# Synergistic Effects of Oxidation and Load on SiC/BN/SiC Ceramic Matrix Composite Degradation at Intermediate Temperatures

А

## Dissertation

Presented to

the faculty of the School of Engineering and Applied Science University of Virginia

> in partial fulfillment of the requirements for the degree

> > Doctor of Philosophy

by

Kaitlin Detwiler

May 2022

## **APPROVAL SHEET**

This

Dissertation

# is submitted in partial fulfillment of the requirements for the degree of

## Doctor of Philosophy

## Author: Kaitlin Detwiler

This Dissertation has been read and approved by the examing committee:

Advisor: Dr. Elizabeth Opila

Advisor:

Committee Member: Dr. Bi-Cheng Zhou

Committee Member: Dr. James Burns

Committee Member: Dr. Xiaodong (Chris) Li

Committee Member: Dr. David Marshall

Committee Member:

Committee Member:

Accepted for the School of Engineering and Applied Science:

J~62. W~+

Jennifer L. West, School of Engineering and Applied Science

May 2022

### Acknowledgments

Thank you to Rolls-Royce and Rolls-Royce HTC for providing program funding and material for the project, as well as my Program Manager Dr. Adam Chamberlain for his support of the work. I would also like to thank Dr. Louise Gale, Dr. Stephen Harris, Dr. Stephen Pattison, and Dr. Ian Edmonds from Rolls-Royce UK for their collaboration and comments on the work.

I would like to thank the DoD SMART program for supporting me during this project. My internships at the Materials & Manufacturing Directorate at the Air Force Research Labs at Wright-Patterson Air Force Base were instrumental in the work. Many thanks to my colleagues at AFRL for all of the support they have given me since I was an undergraduate researcher. I would especially like to acknowledge my mentors Dr. Craig Przybyla and Ms. Jenny Pierce for their guidance over the years. Thank you to Dr. Jennifer Fielding and Mr. Bret Rogers for their support and help as I navigated through my career at AFRL. Thank you to Mr. Reece Hunt and Dr. Robert Wheeler for their help with the micro-tensile stage. Thank you to Dr. Pavel Mogilevsky for his assistance with the UES CMC Micro-Model utilized in this work.

Thank you to the entire Materials Science Department at UVA. The Opila Research Group at UVA has been a constant source of comradery and friendship during my Ph.D. Thank you to Mr. Marcus Dozier for his help as an undergraduate research assistant. I am extremely grateful to have worked with my advisor, Dr. Elizabeth Opila; her mentorship and support have been instrumental and she has been an excellent role model to learn from. I would also like to thank Ms. Tonya Reynolds, Ms. Sherri Sullivan, Ms. Peggy Gibson, Ms. Bryana Amador, Mr. Barry Baber, Mr. Jerry Weaver, and Mr. Ig Jakovac for their logistical help throughout the years. I would also like to acknowledge the UVA Nanomaterials Characterization Facility and the research staff that have assisted and trained me, including Mr. Richard White, Dr. Helge Heinrich, and Mr. Joe Thompson. I would especially like to thank Ms. Catherine Dukes for her assistance using X-ray photoelectron spectroscopy for this work.

Thank you to my friends and family for all of their support. Thank you to my sisters Kelsie and Kiersten, and my Mom and Dad everything you all have done for me. Thank you to my husband Andrew for always being there for me.

# Table of Contents

List of Figures vi
List of Tablesxxv
Abstractxxvii
Chapter I. Introduction1
1.1 SiC/BN/SiC ceramic matrix composites
1.2 Objective I: Baseline oxidation of SiC/BN/SiC CMCs at intermediate temperatures6
1.3 Objective II: Micro-tensile mechanical behavior of SiC/BN/SiC CMCs11
1.4 Objective III: Synergistic effects of oxidation and load on SiC/BN/SiC CMCs13
Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen
2.1 Introduction
2.2 Materials and Methods22
2.3 Results
2.4 Discussion
2.5 Conclusions
Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in
3.1. Introduction 40
3.2 Materials and Methods43
3.3 Results
3.4 Discussion54
3.5 Conclusions60

Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composi a tensile stage	te using 62
4.1 Introduction	62
4.2 Materials and Methods	67
4.3 Results	76
4.4 Discussion	
4.5 Conclusions	92
Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air 5.1 Introduction	93 93
5.2 Material and Methods	97
5.3 Results	103
5.4 Discussion	127
5.5 Conclusions	133
Chapter VI. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in dry oxygen 6.1 Introduction	135 135
6.2 Material and Methods	136
6.3 Results	140
6.4 Discussion	150
6.5 Conclusions	155
Chapter VII. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in wet oxygen 7.1 Introduction	156 156
7.2 Materials & Methods	158
7.3 Results	160
7.4 Discussion	174

7.5 Conclusions	
Chapter VIII. CMC Degradation Modeling 8.1 Introduction	182 182
8.2 Methods	
8.3 Results and Discussion	190
8.4 Conclusions	198
Chapter IX. Conclusions 9.1 Summary of the work and findings	200 200
9.2 Recommendations for material improvement and operating conditions	202
9.3 Recommendations for future work	203
Chapter X. Resulting Presentations, Publications, & Awards 10.1 Presentations	207 207
10.2 Publications	208
10.3 Awards	208
Appendix Chapter 1. Introduction	209 209
Chapter 4. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix c	omposite using
a tensile stage	210
Chapter 5. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air	<i>-</i> 216

# List of Figures

Figure 1: Potential applications for SiC/BN/SiC CMCs in a jet engine. Image reproduced from [4].
2
Figure 2: Schematic of data relationships in this dissertation. Data from each chapter is related to
subsequent chapters to understand synergistic effects of oxidation and load on SiC/BN/SiC CMC
degradation3
Figure 3: Rolls-Royce High Temperature Composites (RRHTC) SiC/BN/SiC MI CMC microstructure.
5
Figure 4: SEM/EDS maps of as-received SiC/BN/SiC CMC used in this study. EDS map colors are
used throughout thesis document6
Figure 5: SEM/EDS maps of a FIB-milled cross-section of SiC fibers in the as-received SiC/BN/SiC
CMC used in this study6
Figure 6: $B_2O_3$ -SiO <sub>2</sub> phase diagram based on thermodynamic calculations and experimental data
[10]8
Figure 7: Two-dimensional schematic drawings of A) Silica glass network with SiO4 tetrahedron
[22] B) Boria glass network containing boroxol rings and planar triangles [23] and C) Borosilicate
glass network with various bond types opening up glass network [24]. Images reproduced from
[22-24]

Figure 8: SiC/BN/SiC CMC stress-strain behavior, where 1) micro-cracks initiate between transverse fibers and in the matrix material at the matrix cracking stress ( $\sigma_{MC}$ ), 2) more cracks initiate and the existing cracks widen past the proportional limit ( $\sigma_{PL}$ ), 3) crack opening displacements widen further and stochastic fiber failure occurs and 4) the sample fails at the Figure 9: Schematic depicting relationship between cracking and embrittlement in the SiC/BN/SiC CMC with oxidation exposure. Black fiber coatings indicate unaffected areas, blue indicate oxidized, and white indicates volatilized coatings......14 Figure 10: Graphic of SiC/BN/SiC CMC oxidation model by Parthasarathy et al. A crack connected to the surface allows oxidant into the CMC to react with a BN fiber coating. Retrieved from [30]. Figure 11: Borosilicate viscosity versus temperature. Viscosities are reported from Yan et al. (0, 3, 5, and 48 mol%  $B_2O_3$ ) [35] and Bruckner and Navarro (98 mol%  $B_2O_3$ ) [25]. Figure was reproduced Figure 12: Thermogravimetric analysis (TGA) setup for dry oxygen......23 Figure 13: Characterization schematic for SiC/BN/SiC CMC after TGA exposure. Plan view images and FIB cross-sections were taken in the box. Cross-sections were taken 10mm from the bottom edge of the sample at the red dashed line......25 Figure 14: Specific weight change data for SiC/BN/SiC exposed to dry  $O_2$  for 50 hours at 400, 600, Figure 15: Plan view of fiber tow of SiC/BN/SiC sample exposed for 1 hour at 600°C in dry oxygen. vii

Figure 16: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in dry oxygen showing
boria-rich and silica-rich regions of oxide growth28
Figure 17: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 600°C in dry oxygen with
surface oxide coverage. The red arrow in the oxygen map indicates oxygen solubility length in the
fibers
Figure 18: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 600°C in dry oxygen with
little to no surface oxide coverage. The "shadow" in the bottom right corner is due to a loss of
EDS signal from the SEM/EDS and sample geometry configuration. The red arrows in the oxygen
map indicates oxygen solubility length in the fibers29
Figure 19: Backscatter SEM images of silica-rich oxide formed after 1 and 50 hours at 800°C in dry
02
Figure 20: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 800°C in dry oxygen. Note
the intact BN interphase and lack of oxygen solubility in the fibers
Figure 21: Specific weight change data for SiC/BN/SiC exposed to dry O2 for 50 hours at 800°C
immediately followed by an exposure for 50 hours at 600°C
Figure 22: FIB Cross-section of SiC/BN/SiC fibers exposed for 50 hours at 800°C in dry oxygen
followed by 50 hours at 600°C. Note the intact BN interphase and lack of oxygen solubility in the
fibers
Figure 23: Ellingham Diagram for SiC/BN/SiC system calculated using the FactPS database in
FactSage
Figure 24: Activities of boron and silicon hydroxide species versus temperature for 0.5 mol $H_2O$
and 0.5 mol $O_2$ at 1 atm. The temperature region of interest is shaded in grey41 viii

Figure 25: Schematic of thermogravimetric analysis (TGA) with a presaturator and saturator to
inject water vapor into the environment
Figure 26: TGA specific weight change data for SiC/BN/SiC exposed to 50% $O_2/50\%$ H <sub>2</sub> O for 50
hours at 400, 600, and 800°C versus a) time and b) root time46
Figure 27: Comparison of TGA specific weight change vs. time for SiC/BN/SiC exposed to wet and
dry oxygen for 50 hours at 600 and 800°C47
Figure 28: Fiber tow of SiC/BN/SiC sample exposed for 1 hour at 600°C in 50% $H_2O/50\%$ $O_2$ gas
mixture
Figure 29: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in 50% $H_2O/50\%$ $O_2$ gas
mixture
Figure 30: FIB cross-section of fiber tow showing a larger, hollow droplet (left) and a smaller solid
droplet (right) for a SiC/BN/SiC sample exposed for 50 hours at 600°C in 50% $H_2O/50\%$ $O_2$ gas
mixture
Figure 31: FIB cross-section of fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in
50% $H_2O/50\%$ $O_2$ gas mixture. The red arrows point to the annular void region. The lack of
nitrogen signal indicates that the BN fiber coating is no longer present and the lack of oxygen signal
indicates that no glass has filled in the annular void50
Figure 32: Polished cross-section of SiC fibers and CVI SiC after exposure at $600^{\circ}$ C in $50\%$ H <sub>2</sub> O/ $50\%$
$O_2$ gas mixture showing a) interface between annular void and oxidized coating and b) between
oxidized coating and BN coating51
Figure 33: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 800°C in 50% $H_2O/50\%$ $O_2$ gas
mixture

C	58

Figure 43: Example of markings to analyze crack composition. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN Figure 44: Lineal intercept method used to calculate crack spacing in SiC/BN/SiC CMCs while under load. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating. ......74 Figure 45: Tensile stage inside of SEM with CMC specimen and button heater......75 Figure 46: Light optical images of a SiC/BN/SiC CMC tested at room temperature with tensile stage at 175, 225, 275 and 325 MPa. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating......77 Figure 47: Masks of cracks marked on a SiC/BN/SiC CMC tested at room temperature with tensile stage at 175, 225, 275 and 325 MPa. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating......78 Figure 48: Micro-crack spacing vs. applied stress for a SiC/BN/SiC CMC tested at room temperature. Error bars are standard deviations. ......79 Figure 49: Micro-crack spacing for each line measured vs. applied stress for SiC/BN/SiC CMC tested at room temperature with tensile stage. .....79 Figure 50: Micro-crack composition vs. applied stress for a SiC/BN/SiC CMC tested at room Figure 51: Backscatter SEM images of micro-cracks 3 and 4 at increasing stress levels. Loading 

Figure 52: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC
loaded at room temperature in SEM82
Figure 53: Crack opening displacements in transverse fiber tow vs. applied stress in SiC/BN/SiC
CMC loaded at room temperature in SEM82
Figure 54: Crack opening displacement vs. the distance from the longitudinal fiber tow for crack
12 in a SiC/BN/SiC CMC. Crack 12 can be seen in Figure 55
Figure 55: Stitched SEM micrographs of micro-crack 12 tested at room temperature. The COD
increases with increased distance from the longitudinal, load-bearing fiber tow. Loading direction
is vertical. Material is a SiC/BN/SiC CMC
Figure 56: Backscatter SEM image of crack propagating through transverse fiber tow in SiC/BN/SiC
CMC tested at room temperature. Red arrows indicate the BN fiber coating. Inside debonding is
observed, where the debond occurs between the fiber and the BN coating
Figure 57: Secondary SEM images of micro-crack B2 in a SiC/BN/SiC CMC at increasing stress levels.
Loading direction is horizontal. Testing temperature is 600°C86
Figure 58: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC
loaded at 600°C in SEM
Figure 59: Crack opening displacements in transverse fiber tow vs. applied stress in SiC/BN/SiC
CMC loaded at 600°C in SEM87
Figure 60: Secondary SEM images of matrix micro-cracks F1 and F2 at 275, 300, 325 and 350 MPa.
Zoomed in red box is the same region for each loading step. The SiC/BN/SiC CMC sample was
tested at 600°C. Loading direction is horizontal

Figure 61: a) Crack density vs. applied stress for SiC/BN/SiC CMC tested at room temperature with tensile stage in this work and b) Crack density vs. applied stress for a different 5HSW SiC/BN/SiC CMC (stress values studied in this work shaded in grey), reproduced from Gowayed et al. [66]. 90 Figure 62: "Picture-frame" fracture surface of a SiC/BN/SiC CMC, where fibers near the edge exhibit flat, brittle failure and fibers on the interior surface exhibit longer lengths of fiber pullout. Reproduced from Morscher et al. [72]......95 Figure 63: Dimensions for SiC/BN/SiC CMC dogbones for fast fracture mechanical testing. All Figure 64: X-ray CT slices of SiC/BN/SiC CMC tensile dogbone. Black spots are porous regions...99 Figure 65: SiC/BN/SiC CMC dogbone in MTS servo-hydraulic load frame equipped with acoustic Figure 66: SiC/BN/SiC CMC in load frame with half of high temperature furnace......101 Figure 68: Mechanical properties vs. temperature for fast fracture tests of SiC/BN/SiC CMCs ran at room and elevated temperatures. ......104 Figure 69: Backscatter SEM image of CMC surface oxide morphologies at 600 and 800°C after 50 Figure 70: Si, B, O, and C EDS maps of SiC/BN/SiC CMC surface oxide at matrix cracking onset tested Figure 71: Oxygen solubility in Hi-Nicalon fibers (white arrows) and oxidation of B-rich intratow MI region (red arrow) in a SiC/BN/SiC CMC. Specimen was exposed to lab air for 100 hours at 600°C xiii

Figure 72: Example of SiC/BN/SiC CMC intratow region that is filled with melt-infiltrated silicon and
is rich in B-containing species. Specimen was exposed to lab air for 100 hours at 600°C at 150
MPa109
Figure 73: Crack in SiC/BN/SiC CMC MI matrix material. Yellow arrows point to unfilled crack. Red
line depicts where FIB cross-section in Figure 74 was taken, with an oxide droplet on top of the
crack. Sample was exposed to lab air at 800°C for 100 hours at 180 MPa111
Figure 74: FIB cross-section of oxide filled crack from Figure 73. SiC/BN/SiC CMC was exposed to
lab air at 800°C for 100 hours at 180 MPa111
Figure 75: Oxide filling in interior cracks in the matrix of SiC/BN/SiC CMC. Specimens were exposed
in lab air at 800°C at 180 MPa for 1, 50, and 100 hours. Red arrows on the backscatter image
indicate loading direction
Figure 76: Oxide filling in interior cracks near fibers in SiC/BN/SiC CMC. Specimens were exposed
in lab air at 800°C at 180 MPa for 1, 50, and 100 hours. Red arrows on the backscatter image
indicate loading direction
Figure 77: Oxidation of porous region in interior of SiC/BN/SiC CMC. The inset in the upper right
corner shows location (red box) of image on the cross-section. Sample was tested for 50 hours at
180 MPa at 800°C114
Figure 78: SEM/EDS maps showing crack in SiC/BN/SiC CMC interior after 50 hours at 800°C in lab
air at 180 MPa. Red arrows point out oxidized BN fiber coating115
Figure 79: SEM/EDS maps of crack in SiC/BN/SiC CMC interior after 100 hour exposure at 800°C in
lab air at 180 MPa. Red arrows point out oxidized coating

Figure 80: MTS furnace temperature profile for furnace with a hot zone temperature of 800°C. Specimen failure regions are marked with the red dots, with 0891-12 failing after 13 hours and Figure 81: Oxygen and boron EDS maps for oxides on the machined SiC/BN/SiC edge formed in the hot zone and the fracture surface after exposures at 13 and 49 hours at 800°C in lab air at 200 Figure 82: FIB milling of micro-cracks in the Si-SiC matrix material of SiC/BN/SiC CMC after 23 and 100 hour exposures at 600°C in lab air at 200 MPa. White arrows indicate oxidation on the crack Figure 83: Comparison of unfilled and oxide-filled cracks in SiC/BN/SiC CMC of similar crack Figure 84: Top and bottom fracture surfaces from stress ruptured SiC/BN/SiC CMC specimen after 13 hour exposure at 800°C in lab air at 200 MPa. The red box is a magnified region of the fracture surface to show more detail. The white dots indicate the same location on the sample on the top Figure 85: Top and bottom fracture surfaces from stress ruptured specimen SiC/BN/SiC CMC after 49 hour exposure at 800°C in lab air at 200 MPa. The blue box is a magnified region of the fracture surface to show more detail. The white dots indicate the same location on the sample on the top Figure 86: Mid-plane polish of SiC/BN/SiC CMC sample exposed to lab air at 600°C for 23 hours at 200 MPa. Yellow arrows point out a crack in the matrix that allowed oxidant travel to the porous

region where the outer edge of CVI SiC on a fiber tow oxidized. Red arrows indicate loading
direction
Figure 87: Oxide droplets on melt-infiltrated material in interior of SiC/BN/SiC composite for
specimen exposed at 600°C for 100 hours at 200 MPa. Yellow arrows point to a matrix crack.124
Figure 88: Crack in interior of SiC/BN/SiC CMC after exposure after at 800°C for 13 hours at 200
MPa. Images were taken near the hot zone region. Blue, red, and green boxes are zoomed in
below to show more detail and the oxygen EDS map that correlates to that region
Figure 89: B-containing phase in matrix oxidized when in crack path in SiC/BN/SiC CMC interior
after exposure at 800°C for 49 hours at 200 MPa126
Figure 90: Oxidized crack near interior fiber tow after exposure at 800°C for 49 hours at 200 MPa.
EDS point analysis was conducted at the points indicated with red arrows and are listed in Table
9126
Figure 91: SiC/BN/SiC CMC behavior as a function of temperature, stress, and water vapor volume
percentage. Green dots indicate that no failures occurred at that condition and red dots indicate
that stress-rupture occurred in at least one test conducted in that condition. Each dot represents
two tests. Only results obtained in lab air are included here
Figure 92: Fused quartz environmental chamber encasing SiC/SiC tensile bar for load frame testing.
Figure 93: Evaluation of dry oxygen test setup. A CVD SiC TGA coupon is suspended inside of the
fused quartz environmental chamber and exposed at high temperature. Note that the furnace is
open and at room temperature in this photo138

Figure 94: Concentration of element in the exposed CVD SiC coupon versus sputtering time. Figure 95: SEM backscatter plan view images of surface oxide morphologies on machined edges of SiC/BN/SiC CMC sample in dry oxygen exposures after 50 hours at a) 600°C in the TGA, b) 600°C Figure 96: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 50 hour exposure at 600°C loaded to 200 MPa in dry oxygen.....142 Figure 97: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after Figure 98: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 50 hour exposure at 800°C loaded to 200 MPa in dry oxygen......143 Figure 99: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after Figure 100: Oxygen solubility lengths for Hi-Nicalon SiC fibers in SiC/BN/SiC CMCs exposed in dry oxygen as a function of temperature, time, and load......144 Figure 101: Matrix crack on exposed surface of a SiC/BN/SiC CMC sample after 50 hour exposure at 800°C loaded to 180 MPa......146 Figure 102: Matrix crack on exposed surface of a SiC/BN/SiC CMC sample after 100 hour exposure at 800°C loaded to 180 MPa......146 Figure 103: Polished cross-section of mid-plane of SiC/BN/SiC CMC sample exposed for 50 hours in dry oxygen at 600°C loaded to 150 MPa. Red arrows point to regions filled with oxide......147

Figure 104: SEM image of polished cross-section of mid-plane of SiC/BN/SiC CMC sample exposed for 50 hours in dry oxygen at 800°C loaded to 150 MPa. Blue arrows indicate loading direction. Inset shows an oxide filled crack (red arrow) propagated through a longitudinal, load-bearing fiber tow. The yellow arrow points to a cracked SiC fiber......147 Figure 105: EDS maps of oxide filled crack near fiber tow in SiC/BN/SiC CMC exposed to 50 hours in dry oxygen at 800°C loaded to 150 MPa. A cracked SiC fiber (yellow arrow) displays oxygen solubility (red arrow)......148 Figure 106: Backscatter SEM images of interior crack filling in SiC/BN/SiC CMC after 50 and 100 Figure 107: Fracture surfaces for SiC/BN/SiC CMC specimen exposed at 800°C at 200 MPa that ruptured after 28 hours in dry oxygen. White dot marks the same location on both surfaces..150 Figure 108: Illustration displaying the effects of temperature, stress, and water vapor content with results from dry oxygen and lab air. Green dots represent no stress-rupture at that condition and red dots represent at least one sample rupturing at that condition. Each dot represents two tests. Figure 111: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 600°C in the TGA for 50 hours and the load frame for 26 hours at 150 MPa. Note the lack of oxide droplets for the load frame exposure. Blue arrows indicate porosity pipes. 

Figure 112: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the load frame for 26 hours at 150 MPa. Red arrows indicate locations where B-containing phases oxidized and volatilized in MI-rich regions in longitudinal fiber tows and in MI matrix material......162 Figure 113: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 800°C in the TGA for 50 hours and the load frame for 100 hours at 150 Figure 114: Backscatter SEM images of top and bottom fracture surfaces of SiC/BN/SiC CMC that stress-ruptured after exposure to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 600°C for 26 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit flat, brittle failure. Figure 115: Backscatter SEM images of exterior and interior fiber tow from top fracture surface of SiC/BN/SiC CMC that stress-ruptured after exposure to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C for 26 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit Figure 116: Backscatter SEM images of top fracture surfaces of SiC/BN/SiC CMC that stressruptured after exposure to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 600°C for 26 hours and with a 30 hour pre-exposure + 12.7 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit flat, brittle failure. Red arrows indicate regions of porosity in the matrix. 165 Figure 117: Backscatter SEM images of top fracture surfaces of SiC/BN/SiC CMC that stressruptured after exposure to 50%  $H_2O/50\%$  O<sub>2</sub> mixture with a 30 hour pre-exposure + 12.7 hours at

150 MPa. Red arrows indicate flat fiber bundle and blue arrows indicate multi-ply topography in Figure 118: Backscatter SEM stitched image of top fracture surface of SiC/BN/SiC CMC that stressruptured after exposure to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 800°C for 5 hours. The fiber tow fractures Figure 119: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exposed surface in SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C the load frame for 26 hours at 150 MPa. Note the lack of B, O, and N signal in the fiber coating region. .........167 Figure 120: Backscatter SEM images and EDS maps of SiC fibers on interior of fracture surface in SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C the load frame for 26 hours at 150 Figure 121: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on interior of fracture surface in SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C the load frame for 26 hours at 150 MPa. Cross-section taken from location marked with white dashed line on left hand image. Oxygen signal at coating regions indicated by red arrows. ......169 Figure 122: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exterior of fracture surface in SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the load frame for 26 hours at 150 MPa. Cross-section taken from location marked with white dashed line on left hand image. Oxygen signal in fiber coating regions indicated by red arrows. 

Figure 123: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exposed surface in SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 800°C the load frame Figure 124: Backscatter SEM images cross-section C of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the load frame for 14 hours at 150 MPa. The test was interrupted after 14 hours. Blue arrows indicate loading direction. Red arrows indicate oxidized fiber coatings and Figure 125: Backscatter SEM images cross-section C of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the load frame for 26 hours at 150 MPa. Blue arrows indicate loading direction. Red arrows indicate filled matrix crack and white arrows indicate unfilled matrix crack in red inset. Green inset shows intratow MI rich region where B-containing phase oxidized and volatilized, leaving voids, indicated by green arrows......172 Figure 126: Backscatter SEM image of cross-section C SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 800°C in the load frame for 100 hours at 150 MPa. Red arrows in inset image indicate Figure 127: Backscatter SEM images and EDS maps of cross-section of SiC fibers in interior of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$  O<sub>2</sub> mixture at 800°C in the load frame for 2 hours at Figure 128: Schematic showing example of sudden expansion phenomena that occurs in the wet Figure 129: Oxidation mechanisms observed at 600°C in water vapor where a) SiC/BN/SiC CMC has porosity pipes at the surface that b) allow oxidant ingress into the material resulting in xxi

embrittlement that c) promotes cracking and further oxidation. Black interphase is unaffected, Figure 130: Oxidation mechanisms observed at 800°C in water vapor where a) SiC/BN/SiC CMC that b) cracks with applied load allowing oxidant ingress into the material resulting in embrittlement that c) promotes cracking and further oxidation. Black interphase is unaffected, Figure 131: Illustration displaying the effects of temperature, stress, and water vapor content with results from dry oxygen, lab air, and wet oxygen. Green dots represent no stress-rupture at that condition and red dots represent at least one sample rupturing at that condition. Each dot Figure 132: Schematic depicting the oxidation processes for SiC/C/SiC composites. Oxygen oxidizes the pyrocarbon fiber coating, forming CO and CO<sub>2</sub>, leaving an annular void between the matrix and fiber. Oxidant diffuses in while the CO and CO<sub>2</sub> products diffuse out via the annular void. Meanwhile, oxygen reacts with the SiC constituents to form SiO<sub>2</sub> to seal the annular void. Schematic reproduced from [87]......183 Figure 133: Schematic depicting BN oxidation and recession behavior in SiC/BN/SiC CMCs modeled by Jacobson et al. [17]. Oxidant travels through boundary layer and annular void region to react with borosilicate and boron hydroxide species diffuse out of the annular void and boundary layer. SiO<sub>2</sub> growth occurs on the annular void walls to close annular void channel. Schematic reproduced from [17]......184 Figure 134: Model schematic for SiC/BN/SiC CMCs at intermediate temperature where the predominant failure mechanism is oxidation of the BN fiber coatings bonding the fibers to themselves xxii

or matrix material. X(t) is the embrittlement depth and $\sigma_f$ is the stress on the fiber in a bridged
matrix crack. Schematic obtained from [89]185
Figure 135: Graphic of SiC/BN/SiC CMC oxidation model by Parthasarathy et al. A crack connected
to the surface allows oxidant into the CMC to react with a BN fiber coating. Reproduced from [30].
Figure 136: Predicted effect of applied force on SiC/BN/SiC CMC fiber tow elastic modulus at 600
and 800°C in a) 100% O <sub>2</sub> and b) 50% H <sub>2</sub> O/50% O <sub>2</sub> . Force values used were 70, 80, and 90 N…191
Figure 137: Stress-rupture predictions for SiC/BN/SiC CMCs at 70, 80, and 90N in dry and wet
oxygen at 800°C192
Figure 138: Stress-rupture predictions for SiC/BN/SiC CMCs at 70, 80, and 90N in dry and wet
oxygen at 800°C. Crack opening displacements used were 0.2, 0.5, and 1.0 $\mu$ m. The data for 0.5
and 1 $\mu m$ in 50% H_2O/50% O_2 are equal and are indistinguishable in the chart
Figure 139: Crack opening displacement predictions for SiC/BN/SiC CMC vs. time for $aB_2O_3 = 0.01$ ,
0.10, 0.25, and 0.50 in a) 100% O2 and b) 50% H2O/50% O2. Starting COD is 0.5 $\mu m.$ 194
Figure 140: Predictions of SiC/BN/SiC CMC a) BN annular void width vs. time and b) Degraded tow
length vs. time for $aB_2O_3 = 0.01$ , 0.10, 0.25, and 0.50 in a) 100% $O_2$ and b) 50% $H_2O/50\% O_2$ .
Starting COD is 0.5µm
Figure 141: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 175
and 200 MPa
Figure 142: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 225,
250, and 275 MPa

Figure 143: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 300
and 325 MPa212
Figure 144: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile
stage at 175, 200, and 225 MPa213
Figure 145: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile
stage at 250, 275, and 300 MPa214
Figure 146: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile
stage at 325 MPa215
Figure 147: Micro-crack spacing for each line measured vs. applied stress for SiC/BN/SiC CMC
tested at room temperature with tensile stage215
Figure 148: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC
loaded at 600°C in SEM216
Figure 149: Bilinear stress-strain curve seen in CMCs at room temperature216

## List of Tables

Table 1: Oxygen Solubility Lengths measured in Hi-Nicalon SiC fibers after 50 hours of exposure
Table 2: Lengths of volatilized and oxidized boron nitride fiber coatings in SiC/BN/SiC CMCs in wet
oxygen after 50 hours
Table 3: Mechanical properties for RR-HTC SiC/SiC CMC at room and elevated temperatures104
Table 4: Hi-Nicalon oxygen solubility length measurements for SiC/BN/SiC CMC specimens
exposed to lab air as a function of stress, time, and temperature108
Table 5: Crack spacings for SiC/BN/SiC CMC specimens tested at 180 MPa in lab air at 800°C 110
Table 6: EDS Point ID compositional analysis of oxides formed at hot zone and fracture surface
after 13 hours117
Table 7: Crack spacings for specimens tested at 200 MPa119
Table 8: Point EDS Analysis taken from cracks in SiC/BN/SiC CMC matrix material near the hot zone
and fracture surface after exposure at 800°C for 13 hours at 200 MPa. The points for the hot zone
are taken from the crack featured in the red box in Figure 88125
Table 9: EDS Point Analysis for locations in Figure 90. 127
Table 10: Damage mechanisms observed in SiC/BN/SiC CMCs at different load levels in lab air at
600 and 800°C. ( ) signifies that the mechanism was observed and (-) signifies that the
mechanism was not observed128

#### Abstract

SiC/BN/SiC ceramic matrix composites (CMCs) are desirable for use in the hot section of jet engines, where temperatures can reach 1200°C or higher. However, due to thermal gradients and backside cooling, many SiC/BN/SiC CMC components will experience intermediate temperatures ranging from 600-800°C. Oxidation mechanisms in this intermediate temperature range are not well understood. CMCs in this region will also experience micro-cracking arising from mechanical and thermal stresses, increasing pathways for oxidant ingress. The following standalone and synergistic effects of oxidation and micro-cracking on SiC/BN/SiC CMC degradation were explored:

- The baseline oxidation mechanisms of the SiC/BN/SiC CMC in dry and wet oxygen from 400-800°C were observed without load using thermogravimetric analysis (TGA).
- 2. Micro-crack spacing, crack opening displacement, and micro-crack composition were quantified for a SiC/BN/SiC CMC under increasing tensile stress at room temperature and 600°C utilizing a micro-tensile stage with light and scanning electron microscopy.
- The synergy between oxidation and applied load was determined by performing oxidation load holds in lab air, dry oxygen, and wet oxygen at 600 and 800°C. The experimental results were compared to CMC damage models.

#### Chapter I. Introduction

Ceramic matrix composites (CMCs) are being developed and introduced into commercial jet engines to replace Ni-base superalloys. CMCs are less dense and can operate at higher temperatures compared to the current metal components used. CMCs are typically composed of coated ceramic fibers embedded in a ceramic matrix. Of particular interest for high temperature, moderate stress regimes in the engine are boron nitride (BN) coated silicon carbide (SiC) based fibers surrounded by a SiC matrix, termed a SiC/BN/SiC CMC. The maximum operating temperature for current state-of-the-art SiC/BN/SiC CMCs is reported to be 1200°C [1, 2].

Potential applications for CMCs inside of a jet engine include the combustor liners, shrouds, and airfoils, as imaged in Figure 1. Temperatures vary throughout the engine depending on component location and the flight profile. The operating temperature is highest during ascent and drops to a steady state temperature during idling and cruising. The temperature can also vary across a single part due to thermal gradients and part cooling. Temperature profiles show that in service, some regions of the CMC component of interest for this work initially spike to 800°C during ascent, and then remain at 600°C during cruising [3]. This temperature range (600-800°C) is considered the intermediate temperature regime for a SiC/BN/SiC CMC. While this temperature range is not the highest temperature a CMC can withstand, degradation of the CMC is a concern as non-protective oxidation reactions will occur with oxygen and water vapor that are present in the engine environment due to combustion.



Figure 1: Potential applications for SiC/BN/SiC CMCs in a jet engine. Image reproduced from [4].

CMCs will experience both chemical and mechanical degradation during flight. The standalone effects of both modes are considered in this work, as well as their combined, synergistic effects. The oxidation reactions and mechanisms for the SiC/BN/SiC CMC are studied in Objective I in *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen* and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen* and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen.* CMCs will experience stress during flight from both thermal stresses and mechanical loading. If the stresses are high enough, cracks will initiate and provide access for oxidant attack into the interior of the CMC. Crack opening displacements, spacings, and general mechanical behavior without oxidation are explored in Objective II in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage.* The

mechanical performance will degrade as oxidant attacks the CMC through micro-cracks in the matrix and through porosity. The synergy between oxidation and stress on CMC performance is evaluated and compared to degradation models in Objective III in *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air, Chapter VI. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in dry oxygen, Chapter VII. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in dry oxygen, Chapter VII. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in wet oxygen, and Chapter VII. CMC Degradation Modeling. Figure 2 shows a schematic of how data from the different objectives relate to each other and how the synergy between oxidation and stress on SiC/BN/SiC CMC degradation is elucidated. A brief literature review is provided below in this chapter, and a more focused review is given as it relates to each chapter's research objectives.* 



Figure 2: Schematic of data relationships in this dissertation. Data from each chapter is related to subsequent chapters to understand synergistic effects of oxidation and load on SiC/BN/SiC CMC degradation.

#### 1.1 SiC/BN/SiC ceramic matrix composites

SiC/BN/SiC CMCs are being utilized for their thermochemical stability and structural integrity at high temperatures. SiC fibers are woven into a five harness satin weave (5HSW) fabric and laid up into various flat panel and complex component geometries. Hi-Nicalon SiC fibers are used in the composite being studied. Hi-Nicalon fibers contain excess C; with a composition of 57.9 mol% C, 41.5 mol% Si, and 0.6 mol% O [5]. Fibers running parallel to the loading direction are called longitudinal fibers and those running perpendicular to the loading direction are called transverse fibers. Thin (on the order of a couple hundred nanometers) BN fiber coatings are used as an interphase between the fiber and matrix to allow for both crack deflection for toughening and interfacial sliding for increased strain capability. A chemical vapor infiltration (CVI) layer of SiC is deposited around the coated fibers prior to melt-infiltration (MI) of silicon within a SiC particulate matrix to fill in remaining porosity. A micrograph of the CMC being studied is shown in Figure 3.



Figure 3: Rolls-Royce High Temperature Composites (RRHTC) SiC/BN/SiC MI CMC microstructure.

State of the art CMCs were provided by Rolls-Royce High Temperature Composites (RR-HTC). Scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS) were used to characterize as-received material, as seen in Figure 4. EDS maps are used throughout the dissertation to assess the post-exposure state of the material, and the same color scheme is kept throughout the work. It should be noted that in the as-received material, little oxygen signal is detected in the coatings at the surface, or in cross-sections of the coatings seen in a focus ion beam (FIB) milled cross-section in Figure 5. Nitrogen signal is used to assess the presence of the BN interphase post-exposure.



Figure 4: SEM/EDS maps of as-received SiC/BN/SiC CMC used in this study. EDS map colors are used throughout thesis document.



Figure 5: SEM/EDS maps of a FIB-milled cross-section of SiC fibers in the as-received SiC/BN/SiC CMC used in this study.

#### 1.2 Objective I: Baseline oxidation of SiC/BN/SiC CMCs at intermediate temperatures

CMC micro-constituents will oxidize in the presence of oxygen and water vapor at elevated temperatures. Yb<sub>2</sub>Si<sub>2</sub>O<sub>7</sub> environmental barrier coatings (EBCs) are often applied to mitigate

oxidation and volatilization of the underlying CMC via reactions with water vapor [6]. However, EBCs may degrade, via thermochemical reactions with high-velocity water vapor or fail thermomechanically due to stresses associated with thermal cycling during engine operation [7]. EBCs can also form crack channels during loading, reducing their ability to prevent oxidative attack. Also, in some cases, an EBC may not be applied to a surface to minimize component weight if it is thought that the CMC surface exposed is chemically stable for the environment. Baseline CMC oxidation without an EBC must be studied for the aforementioned reasons.

Temperatures of interest in this study are 400, 600, and 800°C. At 800°C, a silica (SiO<sub>2</sub>) rich glass will form on the surface of the CMC, as seen previously in the Rolls-Royce High Temperature Composite (RRHTC) CMC [8]. At 600°C, a borosilicate glass will form, with boron oxidizing from the BN fiber coatings and other B-containing phases in the matrix material. Boria (B<sub>2</sub>O<sub>3</sub>) reacts with the silica glass network and modifies the structure, allowing for a higher oxygen diffusivity through the oxide, resulting in increased amounts of material degradation. Finally, 400°C is of interest as it is below the melting point of B<sub>2</sub>O<sub>3</sub> (458°C) and below the B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> eutectic temperature (451°C) as seen in Figure 6, providing a lower temperature limit for investigation [9].


Figure 6:  $B_2O_3$ -SiO<sub>2</sub> phase diagram based on thermodynamic calculations and experimental data [10].

Relevant dry oxidation reactions include the matrix silicon reacting with oxygen to form silica, via:

$$Si + O_2(g) = SiO_2$$
 (Eq. 1.1)

Silicon oxidation in dry oxygen follows Deal-Grove kinetics, exhibiting linear kinetics at short times, followed by parabolic oxidation at long times as the silica layer grows [11]. Silicon oxidation proceeds by inward diffusion of molecular oxidant through the oxide to react at the Si-SiO<sub>2</sub> interface [11].

SiC oxidation will also result in silica formation, per:

$$\frac{2}{3}SiC + O_2(g) = \frac{2}{3}SiO_2 + \frac{2}{3}CO(g)$$
(Eq. 1.2)

SiC dry oxidation also exhibits Deal-Grove kinetics and has a similar activation energy (118 kJ/mol) as silicon oxidation (117 kJ/mol), indicating that SiC oxidation proceeds via the same mechanism as silicon oxidation [11, 12]. The SiC oxidation rate is slower than silicon oxidation due to the additional formation of CO(g) [12]. The SiC oxidation rate is slowed by crystallization of the scale into cristobalite at 1300°C [13] but this is not relevant to the present study due to the much lower temperature regime being studied.

Boria and borosilicates of varying compositions will form due to oxidation of BN coatings in the composite:

$$\frac{4}{3}BN+O_2(g) = \frac{2}{3}B_2O_3(I) + \frac{2}{3}N_2(g)$$
(Eq. 1.3)

$$xB_2O_3(l) + ySiO_2(s) = xB_2O_3 \cdot ySiO_2(l,s)$$
 (Eq. 1.4)

BN oxidation rates are not readily predicted, as they depend on multiple factors, such as crystallinity, crystallographic orientation, and density [14, 15]. However, it is well known that its oxidation product, boria, has a low melting point of 450°C and it volatilizes readily in the presence of ppm levels of water vapor to form boron hydroxides [9, 16, 17].

The phenomenon of boria fluxing is a contributor to increasing the oxidation rate of SiC. Molten boria results in the dissolution of SiC in the presence of oxygen to form a borosilicate glass [18-21], accelerating SiC oxidation. Silica glass is composed of randomly oriented tetrahedra, seen in Figure 7A [22]. The boria structure is composed of a mixture of boroxol rings and planar triangles [23]. When combined into a borosilicate glass, boria interrupts the silica tetrahedra structure to form Si-O-B bonds, opening up the glass network for higher oxygen permeation rates [24] and lowering the viscosity [25]. The oxidation rate of SiC in contact with a borosilicate is higher than the oxidation rate of SiC alone [18]. It has been shown that with increased presence of SiO<sub>2</sub> in the borosilicate, the reactivity with SiC is reduced [18]. In the case of the thermally grown oxides seen in this work, both borosilicates and silica are relevant.



Figure 7: Two-dimensional schematic drawings of A) Silica glass network with SiO<sub>4</sub> tetrahedron [22] B) Boria glass network containing boroxol rings and planar triangles [23] and C) Borosilicate glass network with various bond types opening up glass network [24]. Images reproduced from [22-24].

In the presence of water vapor, silica will form and volatilize for both Si and SiC:

$$\frac{1}{2}Si + H_2O(g) = \frac{1}{2}SiO_2 + H_2(g)$$
 (Eq. 1.5)

$$\frac{1}{3}SiC + H_2O(g) = \frac{1}{3}SiO_2 + H_2(g) + \frac{1}{3}CO(g)$$
 (Eq. 1.6)

$$\frac{1}{2}SiO_2 + H_2O(g) = \frac{1}{2}Si(OH)_4(g)$$
 (Eq. 1.7)

SiC oxidation kinetics have been shown to increase with increasing water vapor contents [26].

Similarly, boria will form and volatilize in wet oxygen conditions, as well as forming borosilicates per Eq. 1.4:

$$\frac{2}{3}BN + H_2O(g) = \frac{1}{3}B_2O_3(I) + H_2(g) + \frac{1}{3}N_2(g)$$
 (Eq. 1.8)

$$B_2O_3(I) + H_2O(g) = \frac{2}{3}(HBO_2)_3(g)$$
 (Eq. 1.9)

$$\frac{1}{3} B_2 O_3(I) + H_2 O(g) = \frac{2}{3} H_3 B O_3(g)$$
 (Eq. 1.10)

$$B_2O_3(I) + H_2O(g) = 2HBO_2(g)$$
 (Eq. 1.11)

The oxidation mechanisms and behavior for CMCs is discussed in *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen* and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen.* 

#### 1.3 Objective II: Micro-tensile mechanical behavior of SiC/BN/SiC CMCs

CMCs exhibit bilinear stress-strain behavior, as shown in the stress-strain curve in Figure 8. Elastic behavior occurs below the matrix cracking stress ( $\sigma_{MC}$ ), where load is distributed to the fibers and matrix according to their volume fraction ratios. At  $\sigma_{MC}$  cracks initiate in the matrix to accommodate stress. As load increases, matrix cracks deflect around fibers leading to debonding between transverse fibers and matrix material. More micro-cracks occur in the matrix as stresses are applied up to the proportional limit ( $\sigma_{PL}$ ). SiC fibers carry larger portions of the load in the second portion of the stress-strain curve. Matrix cracks widen with increased load, and fibers running parallel to the loading direction will start to fail stochastically. Fiber sliding occurs, and for the CMC being studied, inside debonding occurs, wherein the BN coating remains on the CVI SiC, leaving the SiC fiber exposed. The above failure mechanisms then lead to final rupture of the CMC at the ultimate tensile strength ( $\sigma_{UTS}$ ) [27].

Micro-cracking data, such as crack opening displacement (COD), are utilized in CMC damage and oxidation modeling. The COD at the exposed surface will affect the ingress rate of oxidant into the CMC interior. A micro-tensile stage was utilized to measure COD, as well as other metrics including micro-crack spacing and cracking behavior in relation to micro-constituents. This work is discussed in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage.* 



Figure 8: SiC/BN/SiC CMC stress-strain behavior, where 1) micro-cracks initiate between transverse fibers and in the matrix material at the matrix cracking stress ( $\sigma_{MC}$ ), 2) more cracks initiate and the existing cracks widen past the proportional limit ( $\sigma_{PL}$ ), 3) crack opening displacements widen further and stochastic fiber failure occurs and 4) the sample fails at the ultimate tensile stress ( $\sigma_{UTS}$ ).

# 1.4 Objective III: Synergistic effects of oxidation and load on SiC/BN/SiC CMCs

The CMC is exposed to oxidant while the above damage mechanisms are occurring. Matrix cracks allow for oxidant to travel from the surface of the composite to the interior constituents. Once fiber debonding occurs, there is an increased surface area for degradative attack of the BN coating [28]. When inside debonding occurs, the interface debond occurs between the fiber and the BN interphase, as opposed to outside debonding where the debond occurs between the fiber coating and the matrix [29]. Inside debonding results in the fiber coating adhering to the CVI SiC matrix when fiber pullout occurs. Inside debonding will allow oxidant to directly reach the fiber, whereas outside debonding would cause oxidant to first contact the BN interphase [29].

As fibers begin to break and fiber sliding occurs, more pathways are opened for oxidative attack. It is unclear how mechanical damage affects oxidation rates and how oxidation affects the extent of mechanical damage. The current work seeks to understand the synergies in oxidation and applied load and their effect on CMC degradation. Stress regimes at the  $\sigma_{MC}$  and above the  $\sigma_{PL}$  stress values in lab air, dry oxygen and wet oxygen at intermediate temperatures (600-800°C) were studied.

It was anticipated that stressed oxidation testing would result in increased damage of the CMC, resulting in stress-rupture at loads well below the  $\sigma_{UTS}$ . Cracking in the matrix would open up more pathways for oxidant ingress, resulting in oxidation of interior constituents that would not otherwise be exposed, as depicted in Figure 9b. As oxidation and the resultant reduction in mechanical strength from embrittlement proceed, crack initiation and propagation will occur.

13

More pathways would be open for oxidant ingress for further attack of the CMC interior, resulting in the eventual rupture of the CMC.



Figure 9: Schematic depicting relationship between cracking and embrittlement in the SiC/BN/SiC CMC with oxidation exposure. Black fiber coatings indicate unaffected areas, blue indicate oxidized, and white indicates volatilized coatings.

Models of SiC/BN/SiC behavior in engine conditions have been produced to predict component life [30, 31]. A surface crack in the SiC matrix acts as a fast path for oxidant to reach the BN coated fibers, depicted in Figure 10 [30]. The BN subsequently oxidizes and volatilizes leaving an annular void that fills with silica at long times and higher temperatures. The model allows for matrix oxidation to seal cracks and mitigate further oxidative attack into the interior of the composite.

These models conflict with recent work completed on the RR-HTC CMC [8]. Oxidation studies were completed via thermogravimetric analysis on unstressed material from 800-1200°C. In this case, the BN coating did oxidize, but was sealed off with a borosilicate droplet at the free surface, followed by SiC fiber oxidation and finally SiC matrix oxidation [8]. The subsurface BN coating remained beyond the initial amount of fiber coating oxidation, and annular voids were not

observed via any method, including transmission electron microscopy (TEM). The current work interrogates the fiber coating behavior on exposed specimens with and without load, and will determine if the model is applicable at the intermediate temperature regime.



Figure 10: Graphic of SiC/BN/SiC CMC oxidation model by Parthasarathy et al. A crack connected to the surface allows oxidant into the CMC to react with a BN fiber coating. Retrieved from [30].

Modeling these complex oxidation mechanisms requires input parameters that describe the environment, material, and quantify the extent of damage. Environmental inputs include partial pressures of water vapor and oxygen, temperature, time of exposure, and the force on the fiber tow. These variables were controlled and varied in the current work. Prior inputs for quantified damage of the CMC were from predicted values, and were not measured. COD measurements were experimentally determined in Objective II in this study to provide inputs for the model. A geometric input that was also be measured in the proposed work is the distance of an oxidized fiber tow along a crack from the free surface (L<sub>deg</sub> in Figure 10). The outputs from the model include a residual tow strength and stiffness, length of the degraded BN interface, and stress-rupture predictions. Stress-rupture predictions can be compared to actual stress-rupture times for different temperatures, environments, and loads. A complete list of the variables required for the model can be found in the *Appendix*.

Synergy between oxidation and applied load is discussed in *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab* air, *Chapter VI. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in* dry oxygen, and *Chapter VII. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in* wet oxygen. Comparisons to the Parthasarathy environmental damage model is given in chapter discussions throughout the thesis and are quantified in *Chapter VII. CMC Degradation Modeling*.

# Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen

#### 2.1 Introduction

Gaseous species in the engine environment, including oxygen from excess air and water vapor as a product of combustion, result in an environment that is detrimental to a CMC [30]. This chapter considers reactions between dry O<sub>2</sub> and a SiC/BN/SiC CMC while *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen* interrogates additional reactions with H<sub>2</sub>O. The relative rates of BN and SiC oxidation in each environment are critical to predict oxidative degradation.

An early study, from which current CMC oxidation models are derived, was performed on mini-composites, which were fabricated from a single tow of BN-coated fibers (BN thicknesses ranging from 0.5-3µm) with a chemical vapor infiltrated (CVI) SiC overcoat [32]. The mini-composites were pre-cracked, and then held at a constant load in lab air to rupture or up to 100 hours. It was observed at lower temperatures (~500-700°C) that an annular void was left around fibers where the BN fiber coating volatilized, and at higher temperatures (T>950°C) this void filled with silica for times greater than 98 hours [32]. Oxidation and volatilization of the BN fiber coatings is detrimental to the mechanical properties of the CMC, as the BN coating allows for crack

deflection and interfacial sliding of the SiC fibers, both toughening mechanisms for the CMC. The formation of a  $SiO_2$  layer from oxidation of SiC is desired to limit BN oxidation.

The results from the study on mini-composites [32] were extrapolated to models describing composite behavior, with the most recent by Parthasarathy, et. al [30]. In this model, a surface crack in the melt-infiltrated (MI) matrix acts as a fast path for oxidant to reach the BN coated fibers. The BN subsequently oxidizes and volatilizes leaving an annular void that fills with silica at long times and higher temperatures. The model allows for matrix oxidation to seal cracks and mitigate further oxidative attack into the interior of the composite. Matrix oxidation predictions are dependent on the amount of boron containing species in the matrix. Additionally, models produced by Xu et al., which focus on two oxidative processes from 700-1000°C, in SiC/SiC CMCs also consider the effect of oxidant traveling through micro-cracks [31]. Two models were produced from the work, with 1) considering the effect of SiO<sub>2</sub> scale formation around a fiber with BN coating loss, resulting in tensile stresses in the fiber and 2) when the annular voids filled with oxide and oxide growth is constrained, resulting in stress intensities in the fibers [31].

These models conflict with recent work completed on unstressed SiC/BN/SiC CMCs [8]. Oxidation studies were completed via thermogravimetric analysis on unstressed material from 800-1200°C. In this case, the BN coating did oxidize, but was sealed off with a borosilicate droplet at the free surface, followed by SiC fiber oxidation and finally SiC matrix oxidation [8]. The subsurface BN coating was protected from further oxidation under all conditions, and annular voids were not observed via any characterization method, including transmission electron microscopy. Borosilicate droplets were also previously noted to form at the fiber coating region

18

in SiC/BN/SiC CMCs exposed at 600°C in lab air [33]. Wing & Halloran studied ends-on oxidation from 1200-1285°C in lab air in an unstressed HiPerComp<sup>TM</sup> SiC/BN/SiC CMC, and observed oxidized BN coating lengths (filled with borosilicate) as high as  $1000\mu$ m deep after 80 hours, and no annular voids were observed [34].

The protectiveness of the oxide formed is dependent on boria content. First, an oxide that wets the surface and covers more constituents will provide more protection for the underlying material. Oxide morphology behavior is dictated by glass composition, which affects the surface energy, viscosity, and wettability. Borosilicate viscosity has been measured as a function of B<sub>2</sub>O<sub>3</sub> content and temperature, as shown in Figure 11. Borosilicate viscosity reduces with increased B<sub>2</sub>O<sub>3</sub> content and increased temperature [25, 35]. It is important to note that if a sufficient amount of glass is formed, gravity, rather than surface energy, will dominate and the oxide will flatten instead of being droplet shaped [8, 36]. The second effect that boria content has on oxide protectiveness is due to its effect on the glass network. An increased boron content in the glass will result in higher oxygen permeation rates, as boria interrupts the silica tetrahedra structure to form Si-O-B bonds [24]. The oxidation rate of SiC in contact with a borosilicate is higher than the oxidation rate of SiC alone [18].



Figure 11: Borosilicate viscosity versus temperature. Viscosities are reported from Yan et al. (0, 3, 5, and 48 mol%  $B_2O_3$ ) [35] and Bruckner and Navarro (98 mol%  $B_2O_3$ ) [25]. Figure was reproduced from [18].

# 2.1.1 Objective I Knowledge Gaps

Oxidation behavior for the provided Rolls-Royce SiC/BN/SiC at intermediate temperatures (400-800°C) has not been studied. The effect of the B-containing species that is present in the matrix of the RRHTC CMC on oxidation is unclear, and this effect is studied in detail. It is also unknown if the annular voids in the BN coating regions depicted in many models will occur for the RRHTC CMC at intermediate temperatures, as they have not been previously observed at high temperature [8]. Finally, while it is known that water vapor interactions with the resultant CMC

oxide (borosilicate) results in volatilization of the oxide, it is unclear how this will affect the underlying RRHTC CMC.

#### 2.1.2 Objective I Research Questions

The aim of this chapter was to investigate the oxidation mechanisms for an unstressed SiC/BN/SiC CMC in dry oxygen from 400-800°C, particularly determining conditions, if any, where annular void formation is observed. It was anticipated that annular voids would not form without the presence of water vapor to volatilize the oxidized coatings. Transition temperatures between different oxidation mechanisms are reported. Oxidation penetration depths were measured relative to local oxide formation. Oxygen solubility in Hi-Nicalon SiC fibers was observed and measured, which was unexpected behavior as it had not been previously reported in literature. These mechanisms are compared to the current oxidation models for stressed SiC/BN/SiC CMCs.

The following research questions are explored and discussed in *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen* and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen*:

- 1. What are the oxidation mechanisms in the intermediate temperature regime?
- 2. What are the transition temperatures for different oxidation mechanisms to occur?
- 3. What is the effect of exposure time on the oxide microstructure?
- 4. How do the underlying local microstructure and constituents affect the oxidation behavior?
- 5. How does the addition of H<sub>2</sub>O influence the oxidation mechanisms?

#### 2.2 Materials and Methods

## 2.2.1 Materials

CMC plates provided by RR-HTC had dimensions of approximately 178mm X 178mm X 4.5mm. Test specimens were machined by Bomas Machine Specialties (Somerville, MA) into coupons with dimensions of 25.4mm X 10.2mm X 4.5mm with a geometric surface area of 8.7cm<sup>2</sup>. A 3.175mm diameter hole was machined 5mm from the top edge of the sample to suspend the coupon during elevated temperature oxidation testing. As-machined edges exposed all CMC constituents to the oxidizing environment.

## 2.2.2 Oxidation Exposures

Thermogravimetric analysis (TGA) was used to supply a controlled environment for oxidation exposure of a sample while measuring weight change [18]. The sample was suspended within a fused quartz tube with an inner diameter of 22mm using an alumina hanger, as depicted in Figure 12, which was connected to a sensitive (0.01mg resolution) Setaram B SETSYS 100g microbalance (Setaram, Inc., Hillsborough, NJ) via platinum chain and NiCr wires. Weight changes were acquired during testing to interpret oxidation reactions and mechanisms. The furnace (Lab-Temp Furnace, Thermcraft, Winston-Salem, NC) was heated to the test temperature and raised to the specimen position once at temperature, allowing for rapid heating of the sample and mitigating oxidation at lower temperatures. Oxygen (99.99% pure, Linde) flowed to the sample through a desiccant (MT-Series Drierite, Agilent Technologies) and flow was maintained at a constant supply of 100 sccm using mass flow controllers (G-series and 247 controller, MKS Instruments).



Figure 12: Thermogravimetric analysis (TGA) setup for dry oxygen.

Oxidation exposures were conducted for 1 and 50 hours at temperatures of 400, 600, and 800°C. Intermediate temperatures were also investigated to identify transition temperatures between oxidation mechanisms. Additionally, a bithermal exposure was performed at 800°C for 50 hours, followed by an exposure at 600°C for 50 hours to observe the effect of a pre-grown silica layer on composite oxidation.

#### 2.2.3 Characterization

Samples were characterized using a FEI Quanta 650 field emission scanning electron microscopy (SEM) and Oxford Instruments Aztec X-Max<sup>N</sup> 150 energy dispersive X-ray spectroscopy (EDS) following TGA exposures. Plan view images were taken of the exposed long edge that exposes both transverse and longitudinal fibers, as shown in the box on Figure 13.

Samples were also characterized using a FEI Helios dual-beam focused ion beam (FIB) to make cross-sections that were subsequently analyzed with SEM and EDS. Milling was performed on the machined face exposing longitudinal and transverse fibers, seen in the box on Figure 13. Cross-sections of selected fibers in a fiber bundle were milled using the ion beam and then compositionally mapped using EDS to provide high fidelity images and composition maps. The FIB samples were used to correlate local surface oxide to the underlying material microstructure.

The sample was then cross-sectioned and polished to allow SEM/EDS investigation of oxidation occurring on the edges and interior of the composite. Cross-section images were taken at the weave side (marked on Figure 13) and along the fibers and coatings on the machined edge. A schematic showing the imaging and cross-section locations is shown in Figure 13.



Figure 13: Characterization schematic for SiC/BN/SiC CMC after TGA exposure. Plan view images and FIB cross-sections were taken in the box. Cross-sections were taken 10mm from the bottom edge of the sample at the red dashed line.

# 2.3 Results

# 2.3.1 Oxidation onset and transition temperatures

Specimens exposed to dry O<sub>2</sub> for 1 and 50 hours at 400°C did not exhibit any signs of oxidation via SEM/EDS. Minimal weight change was observed after 50 hours at 400°C, as seen in the specific weight change data in Figure 14. Exposure temperatures were sequentially increased by 50°C to find the onset temperature for oxidation after 1 hour, and initial signs of oxidation, evidenced by oxygen signal in SEM/EDS plan view images. Onset was found to occur between 450-480°C. A boron-rich oxide was observed at 600°C, which transitioned to silica-rich oxide at temperatures between 650-700°C.



Figure 14: Specific weight change data for SiC/BN/SiC exposed to dry  $O_2$  for 50 hours at 400, 600, and 800°C vs. (a) time and (b) root time.

# 3.2 Boron-rich oxide regime at 600°C

Oxidation on the machined surface preferentially occurred in the MI matrix material at 600°C after exposure for 1 hour, shown in plan view in Figure 15. This oxide is rich in both boron and silicon, forming a borosilicate glass that is homogeneous at the length scale studied. A limited amount of oxide formed over the BN coatings, but a majority of the oxide formed in the MI matrix material where an underlying B-containing phase resides. Nitrogen signal around the fibers is strong, indicating that the fiber coatings remain intact after 1 hour. Note that intratow areas that are filled with MI silicon also exhibited oxidation similar to that in the MI matrix material.



Figure 15: Plan view of fiber tow of SiC/BN/SiC sample exposed for 1 hour at 600°C in dry oxygen.

The entire fiber tow surface was oxidized along with the edge of the CVI SiC after 50 hours. Two distinct oxide phases are seen after a 50 hour exposure in Figure 16, where boria and silica co-exist in contrast to the homogeneous borosilicate phase formed after one hour. Boria-rich areas are typically located near thicker areas of the BN fiber coatings where two or more fiber coatings meet. The silica phase covers the fiber tow and the edge of the CVI SiC. Nitrogen signal is not detected where the fiber coatings reside due to oxide covering the coatings and impeding the signal. The BN coatings remain intact when observed in cross-section. Several studies were also performed to understand the transition time for these phases to occur, and the transition between the single-phase borosilicate and two-phase boria-silica phases occurred between 1 and 25 hours.



Figure 16: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in dry oxygen showing boria-rich and silica-rich regions of oxide growth.

Fiber cross-section oxidation behavior varies based on the local surface oxide. Near the outer edge of the CVI tow where there is a layer of oxide, fiber cross-sections in Figure 17 show oxygen solubility (red arrows), and a depleted carbon signal. The depleted carbon signal aligns with the increased oxygen signal, suggesting silicon oxycarbide formation and CO(g) formation. Where little surface oxide is present, such as the middle of a fiber tow as imaged in Figure 18, longer oxygen solubility lengths are observed in the Hi-Nicalon fibers. This phenomenon has not been previously reported in the literature.



Figure 17: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 600°C in dry oxygen with surface oxide coverage. The red arrow in the oxygen map indicates oxygen solubility length in the fibers.



Figure 18: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 600°C in dry oxygen with little to no surface oxide coverage. The "shadow" in the bottom right corner is due to a loss of EDS signal from the SEM/EDS and sample geometry configuration. The red arrows in the oxygen map indicates oxygen solubility length in the fibers.

The average oxygen solubility length, measured from 81 fibers using polished crosssections, is 6.4 ± 3.3 microns. While the borosilicate glass is less protective of the fibers than the silica glass (discussed below), it is still more protective than no oxide at all. There is a strong nitrogen and boron signal at the fiber coating location, consistent with retention of BN and the lack of an annular void for samples exposed at 600°C. Oxygen signal is also present at the fiber coating location near the surface, seen via FIB cross-sections, and unsuccessful attempts were made to measure this depth via SEM/EDS of polished cross-sections. There is also an area of silicon-rich MI matrix material between the two fibers. The intratow MI matrix material, where the B-containing phase is heavily concentrated, has an oxygen signal that is deeper than that seen in the CVI SiC, indicating a higher oxidation rate for boron-rich areas of the matrix.

#### 2.3.3 Silica oxidation regime at 800°C

A silica-rich glass forms at the outer edge of the CVI SiC on the surface after a 1 hour exposure at 800°C. The silica-rich glass covers the entire surface of the CMC after 50 hours. In the matrix-rich region of the machined face, silica-rich glass is also seen. SEM micrographs of the oxide formed at 800°C after 1 and 50 hours are imaged in Figure 19. In contrast to the 600°C samples, boron is not detected in the glass by EDS.



Figure 19: Backscatter SEM images of silica-rich oxide formed after 1 and 50 hours at 800°C in dry O2.

FIB cross-sections were also performed. Figure 20 shows a thick (~5 micron) protective silica layer formed after a 50 hour exposure on top of the fibers in cross-section, resulting in little to no oxygen solubility in the fibers as compared to the 600°C results. This external oxide is much thicker than 0.12 microns, calculated for silica growing on Hi-Nicalon SiC fibers under the same conditions [37], and thicker than a predicted silica thickness of 0.08 microns on CVD SiC (calculated using CVD-SiC fast rate constants) [38]. There are likely boron effects from the matrix that are accelerating the growth of the oxide. The boron and nitrogen signals also show very strongly in the fiber coating, and no annular void is seen. The oxygen maps indicate a slight amount of oxygen solubility into the fiber, but at lower ingress lengths than seen at 600°C. Polished cross-sections were performed and oxygen solubility lengths were measured from 47 fibers, with an average measurement of  $1.6 \pm 1.4$  microns.



Figure 20: FIB cross-section of SiC/BN/SiC fibers exposed for 50 hours at 800°C in dry oxygen. Note the intact BN interphase and lack of oxygen solubility in the fibers.

# 2.3.4 Bithermal study

A bithermal oxidation hold was performed at 800°C for 50 hours to produce a silica layer on all sides of the composite, followed by an exposure at 600°C for 50 hours to observe the protective nature of the silica layer on a cut edge (where much more boron is available locally in contrast to the weave face) at lower temperature exposures. The TGA weight data from the bithermal exposure are presented in Figure 21. A minimal amount of weight gain (0.017 mg/cm<sup>2</sup>) was observed after the temperature change from 800°C to 600°C. This indicates that the pregrown SiO<sub>2</sub> layer protected the CMC from further oxidative attack. Both polished and FIB crosssections were performed at the fiber tow region, as seen in Figure 22. Minimal oxygen dissolution was observed in the fiber cross-sections, similar to that seen in the 50 hour 800°C exposure. The intratow MI material again exhibited a deeper oxidation depth than the surrounding material.



Figure 21: Specific weight change data for SiC/BN/SiC exposed to dry O2 for 50 hours at 800°C immediately followed by an exposure for 50 hours at 600°C.



Figure 22: FIB Cross-section of SiC/BN/SiC fibers exposed for 50 hours at 800°C in dry oxygen followed by 50 hours at 600°C. Note the intact BN interphase and lack of oxygen solubility in the fibers.

# 2.4 Discussion

#### 2.4.1 General oxidation mechanisms

The oxidation onset temperature ranges from 450-480°C, corresponding to the melting temperature of boria (450°C) [9]. This onset temperature has been noted before for BN fiber coatings forming boria in a SiC/BN/SiC system [15, 17, 32].

A two phase borosilicate glass was observed after exposures for 25 hours at 600°C. Phase separation has been studied before in borosilicate-containing glass mixtures, although it has been reported at much smaller length scales (sub-micron) than observed here (approximately 10 microns) [39, 40]. The boria-silica phase diagram in Figure 6 has a shoulder in the liquidus line, indicative of a potential miscibility gap in the boria-rich region with a thermodynamically predicted critical temperature of 520°C [9, 10]. This shoulder terminates at temperatures lower than 800°C in the phase diagram. The difference in the oxide behavior observed at 600 and 800°C after 50 hours may be attributed to this potential miscibility gap, although this observation requires further investigation.

Oxidation at both 600 and 800°C exhibit neither linear nor parabolic oxidation, seen in the TGA curves in Figure 14. Rapid oxidation occurs from 0-15 hours followed by a decrease in the rate of weight change. The initial weight gain is likely attributed to the oxidation of B-containing phases surrounding the CVI SiC as observed in the SEM micrographs after 1 hour exposures.

The B-containing phase in the MI matrix material results in preferential oxidation in all conditions studied. Previous studies of SiC/BN/SiC oxidation show that SiC, either in the form of fiber or matrix, will be the first constituent to oxidize when given limited amounts of oxygen [17, 41, 42]. This is due to the relative thermodynamic stability of SiO<sub>2</sub> compared to B<sub>2</sub>O<sub>3</sub>, as seen in the Ellingham diagram in Figure 23. However, in the present study, the addition of the B-containing phase in the MI matrix material results in preferential oxidation as it is kinetically favored to oxidize given unlimited access to oxygen. Once the oxide on the B-containing phase reaches an unknown critical thickness, the surrounding SiC oxidizes. Boria accelerated SiC oxidation has been observed in prior studies [21].



Figure 23: Ellingham Diagram for SiC/BN/SiC system calculated using the FactPS database in FactSage

The intratow B-rich MI material between the fibers in Figure 17 displays a deeper oxidation length than the surrounding CVI SiC material. Other polished cross-sections also show these intratow MI regions having deeper oxidation lengths than the surrounding SiC. The increased oxidation depths of these regions compared to other microconstituents can be attributed to 1) the thermodynamic stability of SiO<sub>2</sub> forming from Si relative to SiC and 2) the increased kinetics of oxidation when in contact with the B-containing phase in the matrix.

The silica-rich oxide formed at 800°C is shown to be much more protective of the fibers than the boron-rich oxide formed at 600°C. The silica-rich oxide formed at 800°C provided more coverage across fibers and matrix material than the boron-rich oxide formed at 600°C. The boron-rich oxide formed oxide droplets above the matrix material, and did not provide significant coverage atop the SiC fibers. The bithermal exposure also resulted in an oxide with no boron and limited oxygen solubility was found in the fiber cross-sections. The incorporation of boria molecules into the glass network results in a higher oxygen permeability for the oxides formed at 600°C. Oxygen solubility lengths in the fiber are much higher for the 600°C exposure ( $6.4 \pm 3.3$  microns) than at 800°C ( $1.6 \pm 1.4$  microns), but the boron rich oxide still provides protection for the fibers relative to no oxide at all. Oxygen solubility has been reported for SiC thin films previously [43], but there are no known studies observing oxygen solubility in Hi-Nicalon SiC fibers, as seen in this work. Implications of dissolved oxygen are discussed below.

# 2.4.2 Lack of annular void

Annular voids were not observed at the BN fiber coating locations for any exposure conditions in dry oxygen. Boron and nitrogen signals from EDS remain strong below the surface oxide for both 600 and 800°C exposures. The glasses formed in dry oxygen do not show signs of volatility and instead seal off the fiber coatings from oxidation and subsequent volatilization. *Chapter III* of this work will investigate the effect of water vapor in the gas mixture in the same temperature range as this study, which is more relevant for a combustion environment.

Published CMC oxidation models includes crack pathways as a means for oxygen travel to the interior of the composite to reach fiber coatings [30, 31]. Previous work on stressed material in the intermediate temperature range of 600-800°C displayed a pesting mechanism, where the exposure temperature is too low to form a protective silica scale that covers the outer surface and fill surface cracks of the CMC that would limit additional oxidation exposure within the composite [28, 44]. It is unknown if this pesting mechanism would occur in the current material at these temperatures. *Chapters V-VII* describes the effect of applied stress and micro-cracking on fiber coating oxidation, again, addressing more relevant use conditions. The oxidized fiber coating length data obtained in this study can provide input for oxidation phenomena in existing oxidation models.

#### 2.4.3 Implications on CMCs in service

CMCs in service will have an environmental barrier coating (EBC) to help mitigate oxidative attack of SiC/BN/SiC CMC constituents. EBCs can crack and spall off due to thermal cycling and CTE mismatch. If the EBCs spall off in an oxygen rich environment, the underlying SiC/BN/SiC CMC will undergo the aforementioned oxidative mechanisms at 600 and 800°C, where higher oxygen solubility lengths were observed in the Hi-Nicalon fibers at 600°C due to a less protective B-rich oxide compared to a more protective silica-rich oxide formed at 800°C. For the Nicalon series of fibers, it has been shown that higher oxygen content fibers (Nicalon) have lower tensile strengths and lower moduli than their lower oxygen counterparts (Hi-Nicalon) [45, 46]. Also, when oxygen content was increased in Hi-Nicalon fibers after 1 hour exposures from 1000-1400°C, it resulted in a reduction of the tensile strength [45]. The observed oxygen solubility in the Hi-Nicalon fibers at 600°C will likely result in a decrease in fiber strength within the CMC, negatively affecting the mechanical properties. Exposure at 800°C results in a protective silica layer that protects the CMC from further oxidative attack. CMCs in service will be exposed to water vapor due to combustion and will experience mechanical stress. The effects of water vapor on SiC/BN/SiC CMC oxidation behavior at intermediate temperatures is discussed in Chapter III.

#### 2.5 Conclusions

The oxidation behavior of SiC/BN/SiC CMCs was studied via thermogravimetric analysis at 400-800°C in dry oxygen, followed by characterization via SEM/EDS and FIB. Oxidation onset

occurs at ~450°C, with a boron-rich oxidation regime occurring until 650-700°C. The 600°C exposure condition is more detrimental to the composite than 800°C as the boron-rich oxide has a higher oxygen permeability leading to deeper oxygen solubility lengths in the fibers. The silica formation observed at 800°C provided better protection to the fibers in both the isothermal and bithermal conditions. The use of FIB paired with EDS was powerful in relating the resultant surface oxides to underlying material degradation. Annular voids from BN fiber coating loss were not observed, contrary to current oxidation models.

# Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen

#### 3.1. Introduction

The addition of water vapor in the gas mixture causes an increase in oxidation rates for CMC constituents when compared to dry oxygen. Si and SiC oxidation kinetics have been shown to increase by a factor of 10 to 100 with the addition of water vapor [11, 26]. This increase in kinetics, which varies with temperature, is attributed to an increased solubility of H<sub>2</sub>O in the SiO<sub>2</sub> scale [11]. BN oxidizes to form boria, which then reacts with water vapor, forming volatile boron hydroxide species [16, 17, 47].

Oxidation in the presence of water vapor is more complex than dry oxygen, since the water vapor can react with the oxides to form volatile gaseous species, per Equations 1.9-1.11 The FactSage FactPS and SGPS databases were used to calculate gaseous boron hydroxide activities and gaseous silicon hydroxide species that form when 0.5 mol  $O_2$  and 0.5 mol  $H_2O$  react with 1 mol  $B_2O_3$  and 1 mol SiC, respectively, as a function of temperature [48]. Figure 24 shows that  $(HBO_2)_3$  and  $H_3BO_3$  have the highest activities for the gaseous boron hydroxide species at 600 and  $800^{\circ}C$ , and are the most prevalent for the present work.



Figure 24: Activities of boron and silicon hydroxide species versus temperature for 0.5 mol  $H_2O$  and 0.5 mol  $O_2$  at 1 atm. The temperature region of interest is shaded in grey.

The concentration of boria in the resultant oxide is higher at lower temperatures, as seen in *Chapter II*. As boria content in the borosilicate is increased, the silica glass network becomes more disrupted, leading to higher oxygen permeability through the oxide scale. This will result in increased oxidation of the underlying CMC substrate. The borosilicate glass is less viscous and becomes more wetting with higher boria content [25]. From *Chapter II*, it was shown that as temperature increased to 800°C, a protective silica scale formed in dry oxygen, protecting the CMC interior from further oxidative attack. The volatility of the scale in wet oxygen may lead to i) less protection of the CMC when compared to dry oxygen or ii) the preferential volatility of  $B_2O_3$  leaving a SiO<sub>2</sub>-rich scale.

The CMC degradation model by Parthasarathy et al., proposes that a surface crack provides a pathway for oxidant to travel to the interior of the composite [30]. The oxidant reacts with the BN coating, forming boria, which subsequently volatilizes, leaving an annular void where the BN coating once was. The model is focused on temperatures from 800-1200°C. Annular voids, as discussed in the Parthasarathy model, were originally observed in prior experimental work on stress-rupture tests of SiC/BN/SiC mini-composites at intermediate temperatures [15]. This model differs from recent oxidation studies of unstressed SiC/BN/SiC CMCs from 800-1200°C, in which the BN coating preferentially oxidized on the surface, forming an oxide droplet that did not volatilize and did not leave an annular void [8]. In *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen*, the BN coatings were found to remain stable in dry oxygen at temperatures between 400 and 800°C and did not volatilize or leave an annular void.

Previous testing for the unstressed RRHTC from 800-1200°C in wet oxygen resulted in borosilicate glass formation and no annular voids in the BN coating regions [8]. Fatigue tested SiC/SiC CMCs tested at 1200°C in steam displayed failure indicative of borosilicate bonding fibers together, but no comment was made if annular voids were present in the coating region [49]. Zok et al. studied stressed oxidation of a SiC/BN/SiC CMC from at 800 and 1100°C in steam; borosilicate glass was observed at the fiber coating regions, as well as some porosity [50].

42

In this chapter the oxidation mechanisms are explored for an unstressed SiC/BN/SiC CMC from 400-800°C in a 50%  $H_2O/50\%$   $O_2$  gas mixture. It was expected that water vapor reactions with the oxide would produce hydroxide species, resulting in a less protective oxide than that seen in dry oxygen. The presence or absence of annular voids due to BN loss in wet oxygen is evaluated. The oxidation mechanisms are compared to those that occurred in dry oxygen and compared to the current oxidation models for SiC/BN/SiC CMCs. Oxidation behavior is related to the underlying local microstructure, and oxygen solubilities in Hi-Nicalon SiC fibers are observed and measured.

#### 3.2 Materials and Methods

# 3.2.1 Materials

The same material and manufacturing techniques were utilized as *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen.* Refer to *2.2 Materials and Methods* for more information.

#### 3.2.2 Oxidation exposures

Thermogravimetric analysis (TGA) was used to control the environment for oxidation exposure of a sample while tracking weight change [51]. An as-machined sample was suspended using an alumina hanger, which was connected to a sensitive Setaram B SETSYS 100g microbalance (Setaram, Inc., Hillsborough, NJ) via platinum chain and NiCr wires. Weight changes were tracked during testing to interpret oxidation reactions and mechanisms. The furnace (Lab-Temp Furnace,
Thermcraft, Winston-Salem, NC) was heated to the test temperature and raised once at temperature, allowing for rapid heating of the sample and mitigating oxidation at lower temperatures.

A 50% H<sub>2</sub>O/50% O<sub>2</sub> gas mixture was used for sample exposures. A presaturator bath was held at 99°C to saturate the gas with H<sub>2</sub>O, followed by flow through a saturator bath that was held at 81.7°C to control the H<sub>2</sub>O/O<sub>2</sub> ratio, depicted in Figure 25. The gas mixture flowed upward through fused quartz tubes around the test specimen at a velocity of 4.4 cm/s (measured at room temperature). Dry O<sub>2</sub> flowed downward through the microbalance to protect the balance from H<sub>2</sub>O condensation. The 50% H<sub>2</sub>O/50% O<sub>2</sub> gas mixture and O<sub>2</sub> gas exhausted into a bubbler to ensure there were no gas leaks, and the condensed water vapor was collected to confirm H<sub>2</sub>O concentration during testing.



Figure 25: Schematic of thermogravimetric analysis (TGA) with a presaturator and saturator to inject water vapor into the environment.

Sample exposures were conducted for 1 and 50 hours at temperatures of 400, 600, and 800°C. Two to three tests were conducted at each time and temperature. Intermediate temperature exposures were performed to detect oxidation onset.

#### 3.2.3 Characterization

The same characterization techniques were utilized as *Chapter II. Oxidation of SiC/BN/SiC* ceramic matrix composites at intermediate temperatures in dry oxygen. Refer to Section 2.2 Materials and Methods for more information.

## 3.3 Results

#### *3.3.1 Oxidation onset and transition temperatures*

No oxidation was observed on samples exposed at 400°C for 1 and 50 hours. Temperatures were incrementally increased by 50°C, and oxidation onset was observed to occur at 450°C after 1 hour, with oxidation initially occurring in the matrix material where the Bcontaining phase resides. A boron-rich borosilicate was observed at 600°C after 1 and 50 hours. The oxide was silica-rich at 800°C after 1 and 50 hour exposures. At 600 and 800°C, there is an initial period of rapid weight gain, seen in Figure 26a. The rapid weight gain is attributed to B-rich phase oxidation and then the weight gain slows as the B-containing oxide seals the matrix. The specific weight gain difference between 600 and 800°C was not statistically significant. A comparison of specific weight change data for dry and wet oxygen can be found in Figure 27. The specific weight gains measured in wet oxygen are 2.8x higher at 600°C and 1.4x higher at 800°C than those measured in dry oxygen, indicating that oxidation occurs more rapidly with the addition of water vapor to the gas mixture. These increases were found to be statistically significant. Noise in the TGA signal (that was not previously seen in dry oxygen) is attributed to i) a higher gas velocity and ii) potential  $H_2O$  condensation/vaporization on the platinum chain that the alumina rod was suspended from.



Figure 26: TGA specific weight change data for SiC/BN/SiC exposed to 50%  $O_2/50\%$  H<sub>2</sub>O for 50 hours at 400, 600, and 800°C versus a) time and b) root time.



Figure 27: Comparison of TGA specific weight change vs. time for SiC/BN/SiC exposed to wet and dry oxygen for 50 hours at 600 and 800°C.

# 3.3.2 Exposures at 600°C

Oxidation preferentially occurred after 1 hour at 600°C on the perimeter of the CVI SiC as seen in the plan view surface in Figure 28. The oxide was a mixed borosilicate, with a strong boron signal measured via EDS. The oxide was wetting and did not form any droplets after 1 hour. The BN coatings were stable after 1 hour at 600°C as shown by the EDS nitrogen signal.



Figure 28: Fiber tow of SiC/BN/SiC sample exposed for 1 hour at 600°C in 50%  $H_2O/50\%$   $O_2$  gas mixture.

The oxide thickness grew after 50 hours at 600°C and droplets were observed around the perimeter of the CVI SiC and in the MI matrix, seen in Figure 29. The oxide droplets vary in size, with larger droplets present on the outer edge of the CVI SiC and smaller droplets present in the MI matrix. FIB cross-sections were completed showing that smaller droplets are solid until an unknown critical droplet radius is reached and droplets become thick-walled hollow spheres, as seen in Figure 30. Oxygen solubility in the Hi-Nicalon SiC fibers was observed and measured, listed in Table 1. The solubility length in wet oxygen is ~2x deeper for than that measured for dry oxygen exposures after 50 hours at 600°C, and ~4x deeper than after dry oxygen exposures after 50 hours at 800°C. The differences between 600 and 800°C and the differences between dry and wet oxygen were statistically significant.



Figure 29: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in 50%  $H_2O/50\%$   $O_2$  gas mixture.



Figure 30: FIB cross-section of fiber tow showing a larger, hollow droplet (left) and a smaller solid droplet (right) for a SiC/BN/SiC sample exposed for 50 hours at 600°C in 50%  $H_2O/50\%$   $O_2$  gas mixture.

Table 1: Oxygen Solubility Lengths measured in Hi-Nicalon SiC fibers after 50 hours of exposur
------------------------------------------------------------------------------------------------

Exposure Condition	Average ± Standard Deviation of	Measurements Taken
	Oxygen Solubility Length (microns)	
600°C 100% O <sub>2</sub>	6.4 ± 3.3	81
800°C 100% O <sub>2</sub>	$1.6 \pm 1.4$	47
600°C 50% H <sub>2</sub> O/50% O <sub>2</sub>	13.0 ± 4.9	59
800°C 50% H <sub>2</sub> O/50% O <sub>2</sub>	6.6 ± 4.8	89

Figure 31 shows a FIB cross-section of two SiC fibers after a 50 hour exposure at 600°C. Silicon, oxygen, and nitrogen signals are absent in the fiber coating region. The absence of these signals indicates that the fiber coating has oxidized and volatilized away, and borosilicate glass has not filled the annular void region. Beneath the annular void lies an annulus of oxidized fiber coating over the unaffected BN coating, imaged in Figure 32. Measurements of volatilization lengths and oxidized fiber coating lengths were taken from polished cross-sections from wet oxygen exposures, and are reported in Table 2. Attempts were made to measure oxidation lengths in the dry oxygen exposures; however, the oxygen signal was not strong enough in the BN coating to obtain reliable measurements in the polished cross-sections. The volatilized coating length is referred to as Ldeg in the Parthasarathy CMC degradation model [30].



Figure 31: FIB cross-section of fiber tow of SiC/BN/SiC sample exposed for 50 hours at 600°C in 50%  $H_2O/50\%$   $O_2$  gas mixture. The red arrows point to the annular void region. The lack of nitrogen signal indicates that the BN fiber coating is no longer present and the lack of oxygen signal indicates that no glass has filled in the annular void.



Figure 32: Polished cross-section of SiC fibers and CVI SiC after exposure at 600°C in 50%  $H_2O/50\%$   $O_2$  gas mixture showing a) interface between annular void and oxidized coating and b) between oxidized coating and BN coating.

Table 2: Lengths of volatilized and oxidized boron nitride fiber coatings in SiC/BN/SiC CMCs in wet oxygen after 50 hours

Exposure Condition	Volatilized length (microns	coating )	Oxidized fiber length (microns	coating )	Measurements Taken
	Average	Median	Average	Median	
600°C 50% H <sub>2</sub> O/50% O <sub>2</sub>	47.2 ± 27.1	40.0	123.2 ± 51.4	122.8	52
800°C 50% H <sub>2</sub> O/50% O <sub>2</sub>	n/a	n/a	26.1 ± 25.4	15.3	113

## 3.3.3 Exposures at 800°C

The oxide on the surface is concentrated at the perimeter of the CVI SiC after 1 hour at 800°C. The oxide is silica-rich, with little boron signal detected via EDS mapping. After 50 hours, the oxide around the edges of the CVI SiC have grown into large droplets, along with growth of oxide droplets above areas within the fiber tow, seen in Figure 33. Intratow MI regions are also oxidized, and show extensive oxidation in cross-section.



Figure 33: Fiber tow of SiC/BN/SiC sample exposed for 50 hours at 800°C in 50%  $H_2O/50\% O_2$  gas mixture.

The FIB cross-section in Figure 34 shows oxide growth over SiC fibers. On the left, a large oxide droplet covers a fiber, fiber coating location, and an intratow MI region. The fiber coating region does not display a nitrogen signal, but oxygen and silicon signals are present. Multiple fiber coatings were analyzed in plan view, and measurements were taken of fiber coating oxidation lengths, listed in Table 2. The fiber on the right side of the micrograph has a fiber coating with a ~1 micron deep pore at the fiber coating surface, but nitrogen signal is retained below. It is important to note that of the five fibers studied with FIB cross-section and 89 fibers studied in polished cross-section after 800°C/50 hour exposure, this was the only observed instance of a void near a fiber coating region at 800°C. Small oxide droplets often cover the BN coating region, imaged in Figure 35 and also seen in plan view in Figure 33. The oxide droplets typically occur on regions where two fiber coatings join and form a thicker interphase region. Lastly, in Figure 34

and Figure 35, oxygen solubility is observed in the SiC Hi-Nicalon fiber cross-section. Oxygen solubility is observed in both fibers with and without a surface oxide layer.



Figure 34: FIB cross-section of fiber tow of SiC/BN/SiC sample exposed for 50 hours at 800°C in 50%  $H_2O/50\%$   $O_2$  gas mixture. White arrow points to oxide and red arrows point to porous zones in BN fiber coating region. Note oxygen solubility in Hi-Nicalon fibers.



Figure 35: FIB cross-section of fiber tow of SiC/BN/SiC sample exposed for 50 hours at 800°C in 50%  $H_2O/50\%$   $O_2$  gas mixture. White arrow points to oxide atop of BN fiber coating. Note oxygen solubility in Hi-Nicalon fibers.

## 3.4 Discussion

#### 3.4.1 General oxidation mechanisms in wet oxygen

The main oxidation mechanisms observed in wet oxygen are:

- Preferential oxidation occurs in the MI matrix material where a B-containing phase resides.
  The oxide grows with increased exposure time and temperature. Intratow MI-rich regions with high B phase concentrations act as fast paths for oxygen ingress into the material.
- 2. Oxygen solubility is observed in the Hi-Nicalon fibers, with longer solubility lengths measured at 600°C than 800°C. Oxygen solubility lengths are deeper for fibers exposed to wet oxygen.
- 3. BN fiber coatings oxidize and volatilize, leaving an annular void at 600°C. At 800°C, the coatings oxidize and the subsequent borosilicate glass remains. Annular voids are not observed after 800°C exposures.

#### 3.4.2 Oxide wetting

The oxide wetting properties are affected by temperature, time, and environment. At 600°C in dry oxygen, the borosilicate glass wets the surface after 1 hour, and then phase separates into boron and silicon-rich phases after 50 hours. In wet oxygen at 600°C, the borosilicate also wets the surface after 1 hour, but after 50 hours the oxide is non-wetting and large droplets form. No phase separation is observed in wet oxygen. With the addition of H<sub>2</sub>O to the gas mixture, boron hydroxide species will form, resulting in a more silica-rich borosilicate glass. The thick-walled hollow droplets seen in the FIB cross-sections are also indicative of gas formation.

decrease in boria content in the glass results in a more viscous oxide, resulting in the large oxide droplets seen after 50 hours in wet oxygen at 600°C.

Silica-rich glass wets the CMC surface after 1 hour and 50 hours at 800°C in dry oxygen. In wet oxygen at 800°C, the oxide is non-wetting after 1 hour, and droplets grow after 50 hours. Boria is depleted from the glass at 800°C in both dry and wet oxygen and does not appear strongly in the EDS map signals. The addition of water vapor to the gas mixture resulted in dewetting of the oxide, indicating an increase in the glass viscosity. Reactions 3.5-3.8 and Figure 24 show that water vapor reactions result in preferential volatility of B2O3 from the oxide scale. The thermodynamically predicted Si(OH)<sub>4</sub> activity is low compared to the boron hydroxide species. As a result, the boron content may be depleted from the oxide, resulting in a silicon-rich oxide with higher viscosity. Viscosities for borosilicate glasses can be seen in Figure 11. However, depleted boron content of the oxide formed at 800°C was observed in both dry and wet oxygen. The rate of boron depletion is likely occurring more rapidly in wet oxygen than dry oxygen, possibly altering the wetting properties of the glass. Oxidation studies between 1 and 50 hours paired with quantitative compositional analysis of the oxide should be completed to understand the evolution of boron content in the glass. It has also been shown that the addition of  $H_2O$  in a silicate reduces viscosity [52]. It is unlikely that the H<sub>2</sub>O content in the oxide itself is affecting the wetting properties since 1) the viscosity is likely increased evidenced by droplet formation in wet oxygen and 2) pressures much greater than the 1atm TGA environment are required to achieve sufficient H<sub>2</sub>O content in the glass to affect the viscosity [52-54]. Quantitative compositional analysis, such as a surface-sensitive technique like X-ray photoelectron spectroscopy, should be conducted to

55

understand the oxide composition through the thickness of the scale. This compositional analysis through the thickness may provide more insight on the wetting properties of the oxide.

A wetting glass that is silicon-rich is more desirable for protection of the CMC. In the cases of dry oxygen, at 800°C, the silicon-rich glass formed at 800°C resulted in minimal oxygen solubility in the SiC fibers after 50 hours. For wet oxygen exposures, the oxides after 50 hours were concentrated at the perimeter of the CVI SiC in large droplets, and did not wet across the fiber tow or close off any surface porosity. This resulted in oxygen solubility in the fibers at both 600 and 800°C. Furthermore, in actual engine applications, stresses can cause micro-cracking in a CMC component. Cracks filling with oxide can mitigate further oxidative attack of the interior of the composite. A more wetting, less viscous oxide will be able to better fill cracks than a more viscous oxide. The effect of micro-cracking on oxidation and oxide filling cracks in dry and wet environments is explored in *Chapters V-VII*.

## *3.4.3 Oxygen solubility in fibers*

Oxygen solubility was observed in fibers exposed at 600°C in dry oxygen for both those fibers covered with a boron-rich oxide and uncovered fibers. Boria was depleted from the glass at 800°C in dry oxygen, and the silica rich glass provided protection to the fibers, which had minimal oxygen solubility lengths. However, at 800°C in wet oxygen, oxygen solubility in fibers was observed, but the oxygen solubility lengths were 0.5x the solubility length of the 600°C condition.

56

The increased oxygen solubility length of the SiC fibers in wet oxygen can be attributed to two factors. First, the oxide is concentrated around the perimeter of the CVI SiC and does not wet the surface as seen for specimens exposed in dry oxygen. Therefore, the lack of a protective scale local to the fibers results in increased oxygen dissolution in the SiC fibers. Second, for areas that do have an oxide present, the permeation of H<sub>2</sub>O through a silica scale is 10-100x higher than that of O<sub>2</sub> [11], which will also result in an increase in the oxygen solubility length for fibers with a local surface oxide. Oxygen solubility lengths are higher for 600°C due to smaller oxide droplets that do not cover and protect fibers as well as the 800°C oxide.

#### 3.4.4 Comparison to oxidation models

A surface crack allows for oxidant to travel to the interior of the composite in the Parthasarathy CMC oxidation model [30]. Oxidant then oxidizes the BN coating to boria, which then volatilizes, leaving an annular void where the fiber coating once existed. In dry oxygen no annular voids were observed. BN coatings remained intact, but oxygen was present in the fiber coating after TGA exposure in dry oxygen, seen via SEM/EDS investigations of FIB cross-sections. BN fiber coating behavior varied in wet oxygen at 600 and 800°C. Fiber coatings oxidized and volatilized away, leaving annular voids at 600°C. At 800°C, fiber coatings oxidized without evidence of volatilization. A comparison of the behavior at the two temperatures is found in Figure 36. The only porosity observed at 800°C, imaged in Figure 34, may be attributed to transport of volatile gaseous species (N<sub>2</sub>, CO, H<sub>2</sub>) through the high viscosity silica-rich glass.





Figure 36: Summary of oxidation behavior of SiC/BN/SiC CMCs at 600 and 800°C after a 50 hour exposure in a 50%  $H_2O/50\%$   $O_2$  gas mixture. BN fiber coatings oxidize and volatilize at 600°C, which then leads to further oxidation of the BN coating. BN fiber coatings oxidize and remain at 800°C.

The CMC degradation model put forth by Parthasarathy et al. [30] expands upon a previous model [17] based on experimental work completed on SiC/BN/SiC mini-composites in 1997 [32]. Stress-rupture testing was conducted from 700-1200°C, and annular voids around the fiber coatings were only observed in regions of the mini-composite that were below 950°C. The CMC degradation model [30] extends these findings to temperatures ranging from 800-1200°C. Annular voids are present in the SiC/BN/SiC CMC in this study at 600°C in wet  $O_2$ . However, annular voids are not present in this study at 800°C or at 1000-1200°C for the SiC/BN/SiC CMC in a prior study [8]. Another recent study on a different class of SiC/BN/SiC CMCs (HiPerComp<sup>TM</sup>) also shows that the BN fiber coatings oxidize and remain at 1200-1285°C [34].

Another notable difference between the results at 600°C in the present work and the CMC degradation model are the depictions of the volatility length and the underlying oxidized coating

length. The volatility length (also referred to as the fiber coating degradation length) is depicted as being much longer than a silica plug that subsequently forms over the BN coating in the CMC degradation model. The silica plug is thought to protect the BN coating from further oxidative attack. In the present work, the oxidized coating length is longer than the volatility length in 47 of 52 measurements. A protective silica plug does not form over the BN coating resulting in coating oxidation lengths of up to ~250 microns after 50 hours in wet oxygen at 600°C. These large lengths of annular oxide suggest fast transport paths of oxidant to the underlying BN fiber coating, likely at the oxide-SiC interface.

While the CMC degradation model is applied to higher temperatures (800-1200°C), it may more accurately describe behavior in the intermediate temperature regime (~450-700°C) in wet O<sub>2</sub> only for modern CMCs. From 450-700°C, boria-rich oxides dominate, and volatility of the glass is faster due to boron hydroxide species volatilizing, resulting in annular voids around the SiC fibers. Differences from the past and present work may be due to the use of mini-composites instead of full-scale CMCs. Mini-composites may be unrepresentative to use for modeling the oxidation behavior of full-scale CMCs as they lack the MI matrix material, in which the silicon and B-containing phase in this work preferentially oxidized. Also, the previous experimental work was conducted on stressed material where micro-cracks provide access for oxidant to attack the BN fiber coatings. The effect of micro-cracking on the oxidation behavior of the Rolls-Royce SiC/BN/SiC CMC in lab air, dry oxygen, and wet oxygen is evaluated in *Chapter V-VII*, with specific focus on the presence or non-presence of annular voids and micro-crack sealing.

#### 3.4.5 Implications on CMCs in service

SiC/BN/SiC CMCs will oxidize at 600 and 800°C in a combustion environment containing water vapor. In the presence of water vapor, the oxides are non-wetting and provide little protection for the underlying material. Oxygen solubility in the Hi-Nicalon fibers will occur, resulting in reduced tensile strengths of the fibers [45]. Notably, the BN coatings will oxidize to boria and volatilize at 600°C, leaving an annular void between fibers and the CVI SiC. The lack of a mechanically weak BN fiber coating results in a loss of toughness for the CMC. At both 600 and 800°C, oxidation of the fiber coatings was observed. The oxide bonds neighboring fibers together, again weakening the composite material by inhibiting fiber sliding. Oxidative attack on the CMC in service can be mitigated by the use of environmental barrier coatings (EBCs); however, EBCs may spall off due to thermal cycling and coefficient of thermal expansion mismatch between the CMC and EBC. CMCs, and their EBCs, can crack due to mechanical stresses experienced in service.

## **3.5 Conclusions**

Oxidation mechanisms for an unstressed SiC/BN/SiC CMC were elucidated for isothermal exposures in a 50% H<sub>2</sub>O/50% O<sub>2</sub> gas mixture and compared to results obtained in dry oxygen at 400-800°C. Measurements of oxygen solubility in the SiC fibers, fiber coating oxidation lengths, and annular void lengths were taken to understand behavior under different environments. Several key takeaways from the work are as follows:

- The addition of water vapor in the gas mixture results in a more degradation for the CMC.
  Water vapor exposures result in material loss (in the form of BN coatings) and in nonwetting oxide droplet formation on the surface.
- Annular voids in the fiber coating region were only observed at 600°C in wet O<sub>2</sub> for the Rolls-Royce SiC/BN/SiC CMC. This differs from phenomena described in the CMC oxidation models where annular voids are modeled at temperatures greater than 800°C.
- Oxygen solubility was observed in the Hi-Nicalon SiC fibers at intermediate temperatures.
  This behavior could prove to be deleterious for CMC mechanical properties. *Chapters V-VII* CMC mechanical behavior while under oxidative attack.
- 4. A wetting, silica-rich external scale mitigates oxidative attack of the underlying CMC. Oxygen solubility lengths in the SiC fiber and fiber coating oxidation lengths were shorter with the protective scale. It was shown that a pre-formed scale at 800°C protects the CMC during subsequent lower temperature exposures in dry oxygen.

# Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage

## 4.1 Introduction

## 4.1.1 CMC mechanical behavior

The addition of ceramic fibers to a ceramic matrix material result in a tougher material than standard monolithic ceramics. CMCs exhibit bilinear stress-strain behavior, as depicted in Figure 8. The CMC displays linear elastic behavior during the initial period of loading, in which the matrix and fibers share the applied load. The load is distributed across the different microconstituents via a rule of mixtures according to the volume fraction and strength of the constituents within the material, where  $\sigma_f$  and  $\sigma_m$  are the stress experienced by the fibers and matrix respectively, and  $v_f$  and  $v_m$  are the volume fractions of the fibers and matrix:

$$\sigma_{total} = \sigma_f v_f + \sigma_m v_m \tag{Eq. 4.1}$$

The applied load will increase to a point where the weaker matrix material will crack, called the matrix cracking stress,  $\sigma_{MC}$ . On a micro-scale level, there are variations in the local loading due to fiber architecture, local fiber content, or defects (pores). Matrix cracks will initiate in areas where the local stress is at  $\sigma_{MC}$ . The stress is relieved at the crack plane, and the local stress on the matrix increases as one moves away from the crack plane, as depicted in Figure 37. Fibers in the

immediate area of the matrix crack plane will predominately carry the load in that local region. As the applied load is increased, new matrix cracks will form, and the crack opening displacement (COD) of existing cracks will increase.



Figure 37: A crack in the matrix material relieves the stress on the matrix at the crack plane, and the far-field stress increases away from the crack until a new crack is formed. Graphic reproduced from LaRochelle [55]. u is the crack opening displacement,  $\delta/2$  is the stress transfer length,  $\sigma_{MC}$  is the matrix cracking stress, and  $\sigma_{f,c}$  is the stress on the fiber in the crack opening.

New matrix cracks will continue to initiate and propagate through the material as applied load increases. Failure of the weakest fibers or those with higher local loads may also occur. The matrix eventually saturates with cracks, and the cracks will be so close together that load can no longer be shed to the matrix. Several mechanisms occur during loading that increase fracture toughness, including crack deflection and bridging. The SiC fibers will carry the entirety of the applied load, until enough fibers fail that the CMC ruptures. Matrix crack CODs are directly implemented into CMC oxidation degradation models, as oxidant diffusion is dependent upon the COD width. The COD widths obtained in this chapter are used for degradation modeling in *Chapter VIII. CMC Degradation Modeling*. The spacing between the micro-cracks is important as 1) a reduced crack spacing means more pathways for oxidant ingress and 2) this parameter is used in mechanical modeling to predict mechanical properties; for example stress profiles for the SiC fibers, fiber debond length, and shear lag distance [56-58]. The micro-crack spacing measurements will not be directly used in modeling for this dissertation.

#### 4.1.2 Micro-scale testing of SiC/SiC CMCs

Matrix crack spacing and CODs have been observed with in-situ micro-scale testing, utilizing tensile stages with optical and scanning electron microscopy and X-ray computed tomography (CT). Previous work has been completed with woven CMCs, unidirectional CMCs, and CMC mini-composites [57, 59-61]. Sevener et al. tested SiC/BN/SiC woven CMCs using a tensile stage inside of an SEM at room temperature, imaging edges with exposed fibers [59]. Stress fields were imaged at cracking events using digital image correlation (DIC) and matrix cracks resulted in a reduction of far-field stresses (approximately a few hundred microns away) [59]. Digital extensometers were also used to measure CODs, and it was observed that CODs increase linearly with applied stress [62]. SiC/BN/SiC mini-composites (a single fiber tow with a BN coating and CVI SiC overcoat) were studied with a tensile stage inside of an SEM with acoustic emission (AE) sensors attached to the sample [60]. Micro-cracks, detected by AE, were observed before the proportional limit, and were the result of pre-existing surface flaws on the mini-composite [60].

Hilmas et al. utilized synchrotron X-ray CT to observe internal micro-cracking behavior in a unidirectional SiC/BN/SiC CMC during tensile loading [57]. It was observed that internal cracking is often torturous, with cracks often bifurcating and merging as crack spacing decreases. Internal crack density ranged from 1.0 to 3.5 cracks/mm and the crack spacing for two different samples prior to failure was 210 and 430  $\mu$ m [57]. It was also noted that fiber breaks only occurred after the onset of matrix cracking.

There are several advantages of using a tensile stage inside of an SEM. First, the use of SEM imaging allows for high-resolution images for accurate COD measurements. Heating systems can also be used inside of the SEM to observe COD at elevated temperatures with no oxidative effects. However, experimentation in the SEM requires a significant amount of time for setup and imaging, and some data can be missed because of time restrictions on the equipment. These issues can be resolved by using the tensile stage with a light microscope, allowing for faster data acquisition and the ability to image large areas to interrogate the entire surface microstructure, however with lower resolution. The current study will implement light microscopy and SEM to obtain different measurements. Crack spacing and crack composition (explained below) were measured on light microscopy images. CODs at room and elevated temperature were measured from SEM images due to their high resolution. The paired use of SEM and light microscopy allow for a deeper understanding of micro-cracking behavior in SiC/BN/SiC CMCs.

#### 4.1.3 Objective II Knowledge Gaps

Previous work has been completed on micro-cracking behavior in SiC/BN/SiC CMCs at room temperature with in-situ tensile stages in a scanning electron microscope and an x-ray computed tomography machine [57, 62]. CODs and crack spacings have been measured for some SiC/BN/SiC CMCs; however, CODs have not been measured at elevated temperature and the crack spacing is dependent on many factors, including but not limited to fiber architecture and constituent volume fraction, which differ between different CMCs. Accurate COD measurements for the RRHTC CMC were determine and used for CMC degradation modeling in *Chapter VIII. CMC Degradation Modeling*. Also, previous studies have not correlated the local microstructure to micro-cracks, called the "crack composition" in this work. Different microstructural features, such as the BN coatings and B-rich phase, have a higher propensity for oxidation than the SiC phases, as previously seen in the TGA work. The proximity of these phases to a micro-crack will result in different oxide filling behavior on the surface of the composite. Oxide filling in the micro-cracks will mitigate oxidant attack into the CMC interior, and the local effects of microstructure should be considered in CMC oxidation modeling.

#### 4.1.4 Objective II Research Questions

This chapter focuses on the micro-cracking behavior of a SiC/BN/SiC CMC at room and elevated temperature. Micro-crack spacing/density was measured at room temperature using a tensile stage with light microscopy. It was anticipated that the crack spacing would decrease with increased stress. CODs were measured at room and elevated temperature with a tensile stage and scanning electron microscopy. It was unclear if COD would increase at elevated temperature 66

due to a relief in compressive residual stress from the MI silicon or if the COD would decrease due to thermal expansion of the material.

This following research questions are explored and discussed in this chapter:

- 1. What is the local microstructure in contact with the micro-crack? How does the distribution for this microstructure change with applied load?
- 2. What is the relationship between applied load and micro-crack spacing?
- 3. How do local micro-constituents affect COD?
- 4. How does the COD change with applied load?
- 5. What is the effect of increased temperature on the COD?

## 4.2 Materials and Methods

## 4.2.1 Materials

A SiC/BN/SiC CMC panel layed up in a 5HSW was provided by Rolls-Royce HTC. Samples were sectioned with a diamond wafering blade to a thickness of approximately 1.5mm. The samples were then mounted in epoxy and polished to a 0.25µm finish. The sample was removed from the epoxy, and final dimensions were 32mm X~4.5mm X~1mm. The sample was rectangular in shape as required for the grips used for the tensile stage. Aluminum tabs were adhered to the sample with epoxy (Loctite EA 9394 AERO Epoxy Adhesive) to accommodate gripping and to reduce the potential for breaking in the grips. Tabs were 8mm in length, leaving approximately a 16mm length of the specimen surface exposed to be imaged. The tabs could not be used for

elevated temperature exposures, and instead the surfaces to be gripped were roughened with 15µm polishing film.

# 4.2.2 Micro-tensile stage loading

Testing was completed at the Materials & Manufacturing Directorate at the Air Force Research Laboratory. A micro-tensile stage made by Ernest F. Fullam, Inc. was used for both optical and scanning electron microscopy, and is shown in Figure 38. The stage was equipped with a 5kN load cell. MTestW software was used to write and control the loading programs.



Figure 38: Tensile stage used to study micro-cracking in SiC/BN/SiC CMCs.

Samples were gripped with sawtooth edged grip inserts that were clamped with screws. The tensile program was started prior to gripping in order to maintain a load of 0 newtons during gripping. Once the sample was gripped, an image was taken of the sample prior to loading, followed by the subsequent loading procedure. Loading profiles for experiments with the light microscope and SEM were similar in nature, with a ramp to a specified load followed by a hold period where images were acquired, depicted in the graphic in Figure 39. Due to limitations in the amount of data the software could acquire, there was a limit of nine loading steps.



Figure 39: Loading and imaging profile for experiments conducted with tensile stage.

It was observed that cracks occurred at higher loads than expected during previous work completed with the tensile stage [63]. Previous unpublished work has shown that strain gaged specimens tested with the tensile stage were more compressive on the top surface than the bottom surface [63]. For this reason, strain gages were applied to the top and bottom of two CMC specimens. The specimens were loaded into the tensile stage using the standard loading procedure, and the loading profile in Figure 40 was employed, with each load hold lasting approximately five minutes. The specimen slipped at 275 MPa.



Figure 40: Stress (MPa) vs. Time (s) profile for strain gaged test specimen. Specimen was held at the desired load for approximately five minutes.

The strain data from the bottom (blue) and top (orange) strain gages is shown in Figure 41. The bottom surface remains in tension the entire test, where the top surface starts in compression and then switched to tension when the load reached 99 MPa. The strain stayed nearly constant for the bottom surface during load holds, but a slight increase is observed in the strain response for the top surface during load holds. The overall differences between the top and bottom strains was greatest when the top was in compression at 75 MPa, and then decreased as the top went into tension. A second strain gaged specimen was run to confirm the results, and the same phenomena occurred, with the top going from compression to tension at 118 MPa.



Figure 41: Strain (mm/mm) vs. Time (s) for bottom (blue) and top (orange) strain gages on CMC in tensile stage. Specimen was held at each load for approximately five minutes.

Sevener et al. noted that load relaxation occurred after each load hold, and waited for relaxation to occur prior to imaging [59]. Figure 42 shows a region in the CMC from the current study that was imaged immediately after the system reached 225 MPa and then reimaged after five minutes at load. Matrix cracks initiated during those five minutes. Therefore, for both the light microscope and SEM experiments, the sample was held at load for five minutes prior to imaging to allow relaxation to occur and damage to occur.

#### Imaged immediately

## Imaged 5 minutes after



Figure 42: SEM image of SiC/BN/SiC immediately and 5 minutes after load of 225 MPa was reached. Red arrows point out cracks that appeared after relaxation period.

#### *4.2.3 Micro-scale testing with light microscope*

A Zeiss Imager.M2m optical microscope with Zen 2.3 software was used to image the sample. A 20x lens with 2.5x Optovar modifier was used with the 10x eyepiece for an overall magnification of 500x per tile. Thousands of tile images were taken at each load level that were stitched together a montage image of approximately 14mm x 4.5mm. The montage took approximately 40 minutes to acquire.

Photoshop was used to analyze the stitched images. Cracks were marked using the paint brush tool, and were marked according to the constituent they were in contact with. This allowed for a measurement named the "crack composition" to be taken. Crack composition is a novel measurement quantifying the fraction of a crack running through each phase. To the author's knowledge, this measurement has never been taken before on any composite material. For example, in Figure 43, the crack is highlighted as running through MI matrix, CVI SiC, and fiber coating. Once the location of the crack is marked, the percentage of each phase that the crack runs through is calculated.



Figure 43: Example of markings to analyze crack composition. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating.

The spacing between micro-cracks was also measured. It is difficult to determine crack spacing because cracks deflect around fiber tows and travel beneath the visible surface. Therefore, a lineal intercept method was used to determine crack spacing. Sixteen horizonal lines (one for each ply) were spaced evenly along the image perpendicular to the load direction and crack spacing was measured where cracks intersected the line. Micro-crack spacing at each load was averaged for all sixteen lines. This method is visualized in Figure 44.



Figure 44: Lineal intercept method used to calculate crack spacing in SiC/BN/SiC CMCs while under load. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating.

# 4.2.4 Micro-scale testing with scanning electron microscopy

Room and elevated temperature testing were conducted inside a Quanta 650 SEM to measure COD. Specimen heating was performed with a button heater outfitted for the tensile stage. Figure 45 shows the tensile stage inside of the SEM with the heater equipped. The button heater was a resistive heating setup in which temperature was user-controlled with voltage and current output from a power supply. Calibrations were completed with thermocouples prior to experimentation to validate the temperature of the heater. Liquid cooling for extremities of the stage was supplied via an external cooling unit. It was difficult to achieve a successful test at elevated temperature as specimen tabs did not work with the heating setup. Only one successful test was achieved at 600°C.



Figure 45: Tensile stage inside of SEM with CMC specimen and button heater.

Specimens were loaded to desired loads and when a crack was observed, images were taken at 1000x. Room temperature images were taken in both backscatter and secondary modes. The backscatter detector was removed for elevated temperature exposures. A crack and its propagation path were measured throughout the entirety of the loading profile. Care was taken to image in the exact same location after each loading step so COD measurements vs. stress would be accurate. ImageJ was used to place ten lines on the image, and measurements were taken when a line intersected the crack. The COD measurement was taken such that the crack edges were parallel to one another.

## 4.3 Results

## 4.3.1 Micro-crack spacings at room temperature

Stitched images in Figure 46 and Figure 47 show marked micro-cracks and their masks, respectively, at increasing load levels. Images of all load levels and masks of the crack markings by themselves can be found in the *Appendix* in Figure 141-Figure 146. The average micro-crack spacings for all sixteen lines studied are in Figure 48, and measurements for select lines are charted in Figure 49 (all lines are charted in Figure 147 in the *Appendix*). The error bars in Figure 48 are one standard deviation. The standard deviation of the crack spacings is higher at low loads as there are fewer micro-cracks. As stress increases, cracking becomes more homogenous across the surface, resulting in the standard deviation reducing for each subsequent load. Micro-crack spacing was independent of the line location, with no difference observed near the edge of the CMC or in the middle of the CMC.



Figure 46: Light optical images of a SiC/BN/SiC CMC tested at room temperature with tensile stage at 175, 225, 275 and 325 MPa. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating. Loading direction is horizontal.



Figure 47: Masks of cracks marked on a SiC/BN/SiC CMC tested at room temperature with tensile stage at 175, 225, 275 and 325 MPa. Red lines represent cracks in the MI Si-SiC matrix, blue lines represent cracks in the CVI SiC, and green lines represent cracks in the BN fiber coating. Loading direction is horizontal.



Figure 48: Micro-crack spacing vs. applied stress for a SiC/BN/SiC CMC tested at room temperature. Error bars are standard deviations.



Figure 49: Micro-crack spacing for each line measured vs. applied stress for SiC/BN/SiC CMC tested at room temperature with tensile stage.
#### 4.3.2 Micro-crack composition at room temperature

Measurements of micro-crack composition were taken on the same set of images that crack spacings were taken from. Micro-cracks that propagated through the MI matrix were marked in red, CVI SiC in blue, and fiber coatings in green, as seen in Figure 43. The micro-cracking composition vs. applied stress is plotted in Figure 50. Cracking through the BN fiber coating was predominant at higher loads, followed by cracks in the MI matrix and in the CVI SiC. The CVI SiC composition at low loads is attributed to CVI that cracked in the transverse fiber tows and the slight increase in CVI SiC composition at higher loads is due to new cracking that occurred around the longitudinal fiber tows.



Figure 50: Micro-crack composition vs. applied stress for a SiC/BN/SiC CMC tested at room temperature. Measurements made from light microscopy images.

## *4.3.3 Crack opening displacements at room temperature*

The tensile stage was used inside of the SEM to obtain COD measurements. Measurements were taken when cracks were first visible, and at room temperature the first observed surface cracking occurred at 200 MPa. An example of the obtained images can be seen in Figure 51. Figure 51 initially shows two cracks, 3 and 4, with 3 being connected to a pore and 4 propagating into a transverse fiber tow. Their CODs are equivalent at 200 MPa. Crack 4 then propagates towards the pore at 225 MPa, resulting in near closure of crack 3. The COD of crack 4 continues to increase with load and the COD of crack 3 does not increase appreciably until 300 MPa.



300 MPa 325 MPa 350 MPa Figure 51: Backscatter SEM images of micro-cracks 3 and 4 at increasing stress levels. Loading direction is horizontal.

COD measurements vs. load are separated between those in the MI matrix material in Figure 52 and CODs in transverse fiber tows in Figure 53. CODs in the matrix and in the transverse fiber tows are close in value. Initial CODs range from 0.25 to  $1\mu$ m wide at 200 MPa, and increase to as high as 3.2 microns wide at 350 MPa. CODs typically increase with increased applied load, with crack 3 being an exception due to the interactions with crack 4 nearby. Cracks that have a high COD at the initial measurement tend to be the cracks with the highest CODs at the final measurement.



Figure 52: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC loaded at room temperature in SEM



Figure 53: Crack opening displacements in transverse fiber tow vs. applied stress in SiC/BN/SiC CMC loaded at room temperature in SEM

One micro-crack (crack 12) was observed that interacted with transverse fiber tows, matrix material, and longitudinal fiber tows for the majority of the test. COD measurement data is found in Figure 54 and SEM images are in Figure 55. The COD increases further away from the load-bearing longitudinal fiber tows. One longitudinal fiber broke at 225 MPa, and all five of the fibers imaged on the left side of Figure 55 at 350 MPa. CODs in the transverse fiber tow are some of the highest measured with a maximum of 3  $\mu$ m. Interestingly, this transverse fiber tow is right next to a porous region, resulting in a lack of additional strength (and compressive residual stresses from the MI silicon) that may be provided if there were MI matrix material there.



Figure 54: Crack opening displacement vs. the distance from the longitudinal fiber tow for crack 12 in a SiC/BN/SiC CMC. Crack 12 can be seen in Figure 55.





Figure 55: Stitched SEM micrographs of micro-crack 12 tested at room temperature. The COD increases with increased distance from the longitudinal, load-bearing fiber tow. Loading direction is vertical. Material is a SiC/BN/SiC CMC.

Another phenomenon observed is inside debonding between the BN fiber coating and the SiC fiber. Figure 56 shows a crack propagating through a transverse fiber tow. The BN coating debonded from the fiber and adhered to the CVI SiC. Inside debonding was observed for all cracks in the transverse fiber tows.



Figure 56: Backscatter SEM image of crack propagating through transverse fiber tow in SiC/BN/SiC CMC tested at room temperature. Red arrows indicate the BN fiber coating. Inside debonding is observed, where the debond occurs between the fiber and the BN coating.

# *4.3.4 Crack opening displacements at elevated temperature*

COD measurements were also taken at 600°C. Example of images taken for the COD measurements are shown in Figure 57, and COD measurements vs. stress in matrix material and transverse fiber tows are charted in Figure 58 and Figure 59, respectively. Multiple images of the same crack were taken, and the cracks are grouped by letter, and in the order they were taken in. For instance, Crack F1 and Crack F2 are the same crack but a different region of that crack. Cracks displayed in Figure 58 show representative cracks of each grouping, and all of the cracks can be seen in Figure 148 in the Appendix. COD typically increases with applied stress in both the matrix

and fiber tows, as was seen in the room temperature results. CODs in the matrix and transverse fiber tows were also close in width, barring a few cracks in the matrix with higher CODs than others.



275 MPa300 MPa325 MPa350 MPaFigure 57: Secondary SEM images of micro-crack B2 in a SiC/BN/SiC CMC at increasing stress levels.Loading direction is horizontal.Testing temperature is 600°C.



Figure 58: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC loaded at 600°C in SEM



Figure 59: Crack opening displacements in transverse fiber tow vs. applied stress in SiC/BN/SiC CMC loaded at 600°C in SEM

Cracks F1 and F2 are imaged in Figure 60. Crack F1 was first observed at 200 MPa and the COD was constant until it increased at 275 MPa. At 300 MPa, Crack F2 initiated and resulted in the COD width reducing in the upper region of Crack F1 that was in-plane with the new Crack F2. The lower portion of Crack F1 that did not have a nearby crack in the same plane continued to increase in width as load was increased. Crack F2 also increased with applied load, while the upper portion of Crack F1 did not change with increased load at 300 MPa and above.



325 MPa

350 MPa

Figure 60: Secondary SEM images of matrix micro-cracks F1 and F2 at 275, 300, 325 and 350 MPa. Zoomed in red box is the same region for each loading step. The SiC/BN/SiC CMC sample was tested at 600°C. Loading direction is horizontal.

# 4.4 Discussion

# 4.4.1 General micro-cracking behavior

The paired use of light microscopy for large-scale measurement of micro-crack spacing and SEM for detailed crack opening displacement measurements highlighted two micro-cracking regimes. In the first regime, from stress values 175 MPa to 250 MPa, the micro-crack spacing decreases 82%, from 3.9mm to 0.7mm. The CODs, at both room temperature and 600°C have variations in behavior; in general, the COD in the MI matrix and in the transverse fiber tows increases from 175 MPa to 250 MPa, but there are instances where the COD decreases. The COD

decreases are due to interactions of stress fields from other nearby cracks, where new cracks propagate next to existing cracks and result in COD reduction of the pre-existing crack. The crack composition is primarily composed of cracking in the transverse fiber tows at the BN coating/fiber interface, followed by the MI matrix and CVI SiC in the transverse fiber tows.

The saturation of micro-cracking transitions the CMC micro-cracking behavior into a second regime. The micro-crack spacing only decreases an additional 8% from 3.9mm between 250-325 MPa. While the overall fiber coating and MI matrix crack content still increased at higher loads, the CVI SiC composition increased the most in this regime. This is attributed to cracking that occurred in the CVI SiC near or in the longitudinal, load-bearing fiber tows. The average CODs increase nearly linearly in this regime (250-325 MPa) to their maxima.

# 4.4.2 Micro-crack spacing

The surface micro-crack spacing (0.4-3.9mm) converts to a crack density of 0.25-2.5 cracks/mm, seen in Figure 61a. This is in good agreement with previous studies with crack densities of 1.0-3.5 cracks/mm for a X-ray CT tested unidirectional SiC/BN/SiC CMC [57] and 0.5-4.5 cracks/mm for load frame tested unidirectional and cross-ply SiC/BN/SiC CMCs [64]. However, this is not in good agreement with another 5HSW SiC/BN/SiC CMC, which had crack densities of up to 10 cracks/mm [65], shown in Figure 61b [66]. The crack density varies greatly between different CMCs, and should be measured for each individual system when relevant for damage modeling.



Figure 61: a) Crack density vs. applied stress for SiC/BN/SiC CMC tested at room temperature with tensile stage in this work and b) Crack density vs. applied stress for a different 5HSW SiC/BN/SiC CMC (stress values studied in this work shaded in grey), reproduced from Gowayed et al. [66].

# 4.4.2 Micro-cracking interactions with microstructure and other cracks

COD is variable in SiC/BN/SiC CMCs due to multiple factors. The geometry of the woven architecture may influence the cracking behavior [66]. Different micro-constituents in the composite will have different cracking behavior. For example, the transverse fiber tows had the highest amount of cracking due to delamination of the weak fiber-fiber coating interface. Observations with DIC show strain localizations occurring in these transverse fiber regions at lower loads [62]. It was also seen in this work that closer proximity to longitudinal fiber tows resulted in lower COD in those regions. Longitudinal fiber tows bridging the micro-crack carry load in these local regions, reducing the COD.

Another effect not studied here is the potential effect of excess silicon in the matrix material. During processing, some regions do not fill with SiC particulate, resulting in areas with large amounts of MI silicon. Silicon in the matrix results in compressive residual stresses at room temperature as silicon expands upon solidification [67-69], and these compressive residual

stresses will attenuate cracking in these regions. Future work could be completed on relating local regions of silicon in the matrix to cracking behavior.

CODs are also dependent on other micro-cracks in the region. As seen in Figure 51 and Figure 60, CODs decreased for a pre-existing crack when a nearby crack propagated in the same plane as the existing crack. This effect was also seen by Sevener et al., where a nearby matrix crack resulted in a reduction of the far-field strains [59].

#### 4.4.3 Effect of temperature

CODs were wider at room temperature than at 600°C. This can be attributed to two potential factors. First, thermal expansion of the CMC constituents will result in a smaller COD, which has been seen in modeling and experimental work of C/SiC CMCs [70]. Second, the matrix crack density is unknown for the elevated temperature exposures. If the matrix crack density increases at elevated temperature, it may result in a reduced COD for cracks across the CMC surface. Future work should be completed on measuring crack spacing/density at elevated temperatures.

#### 4.4.4 Implications for CMC oxidation modeling

CMC oxidation modeling assumes a matrix crack that allows oxidant to interact with a fiber tow beneath the CMC surface. However, it is seen in this work that a large portion of microcracking occurs in the transverse fiber tows, through the BN coating regions and in the CVI SiC. Micro-cracks that occur in this region with a high amount of B-containing phase will oxidize differently from micro-cracks that are in the MI-matrix, as seen in results for Objective III. Oxidation behavior at the crack opening on the surface will influence the oxidant transport into the depth of the material. Considerations for local oxidation behavior based on crack composition should be considered in modeling.

This is the first study to investigate elevated temperature CODs for SiC/BN/SiC CMCs to the author's knowledge. Previous modeling efforts assume a COD; for example, the Parthasarathy model assumes a COD of 1 and 10 $\mu$ m for their case studies [30]. While COD may vary across different SiC/BN/SiC CMCs, it is seen here that for the RRTHC a maximum value of about 2 $\mu$ m should be used for elevated temperature modeling. CODs measured at 600°C can be implemented into oxidation modeling for different load levels, as done in *Chapter VIII. CMC Degradation Modeling*.

## 4.5 Conclusions

The paired use of light and scanning electron microscopy techniques were powerful in obtaining crack spacing and crack opening displacement measurements for SiC/BN/SiC ceramic matrix composites. Micro-crack spacings of 0.4-3.9mm (crack density of 0.25-2.5 cracks/mm) were measured at room temperature. CODs of up to  $3.2\mu$ m in room temperature and up to  $1.9\mu$ m were measured at 600°C at 350 MPa were measured. It was observed that local microstructural features, such as longitudinal fiber tows, affected the COD. Nearby micro-crack interactions resulted in COD decreases, but COD generally increased with applied stress.

# Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air

## 5.1 Introduction

Prior experimental work on the SiC/BN/SiC CMC studied in this work was completed to understand unstressed oxidation behavior. In dry oxygen, a non-protective boron-rich oxide was formed at 600°C, resulting in oxygen solubility in the SiC fibers and fiber coating oxidation. A protective silica-rich oxide formed at 800°C resulting in limited oxidation of SiC fibers. A more detailed analysis of behavior in dry oxygen can be found in *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen*. Non-protective oxides formed at both 600 and 800°C in wet oxygen, and oxygen solubility in the SiC fibers was observed at both temperatures. Fiber coatings oxidized and volatilized at 600°C, leaving an annular void where the coating once was. Fiber coatings at 800°C oxidized but did not volatilize. Oxidation behavior in wet oxygen is detailed in *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen*. The current chapter will introduce micro-cracking, studied in detail in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage*, in the CMC to allow oxidant transport into the interior of the CMC at elevated temperature in lab air, and oxidize various micro-constituents, including the SiC fibers. The additional strain capability for CMCs, as compared to their monolithic counterparts, seen in the second regime of the stress-strain curve is afforded by the added support of the fibers [71]. In the case that fibers become embrittled from oxidation, the potential strain addition is not fully realized [44]. The mechanisms that cause this embrittlement in CMCs in the intermediate temperature regime are referred to as pesting.

#### 5.1.1 Pesting in Ceramic Matrix Composites

There are two cited modes of pesting in CMCs [28]. In both pesting cases, the exposure temperature is too low to form a protective silica scale that covers the outer surface of the CMC that would limit additional oxidation exposure within the composite. In the first mode of pesting, the unprotected interphase volatilizes away via ends-on oxidation and oxidation occurs through cracks [28, 44]. The void is subsequently filled with silica that bonds the fibers together and does not allow for fiber sliding, resulting in poor mechanical properties. The oxidative damage is exhibited in the fracture surface, where oxidized fibers have short fiber pullout in contrast with unoxidized fibers that exhibit long pullout lengths. This results in a "picture-frame" fracture surface, where fiber pullouts close to the oxidized edges are shorter than fiber pullouts in the unoxidized center region [44, 72].



Figure 62: "Picture-frame" fracture surface of a SiC/BN/SiC CMC, where fibers near the edge exhibit flat, brittle failure and fibers on the interior surface exhibit longer lengths of fiber pullout. Reproduced from Morscher et al. [72].

The second mode of pesting arises from composite processing conditions that result in excess carbon forming beneath the BN interphase next to the fiber [20]. This carbon layer was observed for SiC/BN/SiC CMCs with carbon-rich Hi-Nicalon and Hi-Nicalon S fibers. When exposed to burner-rig conditions (high-speed flame with combustion products), the carbon rapidly oxidizes leaving a pathway for inward oxidant transport, exposing a large surface area of BN fiber coating and SiC fiber [20]. This subsequently fills with borosilicate glass and silica. It is uncertain to what extent this pesting mode is observed across a variety of CMC materials.

#### 5.1.2 CMC Environmental and Damage Modeling

Various models have been produced to integrate the effects of environmental damage on mechanical behavior of SiC/BN/SiC CMCs [30, 31, 73, 74]. While the execution of the models vary, the basic phenomenological behavior remains. Load is applied to the CMC, resulting in microcracking in the matrix. Oxidant (H<sub>2</sub>O and O<sub>2</sub>) travels from the surface through the micro-cracks of the CMC to attack interior constituents. The micro-cracks can also close due to oxide growth on the crack walls, but this oxide growth slows in the intermediate temperature (600-800°C) regime due to slower SiC oxidation. The oxidant attacks the BN coatings, oxidizing to a borosilicate glass, which subsequently volatilizes away with H<sub>2</sub>O interaction, leaving an annular void surrounding the SiC fiber. This ultimately results in a knockdown of strength as there is a loss in load transfer from matrix to fibers in the oxidized regions.

## 1.3.1 Objective III Knowledge Gaps

It is unclear how the oxidation mechanisms may change for the RRHTC SiC/BN/SiC CMC when under load. It was expected that the addition of micro-cracking would allow for oxidant ingress into the material, which would result in reduced mechanical performance. The oxide compositions were expected to remain similar to that seen in the TGA work in *Chapter II and III*. It was however, unclear how much the B-containing phase in the matrix material would contribute to crack filling. It was expected that increases in stress would increase the crack density, as seen in *Chapter IV*, and result in increased oxidative degradation and shorter stress-rupture times. It was also necessary to interrogate the effect of environment on the mechanical properties for the RRHTC SiC/BN/SiC CMC. In the case of dry oxygen, more protective oxides would form, but it was

expected that with less volatility the remaining oxide may result in embrittlement of the material and cause stress concentrations leading to stress-rupture. It was unclear if the  $H_{H2O}$  in lab air would result in a significant difference from dry oxygen testing. Water vapor testing was expected to result in a less protective oxide that would not protect the CMC from interior damage. It was also of interest to see how each condition compared to the oxidation model set forth by Parthasarathy et al. [30].

The following research questions were explored and discussed for Objective III:

1. Does the BN interface oxidize, volatilize, and leave an annular void when a SiC/BN/SiC CMC is oxidized under load?

What is the effect of micro-cracking on oxidation behavior for SiC/BN/SiC CMCs?
How does the loading regime (first matrix cracking, below the proportional limit, above the proportional limit) affect the oxidation behavior? Is kinetic behavior affected by with loading regime?

4. What are the synergistic effects of oxidation and load for RR-HTC SiC/BN/SiC CMCs in an intermediate temperature regime?

# 5.2 Material and Methods

#### 5.2.1 Materials

State of the art CMCs were provided by Rolls-Royce High Temperature Composites (RR-HTC). The composites consist of Hi-Nicalon fiber layups in a 2D five-harness satin weave geometry.

97

The fibers were coated with a boron nitride (BN) interphase, and a chemical vapor infiltration (CVI) layer of SiC around the fibers. A matrix of SiC particulate and melt-infiltrated silicon filled the remaining porosity. A boron-containing phase was observed in the matrix material.

Plates provided by RR-HTC had dimensions of approximately 178mm X 178mm X 4.5mm. Test specimens were machined by Cincinnati Testing Labs (Cincinnati, OH). Dogbone coupons were machined for baseline mechanical properties, with dimensions shown in Figure 63. Straight sided test coupons were machined for oxidation load holds, with dimensions of 163 mm X 9.5mm X 4.5mm to conserve material.



Figure 63: Dimensions for SiC/BN/SiC CMC dogbones for fast fracture mechanical testing. All measurements in inches.

# 5.2.2 Baseline mechanical testing

Fast-fracture mechanical tests were completed at the Air Force Research Laboratory at Wright-Patterson Air Force Base. X-ray CT (HMK160, X-Tek) was performed on select dogbone specimens prior to testing. Porosity was distributed throughout the composites, and 4 representative slices are shown in Figure 64. Porosity within a RRHTC CMC with similar processing techniques was previously measured to be 12% of the overall volume fraction [75], so the observed porosity in the current RRHTC is not unexpected.



Figure 64: X-ray CT slices of SiC/BN/SiC CMC tensile dogbone. Black spots are porous regions.

The matrix cracking onset, proportional limit, and ultimate tensile strength were determined at room and elevated temperatures in lab air. A servo-hydraulic load frame (MTS Systems Corporation) was used in conjunction with a high temperature furnace and extensometer.

Acoustic emission sensors (Pico sensors, Digital Wave) were placed on the edge of the sample in the grip section to detect matrix cracking onset, shown in Figure 65. A room temperature extensometer (Model 632.26, MTS Systems Corporation) and a high temperature extensometer (Model 632.50B, MTS Systems Corportation) were used for strain measurement. Samples were loaded to 50 MPa and unloaded at room temperature to ensure proper contact with the extensometer. Samples were then heated to 400, 600, or 800°C, and temperatures were equilibrated for 15 minutes. Samples were loaded to 50 MPa and unloaded at elevated temperature to again check for proper contact with the extensometer. The samples were then loaded to failure. Fracture surfaces were evaluated via scanning electron microscopy (FEI Quanta 650).



Figure 65: SiC/BN/SiC CMC dogbone in MTS servo-hydraulic load frame equipped with acoustic emission (AE) sensors and a room temperature extensometer.

# 5.2.3 Oxidation load holds

An electromechanical tensile test frame (C43.304 Criterion Test System, MTS Systems Corporation) was used to perform oxidation load holds with two-zone elevated temperature furnace (653.02B Furnace, MTS Systems Corporation), seen in Figure 66. Samples were held at a static load for 50 and 100 hours in lab air at 600 and 800°C. Humidity in the lab air was tracked during testing with a humidity sensor (SD500, Extech Instruments). Samples were held at three load levels of interest; the matrix cracking onset stress (150 MPa), above the proportional limit (180 MPa), and an additional load above the proportional limit (200 MPa). Upon reaching 50 or 100 hours at load, the tests were interrupted and removed from the load frame. The samples were first cooled to room temperature under load, and then unloaded to ensure that any liquid oxide would freeze and remain in the cracks to be examined post-test and removed from the load frame. Stress rupture occurred in some of the tests past the proportional limit, and the interrupted test could not be performed.



Figure 66: SiC/BN/SiC CMC in load frame with half of high temperature furnace.

#### 5.2.4 Characterization

Samples were characterized using a FEI Quanta 650 field emission scanning electron microscopy (SEM) and Oxford Instruments Aztec X-Max<sup>N</sup> 150 energy dispersive X-ray spectroscopy (EDS) following exposures. If sample failure occurred, fracture surfaces were also evaluated. Plan view images were taken of the machined long edge that exposes both transverse and longitudinal fibers.

Samples were also characterized with a FEI Helios dual-beam focused ion beam (FIB) with SEM and EDS. Milling was performed on the plan view edge where longitudinal and transverse fibers were exposed. Cross-sections of selected fibers in a fiber bundle were milled using the ion beam and then compositionally mapped using EDS to provide high fidelity images and composition maps. The FIB samples were used to correlate local surface oxide to the underlying material microstructure.

The sample was then cross-sectioned and polished to allow SEM/EDS investigation of oxidation occurring on the edges and interior of the composite. Examples of the cross-sections can be seen in Figure 67. Cross-section A was used to investigate the oxygen solubility lengths and internal oxidation behavior. Cross-sections B and C were used to investigate the internal oxidation behavior, with cross-section C being polished to the mid-plane through the thickness of the sample.



Figure 67: Characterization schematic for static load holds

# 5.3 Results

# 5.3.1 Baseline mechanical testing

Fast-fracture tensile properties were determined at room temperature, 400, 600, and 800°C, and can be found in Table 3. The average matrix cracking (MC) stress value across all temperatures was  $150 \pm 9$  MPa. The proportional limit (PL) stress value across all temperatures was  $163 \pm 11$  MPa. The ultimate tensile strength (UTS) was observed to slightly increase at 600°C, as seen in Figure 68, but the differences are within known variability for this class of materials. The matrix cracking stress was only obtained for one sample at each temperature, so standard error bars have not been calculated for it. The  $\sigma_{PL}$  and  $\sigma_{UTS}$  were obtained for two samples each

at all three temperatures of interest, and standard error bars are shown that display little scatter. There is little variation of the matrix cracking stress and proportional limit across all temperatures. An example stress-strain curve obtained at room temperature is seen in Figure 149 in the *Appendix*.

Specimen Number	Test Temperature (ºC)	Acoustic Emission	Room Temperature Modulus (GPa)	High Temperature Modulus (GPa)	Matrix Cracking Stress (MPa)	Proportional Limit Stress (MPa)	Ultimate Tensile Stress (MPa)	Strain to Failure (%)
1010-1	23	Yes	303	-	-	165	374	0.78
1010-2*	23	Yes	297	-	141	151	-	-
1010-6	400	No	275	275	-	157	326	0.55
1010-7	400	Yes	276	258	148	156	374	0.85
1010-8	600	No	278	266	-	168	413	0.87
1006-4	600	Yes	287	267	163	188	400	1.1
1010-4	800	Yes	280	274	150	159	274	0.36
1010-5	800	No	285	281	-	160	343	0.64

Table 3: Mechanical properties for RR-HTC SiC/SiC CMC at room and elevated temperatures.

\*Specimen slipped in grips prior to failure





The room temperature fracture surface was flat and failed across one transverse ply. Fiber pullout measurements for the room temperature tests were approximately 70% the length of the high temperature tests. The high temperature tests fracture surfaces showed failure through multiple transverse plies. Inside debonding of the fibers/fiber coatings was observed for all fracture surfaces.

#### 5.3.2 Oxidation load holds in lab air

Oxidation load holds were completed at 150 MPa ( $\sigma_{MC}$ ), 180 MPa ( $\sim \sigma_{PL}$ ), and 200 MPa ( $\sigma > \sigma_{PL}$ ) for up to 100 hours. The following chapter sections are separated by load level and discuss surface and subsurface oxidation behavior.

5.3.2.1 CMC oxidation load holds at 150 MPa at 600 and 800°C in air

## 5.3.2.1.2 As-machined surface behavior at 150 MPa

Oxide morphologies on the surface of the composite after testing are shown in Figure 69. Oxidation occurs preferentially in the matrix where B-rich phases reside, as seen previously in both dry and wet unstressed TGA exposures in *Chapter II.* Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen.* The oxide at 600°C is more boron-rich than the oxide at 800°C, as seen in EDS maps in Figure 70. The oxide forms droplets and is non-wetting, similar to behavior seen in wet oxygen thermogravimetric analysis testing containing 50% water vapor/50% oxygen. The non-wetting oxide does not provide protection for the SiC fibers, and oxygen solubility in the fibers is observed in the oxygen composition maps in Figure 70. Oxide is also observed in porosity connected to the surface, or porosity pipes, after 50 and 100 hours at both temperatures.

The plan view surface was interrogated for mechanical damage upon unloading. Microcracks were not observed in any constituent. There were no other signs of mechanical damage present on the surface of the CMC.



Figure 69: Backscatter SEM image of CMC surface oxide morphologies at 600 and 800°C after 50 and 100 hours at  $\sim \sigma_{MC}$  = 150 MPa in lab air



Figure 70: Si, B, O, and C EDS maps of SiC/BN/SiC CMC surface oxide at matrix cracking onset tested in lab air at 600 and 800°C for 50 and 100 hours at 150 MPa

5.3.2.2 Subsurface behavior at 150 MPa

Oxygen solubility lengths in the Hi-Nicalon SiC fibers were measured from polished crosssections of the CMC, as imaged in Figure 71. Oxygen solubility is observed in the fibers at both 600 and 800°C, reported in Table 4. Oxygen solubility in the fibers increase with both temperature and time, which is different from the TGA results where oxygen solubility lengths at 800°C were shorter than those at 600°C. EDS analysis of the fiber coatings shows oxygen signal in the coatings, seen in the oxygen map in Figure 71. Coating oxidation is observed in fiber tows connected to the surface, but not deep into the interior of the CMC. Coating oxidation lengths are variable within the same sample. Table 4: Hi-Nicalon oxygen solubility length measurements for SiC/BN/SiC CMC specimens exposed to lab air as a function of stress, time, and temperature.

Stress (MPa)	Time (hours)	Temperature (°C)	Location	Length (µm)	Std. Dev. (µm)	Number of measurements
150	50	600	Hot Zone	10.3	2.9	4
150	100	600	Hot Zone	14.7	2.9	48
150	50	800	Hot Zone	9.4	9.0	42
150	100	800	Hot Zone	16.2	11.7	62
180	50	800	Hot Zone	10.3	11.2	80
180	100	800	Hot Zone	13.2	9.8	79
200	23	600	Hot Zone	9.49	2.8	25
200	100	600	Hot Zone	20.6	5.3	37
200	13	800	Hot Zone	2	5.6	47
200	13	800	Fracture Surface	23.2	7.8	92
200	49	800	Hot Zone	19.8	10.8	91
200	49	800	Fracture Surface	37.3	13.1	105



Figure 71: Oxygen solubility in Hi-Nicalon fibers (white arrows) and oxidation of B-rich intratow MI region (red arrow) in a SiC/BN/SiC CMC. Specimen was exposed to lab air for 100 hours at 600°C at 150 MPa.

In the interior of a fiber tow, there are pores that get filled with melt-infiltrated silicon. These regions are also rich in B-containing species. An example of this is imaged in plan view in Figure 72. These regions oxidize preferentially, likely due to the presence of the B-rich species. These regions, occurring inside of a fiber tow, show deep oxidation lengths when connected to the open surface exposed to the environment, as seen in Figure 71. Pores that are unfilled also allow for oxidant travel into the interior of the CMC. This is discussed in more detail in subsequent sections. Mechanical damage in the form of open matrix cracks in the interior of the CMC upon unloading was not observed, consistent with the lack of open matrix cracks on the surface of the CMC upon unloading,



Figure 72: Example of SiC/BN/SiC CMC intratow region that is filled with melt-infiltrated silicon and is rich in B-containing species. Specimen was exposed to lab air for 100 hours at 600°C at 150 MPa.

## 5.3.3.1 Surface behavior at 180 MPa

Surface oxidation behavior is similar to that seen at 150 MPa. The oxide preferentially forms at areas where the B-containing phase resides. After 1 hour oxide has formed in regions where B-rich phases are. Oxide droplets are observed after 50 hours. The oxide droplets grow in size after 100 hours. This oxidation behavior aligns with the behavior seen at 150 MPa. Open micro-cracks are observed on the surface of the composite. The micro-crack spacing was measured and reported in Table 5.

Table 5: Crack spacings for SiC/BN/SiC CMC specimens tested at 180 MPa in lab air at 800°C.

Condition	Crack Spacing (micron)	Standard Deviation (micron)
50 hour 800°C Hot Zone	3750	2317
100 hour 800°C Hot Zone	623	688

Micro-cracks intermittently fill with oxide at the surface, and where they have filled with oxide a droplet is typically present at the surface. The occurrence of filling is seemingly consistent with the presence of B-rich phases in the matrix material. FIB milling was performed near microcracks to observe the CMC and oxide microstructure around the cracks. A crack in the matrix is shown in Figure 73, and Figure 74 shows a FIB-milled cross-section from this crack. The oxide fills the crack at the surface, and beneath the crack walls have also started to oxidize. Other areas on the surface remain unfilled, as pointed out by the yellow arrows in Figure 73.



Figure 73: Crack in SiC/BN/SiC CMC MI matrix material. Yellow arrows point to unfilled crack. Red line depicts where FIB cross-section in Figure 74 was taken, with an oxide droplet on top of the crack. Sample was exposed to lab air at 800°C for 100 hours at 180 MPa.



Figure 74: FIB cross-section of oxide filled crack from Figure 73. SiC/BN/SiC CMC was exposed to lab air at 800°C for 100 hours at 180 MPa.

Open cracks are also observed in the interior of the CMC. Cross-sections were polished to the mid-plane of the composite (approximately 2.7mm deep). Cracks in the interior were also intermittently filled with oxide. In the MI matrix material away from fiber tows, cracks had partial filling. The amount of crack filling increased with time, as seen in Figure 75 (some oxygen signal is also coming from carbon containing species, likely polishing media). Near the edge of a fiber tow where B-containing phase was present, oxide was observed and filled the crack in this region, as seen in the 50 and 100 hour conditions in Figure 76.



Figure 75: Oxide filling in interior cracks in the matrix of SiC/BN/SiC CMC. Specimens were exposed in lab air at 800°C at 180 MPa for 1, 50, and 100 hours. Red arrows on the backscatter image indicate loading direction.



Figure 76: Oxide filling in interior cracks near fibers in SiC/BN/SiC CMC. Specimens were exposed in lab air at 800°C at 180 MPa for 1, 50, and 100 hours. Red arrows on the backscatter image indicate loading direction.

Oxidation of CMC constituents in contact with porosity is also observed. Cracks or porosity pipes allow direct access and oxidation of a region that is far from any exterior surface, seen in Figure 77. The porous region has glass that covers the surface of the underlying constituent, which is likely the edge of a fiber tow based off of the close proximity to a fiber tow on the surface.



Figure 77: Oxidation of porous region in interior of SiC/BN/SiC CMC. The inset in the upper right corner shows location (red box) of image on the cross-section. Sample was tested for 50 hours at 180 MPa at 800°C.

The amount of BN fiber coating oxidation is variable. After 1 hour, no oxidation of coatings is observed. After 50 and 100 hours, BN coating oxidation is observed. The coating oxidation is not uniform. For example, in Figure 78, after a 50 hour exposure a BN fiber coating in the middle of the tow that has a crack running through it is heavily oxidized. Some adjacent fiber coatings exhibit oxygen and nitrogen signals, and others exhibit no oxygen signal. Similarly, after 100 hours, BN coatings oxidize when associated with a nearby crack, as seen in Figure 79.



Figure 78: SEM/EDS maps showing crack in SiC/BN/SiC CMC interior after 50 hours at 800°C in lab air at 180 MPa. Red arrows point out oxidized BN fiber coating.



Figure 79: SEM/EDS maps of crack in SiC/BN/SiC CMC interior after 100 hour exposure at 800°C in lab air at 180 MPa. Red arrows point out oxidized coating.
#### 5.3.4 Oxidation load holds at 200 MPa at 600 and 800°C in lab air

Oxidation load holds were completed for 23 and 100 hours at 600°C. The 23 hour test was intended to be a 50 hour test, but a heating element in the furnace broke. Oxidation load holds were completed for 13 and 49 hours at 800°C. The test times at 800°C were shortened due to stress rupture that occurred outside the hot zone in regions that were approximately 750°C, according to furnace temperature profiling, seen in Figure 80. Resultant behavior in the hot zone and at the failure region is discussed.



Figure 80: MTS furnace temperature profile for furnace with a hot zone temperature of 800°C. Specimen failure regions are marked with the red dots, with 0891-12 failing after 13 hours and 0891-8 failing after 49 hours.

The oxide morphology on the surface is similar to that seen at 150 MPa and 180 MPa for the hot zones at 600 and 800°C. SEM/EDS maps of the hot zone and fracture surface are imaged in Figure 81. EDS measurements near the hot zone and fracture surface for the tests run at 800°C were similar, listed in Table 6, and there was not a statistically significant difference between the surface oxides at these locations.



Figure 81: Oxygen and boron EDS maps for oxides on the machined SiC/BN/SiC edge formed in the hot zone and the fracture surface after exposures at 13 and 49 hours at 800°C in lab air at 200 MPa.

Table 6: EDS Point ID compositional analysis of oxides formed at hot zone and fracture surface after 13 hours

Location	B at%	Si at%	Data points
Hot Zone (800°C)	14.8 ± 1.1	18.3 ± 1.1	6
Fracture Surface (~750°C)	15.6 ± 1.1	17.3 ± 1.0	4

Open micro-cracks were observed on the surface for both 600 and 800°C exposures upon

unloading. FIB milling was used to interrogate open cracks in the matrix. Oxygen signal is present

on the crack faces at 600°C after 23 hours, seen in Figure 82. The crack faces are oxidized after 100 hours, pointed out by the white arrows on the image. Debris is also present in the open cracks after both 23 and 100 hours, indicated by the yellow arrows. Two micro-cracks were compared via FIB milled cross-sections after an 800°C exposure for 49 hours. The micro-cracks in Figure 83 are of similar crack opening displacements, but one is not filled with oxide and the other is filled with oxide and had an oxide droplet present on the exposed surface. Oxide droplets occur on the surface at locations where a B-containing phase resides. This filled droplet region is likely associated with an underlying B-rich feature.



Figure 82: FIB milling of micro-cracks in the Si-SiC matrix material of SiC/BN/SiC CMC after 23 and 100 hour exposures at 600°C in lab air at 200 MPa. White arrows indicate oxidation on the crack faces. The yellow arrows indicate debris in the micro-crack.



Figure 83: Comparison of unfilled and oxide-filled cracks in SiC/BN/SiC CMC of similar crack opening displacements after 800°C exposure for 49 hours in lab air at 200 MPa.

Matrix cracks were prevalent across the span of the hot zone and near failure regions.

Stitched images were acquired of these regions, and cracks were marked. Crack spacing

measurements were taken for each condition and are listed in Table 7.

				~				
Tahla	7.	Crack	cnacinac	tor	cnacimanc	toctod	at	$2 \cap \cap \Lambda A D a$
IUDIC	1.	CIUCK	spucings	101	SPECIFICIS	IESIEU	uι	200 IVIF U
			1 3	,	,			

Condition	Crack Spacing (micron)	Standard Deviation (micron)
23 hour 600°C Hot Zone	708	190
100 hour 600°C Hot Zone	746	445
13 hour 800°C Hot Zone	1780	1378
13 hour 800°C Fracture Surface	1628	962
49 hour 800°C Hot Zone	1178	824
49 hour 800°C Fracture Surface	619	506

## 5.3.4.2 Fracture surface behavior at 200 MPa

Specimens tested with a hot zone temperature at 800°C stress-ruptured in regions that were approximately 750°C after 13 and 49 hours. After 13 hours, the fiber bundles exhibited little fiber pullout, seen in the red box in Figure 84. The specimen failed through multiple transverse ply levels, as was seen in the baseline fast fracture tests. Note that the large amount of debris in the bottom fracture surface is broken fibers and matrix material. The other sample tested with a hot zone temperature at 800°C failed after 49 hours at load, and exhibited more fiber pullout in the middle of fiber tows. It is important to note that the outer edge of the fiber tows appeared flat and did not have much fiber pullout, indicating that the outer portion of the fiber tow failed in a more brittle fashion. It is also important to note that after failure the fracture surfaces remained inside the furnace during cooldown (approximately 1 hour), and resulted in some oxide formation on the fracture surface.





Figure 84: Top and bottom fracture surfaces from stress ruptured SiC/BN/SiC CMC specimen after 13 hour exposure at 800°C in lab air at 200 MPa. The red box is a magnified region of the fracture surface to show more detail. The white dots indicate the same location on the sample on the top and bottom fracture surfaces.





Figure 85: Top and bottom fracture surfaces from stress ruptured specimen SiC/BN/SiC CMC after 49 hour exposure at 800°C in lab air at 200 MPa. The blue box is a magnified region of the fracture surface to show more detail. The white dots indicate the same location on the sample on the top and bottom fracture surfaces.

#### 5.3.4.3 Subsurface behavior at 200 MPa

Open micro-cracks in the interior were observed in all test conditions at 200 MPa. Microcracks allow access to interior constituents. In Figure 86, a micro-crack (yellow arrows) is present through the width of the specimen. The micro-crack connects the exterior exposed surface to a large porous region where a CVI SiC-coated fiber bundle was exposed to oxidant. An oxide layer was observed on the CVI SiC. Cracks were observed in the oxide layer, but no cracking was readily observed in the CVI SiC overcoat. FIB was used to mill a cross-section in the fiber tow, indicated by the red box on Figure 86, to interrogate the oxidation behavior of the fibers and coatings in this region. The nitrogen signal indicates that the BN coating was retained, however there is a weak oxygen signal in the coating region. Oxygen solubility was not observed in the SiC fibers. The outer edges of the fiber tow were attacked but the load-bearing fibers and coatings were not affected.



Figure 86: Mid-plane polish of SiC/BN/SiC CMC sample exposed to lab air at 600°C for 23 hours at 200 MPa. Yellow arrows point out a crack in the matrix that allowed oxidant travel to the porous region where the outer edge of CVI SiC on a fiber tow oxidized. Red arrows indicate loading direction.

Open micro-cracks in the interior were also observed in the sample exposed for 100 hours at 600°C. A micro-crack, pointed out by yellow arrows, allowed access to interior MI matrix material and resulted in oxide droplets forming on the interior matrix, observed in Figure 87. The oxide droplets likely formed over B-containing phase in the matrix material. This interior matrix oxidation was observed any time there was a matrix rich region with B-containing phase found.



Figure 87: Oxide droplets on melt-infiltrated material in interior of SiC/BN/SiC composite for specimen exposed at 600°C for 100 hours at 200 MPa. Yellow arrows point to a matrix crack.

Cracks in the CMC interior were observed for samples exposed at 800°C for 13 hours at 200 MPa, both near the hot zone and fracture surface. A crack near the hot zone is pointed out by the yellow arrows in Figure 88. The entire length of the crack imaged was filled with oxide, shown by the oxygen EDS maps for three regions in the crack, and other interior cracks seen in the CMC at this exposure were filled in with oxide. Point EDS was conducted on the oxide filling the crack, and it was a mixed borosilicate, with its composition listed in Table 8. Another crack near the fracture surface was also analyzed with Point EDS and the average composition from that crack is listed in Table 8.





Figure 88: Crack in interior of SiC/BN/SiC CMC after exposure after at 800°C for 13 hours at 200 MPa. Images were taken near the hot zone region. Blue, red, and green boxes are zoomed in below to show more detail and the oxygen EDS map that correlates to that region.

Table 8: Point EDS Analysis taken from cracks in SiC/BN/SiC CMC matrix material near the hot zone and fracture surface after exposure at 800°C for 13 hours at 200 MPa. The points for the hot zone are taken from the crack featured in the red box in Figure 88.

Location	В	0	Si	# of points
Near Hot Zone	12.47	33.74	34.56	3
Near Fracture Surface	8.49	25.44	36.59	2

Cracks observed in the CMC after exposure at 800°C for 49 hours at 200 MPa were also filled with oxide. When cracks propagated through a B-containing phase in the matrix material, the B-containing phase oxidized, as shown in Figure 89. The B-containing phases also oxidized near the fiber tows, filling cracks near these regions. It was often observed that long lengths of cracks would be unfilled, but filling would be observed near the B-containing phases in the matrix near the fiber tows. The fiber coatings in these regions were partially oxidized, as seen in Figure 90. The coating on the left side of the fiber is unoxidized compared to the coating on the right side of the fiber which appears glassy. The compositions for the oxidized and unoxidized coating are listed in Table 9. Cracks provided access to porous regions in the composite, resulting in oxidation of these regions, which had also been seen at 600°C/200 MPa conditions.



Figure 89: B-containing phase in matrix oxidized when in crack path in SiC/BN/SiC CMC interior after exposure at 800°C for 49 hours at 200 MPa. Scale bar purposefully omitted due to Rolls-Royce intellectual property.



Figure 90: Oxidized crack near interior fiber tow after exposure at 800°C for 49 hours at 200 MPa. EDS point analysis was conducted at the points indicated with red arrows and are listed in Table 9. Scale bar purposefully omitted due to Rolls-Royce intellectual property.

Constituent	В	Ν	С	0	Si	
Oxidized Coating	10.7	0.9	21.4	28.7	34.3	
Unoxidized Coating	14.4	5.7	19.9	3.7	36.0	
Oxidized Crack	6.6	0.8	32.61	14.6	41.8	

Table 9: EDS Point Analysis for locations in Figure 90.

# 5.4 Discussion

# 5.4.1 Degradation modes observed

Several degradation modes were observed during testing, with some being more prevalent at loads past the proportional limit. The following modes were noted, and charted as a function of load in Table 10:

- 1. Oxide formation in interior of composite via 'porosity pipes' at free surface
- 2. Oxygen solubility in fibers
- 3. Oxidation of intratow melt-infiltrated regions with high concentrations of B-rich phases
- 4. Oxide formation in matrix cracks
- 5. Surface cracks providing access to porosity pocket in composite

Table 10: Damage mechanisms observed in SiC/BN/SiC CMCs at different load levels in lab air at 600 and 800°C. ( $\checkmark$ ) signifies that the mechanism was observed and (-) signifies that the mechanism was not observed.

Damage Mechanism	Unstressed Oxidation	σ <sub>150</sub>	σ <sub>180</sub>	σ <sub>200</sub>
Oxidation through porosity pipes	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxygen solubility in SiC fibers	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxidation in intratow MI-rich regions	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxidation formation in matrix cracks	N/A	-	$\checkmark$	$\checkmark$
Stress Rupture	N/A	-	-	√ (~750°C)

## 5.4.2 Surface oxidation

On the machined edge of the composite there are pores that extend into the depth of the composite, as seen in Figure 69. Oxide formation is observed on the pore interior. These pores allow access into the interior of the composite and allow for more direct oxidative attack of interior constituents.

Oxygen solubility occurred in fibers due to non-protective nature of the oxide. It has been shown previously in *Chapter II. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry oxygen* and *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen* that when a silica-rich oxide forms across the surface of the fibers at 800°C in dry oxygen that minimal oxygen solubility is observed in the fibers. However, at lower temperatures and when water vapor (50% H<sub>2</sub>O/50% O<sub>2</sub> mixture) is introduced in the gas mixture, the oxide is non-protective and oxygen solubility in the fibers occurs. In the load holds performed in lab air (with approximately 1-2% H<sub>2</sub>O content) a non-protective oxide formed at both 600 and 800°C, and oxygen solubility was observed in the fibers in all cases.

There are silicon-rich regions in the interior of fiber tows, as seen in Figure 71. These regions are also rich in B-containing species on the matrix material. These regions lead to higher oxidation depths due to preferential oxidation of the boron and silicon rich regions. These regions act as fast paths for oxidant transport into the interior of the CMC, potentially providing access to nearby fiber tows if cracking occurs in the fiber tow region. Potential mitigation strategies for this effect would include better infiltration of SiC particulate into the intratow regions and/or reducing the amount of B-containing species in the region.

#### 5.4.3 Oxide filling in micro-cracks

Micro-cracks were observed after unloading on the exterior and in the CMC interior. The residual micro-crack spacing measured after oxidation load holds was on the same order of magnitude observed in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage*. Oxide formation in micro-cracks is dependent upon exposure temperature and time. At 600°C, the micro-cracks remain unfilled in the open matrix region after 50 and 100 hours. Oxide filling that is observed is near the B-containing species. Matrix crack filling is observed at 200 MPa/800°C, to a larger extent in the open matrix material. Oxidation is heavily dependent on the proximity to the B-containing species. Oxide is often

observed near the fiber tow regions, and intermittently in the free matrix (when local to Bcontaining species in the matrix). The oxide filling behavior being dependent on the proximity of a B-containing phase shows that micro-crack composition (obtained in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage*) is an important characteristic of the composite to consider for the oxidation behavior of the CMC.

## 5.4.4 Stress rupture at 200 MPa/800°C

Specimens tested at 200 MPa at 800°C failed after 13 and 49 hours. Fiber pullout was shorter for the specimen that failed after 13 hours. Fiber tows near the outer edges of the specimen were much flatter, exhibiting a "picture frame" fracture surface like that previously seen for SiC/BN/SiC CMCs stress-rupture tested at intermediate temperatures in lab air [72]. Cracking in the CMC likely allowed access to the interior of the composite causing embrittlement, resulting in early failure of the composite. The sample that ruptured after 49 hours had more fiber pullout, but also exhibited flat fiber fracture surfaces near the outer edge of the fiber tows. To understand the impact of temperature, load, and water vapor content on stress-rupture behavior, the graphic in Figure 91 is included throughout the remainder of this thesis document.



Figure 91: SiC/BN/SiC CMC behavior as a function of temperature, stress, and water vapor volume percentage. Green dots indicate that no failures occurred at that condition and red dots indicate that stress-rupture occurred in at least one test conducted in that condition. Each dot represents two tests. Only results obtained in lab air are included here.

The composition of oxide filling the cracks is listed in Table 8. B content, measured via EDS, was lower for the glass in the region near the fracture surface (~750°C) than the hot zone. This composition difference is unexpected based off of the temperatures. It was expected that the glass in the 750°C region would be higher in B content since it would volatilize out of the glass less at lower temperatures. Other factors that may be affecting glass composition are the nearby constituents and partial pressure of oxidant species in that region. If B-rich species are near the crack, such as near a fiber tow or B-containing phase in the matrix, then it is expected that the glass composition will be higher in those regions than if the crack were not near any B-containing species.

#### 5.4.5 Fiber Coating Behavior

Oxidation of fiber coatings was observed; however, the oxidation of the coatings was inconsistent. Coatings within the same fiber tow displayed different oxidation behavior, with some being oxidized and some not. It is hypothesized that cracking in the material allowed attack to certain fiber coatings, such as in Figure 78 after exposure at 180 MPa at 800°C for 50 hours. There are also locations on the same fiber/fiber coating where oxidation occurs on some parts but not on others, such as in Figure 90 after exposure at 200 MPa at 800°C for 49 hours. This occurs even when an oxidized crack is directly touching the unoxidized coating portion. No annular voids were observed in the coating regions for any test condition.

#### 5.4.6 Time effects

All load conditions had attempts for 50- and 100-hour tests. Oxide growth on the surface was observed from 50 to 100 hours. However, it was difficult to ascertain differences in the interior oxidation from 50 to 100 hours, as oxide was observed in the matrix cracks at both times when tested at 180 MPa and above. A 1-hour test was completed at 180 MPa at 800°C to observe oxidation at early times. As seen in Figure 75 and Figure 76, little oxide was present in the micro-cracks (some locations show oxygen signal, but also match with carbon signal, suggesting that it is likely polishing media in the crack). Future work should be conducted on testing at intermediate times between 1 and 50 hours to understand oxidation kinetics of a stressed CMC.

## 5.4.7 Synergistic Effects of Oxidation and Load

Synergy between micro-cracking damage and air ingress into the material results in increased degradation of the CMC. Micro-cracking in the material provides access for air to attack the CMC interior for subsurface degradation. Oxidation of micro-cracks, BN coatings, and B-containing species in the matrix occurred throughout the entire thickness of the specimen. Fiber tows, and the B-containing species around them, are susceptible to attack and are often seen to have oxidized after 50- and 100-hour exposures. Micro-cracking channels will pinch off from oxide growth as exposure continues. However, those channels that do not close will allow air access to fiber tows. As stress states change in the matrix with load hold time, eventually fiber failures will also occur. The regions where fiber breaks and sliding occurs will also allow ample access to surrounding fiber coatings and fibers for oxidant to attack.

Oxidation of the CMC will affect the stress-response of the material. If the BN coating oxidizes and remains, the resultant glassy phase will bond fibers together, resulting in the fibers behaving as a single unit to fail. This is likely the case seen in the specimens that stress ruptured at 800°C/200 MPa, where blocks of fibers near the outer edges of the specimen were seen to fail in a brittle, flat manner.

## **5.5 Conclusions**

Oxidation of SiC/BN/SiC CMCs while under load was studied at 600 and 800°C in lab air below and above the proportional limit. Several degradation modes occurred, including those in

133

previous studies where no load was applied. These modes include oxidation through porosity pipes, oxygen solubility in the SiC fibers, and preferred oxidation in the intratow MI regions. The addition of load beyond the proportional limit during oxidation exposure resulted in matrix cracks that stayed open upon unloading, and oxide partially filled the cracks in the interior of the composite. Oxide growth occurred in locations with B-containing species, both on the surface and interior of the composite, highlighting the importance of micro-crack composition. When loaded to 200 MPa, additional cracking that occurred allowed oxidant access into the interior on the CMC resulting in stress rupture when tested at 800°C. Synergy between the oxidation and stress state of the material resulted in interior oxidation of the CMC via crack pathways that was not previously seen in baseline oxidation studies without applied load.

# Chapter VI. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in dry oxygen

## 6.1 Introduction

This chapter builds on results from the last chapter with results obtained in lab air. This chapter focuses on the stressed oxidation behavior of SiC/BN/SiC CMCs at 600 and 800°C in dry oxygen. Limited work has been completed on mechanically testing SiC/SiC CMCs and their constituents in dry oxygen or dry air. Residual strength testing was completed by Hay & Chater was completed on uncoated Hi-Nicalon S fibers following oxidation in both dry (<10 ppm H<sub>2</sub>O) and wet air from 700-1400°C [76]. It was observed that at 700 and 800°C in dry air, a continuous silica glass layer formed and no drops in strength were reported for these temperatures [76]. Zok et al. investigated mechanical behavior of a 3D woven SiC/BN/SiC CMC with Tyranno ZMI fibers from 800-1100°C in dry air (<7 ppm H<sub>2</sub>O) and water vapor [50]. Three tests were completed in dry air; a monotonic tensile test and two tests with a pre-load exposure of 6h at 0 MPa and 135 MPa (below the matrix cracking stress), followed by monotonic tensile loading to failure. The specimens tested in dry oxygen had no change in tensile properties [50]. The experimental setup for dry oxygen used by Zok et al. is employed in this chapter.

SiC/BN/SiC CMC samples were held at 150, 180, or 200 MPa for either 50 or 100 hours while 100% oxygen is injected into the sample environment. Post-test characterization includes plan view and cross-section analysis of FIB-milled and polished cross-sections. Degradation modes including oxidation on the surface, through porosity pipes, through matrix cracks, as well as oxygen solubility in SiC fibers, were observed and are discussed. These modes are compared to previous results obtained in the TGA (*Chapters II and III*) and oxidation load holds in lab air (*Chapter V*).

#### 6.2 Material and Methods

#### 6.2.1 Materials

The same material and manufacturing techniques were utilized as *Chapter V. Stressed* oxidation of SiC/BN/SiC ceramic matrix composites in lab air. Refer to Section 5.2 for more information.

#### 6.2.2 Static load holds

A fused quartz setup modeled after Zok et al. was employed to control the environment around the sample [50]. The samples were encased in a fused quartz tube with fused quartz wool packed on either end of the specimen, as seen in Figure 92. The fused quartz tube had an outer diameter of 25mm and an inner diameter of 22mm, providing ample room to fit the tensile coupon and a smaller fused quartz tube (outer diameter 8mm, inner diameter 6mm). The smaller fused quartz tube was connected to a flow controller that allowed 200sccm of 100% oxygen to flow into the fused quartz environmental chamber.

The same testing method for the load frame was used as *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air.* Refer to Section 5.2 for more information. Specimens were exposed at 150 and 200 MPa at 600 and 800°C for 50 and 100 hours, or until rupture. Additional exposures were performed at 180 MPa at 800°C for 50 and 100 hours.



Figure 92: Fused quartz environmental chamber encasing SiC/SiC tensile bar for load frame testing.

# 6.2.3 Evaluation of dry oxygen testing setup

A CVD SiC coupon machined for thermogravimetric analysis was suspended from an alumina hook held by the top grip of the load frame. The CVD SiC coupon was encased in the fused quartz tube and either end was packed with fused quartz wool to mimic the test setup for oxidation load hold samples. The CVD SiC coupon was then exposed to the dry oxygen environment at 1000°C for 24 hours. The testing evaluation setup is shown in Figure 93.



Figure 93: Evaluation of dry oxygen test setup. A CVD SiC TGA coupon is suspended inside of the fused quartz environmental chamber and exposed at high temperature. Note that the furnace is open and at room temperature in this photo.

X-ray photoelectron spectroscopy (XPS) (Versaprobe III, Physical Electronics) was utilized to measure the oxide thickness after exposure with assistance from Cathy Dukes (University of Virginia). XPS employs argon sputtering to remove material from the surface and the sputtered material is identified via the spectrometer as a function of sputtering depth. The sputtering rate and depth are calibrated with a known SiO<sub>2</sub> standard, and then this sputtering rate is used to calculate the oxide thickness on the exposed SiC coupon. The concentration profile of the oxide on the SiC coupon determined by XPS is displayed in Figure 94. The SiO<sub>2</sub>-SiC interface position was reached after sputtering for approximately 63.9 minutes, where the O and C concentration profiles intersect. Using the sputtering rate standard previously determined from the SiO<sub>2</sub> standard of 6.63 nm/min, the oxide thickness is  $0.424 \pm 0.015$ microns. Ramberg et al. measured oxide thicknesses and provided kinetic rates for oxide growth on CVD SiC [38]. Using the "CVD SiC Fast" values for 1000°C, the predicted oxide thickness for 24 hours was 0.31 microns. The predicted and measured oxide thickness values were considered to be in sufficient agreement to proceed with the dry oxygen testing setup.



Figure 94: Concentration of element in the exposed CVD SiC coupon versus sputtering time. Sputtering profile provided by Cathy Dukes at the University of Virginia.

#### 6.2.4 Characterization

The same characterization techniques were utilized as *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air.* Refer to Section 5.2 for more information.

## 6.3 Results

## 6.3.1 Surface Oxide Morphologies

The surface oxides produced from exposures in the dry oxygen load frame setup were compared to oxides produced from the 100% O<sub>2</sub> thermogravimetric analysis (TGA) work in Chapter II. The oxides produced in the load frame are similar to those produced in the dry TGA. A boron-rich oxide primarily present on B-rich microstructural features occurs for both the TGA and load frame exposures at 600°C. However, unlike the dry TGA, a two-phase oxide was not observed for the load frame exposure, and instead the glass remains a continuous single-phase borosilicate atop the B-rich phases. Both 800°C exposures produce a silica-rich oxide that covers the surface of the CMC, including the MI matrix material and over the fiber tows.



Figure 95: SEM backscatter plan view images of surface oxide morphologies on machined edges of SiC/BN/SiC CMC sample in dry oxygen exposures after 50 hours at a) 600°C in the TGA, b) 600°C in the load frame, c) 800°C in the TGA, and d) 800°C in the load frame.

## 6.3.2 Oxidation of Fiber Coatings

FIB sections show cross-sections of fiber coatings exposed at 600°C for 50 and 100 hours in Figure 96 and Figure 97, respectively. The retained boron and nitrogen signal in both show that the fiber coatings remain, but have oxidized per the oxygen signal. No annular voids were observed in any polished or FIB cross-section for 600°C exposures at any stress level.



Figure 96: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 50 hour exposure at 600°C loaded to 200 MPa in dry oxygen.



Figure 97: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 100 hour exposure at 600°C loaded to 200 MPa in dry oxygen.

A thick uniform oxide is present on the surface after exposure at 800°C for 50 and 100 hours, seen in Figure 98 and Figure 99. The BN fiber coating is retained in both cases, seen both in the EDS maps and confirmed by EDS linescans. Little oxygen signal is present in the coating as compared to the exposures performed at 600°C. The oxidation behavior in the dry oxygen load frame setup is similar to that seen in the dry  $O_2$  TGA testing.



Figure 98: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 50 hour exposure at 800°C loaded to 200 MPa in dry oxygen.



Figure 99: SEM/EDS analysis of FIB cross-section of SiC fibers in a SiC/BN/SiC CMC sample after 100 hour exposure at 800°C loaded to 180 MPa in dry oxygen.

#### 6.3.3 Oxygen Solubility in Fibers

Oxygen solubility is present in the Hi-Nicalon SiC fibers for all conditions. Oxygen solubility in the fibers can be seen in the EDS oxygen signal map in Figure 96 through Figure 99. Oxygen solubility lengths for each condition are depicted in Figure 100. There is a clear trend where oxygen solubility lengths are longer for specimens exposed at 600°C. The oxide at 600°C does not provide coverage across the entire surface of the composite like that seen at 800°C, leading to less protection of the SiC fibers. There is no clear trend for the oxygen solubility lengths versus time, with shorter times exhibiting longer oxygen solubility lengths in some cases. This is potentially due to the fibers that are being sampled, as the oxygen solubility lengths are likely dependent on the protectiveness of the oxide residing directly above it. The oxygen solubility lengths show variability, as displayed by the high standard deviations for some cases, listed in Table 11.



Oxygen Solubility Length in Hi-Nicalon Fibers in Dry Oxygen

Figure 100: Oxygen solubility lengths for Hi-Nicalon SiC fibers in SiC/BN/SiC CMCs exposed in dry oxygen as a function of temperature, time, and load.

Load	Temperature	Time	Location	Average	Std. Dev.	Number
(MPa)	(°C)	(hours)		(µm)	(µm)	of fibers
150 MPa	600	50	Hot Zone	11.6	4.1	61
	600	100	Hot Zone	7.7	7.7	22
	800	50	Hot Zone	7.4	7.3	42
	800	100	Hot Zone	3.9	5.5	64
180 MPa	800	50	Hot Zone	3.6	5.3	94
	800	100	Hot Zone	2.3	4.4	24
200 MPa	600	50	Hot Zone	10.8	6.5	137
	600	100	Hot Zone	15.8	9	59
	800	28	Hot Zone	1.2	2.4	25
			Frac. Surf.	6.9	8.5	86
	800	50	Hot Zone	2.5	4.6	66

Table 11: Oxygen solubility lengths for Hi-Nicalon SiC fibers in SiC/BN/SiC CMCs exposed in dry oxygen.

#### 6.3.4 Exterior Micro-cracking

Minimal to no micro-cracking was observed on the machined CMC surface upon unloading for all conditions. If any micro-cracking was observed, there was often only one or two microcracks observed in the plan view imaging of the hot-section, and therefore no micro-crack spacing measurements were made as done previously for the lab air oxidation load holds. In Figure 101, a matrix crack that remained open after a 50 hour exposure at 800°C remains unfilled in the matrix material, and filling begins near the fiber tow. Micro-cracks that ran through the fiber tow were typically filled with oxide after an 800°C exposure. After 100 hours at 800°C, the micro-cracks in the matrix remain unfilled and the micro-cracks in the fiber tow were filled, again highlighting the importance of micro-crack composition considerations. At 600°C, where oxide formed in droplets and did not wet the surface, little filling was observed in the fiber tow or matrix regions.



Figure 101: Matrix crack on exposed surface of a SiC/BN/SiC CMC sample after 50 hour exposure at 800°C loaded to 180 MPa.



Figure 102: Matrix crack on exposed surface of a SiC/BN/SiC CMC sample after 100 hour exposure at 800°C loaded to 180 MPa.

# 6.3.5 Interior Matrix Cracking

Samples were polished to the mid-plane to observe oxidation behavior through the thickness of the material (configuration C, as described in Chapter V). Open matrix cracks in the

interior were observed upon unloading at all stress values, including 150 MPa, which is below the matrix cracking stress. Oxide intermittently fills cracks at both 600 and 800°C, imaged in Figure 103 and Figure 104. Oxide filling occurs near areas where B-rich material resides, either in the matrix or the BN coatings. In matrix material not near a fiber tow, some oxide would form in cracks in locations where B-rich matrix phase was located.



Figure 103: Polished cross-section of mid-plane of SiC/BN/SiC CMC sample exposed for 50 hours in dry oxygen at 600°C loaded to 150 MPa. Red arrows point to regions filled with oxide.



Figure 104: SEM image of polished cross-section of mid-plane of SiC/BN/SiC CMC sample exposed for 50 hours in dry oxygen at 800°C loaded to 150 MPa. Blue arrows indicate loading direction. Inset shows an oxide filled crack (red arrow) propagated through a longitudinal, load-bearing fiber tow. The yellow arrow points to a cracked SiC fiber.

The matrix crack imaged in Figure 104 resulted in oxidation of the outer edge of the tow, and also attacked the fiber tow itself. Figure 105 shows SEM/EDS maps of the region where a load-bearing fiber has cracked and oxygen solubility (red arrow) is observed in the fiber on either side of the crack. It is unknown if the fiber cracked first and then oxidized, or if the fiber oxidized and then cracked. However, due to the similar oxygen solubility lengths on either side of the crack, it is assumed that the fiber cracked first and then oxidized. It can also be seen in the oxygen map that the fiber coating near the cracked fiber has also oxidized. Fiber cracking and sliding results in a larger surface area for oxidant attack in the fiber tow, potentially degrading mechanical properties.



Figure 105: EDS maps of oxide filled crack near fiber tow in SiC/BN/SiC CMC exposed to 50 hours in dry oxygen at 800°C loaded to 150 MPa. A cracked SiC fiber (yellow arrow) displays oxygen solubility (red arrow).

The effects of stress and time were also considered. Samples exposed at 180 and 200 MPa also exhibited partial oxide filling in the cracks, with preferential filling occurring near B-rich phases. The stress value did not obviously affect the degree of oxide filling. The exposure time did have an effect on the amount of filling based on limited observations. In Figure 106, the crack exposed for 100 hours has a longer length of continuous filling than the sample exposed to the same 600°C/200 MPa condition for 50 hours. There is still a length of crack that remains unfilled for the 100 hour exposure as well.



Figure 106: Backscatter SEM images of interior crack filling in SiC/BN/SiC CMC after 50 and 100 hours at 600°C at 200 MPa in dry oxygen.

# 6.3.6 Stress-rupture at 200 MPa for 800°C exposure

One of the samples exposed at 800°C, 200 MPa ruptured after 28 hours, and the second sample completed the 50 hour exposure. The sample that ruptured failed in a region that was approximately 760°C, according to the furnace thermal mapping completed prior to testing. Fibers exposed to the environment at the fracture surface had longer oxygen solubility lengths compared

to fibers in the hot zone, as listed in Table 11. The top and bottom fracture surface can be seen in Figure 107. On the edges of the fracture surface, flat fiber bundles with little to no fiber pullout are observed, indicative of embrittlement in these regions. The interior of the fracture surface exhibits longer fiber pullout lengths.



Figure 107: Fracture surfaces for SiC/BN/SiC CMC specimen exposed at 800°C at 200 MPa that ruptured after 28 hours in dry oxygen. White dot marks the same location on both surfaces.

# 6.4 Discussion

# 6.4.1 Damage Mechanisms Observed

The same damage mechanisms were observed for SiC/BN/SiC CMC specimens exposed in dry oxygen as those previously described for the lab air oxidation load holds. These damage mechanisms are summarized per load level for the dry oxygen exposure in Table 12. Table 12: SiC/BN/SiC CMC damage mechanisms observed in dry oxygen at different load levels. ( $\checkmark$ ) signifies that the mechanism was observed and (-) signifies that the mechanism was not observed.

Damage Mechanism	Unstressed Oxidation	σ <sub>150</sub>	$\sigma_{180}$	$\sigma_{200}$
Oxidation through porosity pipes	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxygen solubility in SiC fibers	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxidation in intratow MI-rich regions	$\checkmark$	$\checkmark$	$\checkmark$	$\checkmark$
Oxidation formation in matrix cracks	N/A	-	$\checkmark$	$\checkmark$
Stress Rupture	N/A	-	-	√ (~760°C)

#### 6.4.2 Comparison to dry oxygen oxidation in TGA

The oxidation behavior observed in the dry oxygen load frame setup is similar to that seen in the dry oxygen TGA. A boron-rich oxide is formed at 600°C and a silica-rich oxide is formed at 800°C in both setups. Both setups and temperatures result in oxygen solubility in the SiC fibers, and the oxygen solubility length is longer for the 600°C exposure due to the less protective (i.e. non-wetting) boron-rich oxide. The oxygen solubility lengths are longer for the stressed condition. Applied stress may result in delamination between the fiber and fiber coating in the transverse, non-load bearing fiber tows, which may allow for a larger surface area of the fiber to be oxidized, resulting in the longer oxygen solubility lengths observed. It is unknown if oxygen solubility in the Hi-Nicalon SiC fibers only occurs via the base of the fiber or if it can also occur via the circumference of the fiber. Further work should be completed on understanding the directional dependence of oxygen solubility in Hi-Nicalon fibers. The BN fiber coatings are oxidized after the 600°C exposures in both setups and are not oxidized after the 800°C exposure.
One difference between the oxidation behavior in the two setups is the lack of a two-phase oxide after 600°C exposures in the load frame. A distinct boron-rich phase and silicon-rich phase existed after cooldown in the TGA exposures. It is unknown if the two-phase behavior first occurred at high-temperature or upon cooldown. One difference between the two experimental setups is that in the TGA the sample is quickly heated and cooled as the furnace position is raised and lowered and dry oxygen flows through the system. In the load frame, the sample takes approximately thirty minutes to heat up and one hour to cool down when the furnace turns off. The different heating profiles may result in different oxidation behavior.

## 6.4.3 Comparison to lab air oxidation load holds

The oxidation and damage mechanisms observed in lab air and dry oxygen are similar. Brich phases preferentially oxidize on the exterior and in the CMC interior in both conditions, interior cracks exhibit partial filling, and stress-rupture only occurs at the 800°C condition at 200 MPa, as illustrated in Figure 108. It is likely that the small difference in water vapor content (approx. 1-2 vol%) in the two conditions does not cause a major difference in the mechanical and oxidative performance of the CMC. Water vapor reactions with the borosilicate produce silicon and boron hydroxide gaseous species, resulting in a less protective oxide. The subsurface water vapor content in lab air exposures is likely not enough to produce a significant amount of hydroxide species that would appreciably alter the degradation behavior as compared to dry oxygen exposures.



Figure 108: Illustration displaying the effects of temperature, stress, and water vapor content with results from dry oxygen and lab air. Green dots represent no stress-rupture at that condition and red dots represent at least one sample rupturing at that condition. Each dot represents two tests.

The one major difference noted between the two conditions is the surface oxide morphology at 800°C. Oxide droplets form over B-rich phases in lab air, in contrast to the oxide formed in dry oxygen which covers the surface of the composite in dry oxygen. The difference in oxide morphology affects crack filling on the surface of the composite. In lab air, the droplets do not fill the cracks on the surface near the fiber tows. In dry oxygen the wetting oxide fills surface cracks near the fiber tows where a B-containing phase resides, seen in Figure 101. This inhomogeneous oxide filling behavior again shows that the crack composition measured previously is an important consideration to model the oxidation behavior of a SiC/BN/SiC CMC.

However, in both conditions, cracks in the MI matrix material without nearby fiber tows remain unfilled and act as a penetration path for oxidant to travel into the CMC interior. The different oxide morphology only appears to affect the level of protection of the fibers and fiber tows on the surface. Previous research has noted that an oxide formed on CMCs at higher temperatures may result in a crack-healing effect, where oxide fills cracks on the surface to mitigate attack in the CMC interior [77]. In the present work, it appears that the crack-healing phenomena is not operative at the CMC surface at 600 or 800°C in lab air or dry oxygen.

#### 6.4.4 Implications for CMCs in service

CMCs in service will experience applied load due to thermal stresses. The load may open micro-cracks if it is past the matrix cracking stress, allowing oxidant ingress into the bulk of the material. It has been shown in both lab air and dry oxygen, that crack closure does not occur after 50 or 100 hours via oxidation, and matrix cracks readily allow access for oxidative attack. Thermochemical attack via SiC fiber oxidation and BN coating oxidation occurs at 600°C. Thermomechanical attack via crack opening is prevalent at both 600 and 800°C when the CMC is loaded past the proportional limit. These results show that CMCs utilized below the matrix cracking stress in low water vapor content environments at 800°C will experience negligible degradation.

## **6.5 Conclusions**

The following conclusions can be made after exposures in the dry oxygen load frame setup:

- 1. The setup used for dry oxygen exposures in the load frame is suitable to reproduce oxidation behavior for CVD SiC and SiC/BN/SiC CMCs as observed in dry oxygen TGAs.
- 2. B-rich phases in the matrix preferentially oxidize on the CMC exterior and interior.
- 3. Dry oxygen and lab air exposures result in different surface oxide morphology, but the subsurface oxidation behavior (SiC fiber oxygen solubility, crack filling) is similar for both exposures as the water vapor content in lab air (1 vol%) is likely not enough to produce a significant amount of hydroxide species that would alter the oxide chemistry and affect material degradation.
- 4. Stress-rupture occurs at 760°C/200MPa, where many cracks are open for material attack and the oxide growth rate is sufficient to produce enough oxide to embrittle the material.

# Chapter VII. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in wet oxygen

#### 7.1 Introduction

Water vapor has two main effects on SiC at high temperature. First, water vapor accelerates the oxidation of silicon carbide, as compared to oxidation in dry oxygen [51]. Second, it has previously been shown that in combustion conditions, with temperatures ranging from 1200-1450°C, pressures of 4-15 atm, gas velocities of 15-30 m/s and lean- and rich-burn fuel-to-air ratios, that the SiO<sub>2</sub> scale formed on a SiC substrate will volatilize and recession of the underlying SiC is observed [78, 79]. Environmental barrier coatings (EBCs) are often applied to mitigate oxidation and recession of the SiC-based composite [80]. However, EBCs may fail from stresses due to thermal cycling, and the reactions between an uncoated CMC and water vapor must be considered.

Previous work has been conducted on tensile testing SiC/BN/SiC CMCs (containing Sylramic-iBN fibers) in water vapor containing environments. LaRochelle and Morscher performed stress-rupture tests on woven SiC/BN/SiC CMCs at 550 and 750°C with  $pH_2O = 0.0$ , 0.2, and 0.6 atm [81]. Little to no fiber/matrix embrittlement was observed at  $pH_2O = 0.0$  atm for either temperature, but embrittlement was observed at both temperatures for  $pH_2O = 0.2$  and 0.6 atm. The most embrittlement, and greatest reduction in stress rupture strength, were observed at

750°C and pH<sub>2</sub>O = 0.6 atm [81]. Fatigue tests on SiC/BN/SiC CMCs were performed by Mall and LaRochelle at 750°C with a frequency of 10 Hz and a stress ratio of 0.1 with 0 and 60% moisture content [82]. It was again observed that the 60% moisture content was more degrading, and fatiguing the samples resulted in a shorter lifetime than stress-rupture testing [82]. Mall and Ryba studied the stress rupture of a SiC/BN/SiC CMC at 400, 750, and 950°C in lab air and 100% steam up to 100 hours [83]. Stress rupture strengths reduced with temperature and steam content, and that the specimens exposed at 750°C displayed lower stress-rupture strengths in both lab air and steam than expected based on interpolations of the data between 400 and 950°C. Residual strength was lowest for specimens exposed at 750°C. Fiber coatings exposed at 400 and 950°C were recessed and lost, and borosilicate glass was observed at fiber coating regions for specimens exposed at 750°C [83]. These studies interrogated the fracture surface behavior, but lacked a detailed investigation of the interior oxidation behavior in micro-cracks prior to stress-rupture.

More recent work was performed by Zok et al. on a precursor impregnated and pyrolyzed (PIP) SiC/BN/SiC CMC containing Tyranno ZMI fibers [50]. Mechanical tests were performed in water vapor at 800 and 1100°C under cyclic and quasi-static tensile load. It was observed that 6 hour tests performed below the matrix cracking stress did not affect composite strength. Slightly above the matrix cracking stress, degradation of the SiC fibers and BN coatings via water vapor attack was observed near cracked regions. Silica glass and porosity was observed at oxidized fiber coating locations [50]. The prior literature demonstrates that degraded fiber coatings result in a decrease of the stress rupture strength, especially with the introduction of water vapor.

The current work focuses on the oxidation of the RRHTC SiC/BN/SiC CMC in a 50% H<sub>2</sub>O/50% O<sub>2</sub> gas mixture at and above the matrix cracking stress. It was anticipated that stress rupture lifetimes would be lower at 600°C and 800°C. This was expected due to the oxidation and volatilization of the fiber coatings at 600°C and the oxidation of the coatings at 800°C observed in the TGA work in *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen.* 

#### 7.2 Materials & Methods

#### 7.2.1 Materials

Material and manufacturing techniques are the same as those utilized in *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air*. Refer to Section 5.2 for more information.

## 7.2.2 Static load holds

The testing method for the load frame previously described in *Chapter V. Stressed* oxidation of SiC/BN/SiC ceramic matrix composites in lab air. Refer to Section 5.2 for more information.

A custom fused quartz fixture (Technical Glass Products) was manufactured to control the environment, and is depicted in the schematic in Figure 109. The specimen was slotted into the fused quartz tube, and the gaps were packed with fused quartz wool. A ball joint inlet was connected to the same presaturator and saturator setup described in Section 3.2 in *Chapter III. Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in wet oxygen* to 158 provide a 50%  $O_2/50\%$  H<sub>2</sub>O mixture. Calibrations to confirm the water vapor content in the gas mixture were performed prior to testing. The 50%  $O_2/50\%$  H<sub>2</sub>O gas mixture was injected into the fused quartz fixture at 500 sccm. A graduated cylinder was connected to fixture in an attempt to collect water vapor in the exhaust to avoid water vapor interactions with the load frame grips; however, this method did not work. Instead water vapor condensed on water-cooling tubes on the top grip, pointed out by the red arrows in Figure 110. Minimal rusting was observed on the grip inserts after testing, but no damage was observed on the grips themselves.



Figure 109: Fused quartz fixture to control environment for testing in load frame.



Figure 110: Water vapor condensing on load frame grips, indicated by red arrows.

## 7.2.3 Characterization

Characterization techniques, included SEM, EDS, and FIB as previously described in *Chapter V. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air*. Refer to Section 5.2 for more information.

## 7.3 Results

## 7.3.1 Testing summary

Oxidation load holds in 50%  $H_2O/50\%$   $O_2$  mixture resulted in stress-ruptures at different loads and temperatures than previously seen in lab air and dry  $O_2$ . Previously, testing in lab air and dry  $O_2$  was performed to a maximum stress of 200 MPa. However, stress-ruptures occurred at short times and lower loads in wet oxygen, as seen in Table 13. For this reason, testing was suspended at 180 MPa. The damage mechanisms are presented and discussed in relation to the stress-rupture behavior.

Stress (MPa)	Temperature (°C)	Result	Time (hours)
150	600	Interrupted, no failure	14
150	600	Stress-rupture	26
150	600	Stress-rupture	27
150	600	Stress-rupture	37
150	600	Stress-rupture	30 hour pre-exposure +
			12.7 hours
150	800	Interrupted, no failure	100
180	800	Interrupted, no failure	2
180	800	Stress-rupture	5

Table 13: Summary of oxidation load hold testing in 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture

## 7.3.2 Surface Oxide Morphology

Samples tested in the load frame at 600°C in wet O<sub>2</sub> exhibit different oxidation behavior than that previously seen in wet oxygen TGA testing, as seen in Figure 111. After removal from the load frame (five minutes after the specimen ruptured), there were minimal oxide droplets present on the sample surface. Black spots, indicated by the blue arrow in Figure 111, are voids/porosity pipes, and remain unfilled after exposure in the load frame. No oxide droplets were present near the fiber tows and only a few droplets were observed in the MI matrix material, as seen in Figure 112. B-containing phases in the material also oxidized and volatilized away, leaving voids where the phase had once been.



Figure 111: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the TGA for 50 hours and the load frame for 26 hours at 150 MPa. Note the lack of oxide droplets for the load frame exposure. Blue arrows indicate porosity pipes.



# fiber tow

material

Figure 112: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at 600°C in the load frame for 26 hours at 150 MPa. Red arrows indicate locations where B-containing phases oxidized and volatilized in MI-rich regions in longitudinal fiber tows and in MI matrix material.

Oxidation for specimens exposed at 800°C in the load frame were similar to those exposed

in the wet TGA setup, as imaged in Figure 113. Silica-rich oxide droplets are present in the MI

matrix material, around the edges of the fiber tow, and in the fiber tow itself. The oxide is not protective and does not cover the entire surface of the CMC as observed for dry oxygen exposures.



Figure 113: Backscatter SEM images of exposed surface of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\% O_2$  mixture at 800°C in the TGA for 50 hours and the load frame for 100 hours at 150 MPa. The fibers on the surface of the load frame sample are from furnace insulation.

## 7.3.3 Stress-rupture at 600 and 800°C

Stress-rupture occurred in three specimens tested at 600°C at 150 MPa after 26, 27, and 37 hours. Stress-rupture did not occur previously for any sample tested at 600°C in lab air or dry oxygen. The top and bottom fracture surfaces from the specimen that failed after 26 hours are shown in Figure 114. The outer edge of the fracture surface exhibits more fiber pullout than the interior of the surface. This is qualitatively observed with the dark contrast in the outer tows (caused by fiber pullout) and the low contrast in the interior (caused by a flat fracture surface). This behavior is opposite of the previously described "picture-frame" fracture surfaces described in *Chapter V*. Higher magnification images of the fiber pullout exhibited in the exterior fiber tows and the flat fiber tow failure are seen in Figure 115.



**Top Fracture Surface** 

**Bottom Fracture Surface** 

Figure 114: Backscatter SEM images of top and bottom fracture surfaces of SiC/BN/SiC CMC that stress-ruptured after exposure to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C for 26 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit flat, brittle failure.



Figure 115: Backscatter SEM images of exterior and interior fiber tow from top fracture surface of SiC/BN/SiC CMC that stress-ruptured after exposure to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C for 26 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit flat, brittle failure.

Since stress-rupture occurred at the lowest stress ( $\sigma_{MC}$  = 150 MPa) studied at similar times for three tests (approximately 30 hours) it was of interest to understand the standalone and synergistic effects of oxidation and load in this condition. In order to do this, a 30 hour preexposure was performed in the wet oxygen load frame at 0 MPa. The sample was then loaded to 150 MPa and held at load until stress-rupture. The pre-exposure resulted in a 58% reduction in rupture time, occurring after 12.7 hours. Again, the outer edges of the specimen displayed fiber pullout and the interior fiber bundles of the CMC had flat, brittle failure, as imaged in Figure 116. There was topography in the matrix material in the interior, but the fiber tows themselves were flat, as imaged in Figure 117. H<sub>2</sub>O rapidly oxidized the outer fiber tows, requiring no micro-cracks to penetrate the material. Red arrows in Figure 116 indicate porous regions in the CMC, which provides another pathway besides micro-cracks for oxidation into the CMC interior. Porosity in the CMC has been previously observed with X-ray CT in *Chapter V*. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air. The pre-exposure resulted in a reduction of the stress-rupture time at 150 MPa at 600°C.



26 hours

30 hours pre-exposure + 12.7 hours

Figure 116: Backscatter SEM images of top fracture surfaces of SiC/BN/SiC CMC that stress-ruptured after exposure to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C for 26 hours and with a 30 hour pre-exposure + 12.7 hours at 150 MPa. Fiber tows on the outer edges exhibit fiber pullout and interior tows exhibit flat, brittle failure. Red arrows indicate regions of porosity in the matrix.



Figure 117: Backscatter SEM images of top fracture surfaces of SiC/BN/SiC CMC that stress-ruptured after exposure to  $50\% H_2O/50\% O_2$  mixture with a 30 hour pre-exposure + 12.7 hours at 150 MPa. Red arrows indicate flat fiber bundle and blue arrows indicate multi-ply topography in matrix material.

Stress-rupture did not occur for the 800°C specimen tested at 150 MPa. However, stressrupture did occur after 5 hours at 800°C for the specimen tested at 180 MPa. The fracture surface is imaged in Figure 118. The fracture surfaces were flat, with little fiber pullout exhibited except for the very outermost fibers on the edge fiber tows.



Figure 118: Backscatter SEM stitched image of top fracture surface of SiC/BN/SiC CMC that stress-ruptured after exposure to  $50\% H_2O/50\% O_2$  mixture at  $800^{\circ}C$  for 5 hours. The fiber tow fractures are flat across the sample.

## 7.3.4 Oxidation of fiber coatings

Fiber coating behavior was investigated with FIB-milled and polished cross-sections on the machined edges and fracture surfaces. Figure 119 shows a FIB-milled cross-section of fibers on the machined edge after exposure at 600°C for 26 hours. The fiber coatings have oxidized and volatilized, leaving an annular void surrounding the fiber coating. There is no oxygen solubility observed in the SiC fibers after the 600°C exposure.



Figure 119: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exposed surface in SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at  $600^{\circ}$ C the load frame for 26 hours at 150 MPa. Note the lack of B, O, and N signal in the fiber coating region.

The fracture surface at 600°C/150 MPa exhibited a reverse picture-frame fracture, with fibers on the outer edge exhibiting fiber pullout and interior fibers exhibiting flat, brittle fracture. Figure 120 shows fiber fracture near the interior, and the nitrogen and oxygen maps associated with the region. Some regions in the nitrogen map show where nitrogen was retained (indicated by red arrows), and oxygen signal displays oxidation of the fiber coatings on this surface. This indicates that the fiber tows likely failed as a single unit due to the glass bonding fibers together. FIB-milled cross-sections were taken from a region that also exhibited flat fiber failure in Figure 121, and in this case no nitrogen signal was observed in the fiber coating region, but oxygen signal at the coating region was observed.



Figure 120: Backscatter SEM images and EDS maps of SiC fibers on interior of fracture surface in SiC/BN/SiC CMC exposed to  $50\% H_2O/50\% O_2$  mixture at  $600^{\circ}C$  the load frame for 26 hours at 150 MPa.



Figure 121: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on interior of fracture surface in SiC/BN/SiC CMC exposed to  $50\% H_2O/50\% O_2$  mixture at 600°C the load frame for 26 hours at 150 MPa. Cross-section taken from location marked with white dashed line on left hand image. Oxygen signal at coating regions indicated by red arrows.

A FIB-milled cross-section was performed near the edge of the fracture surface, as imaged in Figure 122. Attempts were made to FIB fibers that displayed long lengths of fiber pullout, but were unsuccessful. Instead, nearby fibers were investigated, and it was observed via EDS that no fiber coatings were retained for the fibers studied in the cross-section, and some oxygen signal was observed on the fiber coating region.



Figure 122: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exterior of fracture surface in SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at  $600^{\circ}$ C in the load frame for 26 hours at 150 MPa. Cross-section taken from location marked with white dashed line on left hand image. Oxygen signal in fiber coating regions indicated by red arrows.

Figure 123 shows a FIB-milled cross-section for a sample exposed to 50%  $H_2O/50\% O_2$  mixture at 800°C in the load frame for 100 hours at 150 MPa. The fiber coatings oxidized near the

exposed edge, and beneath the oxidized fiber coatings nitrogen signal is retained. The Hi-Nicalon SiC fibers also exhibit oxygen solubility. These oxidation mechanisms were also seen in the wet oxygen TGA work.



Figure 123: Backscatter SEM images and EDS maps of FIB-milled cross-section of SiC fibers on exposed surface in SiC/BN/SiC CMC exposed to 50% H<sub>2</sub>O/50% O<sub>2</sub> mixture at  $800^{\circ}$ C the load frame for 100 hours at 150 MPa.

## 7.3.5 Subsurface oxidation

Micro-cracks in the CMC interior displayed variable behavior for the interrupted 14 hour test at 600°C at 150 MPa. SEM/EDS of these micro-crack regions are seen in Figure 124. The inset image outlined in blue shows a crack partially filled with oxide. Regions of oxide are pointed out with white arrows. On the other hand, a different region shown in the orange inset shows a crack that is unfilled (the oxygen signal in the crack corresponds to carbon signal and is likely polishing media). The fiber coatings in that region have been oxidized and no nitrogen signal remained.



Figure 124: Backscatter SEM images cross-section C of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C in the load frame for 14 hours at 150 MPa. The test was interrupted after 14 hours. Blue arrows indicate loading direction. Red arrows indicate oxidized fiber coatings and white arrows indicate partial matrix crack filling.

Exposure after 26 hours at 600°C, resulting in stress-rupture, did not seemingly increase the amount of oxidation in interior micro-cracks. A micro-crack is indicated by red and white arrows in the red inset in Figure 125. The red arrow points to a location that has oxidized and the white arrows point to an unoxidized region of the micro-crack. All micro-cracks that were observed did not appear to have appreciable amounts of oxide filling. In some cases, B-rich phases in MI intratow regions were also observed to have oxidized, and volatilized, shown in the green inset. Other B-rich regions had oxide droplets present, but did not volatilize.



Figure 125: Backscatter SEM images cross-section C of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 600°C in the load frame for 26 hours at 150 MPa. Blue arrows indicate loading direction. Red arrows indicate filled matrix crack and white arrows indicate unfilled matrix crack in red inset. Green inset shows intratow MI rich region where B-containing phase oxidized and volatilized, leaving voids, indicated by green arrows.

No interior cracks were observed in the specimen tested at 800°C for 100 hours at 150 MPa. Instead, porosity pipes filled with oxide up to  $600\mu$ m deep after exposure to the environment, indicated by the red arrows in Figure 126. The BN fiber coatings were also oxidized.

The B-containing phases in the matrix also oxidized, but the oxide regions remained filled and did not volatilize like seen in the 600°C exposures.



Figure 126: Backscatter SEM image of cross-section C SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 800°C in the load frame for 100 hours at 150 MPa. Red arrows in inset image indicate oxidized regions.

Exposures at 800°C at 180 MPa for two- and five-hours exhibit oxidation of interior cracks and BN fiber coatings. After the two-hour interrupted exposure, cracks were filled near the Bcontaining phases in the matrix. Oxidation of BN fiber coatings connected to the micro-cracks was also observed, as shown in the oxygen EDS maps in Figure 127. The same behavior was observed for the specimen that stress-ruptured after five hours.



Figure 127: Backscatter SEM images and EDS maps of cross-section of SiC fibers in interior of SiC/BN/SiC CMC exposed to 50%  $H_2O/50\%$   $O_2$  mixture at 800°C in the load frame for 2 hours at 180 MPa.

## 7.4 Discussion

## 7.4.1 Damage mechanisms in wet oxygen

Oxidative damage increased via water vapor reactions in the SiC/BN/SiC CMC. The behavior of the BN fiber coatings dominated the mechanical performance. Stress-rupture occurred at 600°C at 150 MPa in the 50% H<sub>2</sub>O/50% O<sub>2</sub> gas mixture due to oxidation of the fiber coatings via porosity pathways. In contrast, micro-cracking pathways for oxidation were required at 800°C for stress-rupture to occur after five hours. The damage mechanisms observed in wet oxygen load holds are summarized in Table 14. Two new mechanisms occurred in water vapor, including annular voids at 600°C and oxidation and volatilization of the B-containing phases at 600°C.

Table 14: Damage mechanisms observed in wet oxygen at different load levels. ( $\checkmark$ ) signifies that the mechanism was observed and (-) signifies that the mechanism was not observed. If a temperature is listed, that behavior only occurred at the listed temperature.

Damage Mechanism	Unstressed Oxidation	$\sigma_{150}$	$\sigma_{180}$
Oxidation through porosity pipes	$\checkmark$	$\checkmark$	$\checkmark$
Oxygen solubility in SiC fibers	$\checkmark$	√ (800°C)	√ (800°C)
Oxidation in intratow MI-rich regions	$\checkmark$	$\checkmark$	$\checkmark$
Oxidation formation in matrix cracks	N/A	$\checkmark$	$\checkmark$
Stress Rupture	N/A	√ (600°C)	√ (~760°C)
Annular voids	√ (600°C)	√ (600°C)	-
Oxidation and volatilization of B-containing phases	-	√ (600°C)	-

## 7.4.2 Stressed oxidation at 600°C in wet oxygen

Oxidation behavior at 600°C was different in the load frame setup than that observed in the wet oxygen TGA in some regards. In the wet oxygen TGA, borosilicate droplets were observed on the surface after removal, and while the B-containing phase did oxidize, it did not noticeably volatilize and leave porosity. Oxygen solubility in the SiC fibers was also observed. In the wet oxygen load frame setup, no oxide droplets were present, volatilization of the B-containing phase occurred, and there were no fibers where oxygen solubility was observed. Oxidation and volatilization of the BN fiber coatings leaving an annular void around the SiC fibers was observed in both experimental setups. The difference in oxidation behavior likely stems from the different gas boundary conditions. In the wet oxygen TGA, there is a well-developed laminar flow over the edges of the TGA coupon. The TGA has a long length of tube where the gas flow is well developed prior to reaching the specimen. In the wet oxygen load frame, the custom fused quartz setup has an inlet tube with an inner diameter of 5mm (D<sub>1</sub> in Figure 128) and has a sudden expansion to the tube surrounding the specimen with an inner diameter of 22mm (D<sub>3</sub> in Figure 128) [84]. This sudden expansion results in turbulent flow near the inlet region, labeled the transitional region in Figure 128. Eventually a well-developed gas flow occurs downstream. The development length is dependent on the Reynolds number and the inner diameter of the tube. It is likely that the development length was not achieved in the load frame, and the CMC experienced an ill-defined turbulent flow during exposure.



Figure 128: Schematic showing example of sudden expansion phenomena that occurs in the wet oxygen load frame setup. Graphic reproduced from [84].

Both laminar and turbulent flow across a sample result in a gas boundary layer. When a reaction product, such as boria, volatilizes, it must travel through the boundary layer. It has been previously demonstrated that a thinner boundary layer (caused by an increase in gas velocity) results in faster weight loss for volatile species like  $Cr_2O_3$  [85]. In turbulent flow, there is a viscous sublayer beneath the turbulent boundary layer that slows vaporization flux and the viscous

sublayer thins with increasing flow rate [86]. Modeling shows that turbulent flow mass transfer is three orders of magnitude higher than that in laminar flow, resulting in much higher recession rates [86]. It is hypothesized in the present work that turbulent flow across the CMC in the load frame setup results in higher  $B_2O_3$  vaporization rates than that seen in the wet TGA.

Stress-rupture was not observed in previous oxidation load hold testing in lab air and dry oxygen at 600°C. Also, no stress-rupture had been previously seen at 150 MPa at any temperature or environmental condition. Water vapor reactions resulted in increased amounts of degradation at 600°C. Similar stress-rupture times (26, 27, 37 hours) suggests oxidation of the CMC is the predominant damage mechanism, rather than crack openings allowing oxidant ingress. The 30 hour pre-exposure at 0 MPa also resulted in a decrease in the stress-rupture time (12.7 hours), likely caused by oxidation of the interior constituents via porosity pipes. Stress-ruptures with and without a pre-exposure exhibited similar "reverse picture-frame" fracture surfaces, where BN coating loss on the outer edges was observed.

Very few matrix cracks, if any, were likely to be open upon initial loading to 150 MPa to allow oxidant ingress into the CMC interior based on baseline fast fracture tests. However, as previously noted, 'porosity pipes' at the surface allow oxidant ingress into the material. The boronrich oxide that forms at 600°C, paired with higher volatilization rates in the wet oxygen load frame setup, lead to an extremely non-protective oxide. BN coatings and the B-containing phase in the matrix oxidize, leading to embrittlement of the material interior. Strength degradation of the CMC micro-constituents in a local region leads to overloading in another region, resulting in microcracking. Micro-cracking leads to more pathways for oxidant travel, resulting in more oxidation. This cycle, depicted in Figure 129, continues until stress-rupture occurs.



Figure 129: Oxidation mechanisms observed at 600°C in water vapor where a) SiC/BN/SiC CMC has porosity pipes at the surface that b) allow oxidant ingress into the material resulting in embrittlement that c) promotes cracking and further oxidation. Black interphase is unaffected, blue is oxidized, and white is where volatilization has occurred.

#### 7.4.3 Stressed oxidation at 800°C in wet oxygen

Oxidation load holds at 800°C at 150 MPa did not result in stress-rupture. Stress-rupture did occur at 180 MPa for 800°C after 5 hours, which was the lowest stress-rupture load observed for 800°C in any environmental condition. The oxide produced at 800°C was present on the surface after testing and was silica-rich, as seen previously in the TGA. The silica-rich oxide provided more protection to the CMC at 150 MPa, and while oxidation of the coatings did occur, no annular voids were observed.

Micro-cracks on the surface at 180 MPa allowed direct access to fiber coatings, resulting in oxidation of the coatings. This oxidation resulted in bonding of the fibers to each other and to the matrix material, resulting in stress-concentrations in these regions. Eventually, bonded fibers would fail as a singular unit, exhibited by the flat fracture surface at the fiber tow, and micro-crack propagation would allow for increased pathways of oxidant travel. More micro-cracking promoted oxidation, and oxidation promoted micro-cracking, as depicted in Figure 130.



Figure 130: Oxidation mechanisms observed at 800°C in water vapor where a) SiC/BN/SiC CMC that b) cracks with applied load allowing oxidant ingress into the material resulting in embrittlement that c) promotes cracking and further oxidation. Black interphase is unaffected, blue is oxidized, and white is where volatilization has occurred.

## 7.4.4 Comparison to stressed oxidation in lab air and dry oxygen

Previous damage mechanisms observed in lab air and dry oxygen were also again observed in wet oxygen, along with additional damage mechanisms. Oxidation through porosity pipes occurred in all three conditions. This mechanism proved most damaging in wet oxygen as it allowed water vapor reactions to occur within the material and cause volatilization of B-containing species at 600°C that eventually caused stress-rupture at 150 MPa.

Oxidation was observed in matrix cracks on the exterior and interior of the CMC in all wet oxygen conditions. Intermittent oxide filling occurred in all conditions, and was most prevalent in regions where B-containing phase resided. The lack of oxide filling in the micro-cracks resulted in pathways for oxidant ingress into the material. Micro-cracking and subsequent oxidation was most degrading for exposures at higher loads at 800°C. Wet oxygen exposure results in increased oxidative degradation for the SiC/BN/SiC CMC under load. As seen in the TGA work, wet oxygen results in increased oxidation of fiber coatings at 800°C and volatilization of coatings at 600°C compared to dry oxygen TGA exposures. These mechanisms occur in the load frame as well, decreasing the mechanical performance of the SiC/BN/SiC CMC. Stress-ruptures occurred at lower loads than those with lab air and dry oxygen, as depicted in Figure 131.



Figure 131: Illustration displaying the effects of temperature, stress, and water vapor content with results from dry oxygen, lab air, and wet oxygen. Green dots represent no stress-rupture at that condition and red dots represent at least one sample rupturing at that condition. Each dot represents at least two tests.

#### 7.5 Conclusions

Wet oxygen exposures caused degradation of SiC/BN/SiC CMC mechanical properties. It was seen that when oxidized under load at 600°C in wet oxygen, BN coatings oxidized and volatilized, causing stress-rupture at 150 MPa after ~30 hours at first matrix cracking loads for fast fracture. Porosity pipes allowed significant access for oxidation to occur while under relatively low loads with little micro-cracking. Increased micro-cracking at 180 MPa for tests conducted at 800°C resulted in oxidation of interior BN fiber coatings via oxidant ingress through the micro-cracks. Oxidative damage rapidly occurs due to the increase of micro-cracks in the material that do not fill with oxide. Synergy between micro-cracking and oxidation results in increased material degradation.

This study provided a detailed look at the resultant micro-structure after stressed oxidation of SiC/BN/SiC CMCs in lab air, dry oxygen, and wet oxygen. A rigorous study of CMC cross-sections on interrupted tests was performed, and analysis of fracture surfaces for ruptured specimens was also provided. A new understanding of the extent of micro-crack oxide filling was gleaned from the polished cross-sections. The amount of B-containing phase in the matrix was not sufficient to rapidly seal cracks and did not mitigate oxidative attack. In fact, the high concentration of the Bcontaining phase near the fiber tows may have contributed to increased amounts of fibers fusing to one another as there was more local available glass in the region. BN fiber coating behavior was evaluated, with the most degradation occurring at 600°C in wet oxygen, where annular voids were present near the edges of the specimen.

181

## Chapter VIII. CMC Degradation Modeling

## 8.1 Introduction

Prior efforts to model CMC oxidation behavior have been made. Recent models for SiC/BN/SiC CMCs are derived from oxidation modeling for SiC/C/SiC composites [87, 88]. Unstressed SiC/C/SiC composites were tested using thermogravimetric analysis from 900-1300°C [87]. The carbon interphases oxidized, leaving an annular void around the SiC fiber. The annular voids provided a path for oxidant ingress to the fiber coating and an exit for CO and CO<sub>2</sub> gas products. The side walls of the SiC fiber and matrix then oxidized, forming  $SiO_2$ . If the carbon interphase was sufficiently thin (on the order of 0.1  $\mu$ m), the annular void would seal due to SiO<sub>2</sub> formation, mitigating further oxidant ingress. A schematic depicting these phenomena is seen in Figure 132. A model was produced that was in good agreement with the experimental results [88]. Inputs for the model include, but are not limited to, temperature, pressure, and initial carbon interphase thickness. Outputs include the concentration of gaseous species and silica thicknesses along the annular void, the length of oxidized carbon, and weight change [88]. It was seen in both the experimental and modeling work that higher temperatures (1100°C and above) and thinner coatings (on the order of 0.1µm) are ideal as a thinner annular void and higher temperatures result in quicker sealing of the annular void with a protective silica layer [87, 88]. Similar oxidative processes from SiC/C/SiC modeling were then extended to SiC/BN/SiC composites.



Figure 132: Schematic depicting the oxidation processes for SiC/C/SiC composites. Oxygen oxidizes the pyrocarbon fiber coating, forming CO and CO<sub>2</sub>, leaving an annular void between the matrix and fiber. Oxidant diffuses in while the CO and CO<sub>2</sub> products diffuse out via the annular void. Meanwhile, oxygen reacts with the SiC constituents to form SiO<sub>2</sub> to seal the annular void. Schematic reproduced from [87].

Experimental work was performed on SiC/BN/SiC mini-composites, which were fabricated from a single tow of BN-coated fibers (BN thicknesses ranging from 0.5-3 $\mu$ m) with a chemical vapor infiltrated (CVI) SiC overcoat [32]. The mini-composites were pre-cracked, and then held at a constant load in lab air to rupture or up to 100 hours. It was observed at lower temperatures (~500-700°C) that an annular void was left around fibers where the BN fiber coating volatilized, and at higher temperatures (T>950°C) this void filled with silica for times greater than 98 hours [32]. This experimental observation led to future experiments with unstressed SiC/BN/SiC model materials using thermogravimetric analysis from 700-1100°C in environments containing water vapor [17]. BN recession was modeled based on the experimental work. BN recession occurs via several steps: 1) H<sub>2</sub>O diffusion through a gas boundary later and then through the annular void around a fiber, 2) H<sub>2</sub>O reacts with liquid B<sub>2</sub>O<sub>3</sub> on at the BN interface to form HBO<sub>2</sub>(g), H<sub>3</sub>BO<sub>3</sub>(g), and  $H_3B_3O_6(g)$ , 3) boron hydroxide species diffuse out of the annular void and through the boundary layer, and 4) the annular void walls begin to oxidize forming SiO<sub>2</sub> and reducing the void width [17]. This process is depicted in Figure 133. Inputs for the model include temperature, water vapor partial pressure, and BN interphase thickness. Outputs for the model include BN recession and times to seal the annular void. This model did not include the effect of matrix cracks sealing, which alters the pO<sub>2</sub> and pH<sub>2</sub>O at the reaction front over time.



Figure 133: Schematic depicting BN oxidation and recession behavior in SiC/BN/SiC CMCs modeled by Jacobson et al. [17]. Oxidant travels through boundary layer and annular void region to react with borosilicate and boron hydroxide species diffuse out of the annular void and boundary layer. SiO<sub>2</sub> growth occurs on the annular void walls to close annular void channel. Schematic reproduced from [17].

A model proposed by Morscher and Cawley aimed to describe the intermediate temperature (600-1000°C) stress-rupture behavior of a SiC/BN/SiC CMC [89]. This model focused on strength degradation that occurs due to neighboring fibers bonding to one another via oxidation of the BN fiber coating. A schematic depicting the model is presented in Figure 134. Once a matrix crack initiates in this region where fibers and matrix are bonded, it will propagate through the strongly bonded fibers rather than deflecting at the matrix-fiber interface. The unbroken fibers in the region will overload and then also fail. Inputs for the model include material mechanical properties, oxidation depths as measured from experimental work, and crack density. Outputs for the model include predictions of the fraction of fiber failures and stress-rupture predictions. This model does not include volatility of the coatings at any temperature.



Figure 134: Model schematic for SiC/BN/SiC CMCs at intermediate temperature where the predominant failure mechanism is oxidation of the BN fiber coatings bonding the fibers to themselves or matrix material. X(t) is the embrittlement depth and  $\sigma_f$  is the stress on the fiber in a bridged matrix crack. Schematic obtained from [89]

Additionally, models produced by Xu et al. focus on two oxidative processes from 700-1000°C in SiC/SiC CMCs and consider the effect of oxidant traveling through micro-cracks [31]. First, the effect of  $SiO_2$  scale formation around a fiber with BN coating loss on tensile stresses in

the fiber is considered and second the effect of annular voids filled with oxide and constrained oxide growth on stress intensities in the fibers is considered [31].

SiC fiber degradation has also been modeled. One such model examines the effect of grain growth and oxidation kinetics on the strength degradation of SiC fibers, and shown to be in good agreement with experimental data [90]. The model by Parthasarathy et al. [30] expands on prior modeling work by including fiber strength degradation [90] and cracking in the matrix material. In this model, depicted in Figure 135, a surface crack in the melt-infiltrated (MI) matrix acts as a fast path for oxidant to reach the BN coated fibers. The BN subsequently oxidizes and volatilizes leaving an annular void that fills with silica at long times and higher temperatures. The model allows for matrix oxidation to seal cracks and mitigate further oxidative attack into the interior of the composite. Matrix oxidation predictions are dependent on the amount of boron containing species in the matrix. Environmental inputs include partial pressures of water vapor and oxygen, temperature, time of exposure, and the force on the fiber tow. The outputs from the model include a residual tow strength and stiffness, length of the degraded BN interface, and stressrupture predictions. Stress-rupture predictions can be compared to actual stress-rupture times for different temperatures, environments, and loads. A complete list of the variables required for the model can be found in the Appendix. The modeling outputs produced in this chapter were conducted with the model produced by Parthasarathy et al., depicted in Figure 135, and is called the "UES MicroModel".



Figure 135: Graphic of SiC/BN/SiC CMC oxidation model by Parthasarathy et al. A crack connected to the surface allows oxidant into the CMC to react with a BN fiber coating. Reproduced from [30].

## 8.2 Methods

The UES CMC MicroModel was provided as a standalone application by Dr. Pavel Mogilevsky of UES to run the environmental micro-model described in Parthasarathy et al. [30]. Parametric studies were conducted to understand the effect of different inputs and to compare to the experimental results obtained in this dissertation. The inputs chosen for the parametric studies are described below:

- Exposure time (hours): The exposure time chosen for all models was 1000 hours. Although no tests in the previous chapters were run for this long, this input could be used as a prediction tool for stress-ruptures that did not occur before 100 hours.
- 2. SiC fiber type: The user can choose between three different SiC fibers: Hi-Nicalon, Hi-Nicalon S, and Sylramic-iBN. The user can also input properties of other fibers if desired.
Hi-Nicalon fibers were chosen as the input for the models, as those were the fibers used in the RR-HTC SiC/BN/SiC CMC.

- 3. Temperature (K): 873K (600°C) and 1073K (800°C) were used in all parametric studies.
- 4. Force on fiber tow (N): 70, 80, and 90 Newtons were chosen as inputs for the stress on the tow based on experimental results. 70, 80, and 90N were chosen by taking the load applied during testing and dividing by the number of load-bearing fiber tows in the cross-section (approx. 95 for the specimen's cross-sectional area). It is assumed in the local region where the matrix crack is, the fibers are carrying the majority of the local load.
- 5. Crack opening displacement (m): Most models run in this work used a COD of 0.5  $\mu$ m. The in-situ tensile testing study in *Chapter IV. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage* had a range of CODs at 200 MPa at 600°C, ranging from 0.2 to 0.6  $\mu$ m. At 225 MPa, CODs reach as high as 1  $\mu$ m. Because these wider CODs were observed, a subset of models were run to observe the effect of COD widths with COD = 0.2, 0.5, and 1.0  $\mu$ m.
- 6. Length to the surface ( $L_{surf}$ ) (m): This parameter describes the crack length to the free surface (see Figure 135). 2mm was used as the input for  $L_{surf}$  for most models. A parametric study was completed for  $L_{surf} = 0.01$ , 0.1, and 1 mm to observe the effect of fiber tows close to the surface.
- 7. Activity of boria in the matrix ( $aB_2O_3$ ): The variable  $aB_2O_3$  is described as "the activity of the borosilicate scale that forms in the interstices of the interface region" [30]. The atomic percent of boron species in the baseline matrix material was used as an estimate for  $aB_2O_3$ as instructed [91]. To obtain this value, twenty images were taken of the matrix material, 188

and thresholding was performed to identify the amount of melt-infiltrated Si, SiC particulate, and B-containing species. An average volume fraction was found for each matrix constituent, and from this, the weight percent and atomic percent were calculated. A value of 0.02 was used for  $aB_2O_3$  in most models, and a subset of models used 0.01, 0.10, 0.25, and 0.50 to observe the effect of  $aB_2O_3$ .

- 8. Partial pressure of oxygen: Partial pressures of oxygen used were 1.0 and 0.5. These values were used in accordance with the experimental work.
- 9. Partial pressure of water vapor: Partial pressures of water vapor were 0.0 and 0.5. These values were used in accordance with the experimental work.

Outputs for the model include:

- 1. Partial pressures of oxygen vs. time at different locations along the matrix crack
- 2. Partial pressures of  $H_2O$  and  $O_2$  at the crack tip vs. time
- 3. Partial pressures of oxygen vs. distance at different times
- 4. Partial pressure of  $H_2O$  and  $O_2$  at receding BN gap vs. time
- 5. Partial pressure of borate species at receding BN gap vs. time
- 6. Oxide scale thickness on the SiC fiber vs. time
- 7. BN gap vs. time
- 8. COD vs. time
- 9. Degraded tow length vs. time
- 10. Relative tow strength vs. time
- 11. Tow modulus vs. time

#### 8.3 Results and Discussion

#### 8.3.1 Effect of applied force

The force applied on the fiber tow was varied between 70, 80, and 90 N. As expected, there was no effect on the oxidation behavior (COD evolution, fiber coating degradation) due to the applied force. The stiffness of the fiber tow was only slightly affected for the 600°C exposures in both dry and wet oxygen, as seen in Figure 136. The lack of progressive fiber failure and stress-rupture predictions for the 600°C results are discussed below in *Section 8.3.5*. Tow modulus reduction in dry oxygen is attributed to fiber failure, and no degradation of the fiber coating is predicted. Water vapor increased the rate at which the modulus of the tow reduced. This is due to both progressive fiber failure and degradation of the fiber coating. The tow modulus is predicted to reduce by approximately 50-60 GPa prior to stress-rupture for a range of times after exposure at 800°C. The tow modulus also reduces more rapidly for wet oxygen than dry oxygen at 800°C.



Figure 136: Predicted effect of applied force on SiC/BN/SiC CMC fiber tow elastic modulus at 600 and 800°C in a) 100%  $O_2$  and b) 50%  $H_2O/50\% O_2$ . Force values used were 70, 80, and 90 N.

Stress-rupture was only predicted at 800°C, which conflicts with the experimental results where stress-rupture was observed at 600°C in wet oxygen at 150 MPa. Predicted stress-rupture times were shorter for wet oxygen at 800°C due to the BN fiber coating degradation, as seen in Figure 137. The stress-rupture times predicted for 800°C were up to 250 hours in dry oxygen for the highest load level, which is longer than the 28 hour stress-rupture observed at 200 MPa in the experimental work. The inputs used thus far result in two conflicts with the experimental work: 1) no stress-rupture predicted for 600°C in wet oxygen and 2) stress-rupture times predicted with the CMC micro-model are higher.



Figure 137: Stress-rupture predictions for SiC/BN/SiC CMCs at 70, 80, and 90N in dry and wet oxygen at 800°C.

#### 8.3.2 Effect of crack opening displacement

CODs of 0.2, 0.5, and 1 $\mu$ m based off of the micro-tensile work were input into the model at 70, 80, and 90 N at 600 and 800°C. There were no variations in the oxidation rates between the different COD inputs. However, the smallest COD, 0.2 $\mu$ m, was predicted to fully fill at 70N in 100% O<sub>2</sub> and 70 and 80N in 50% H<sub>2</sub>O/50% O<sub>2</sub> before stress-rupture could occur. Stress-ruptures were not predicted for the conditions that had full oxide filling of the crack and in all models run at 600°C. The predicted stress-rupture times can be observed in Figure 138. Little difference was predicted in the stress-rupture times between 0.5 and 1 $\mu$ m. Stress-rupture times were slightly longer for 0.2 $\mu$ m as there was a lower pO<sub>2</sub> and pH<sub>2</sub>O along the crack and at the crack tip as diffusion reduces with the COD reducing. This resulted in a lower pO<sub>2</sub> for fiber oxidation. The fiber oxidized at a slower rate until recession of the fiber contributed to a reduction in tow modulus and subsequent rupture. Interestingly, the model also predicts that stress-rupture will not occur for COD = 0.2 $\mu$ m at 80N in wet oxygen but does predict stress-rupture for COD = 0.2 $\mu$ m at 80N in dry oxygen. The difference in this prediction is due to the COD closing at a faster rate in wet oxygen than in dry oxygen, mitigating attack of the fibers and BN coatings. This phenomenon does not match experimental results, where stress-rupture was observed at 180 MPa in wet oxygen after only five hours, and stress-rupture was not observed at 180 MPa in dry oxygen or lab air.



Figure 138: Stress-rupture predictions for SiC/BN/SiC CMCs at 70, 80, and 90N in dry and wet oxygen at 800°C. Crack opening displacements used were 0.2, 0.5, and 1.0  $\mu$ m. The data for 0.5 and 1  $\mu$ m in 50% H<sub>2</sub>O/50% O<sub>2</sub> are equal and are indistinguishable in the chart.

#### 8.3.3 Activity of boria in the matrix

Inputs for boria activity in the matrix were varied from  $aB_2O_3 = 0.01$ , 0.1, 0.25, and 0.50. COD reduces more rapidly with increasing  $aB_2O_3$  and increasing temperature, as seen in Figure 139. This is due to increased oxidation of the boron species as compared to the Si and SiC in the matrix material. The COD is also predicted to reduce quicker in wet oxygen than dry oxygen when  $aB_2O_3 > 0.10$ , due to increased reactivity in water vapor. It was observed experimentally that local regions with higher amounts of B-containing species would preferentially oxidize at both 600 and 800°C, filling cracks near the fiber tow.



Figure 139: Crack opening displacement predictions for SiC/BN/SiC CMC vs. time for  $aB_2O_3 = 0.01$ , 0.10, 0.25, and 0.50 in a) 100%  $O_2$  and b) 50%  $H_2O/50\% O_2$ . Starting COD is  $0.5\mu$ m.

When matrix cracks do not fill in 50% H<sub>2</sub>O/50% O<sub>2</sub>, it results in oxidation and volatilization of the BN coating through the annular void gap (which is also reducing over time via oxidation of the SiC matrix and SiC fiber). Figure 140 shows a) the annular void width and b) the degraded tow length in 50% H<sub>2</sub>O/50%. When the COD rapidly fills with high temperature and high aB<sub>2</sub>O<sub>3</sub>, the BN gap remains as it did not have sufficient oxidant to fill. The BN annular void gap is only filled at 800°C, aB<sub>2</sub>O<sub>3</sub> = 0.10, where the crack did fill but at a slower rate than other cases. Finally, in cases where crack filling rates were slow (lower temperature and lower aB<sub>2</sub>O<sub>3</sub>), the BN annular void gap slowly closes and the predicted degraded tow length is the longest due to constant oxidant access during the exposure. Degradation of the SiC fibers and coatings via this gap results in a loss of tow stiffness and eventual stress-rupture. Stress-rupture was predicted for 800°C in 100% O<sub>2</sub> for the 0.01  $aB_2O_3$  and 0.10  $aB_2O_3$  after 590 and 606 hours, respectively. Stress-rupture was also predicted for 800°C in 50% H<sub>2</sub>O/50% O<sub>2</sub> for 0.01  $aB_2O_3$  after 140 hours.



Figure 140: Predictions of SiC/BN/SiC CMC a) BN annular void width vs. time and b) Degraded tow length vs. time for  $aB_2O_3 = 0.01$ , 0.10, 0.25, and 0.50 in a) 100% O<sub>2</sub> and b) 50% H<sub>2</sub>O/50% O<sub>2</sub>. Starting COD is  $0.5\mu$ m.

#### 8.3.4 Effect of Lsurf

Parthasarathy et al. reported that for small COD (<1 micron) at 3% H<sub>2</sub>O, the predicted degradation ( $L_{deg}$ ) varied significantly for the range 0.1 mm  $\leq L_{surf} \leq 10$  mm [30].  $L_{surf}$  values of 0.01, 0.1, 1, and 2mm were evaluated in this study. It was observed that there was minimal difference in  $L_{deg}$  and the predicted stress-rupture times for the range 0.01 mm  $\leq L_{surf} \leq 2$  mm. No stress-ruptures were predicted by the model for 600°C exposures, and instead lengths of approximately 0.33 meters are predicted after 1000 hour exposures. The predicted values for 50% H<sub>2</sub>O/50% O<sub>2</sub> at 90N can be seen in Table 15.

L <sub>surf</sub> (mm)	L <sub>deg</sub> at 600°C (µm)	Model Run Time (hours)	L <sub>deg</sub> at 800°C (µm)	800°C Stress-Rupture Time (hours)
0.01	33231	1000	1817	55.2
0.10	33227	1000	1818	55.4
1	33186	1000	1824	57.0
2	33141	1000	1831	58.9

Table 15: Predicted degradation lengths at 600 and 800°C and stress-rupture times at 800°C for various  $L_{surf}$  values in 50%  $H_2O/50\%$   $O_2$  at 90N.

#### 8.3.5 Comparisons to experimental work

The CMC micro-model has a matrix crack that allows the environment to react with the BN fiber coating. If the environment contains water vapor, then the BN fiber coating will oxidize and volatilize, leaving an annular void for a length  $L_{deg}$  until the BN annular void gap fills with oxide. The model correctly predicts that  $L_{deg}$  will be zero at 600 and 800°C in dry oxygen. It is important to note that in all of the models, an initial annular void gap is assumed, even if the BN coating is not degraded. This assumption is still valid as it can be thought of as the fiber region that would be exposed to oxidant due to inside debonding (where the debonded fiber remains on the CVI SiC). In wet oxygen, the model predicts an  $L_{deg}$  that is greater than zero for both 600 and 800°C when  $aB_2O_3 = 0.02$ . This differs from the experimental work previously presented where there were no annular voids observed for exposures at 800°C, and instead the BN fiber coatings are oxidized. The model does not account for oxidation of the fiber coatings beyond the region where the annular void has occurred.

Stress-rupture is not predicted for any of the conditions modeled at 600°C. No stressruptures were observed experimentally at 600°C in 100%  $O_2$ , however it was observed that stressrupture occurs after approximately 30 hours at 600°C/150 MPa in 50%  $H_2O/50\% O_2$ . The model does not predict progressive fiber failure at 600°C. This is due to the model predicting rupture 196 based off of a) strength loss due to grain growth, b) fiber recession from oxidation, and c) oxide scale cracking around the fiber resulting in flaws that, if larger than a pre-existing fiber flaw, control the fiber strength [90]. The aforementioned effects are minimal at this temperature after 1000 hours. Fiber recession and oxide scales from the SiC fiber were not observed experimentally. The model could be improved at this temperature by instead considering the effects of subcritical crack growth in the fibers, which has been experimentally shown to describe fiber failure in static fatigue (stress-rupture) experiments of Hi-Nicalon fibers from 500-800°C [92, 93].

Stress-rupture is predicted in dry and wet oxygen at 800°C, at times higher than that observed experimentally. However, the mechanisms that the model is portraying are incorrect for the RRHTC SiC/BN/SiC CMC 800°C. Progressive fiber failure is predicted in the model via the strength loss due to grain growth, fiber recession from oxidation, and oxide scale cracking, which are not observed experimentally.

In its present state, the UES CMC micro-model is not representative for the RR-HTC CMC from 600-800°C. Lifetime prediction may improve for both 600 and 800°C if subcritical crack growth is considered for fiber failure mechanisms. Predictions may also improve at 800°C if fiber coating oxidation, and the embrittlement that arises from it, is considered instead of an annular void forming around the SiC fiber.

#### *8.3.6 Critiques of CMC micro-model*

The CMC micro-model is a powerful tool for lifetime prediction of SiC/BN/SiC CMCs. There are several suggestions to improve upon the model:

197

- 1. The matrix material composition should be considered. Currently, the model assumes a pure SiC matrix with the addition of boron species via aB<sub>2</sub>O<sub>3</sub>. The matrix material of SiC/BN/SiC CMCs varies widely, and in this work the matrix contains silicon, SiC, and B-containing species. The oxidation rates of silicon need to be considered, as well as the effect that silicon has on residual stresses in the matrix.
- 2. The value of aB<sub>2</sub>O<sub>3</sub> is obtained from the average atomic percent of boron species in the matrix material, and the resulting borosilicate glass composition is predicted. Instead, an initial glass composition could also be used as an input. Future experimental work should accurately determine the initial oxide composition and how it evolves over time. Various starting values of boron species should be considered, as there are local variations in the amount of B-containing species in the matrix material.
- Sub-critical crack growth in the SiC fibers should be considered at temperatures of 500-800°C.

#### 8.4 Conclusions

SiC/BN/SiC CMC mechanical and oxidation behaviors are complex processes that vary between different CMC types due to different constituent chemistries, processing techniques, and microstructure. The UES CMC micro-model does not accurately predict oxidation and stressrupture behavior of the RR-HTC SiC/BN/SiC CMC from 600-800°C in 100% O<sub>2</sub> and 50% H<sub>2</sub>O/50% O<sub>2</sub>. Parametric studies were completed evaluating the effect of applied stress on the fiber tow, crack opening displacement, activity of boria in the matrix, and the distance of the fiber tow from the external surface. It was observed that increases in applied load resulted in a decrease in tow 198 stiffness from progressive fiber failure. The variation in CODs (0.2, 0.5, and 1.0 µm), obtained from in-situ micro-tensile testing experiments, showed little effect on stress-rupture predictions. A higher activity of boria in the matrix resulted in faster crack sealing, mitigating oxidative attack of the BN fiber coating and SiC fiber. The crack length from the free surface to the fiber tow (0.01, 0.1, 1, and 2 mm) had little effect on BN coating degradation lengths and stress-rupture predictions. Oxidation mechanisms predicted for 600°C were representative of experimental results, but no stress-ruptures were predicted. Oxidation mechanisms predicated for 800°C were not representative of experimental results, and the stress-ruptures predicted resulted from inaccurate oxidation mechanisms. Recommendations for improving the UES CMC micro-model were provided.

## Chapter IX. Conclusions

#### 9.1 Summary of the work and findings

The oxidation and mechanical degradation, as well as their synergistic effects, of SiC/BN/SiC ceramic matrix composites in an intermediate temperature range (400-800°C) were evaluated in this work. Baseline oxidation behavior in dry and wet oxygen was evaluated via thermogravimetric analysis at 400-800°C, followed by characterization via SEM/EDS and FIB. Preferential oxidation occurred at a B-containing phase in the matrix material in all conditions tested. In both dry and wet oxygen, a boria-rich borosilicate was formed at 600°C and a silica-rich oxide was formed at 800°C. The boria-rich oxide was less protective than the silica-rich oxide, and the oxides were more protective in dry oxygen than wet oxygen. Oxygen solubility was observed in Hi-Nicalon SiC fibers, which had not been noted previously. Oxidation of the BN coatings was observed and no volatility of the coatings was observed in dry oxygen. In wet oxygen, the BN fiber coatings oxidized and volatilization was only observed at 600°C. Wet oxygen exposures result in more degradation for the CMC than dry oxygen exposures due to volatility of the resultant oxides.

In-situ micro-tensile testing with light and scanning electron microscopy techniques at room and elevated temperature allowed for relation of micro-crack behavior to local microstructural features. Measurements of micro-crack spacing, crack opening displacement, and micro-crack composition vs. stress were obtained. The micro-crack composition highlighted inhomogeneity in observed crack sealing, or lack thereof, in the subsequent load hold oxidation experiments. The crack opening displacement measurements were of specific interest as the measurements were used as inputs for CMC damage modeling.

Oxidation of SiC/BN/SiC CMCs while under load was studied at 600 and 800°C in lab air, dry oxygen, and wet oxygen, below and above the proportional limit. Several degradation modes occurred, including those in previous studies where no load was applied. These modes include oxidation through porosity pipes, oxygen solubility in the SiC fibers, and preferred oxidation in the intratow MI regions. B-containing phases were observed to preferentially oxidize on the exterior and interior of the CMC in all conditions studied. Lab air and dry oxygen results were extremely similar, and in these conditions stress-rupture was only observed at 800°C/200 MPa (past the proportional limit), where micro-cracks allowed oxidant ingress for material attack. Wet oxygen exposures again resulted in the most degrading conditions, where stress-rupture was observed at 600°C/150 MPa and 800°C/180 MPa. Oxidation and volatilization of B-containing species via oxidation through porosity pipes and annular void gaps resulted in rapid degradation of the material below the proportional limit at 600°C. Subsequent micro-cracking allowed oxidant attack of interior BN fiber coatings, resulting in brittle fracture above the proportional limit at 800°C.

Experimental findings were compared to behavior predicted by the UES CMC micro-model. It was found that the micro-model does not accurately predict oxidation and stress-rupture behavior of the RR-HTC SiC/BN/SiC CMC from 600-800°C in 100% O<sub>2</sub> and 50% H<sub>2</sub>O/50% O<sub>2</sub>. Oxidation mechanisms predicted for 600°C were representative of experimental results, but no stress-ruptures were predicted. Oxidation mechanisms predicated for 800°C were not representative of experimental results, and the stress-ruptures predicted resulted from inaccurate 201 oxidation mechanisms. Recommendations for improving the UES CMC micro-model were provided.

In conclusion, it has been shown experimentally that the RR-HTC experiences increased degradation when exposed to water vapor at 600°C in unstressed and stressed conditions. A non-protective, non-wetting surface boria-rich surface oxide is formed. The oxide is susceptible to volatility, resulting in porosity, micro-cracks, and annular void gaps remaining unfilled. These unfilled features provide access for oxidative attack, which occurs more rapidly in water vapor than dry oxygen. Oxidation in water vapor results in volatility of the subsurface BN fiber coatings, resulting in poor load-sharing between the matrix and fibers, and the mechanical performance is reduced, resulting in stress-rupture below the proportional limit. Changes in the material and operating conditions should be considered.

#### 9.2 Recommendations for material improvement and operating conditions

The recommendations for material improvement are as follows:

- 1. The RRHTC SiC/BN/SiC CMC contained porosity pipes that contributed to oxidant travel into the CMC interior. Improved infiltration and reduction of this porosity will help mitigate oxidative attack.
- 2. SiC fibers in fiber bundles are in close proximity to each other in the RRHTC CMC, with the only separation being the BN fiber coating. Oxidation of the BN fiber coating with a glassy phase will cause fiber bonding, resulting in the fiber bundle acting as a monolithic material instead of individual filaments. Separating the fibers will slow the bonding process [89].

- Hi-Nicalon fibers show both oxygen solubility and also show reduced resistance to subcritical crack growth from 500-800°C when compared to Hi-Nicalon S fibers [92].
   Hi-Nicalon S fibers will likely be more stable in the RR-HTC CMC.
- 4. EBCs are often not used on the backsides of parts to reduce overall component weight (increasing engine efficiency). It is proposed to pre-oxidize the backside of the specimen at 800°C in dry oxygen to form a protective, uniform silica-rich thermally grown oxide (TGO) layer across the backside of the component prior to engine exposures. More experimental work should be completed on the stability of the pregrown TGO when exposed to water vapor.

Full details of the actual CMC application are unknown to the author. However, if it is possible to reduce the amount backside cooling, it is recommended to maintain the backside at 800°C. It has been shown experimentally that the most degradation in the conditions studied occurs in wet oxygen at 600°C even when micro-cracking is minimal. Avoiding exposure at 600°C may result in improved mechanical performance and component lifetime in the engine.

#### 9.3 Recommendations for future work

#### *9.3.1 Oxidation studies of SiC/BN/SiC CMCs*

The borosilicate composition evolves with exposure time due to further oxidation of CMC microconstituents, as well as volatility of the oxide in the presence of water vapor. The compositional change will affect the subsequent oxidation of the underlying material. Future work should experimentally evaluate the borosilicate composition evolution with exposure time using 203

quantitative evaluation techniques. The effect of the atomic percent of boron-containing species in the starting material should also be evaluated.

BN fiber coating oxidation behavior should be studied in more detail, utilizing transmission electron microscopy (TEM) analysis. Specifically, the transition regions from oxidized coating to unaffected coating should be interrogated. The fast path for oxidant inward should be identified to improve understanding.

It is unknown if oxygen solubility in the Hi-Nicalon SiC fibers only occurs via the base of the fiber or if it can also occur via the circumference of the fiber. Further work should be completed on understanding the directional dependence of oxygen solubility in Hi-Nicalon fibers. Micro-hardness testing should also be utilized to elucidate the mechanical effect of oxygen solubility on Hi-Nicalon mechanical properties.

Hi-Nicalon S fibers should be evaluated in the RR-HTC SiC/BN/SiC CMC. It is expected that with less unreacted C in the fiber, that oxygen solubility will not be observed and the Hi-Nicalon fibers will be more stable.

#### 9.2.2 Micro-tensile studies of SiC/BN/SiC CMCs

Strain measurement, either through custom extensometry, digital image correlation, or strain gages on the bottom surface, should be implemented during micro-tensile testing. Other damage monitoring techniques, like electrical resistivity and acoustic emission, could also be implemented to understand damage evolution in the CMC. SiC/BN/SiC CMCs are exposed to cyclic and fatigue loading in service. Unload-reload cycles should be performed on the micro-tensile stage to observe the effect of hysteresis on matrix cracking behavior.

#### 9.2.3 Oxidation load hold studies of SiC/BN/SiC CMCs

CMCs in service may experience loads that will result in micro-cracking in the CMC. Depending on the part type or location of the CMC component in the engine, complex loads may occur (i.e., biaxial loading, bending, fatigue, etc.). The aforementioned oxidation load hold studies loaded the samples in simple tension. Future work should explore the different failure modes with environmental exposures.

Additional techniques and fixturing should be implemented to better understand the stressed oxidation behavior. Modeling should be completed of the gas flow in the environmental test fixture to understand the effect that the flow type may have on the oxidation behavior due to different gas boundary layers. Fixturing that allows for an extensometer should be used during oxidation exposures to track strain evolution. This could also allow for displacement or strain-controlled experiments that may allow for more control of test interruption instead of stress-rupture. Likewise, damage monitoring techniques such as electrical resistivity and acoustic emission could be implemented to monitor in-situ behavior. Electrical resistivity measurements may highlight the oxidation and/or volatilization of different micro-constituents during exposure. Finally, carefully designed specimen geometries (i.e., notched) could be implemented to reduce the regions of interest to reduce characterization time.

Further work should be done to evaluate the oxidation effects. Load holds similar to the ones performed in this work should be executed with inert gases. This data could then be used to elucidate the thermal degradation from the oxidative degradation. Oxidation of the fiber coatings results in degraded mechanical properties. Fiber push-out tests should be performed to quantify the mechanical effects of oxidized BN coatings. Additionally, more intermediate time studies should be performed to obtain measurements for kinetic rate parameters. Intermediate values between 0-50 vol% of water should also be tested. All sides besides one should be EBC-coated and a notched specimen should be used to have a specific region of interest for these measurements.

### Chapter X. Resulting Presentations, Publications, & Awards

#### **10.1** Presentations

- Detwiler, K., McFarland, B., Watza, M., & Opila, E.\*, "Properties of thermally grown borosilicate glasses and their impact on CMC oxidation and life prediction," Materials Science & Technology, Columbus, Ohio, October 2021. Oral.
- 2. **Detwiler, K.\*** & Opila, E., "Oxidation behavior of melt-infiltrated SiC/BN/SiC ceramic matrix composites at low to intermediate temperatures in dry O<sub>2</sub>/Air," 44th Annual Conference on Composites, Materials, and Structures, Cape Canaveral. Florida, January 2020. Oral.
- 3. Detwiler, K., Wilson, M., Pierce, J. & Opila, E.\*,"Oxidation behavior and mechanical properties of melt-infiltrated SiC/SiC ceramic matrix composites over a wide temperature range," Materials Science & Technology, Portland, Oregon, October 2019. Oral.
- Detwiler, K.\* & Opila, E., "Low temperature oxidation behavior and mechanical properties of melt-infiltrated SiC/SiC ceramic matrix composites," 10th International Conference on High Temperature Ceramic Matrix Composites (HT-CMC10), Bordeaux. France, September 2019. Oral.
- Detwiler, K.\* & Opila, E., "Low temperature mechanical properties and oxidation behavior of melt-infiltrated SiC/SiC ceramic matrix composites," Gordon Research Conference (GRC) on High Temperature Corrosion, New London, New Hampshire, August 2019. Poster.

- 6. **Detwiler, K.\*** & Opila, E., "Low temperature mechanical properties and oxidation behavior of melt-infiltrated SiC/SiC ceramic matrix composites," Gordon Research Seminar (GRS) on High Temperature Corrosion, New London, New Hampshire, August 2019. Poster.
- Detwiler, K.\*, Pierce, J., & Opila, E., "Low temperature mechanical properties and oxidation behavior of melt-infiltrated SiC/SiC ceramic matrix composites," 43rd International Conference and Exposition on Advanced Ceramics and Composites (ICACC) 2019, Daytona Beach, Florida, January 2019. Oral.

#### \*denotes presenter

#### **10.2** Publications

- 1. **Detwiler, K.**, & Opila, E. (2022). Oxidation of SiC/BN/SiC ceramic matrix composites at intermediate temperatures in dry and wet oxygen. Accepted for publication in *Journal of the European Ceramic Society*.
- 2. **Detwiler, K.**, Hunt, R. & Opila, E. (2022). In-situ observation of micro-cracking in SiC/BN/SiC ceramic matrix composites at room and elevated temperature. Manuscript in progress.
- 3. **Detwiler, K.**, & Opila, E. (2022). Stressed oxidation behavior of SiC/BN/SiC ceramic matrix composites in lab air, dry oxygen, and wet oxygen. Manuscript in progress.

#### 10.3 Awards

- 1. Department of Defense SMART Scholarship for Service, 2019-2022.
- 2. SMART Scholar and Mentor (Dr. Craig Przybyla) of the Year Award, Runner-up, 2021.
- 3. Fred D. Rosi Outstanding Citizen Award, Materials Science & Engineering, UVA 2019.

## Appendix

### **Chapter 1. Introduction**

Table 16: List of variables and outputs used in the Parthasarathy CMC damage model. Table reproduced from [30].

Symbol	Description	Units	Type of variable
$P_{O_2(a)}, P_{H_2O(a)}$	Partial pressure of oxygen, moisture in the ambient	Ра	Environment
ρ	Density of gas in the boundary layer	kg/m <sup>3</sup>	Environment
V <sub>fluid</sub>	Velocity of ambient fluid	m/s	Environment
Т	Temperature	К	Environment
m	Weibull modulus of the fiber		Material (fiber)
$\sigma_0$	As-received fiber strength (reference stress)	Pa	Material (fiber)
a <sub>0</sub>	Initial strength limiting flaw size in the fiber	m	Material (fiber)
K <sub>IC</sub>	Fracture toughness of the fiber	MPa√m	Material (fiber)
$G_0$	Initial grain size of the fiber	m	Material (fiber)
t <sub>BN</sub>	Thickness of BN coating	m	Material (coating)
Ispec	Length of CMC along fluid flow	m	Material
R	Universal gas constant	J/mol·K	Universal constant
$D_{ij}$	Multicomponent diffusivity of gases in a mixture of species $i$ and $j$	m <sup>2</sup> /s	Literature
$D_i$	Diffusivity of gaseous species i	m²/s	Literature
$D_{\rm eff}, D_k$	Effective diffusivity and Knudsen diffusivity of gaseous	m <sup>2</sup> /s	Literature
η	Viscosity of gases in boundary layer	Pa·s	Literature
K <sub>r</sub>	Thermodynamic equilibrium constant for reaction r		Literature
Q	Activation energy for grain growth	kJ/mol	Literature
$P_{H_xB_yO_z}$	Equilibrium vapor pressure of $H_x B_\nu O_z$ gaseous species on $B_2 O_3$ -rich scale	Ра	Literature
$V_{\mathrm{SiC}}, V_{\mathrm{SiO}_2}, V_{\mathrm{SiO}_2}, V_{scale}, V_{BN}$	Molar volume of SiC, SiO <sub>2</sub> , scale, BN	m <sup>3</sup>	Literature
a <sub>B2O3</sub>	Activity of B2O3 in B2O3-rich scale formed at BN/SiC junction		Liter/calibration (d)
h	Empirical constant to account for effect of moisture on permeability		Liter/calibration (d)
$\Pi_{O_2-scale}$	Permeability coefficient of oxygen in silica (SiC matrix), or scale (SiC Fiber)	moles/m·s·Pa	Liter/calibration (d)
$a_{\rm gg}(T, t)$	Flaw size after time t at temperature T in inert environment	m	Predicted
$a_{\rm env}(T,t,P_{\rm O_2},P_{\rm H_2O})$	Flaw size after time t at temperature T in environment of O2, H2O		Predicted
δ <sub>bl</sub>	Boundary layer thickness for surface diffusion	m	Predicted
$\Delta_{\text{COD}}(t)$	Opening available for gaseous diffusion along matrix crack at time t	m	Predicted
G	Grain size of fiber after time t at temperature, T	m	Predicted
$J_{i(v)}$	Rate of evaporation of species i at the external surface	moles/m <sup>2</sup> ·s	Predicted
J <sub>O2</sub> -scale	Permeation rate of oxygen through scale	moles/m <sup>2</sup> ·s	Predicted
$J_{i}$ $P_{i}$	Flux, partial pressure of specie i along the degraded interface	moles/m <sup>2</sup> ·s	Predicted
$L_{\text{scale}}, L_{\text{scale},\text{COD}}$	Thickness of scale on matrix outer surface, on crack open surfaces	m	Predicted
L <sub>scale,f</sub> , L <sub>scale,m</sub>	Thickness of scale on fiber and matrix along degraded interface	m	Predicted
L <sub>deg</sub>	Length of interface degradation	m	Predicted
Π <sub>O2</sub> -scale(H <sub>2</sub> 0)	Permeability coefficient of oxygen in scale in the presence of moisture	moles/m·s·Pa	Predicted
$P_{O_2(s)}, P_{H_2O(s)}$	Partial pressure of oxygen, moisture at the surface of CMC, behind boundary layer	Ра	Predicted
$P_{\mathcal{O}_2(t/m)}, P_{\mathcal{H}_2 \mathbb{O}(t,m)}$	Partial pressure of oxygen, moisture at the tow/matrix junction	Pa	Predicted
$P_{\mathrm{O}_2,\mathrm{i}}, P_{\mathrm{H}_2\mathrm{O},\mathrm{i}}$	Partial pressure of oxygen, moisture at the $B_2O_3\mbox{-rich scale}/H_xB_VO_z$ interface	Pa	Predicted
$R_{f}, R_{m}$	Recession of substrate (fiber or matrix)	m	Predicted
tgap	Width of gap formed along degraded interface	m	Predicted
t	Time	s	Model variable
X	Distance along matrix crack from the free surface	m	Model variable
$\Delta_{\text{cod}}(0)$	Initial opening available for gaseous diffusion along matrix crack	m	input (FEM)
F <sub>tow</sub>	Force on the tow	Ν	input (FEM)
L <sub>surf</sub>	Distance along matrix crack of fiber tow from the free surface	m	input (FEM)
$F_{\rm C}(t)$	Residual tow strength expressed as critical traction force for failure (output to FEM)	N	Output (Numerical)
dF/dδ	Residual tow stiffness (output to FEM)	N/m	Output (Numerical)
$L_{\text{deg}}(t)$	Length of interface degraded at time $t$ (output to FEM)	m	Output (Numerical)

Chapter 4. In-situ observation of micro-cracking in a SiC/BN/SiC ceramic matrix composite using a tensile stage



175 MPa

Figure 141: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 175 and 200 MPa.

225 MPa



## 250 MPa



# 275 MPa



Figure 142: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 225, 250, and 275 MPa.

## 300 MPa



# 325 MPa



Figure 143: Optical images SiC/BN/SiC CMC tested at room temperature with tensile stage at 300 and 325 MPa.



Figure 144: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile stage at 175, 200, and 225 MPa.



Figure 145: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile stage at 250, 275, and 300 MPa.

325 MPa



Figure 146: Mask of marked cracks from SiC/BN/SiC CMC tested at room temperature with tensile stage at 325 MPa.



Figure 147: Micro-crack spacing for each line measured vs. applied stress for SiC/BN/SiC CMC tested at room temperature with tensile stage.



Figure 148: Crack opening displacements in matrix material vs. applied stress in SiC/BN/SiC CMC loaded at 600°C in SEM



Chapter 5. Stressed oxidation of SiC/BN/SiC ceramic matrix composites in lab air

Figure 149: Bilinear stress-strain curve seen in CMCs at room temperature.

### Works Cited

- 1. Steibel, J., *Ceramic matrix composites taking flight at GE Aviation*. Am. Ceram. Soc. Bull, 2019. **98**(3): p. 32-36.
- 2. Dicarlo, J.A., Yun, H.M., Morscher, G. N., & Bhatt, R.T., *SiC/SiC composites for 1200 C and above*, in *Handbook of Ceramic Composites*. 2005, Springer US. p. 77-98.
- 3. Louise Gale, L.N., Unpublished correspondence with Rolls-Royce: Analysis of water vapour through the flight cycle. 2018.
- 4. *Advance and Ultrafan*. January 10 2022]; Available from: <u>https://www.rolls-royce.com/media/our-stories/innovation/2016/advance-and-ultrafan.aspx#challenge</u>.
- 5. Flores, O., et al., Ceramic fibers based on SiC and SiCN systems: current research, development, and commercial status. Advanced Engineering Materials, 2014. **16**(6): p. 621-636.
- 6. Lee, K.N., *Environmental barrier coatings for SiCf/SiC*. Ceramic matrix composites: materials, modeling and technology, 2014: p. 430-451.
- 7. Richards, B.T., M.R. Begley, and H.N. Wadley, *Mechanisms of ytterbium monosilicate/mullite/silicon coating failure during thermal cycling in water vapor*. Journal of the American Ceramic Society, 2015. **98**(12): p. 4066-4075.
- 8. Wilson, M., Oxidation of SiC/BN/SiC Ceramic Matrix Composites and their Constituents, in Materials Science. 2018, University of Virginia.
- 9. Rockett, T. and W. Foster, *Phase relations in the system boron oxide–silica*. Journal of the American Ceramic Society, 1965. **48**(2): p. 75-80.
- 10. Chen, H.M., et al. *Thermodynamic Assessment of B2O3-SiO2 Binary System*. in *Applied Mechanics and Materials*. 2014. Trans Tech Publ.
- 11. Deal, B.E. and A. Grove, *General relationship for the thermal oxidation of silicon*. Journal of Applied Physics, 1965. **36**(12): p. 3770-3778.
- 12. Ogbuji, L.U. and E.J. Opila, *A comparison of the oxidation kinetics of SiC and Si3 N 4*. Journal of the Electrochemical Society, 1995. **142**(3): p. 925.
- 13. Ogbuji, L.U., *Effect of oxide devitrification on oxidation kinetics of SiC*. Journal of the American Ceramic Society, 1997. **80**(6): p. 1544-1550.
- 14. Opila, E.J. and N.S. Jacobson, *Oxidation and corrosion of ceramics*. Ceramics science and technology, 2013. **4**: p. 74-79.
- 15. Morscher, G., D. Bryant, and R. Tressler. *Environmental durability of different BN interphases (for SiC/SiC) in H<sub>2</sub>O-containing atmospheres at intermediate temperatures.* in *Ceram Eng Sci Proc.* 1997.
- 16. Jacobson, N., et al., *High-temperature oxidation of boron nitride: I, monolithic boron nitride.* Journal of the American Ceramic Society, 1999. **82**(2): p. 393-398.
- 17. Jacobson, N.S., et al., *High-temperature oxidation of boron nitride: II, boron nitride layers in composites.* Journal of the American Ceramic Society, 1999. **82**(6): p. 1473-1482.
- 18. McFarland, B., *Boria Effects on the High Temperature Oxidation of Silicon Carbide*, in *Materials Science and Engineering*. 2017, University of Virginia.
- 19. Rebillat, F., E. Garltte, and A. Guette, *QUANTIFICATION OF HIGHER SIC FIBER OXIDATION RATES TN PRESENCE OF B203 UNDER AIR*. Design, Development, and Applications of Engineering Ceramics and Composites, 2010. **215**: p. 135.

- 20. Ogbuji, L.U., *A pervasive mode of oxidative degradation in a SiC-SiC composite*. Journal of the American Ceramic Society, 1998. **81**(11): p. 2777-2784.
- 21. McFarland, B. and E.J. Opila, *Silicon carbide fiber oxidation behavior in the presence of boron nitride*. Journal of the American Ceramic Society, 2018. **101**(12): p. 5534-5551.
- 22. Lamkin, M., F. Riley, and R. Fordham, *Oxygen mobility in silicon dioxide and silicate glasses: a review.* Journal of the European Ceramic Society, 1992. **10**(5): p. 347-367.
- 23. Hwang, S.-J., et al., *Quantitative study of the short range order in B<sub>2</sub>O<sub>3</sub> and B<sub>2</sub>S<sub>3</sub> by MAS and two-dimensional triple-quantum MAS 11B NMR.* Solid state nuclear magnetic resonance, 1997. **8**(2): p. 109-121.
- 24. Plotnikov, E. and V. Stolyarova, *Calculations of the Thermodynamic Properties of Glasses* and Melts in the Na<sub>2</sub>O-SiO<sub>2</sub> and B<sub>2</sub>O<sub>3</sub>-SiO<sub>2</sub> Systems on the Basis of the Generalized Lattice Theory of Associated Solutions. Glass Physics and Chemistry, 2005. **31**(6): p. 763-788.
- 25. Brückner, R. and J. Navarro, *Physikalisch-chemische untersuchungen im system B2O3-SiO2*. Glastech. Ber., 1966. **39**(6): p. 283-294.
- 26. Opila, E.J., *Variation of the oxidation rate of silicon carbide with water-vapor pressure.* Journal of the American Ceramic Society, 1999. **82**(3): p. 625-636.
- 27. Li, L., Damage, fracture, and fatigue of ceramic-matrix composites. 2018: Springer.
- 28. Ogbuji, L.U., *Pest-resistance in SiC/BN/SiC composites*. Journal of the European Ceramic Society, 2003. **23**(4): p. 613-617.
- 29. Morscher, G.N., et al., *Effect of a boron nitride interphase that debonds between the interphase and the matrix in SiC/SiC composites.* Journal of the American Ceramic Society, 2004. **87**(1): p. 104-112.
- Parthasarathy, T.A., et al., *Modeling environmentally induced property degradation of SiC/BN/SiC ceramic matrix composites*. Journal of the American Ceramic Society, 2018. 101(3): p. 973-997.
- 31. Xu, W., F.W. Zok, and R.M. McMeeking, *Model of oxidation-induced fiber fracture in SiC/SiC composites.* Journal of the American Ceramic Society, 2014. **97**(11): p. 3676-3683.
- 32. Morscher, G.N., *Tensile Stress Rupture of SiCf/SiCm Minicomposites with Carbon and Boron Nitride Interphases at Elevated Temperatures in Air.* Journal Of The American Ceramic Society, 1997. **80**(8): p. 2029-2042.
- 33. Lin, H.-T. and P.F. Becher, *Effect of fiber coating on lifetime of Nicalon fiber-silicon carbide composites in air*. Materials Science and Engineering: A, 1997. **231**(1-2): p. 143-150.
- Wing, B.L. and J.W. Halloran, Subsurface oxidation of boron nitride coatings on silicon carbide fibers in SiC/SiC ceramic matrix composites. Ceramics International, 2018. 44(14): p. 17499-17505.
- 35. Yan, M.F., et al., *Sintering of optical wave-guide glasses*. Journal of materials science, 1980. **15**(6): p. 1371-1378.
- 36. Kaplan, W.D., et al., A review of wetting versus adsorption, complexions, and related phenomena: the rosetta stone of wetting. Journal of Materials Science, 2013. **48**(17): p. 5681-5717.
- 37. Wilson, M. and E. Opila, *A review of SiC fiber oxidation with a new study of Hi-Nicalon SiC fiber oxidation*. Advanced Engineering Materials, 2016. **18**(10): p. 1698-1709.

- 38. Ramberg, C.E., et al., *Passive-oxidation kinetics of high-purity silicon carbide from 800° to 1100° C.* Journal of the American Ceramic Society, 1996. **79**(11): p. 2897-2911.
- Elmer, T., et al., *Phase separation in borosilicate glasses as seen by electron microscopy* and scanning electron microscopy. Journal of the American Ceramic Society, 1970. 53(4): p. 171-175.
- 40. Charles, R., *Phase separation in borosilicate glasses*. Journal of the American Ceramic Society, 1964. **47**(11): p. 559-563.
- 41. Sheldon, B.W., et al., *Oxidation of BN-coated SiC fibers in ceramic matrix composites.* Journal of the American Ceramic Society, 1996. **79**(2): p. 539-543.
- 42. Opila, E.J., R.C. Robinson, and M.J. Verrilli, *Borosilicate glass-induced fiber degradation* of *SiC/BN/SiC composites exposed in combustion environments*. International Journal of Applied Ceramic Technology, 2016. **13**(3): p. 434-442.
- 43. Di Ventra, M. and S.T. Pantelides, *Oxygen stability, diffusion, and precipitation in SiC: Implications for thin-film oxidation.* Journal of Electronic Materials, 2000. **29**(3): p. 353-358.
- 44. Evans, A.G., et al., *Models of high-temperature, environmentally assisted embrittlement in ceramic-matrix composites.* Journal of the American Ceramic Society, 1996. **79**(9): p. 2345-2352.
- 45. Li, L., K. Jian, and Y. Wang. Oxidation Behavior of Continues SiC Fibers in Static Air. in 2015 4th International Conference on Sensors, Measurement and Intelligent Materials. 2016. Atlantis Press.
- 46. Kister, G. and B. Harris, *Tensile properties of heat-treated Nicalon and Hi-Nicalon fibres*. Composites Part A: Applied Science and Manufacturing, 2002. **33**(3): p. 435-438.
- 47. Cofer, C.G. and J. Economy, Oxidative and hydrolytic stability of boron nitride—a new approach to improving the oxidation resistance of carbonaceous structures. Carbon, 1995.
  33(4): p. 389-395.
- 48. Bale, C.W., et al., *FactSage thermochemical software and databases*. Calphad, 2002. **26**(2): p. 189-228.
- 49. Ruggles-Wrenn, M., N. Boucher, and C. Przybyla, *Fatigue of three advanced SiC/SiC ceramic matrix composites at 1200° C in air and in steam.* International Journal of Applied Ceramic Technology, 2018. **15**(1): p. 3-15.
- 50. Zok, F.W., et al., *Degradation of a SiC-SiC composite in water vapor environments*. Journal of the American Ceramic Society, 2020. **103**(3): p. 1927-1941.
- 51. Opila, E.J., *Oxidation kinetics of chemically vapor-deposited silicon carbide in wet oxygen.* Journal of the American Ceramic Society, 1994. **77**(3): p. 730-736.
- 52. Reinsch, S., et al., *Water, the other network modifier in borate glasses.* Journal of Non-Crystalline Solids, 2016. **432**: p. 208-217.
- 53. Bauer, U., et al., *Structural investigation of hydrous sodium borosilicate glasses*. Journal of Non-Crystalline Solids, 2017. **465**: p. 39-48.
- 54. Behrens, H., et al., *Structural relaxation mechanisms in hydrous sodium borosilicate glasses.* Journal of Non-Crystalline Solids, 2018. **497**: p. 30-39.
- 55. LaRochelle, K.J., *Tensile Stress Rupture Behavior of a Woven Ceramic Matrix Composite in Humid Environments at Intermediate Temperature*. 2005, Air Force Institute of Technology.

- 56. Budiansky, B., J.W. Hutchinson, and A.G. Evans, *Matrix fracture in fiber-reinforced ceramics*. Journal of the Mechanics and Physics of Solids, 1986. **34**(2): p. 167-189.
- 57. Hilmas, A.M., K.M. Sevener, and J.W. Halloran, *Damage evolution in SiC/SiC unidirectional composites by X-ray tomography*. Journal of the American Ceramic Society, 2020. **103**(5): p. 3436-3447.
- 58. N. P. Bansal, J.L., *Ceramic matrix composites: materials, modeling and technology*. 2015, Hoboken, New Jersey: John Wiley & Sons, Inc.
- 59. Sevener, K.M., et al., *Crack opening behavior in ceramic matrix composites*. Journal of the American Ceramic Society, 2017. **100**(10): p. 4734-4747.
- 60. Swaminathan, B., et al., *Microscale characterization of damage accumulation in CMCs*. Journal of the European Ceramic Society, 2021. **41**(5): p. 3082-3093.
- 61. Tracy, J., A. Waas, and S. Daly, A new experimental approach for in situ damage assessment in fibrous ceramic matrix composites at high temperature. Journal of the American Ceramic Society, 2015. **98**(6): p. 1898-1906.
- 62. Sevener, K., et al., InSitu SEM Investigation of Microstructural Damage Evolution and Strain Relaxation in a Melt Infiltrated SiC/SiC Composite. 2016.
- 63. Hunt, R., *Micro-tensile stage behavior*. 2020: Wright-Patterson Air Force Base, Ohio.
- 64. Morscher, G.N. and N.A. Gordon, *Acoustic emission and electrical resistance in SiC-based laminate ceramic composites tested under tensile loading*. Journal of the European Ceramic Society, 2017. **37**(13): p. 3861-3872.
- 65. Morscher, G.N., *Stress-dependent matrix cracking in 2D woven SiC-fiber reinforced melt-infiltrated SiC matrix composites.* Composites Science and Technology, 2004. **64**(9): p. 1311-1319.
- 66. Gowayed, Y., et al., *Modeling of crack density in ceramic matrix composites*. Journal of Composite Materials, 2015. **49**(18): p. 2285-2294.
- 67. Kollins, K., C. Przybyla, and M.S. Amer, *Residual stress measurements in melt infiltrated SiC/SiC ceramic matrix composites using Raman spectroscopy*. Journal of the European Ceramic Society, 2018. **38**(7): p. 2784-2791.
- 68. Wing, B.L., *Residual stresses and oxidation of silicon carbide fiber reinforced silicon carbide composites*. 2016, University of Michigan.
- 69. Knauf, M., *Effects of Heat Treatment on SiC-SiC Ceramic Matrix Composites*, in *Aeronautics and Astronautics*. 2017, Purdue: West Lafayette, Indiana.
- 70. Yang, C.-P. and F. Jia, *Crack opening model for unidirectional ceramic matrix composites at elevated temperature*. Ceramics International, 2018. **44**(14): p. 17167-17173.
- 71. Karandikar, P.G., Chou, T.W., & Parvizi-Majidi, A., *Ceramic Matrix Composites*, in *Microstructure and Properties of Materials*, J.C.M. Li, Editor. 1996.
- 72. Morscher, G.N., J. Hurst, and D. Brewer, *Intermediate-temperature stress rupture of a woven Hi-Nicalon, BN-interphase, SiC-matrix composite in air.* Journal of the American Ceramic Society, 2000. **83**(6): p. 1441-1449.
- 73. Collier, V.E., et al., *Recession of BN coatings in SiC/SiC composites through reaction with water vapor*. Journal of the American Ceramic Society, 2021.
- 74. Zok, F.W., V.E. Collier, and M.R. Begley, *Coating recession effects in ceramic composite strength.* Journal of the Mechanics and Physics of Solids, 2021. **156**: p. 104608.
- 75. Nowacki, B.M., Verification and Calibration of State-of-the-Art CMC Mechanistic Damage Model. 2016, University of Dayton.

- 76. Hay, R.S. and R.J. Chater, *Oxidation kinetics strength of Hi-NicalonTM-S SiC fiber after oxidation in dry and wet air*. Journal of the American Ceramic Society, 2017. **100**(9): p. 4110-4130.
- 77. Ruggles-Wrenn, M. and M. Lee, *Fatigue behavior of an advanced SiC/SiC ceramic composite with a self-healing matrix at 1300 C in air and in steam.* Materials Science and Engineering: A, 2016. **677**: p. 438-445.
- 78. Robinson, R.C. and J.L. Smialek, *SiC recession caused by SiO2 scale volatility under combustion conditions: I, experimental results and empirical model.* Journal of the American Ceramic Society, 1999. **82**(7): p. 1817-1825.
- 79. Opila, E.J., et al., *SiC recession caused by SiO2 scale volatility under combustion conditions: II, thermodynamics and gaseous-diffusion model.* Journal of the American Ceramic Society, 1999. **82**(7): p. 1826-1834.
- 80. Eaton, H.E. and G.D. Linsey, *Accelerated oxidation of SiC CMC's by water vapor and protection via environmental barrier coating approach*. Journal of the European Ceramic Society, 2002. **22**(14-15): p. 2741-2747.
- 81. LaRochelle, K.J. and G. Morscher, *Tensile stress rupture behavior of a woven ceramic matrix composite in humid environments at intermediate temperature—part I.* Applied Composite Materials, 2006. **13**(3): p. 147-172.
- 82. Mall, S. and K. LaRochelle, *Fatigue and stress-rupture behaviors of SiC/SiC composite under humid environment at elevated temperature*. Composites science and technology, 2006. **66**(15): p. 2925-2934.
- 83. Mall, S. and J. Ryba, *Effects of moisture on tensile stress rupture behavior of a SiC/SiC composite at elevated temperatures*. Composites science and technology, 2008. **68**(1): p. 274-282.
- 84. Roul, M.K. and S.K. Dash, *Two-phase pressure drop caused by sudden flow area contraction/expansion in small circular pipes*. International journal for numerical methods in fluids, 2011. **66**(11): p. 1420-1446.
- 85. Graham, H. and H. Davis, *Oxidation/vaporization kinetics of Cr2O3*. Journal of the American Ceramic Society, 1971. **54**(2): p. 89-93.
- 86. Jacobson, N.S., M.A. Kuczmarski, and B.A. Kowalski, *Vaporization of protective oxide films into different gas atmospheres*. Oxidation of Metals, 2020. **93**(3): p. 247-282.
- Filipuzzi, L., et al., Oxidation mechanisms and kinetics of 1D-SiC/C/SiC composite materials: I, An experimental approach. Journal of the American Ceramic Society, 1994. 77(2): p. 459-466.
- Filipuzzi, L. and R. Naslain, Oxidation mechanisms and kinetics of 1D-SiC/C/SiC composite materials: II, modeling. Journal of the American Ceramic Society, 1994. 77(2): p. 467-480.
- 89. Morscher, G.N. and J.D. Cawley, *Intermediate temperature strength degradationin SiC/SiC composites.* Journal of the European Ceramic Society, 2002. **22**(14-15): p. 2777-2787.
- 90. Parthasarathy, T.A., et al., *Modeling environmental degradation of SiC-based fibers*. Journal of the American Ceramic Society, 2016. **99**(5): p. 1725-1734.
- 91. Mogilevsky, P., SiC/SiC CMC modeling: Matrix material measurements. 2021.

- 92. Gauthier, W. and J. Lamon, *Delayed failure of Hi-Nicalon and Hi-Nicalon S multifilament tows and single filaments at intermediate temperatures (500–800° C).* Journal of the American Ceramic Society, 2009. **92**(3): p. 702-709.
- 93. Gauthier, W., et al., *Oxidation of silicon carbide fibers during static fatigue in air at intermediate temperatures.* Journal of the American Ceramic Society, 2009. **92**(9): p. 2067-2073.