AFRL-RX-WP-JA-2017-0125

FIBER STRENGTH OF HI-NICALON(TM)-S AFTER OXIDATION AND SCALE CRYSTALLIZATION IN SI(OH)4 SATURATED STEAM (POSTPRINT)

S. Hay, R. Corns, A. Ross, B. Larson, P. Kazmierski
AFRL/RX

R. Corns
UES

A. Ross, B. Larson, and P. Kazmierski
Wright State University

25 February 2016
Interim Report

(STINFO COPY)

AIR FORCE RESEARCH LABORATORY
MATERIALS AND MANUFACTURING DIRECTORATE
WRIGHT-PATTERSON AIR FORCE BASE, OH 45433-7750
AIR FORCE MATERIEL COMMAND
UNITED STATES AIR FORCE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1. REPORT DATE *(DD-MM-YY)* 25 February 2016	2. REPORT TYPE Interim	3. DATES COVERED *(From - To)* 22 July 2013 – 25 January 2016

4. TITLE AND SUBTITLE
FIBER STRENGTH OF HI-NICALON™ - -S AFTER OXIDATION AND SCALE CRYSTALLIZATION IN SI(OH)$_4$ SATURATED STEAM (POSTPRINT)

5a. CONTRACT NUMBER IN-HOUSE

5b. GRANT NUMBER

5c. PROGRAM ELEMENT NUMBER

6. AUTHOR(S)
1) S. Hay, R. Corns, A. Ross, B. Larson, P. Kazmierski – AFRL/RX

2) R. Corns – UES

(continued on page 2)

5d. PROJECT NUMBER

5e. TASK NUMBER

5f. WORK UNIT NUMBER X0S7

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)
1) AFRL/RX Wright-Patterson AFB, OH 45433

2) UES, Inc. 4401 Dayton Xenia Rd. Beavercreek, OH 45432

(continued on page 2)

8. PERFORMING ORGANIZATION REPORT NUMBER

9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES)
Air Force Research Laboratory
Materials and Manufacturing Directorate
Wright-Patterson Air Force Base, OH 45433-7750
Air Force Materiel Command
United States Air Force

10. SPONSORING/MONITORING AGENCY ACRONYM(S) AFRL/RXCC

11. SPONSORING/MONITORING AGENCY REPORT NUMBER(S) AFRL-RX-WP-JA-2017-0125

12. DISTRIBUTION/AVAILABILITY STATEMENT
Distribution Statement A. Approved for public release: distribution unlimited.

14. ABSTRACT *(Maximum 200 words)*
Hi-Nicalon™-S SiC fibers were oxidized in Si(OH)4 saturated steam at 500° to 1500°C for 1 – 100 hours. Fiber tensile strengths were measured for fibers that retained reasonable strength, which did not include any fibers oxidized at temperatures over 1000°C. Oxidation and scale crystallization kinetics were characterized by optical and transmission electron microscopy. At 700°C and higher, if SiO2 glass scales got too thick they often dewetted the SiC fibers and would spheroidize. SiO2 glass wicked to the spheroids as fast as it formed on the dewetted SiC surface, causing faster oxidation. SiO2 crystallization to cristobalite began after 100 h at 700°C, but some glass scales were still present after 1 h oxidation at 1400°C. Cristobalite scale that formed as glass before crystallizing was relatively coarse-grained, and scale that formed as cristobalite was fine-grained. Grain growth at 1500°C was inferred to consume fine-grained scale, and formed grains with size comparable to the scale thickness.

15. SUBJECT TERMS
Hi-Nicalon™-S; scale crystallization; saturated steam; volatilization product; growth stress

16. SECURITY CLASSIFICATION OF:

a. REPORT	b. ABSTRACT	c. THIS PAGE
Unclassified	Unclassified	Unclassified

17. LIMITATION OF ABSTRACT: SAR

18. NUMBER OF PAGES 14

19a. NAME OF RESPONSIBLE PERSON (Monitor) William Kennedy

19b. TELEPHONE NUMBER *(Include Area Code)* (937) 255-9987

Standard Form 298 (Rev. 8-98)
Prescribed by ANSI Std. Z39-18

REPORT DOCUMENTATION PAGE Cont'd

6. AUTHOR(S)

   3) A. Ross, B. Larson, and P. Kazmierski - WSU

7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES)

   3) Wright State University, 4401 Dayton Xenia Rd,
       Beavercreek, OH 45432

FIBER STRENGTH OF HI-NICALON[TM]-S AFTER OXIDATION AND SCALE CRYSTALLIZATION IN Si(OH)$_4$ SATURATED STEAM

R. S. Hay[1], R. Corns[1,2], A. Ross[1,3], B. Larson[1,3], P. Kazmierski[1,3]
[1]Air Force Research Laboratory, Materials and Manufacturing Directorate, WPAFB, OH
[2]UES, Inc., Dayton, OH
[3]Wright State University, Fairborn, OH

ABSTRACT

Hi-Nicalon[TM]-S SiC fibers were oxidized in Si(OH)$_4$ saturated steam at 500° to 1500°C for 1 – 100 hours. Fiber tensile strengths were measured for fibers that retained reasonable strength, which did not include any fibers oxidized at temperatures over 1000°C. Oxidation and scale crystallization kinetics were characterized by optical and transmission electron microscopy. At 700°C and higher, if SiO$_2$ glass scales got too thick they often dewetted the SiC fibers and would spheroidize. SiO$_2$ glass wicked to the spheroids as fast as it formed on the dewetted SiC surface, causing faster oxidation. SiO$_2$ crystallization to cristobalite began after 100 h at 700°C, but some glass scales were still present after 1 h oxidation at 1400°C. Cristobalite scale that formed as glass before crystallizing was relatively coarse-grained, and scale that formed as cristobalite was fine-grained. Grain growth at 1500°C was inferred to consume fine-grained scale, and formed grains with size comparable to the scale thickness. SiO$_2$ scale crystallization, microstructure evolution, and the interaction between microstructure evolution and oxidation kinetics are discussed. Oxidation kinetics and oxidized fiber strength are compared with fibers oxidized in dry air, and strength degradation mechanisms are examined.

INTRODUCTION

Hi-Nicalon[TM]-S SiC fibers are used in some of the most advanced SiC-SiC ceramic fiber-matrix composites (CMCs),[1-3] and their properties govern many of the critical mechanical properties of SiC-SiC CMCs.[4] SiC-SiC CMCs are under intense development effort, and will be inserted as first stage shrouds in the Boeing 737 CFM LEAP engine.[5] More demanding applications under development include turbine engine vanes, blades, liners, exhaust washed structures, and various nuclear applications.

Hi-Nicalon[TM]-S fiber has near-stoichiometric β-SiC composition, variously reported as 0.25 to 1 at% excess oxygen, 50.0 to 51.5 at% carbon with 2 to 3.1% free carbon, and 48.1 to 49.1 at% Si. [2, 6-9] Properties of Hi-Nicalon[TM]-S fiber are described in many publications.[6, 8-14] β-SiC grain size is 10 – 50 nm.[8] Tensile strengths of Hi-Nicalon[TM]-S SiC fibers are affected by oxidation.[14-21] Dry air oxidation increases Hi-Nicalon[TM]-S strength slightly when glass SiO$_2$ scales form, but if scales are crystalline the strength degrades.[15, 16] This is attributed to the compressive and tensile residual stresses that form in glass and crystalline scales, respectively.[16] Steam is a major component of the turbine engine combustion environment, but work on SiC fiber oxidation kinetics and strength degradation mechanisms in steam is limited.[22]

SiC oxidation in steam can be either passive or active.[23-27] Active oxidation from Si(OH)$_4$ vaporization is dominant at high gas flow rates. At low gas flow rates or in conditions where steam is partially saturated with the Si(OH)$_4$ volatilization product, scale thickness will reach a steady-state value where the Si(OH)$_4$ volatilization rate balances the oxidation rate.[23, 26, 27] Passive oxidation is the only operating oxidation mechanism in static environments, or when steam is saturated with Si(OH)$_4$. These conditions are expected to be approached during fiber oxidation along microcracks, which is the physical situation of greatest concern to long-term environmental durability of SiC-SiC CMCs. Narrow crack apertures limit gas flow rates to low values, and steam that does penetrate by flow or Knudsen diffusion can be expected to be saturated with Si(OH)$_4$ by the SiC matrix in the crack wakes. The effects of passive oxidation of SiC fibers in Si(OH)$_4$ saturated steam are therefore critical to modeling and prediction of the environmental durability of SiC-SiC CMCs.

Experiment methods and apparatus developed to insure Si(OH)$_4$ saturation are discussed. Preliminary results for Hi-Nicalon[TM]-S SiC fiber oxidation kinetics, SiO$_2$ scale microstructure development, and fiber strength after oxidation in Si(OH)$_4$ saturated steam are presented,

discussed, and compared with similar experiments in dry air.[15, 16, 28] More thorough presentation and analysis will appear in forthcoming papers.

EXPERIMENTS

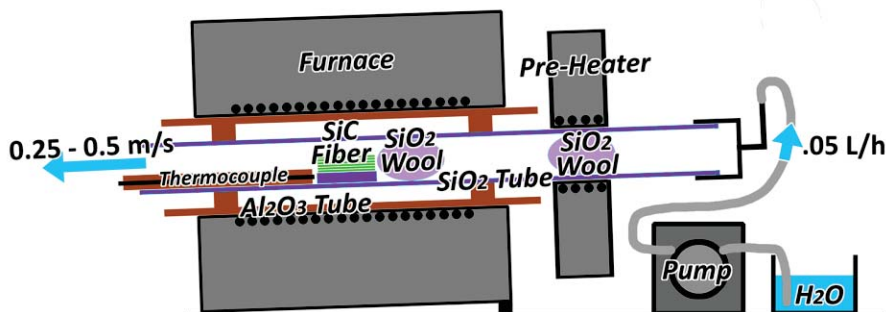   A schematic diagram of the apparatus is shown in figure 1. The polyvinyl alcohol sizing

Figure 1. Schematic diagram of equipment used to oxidize SiC fibers in $Si(OH)_4$ saturated steam.

on Hi-Nicalon™-S was removed by two sequential dissolutions in boiling distilled deionized water in a Pyrex glass beaker for one hour.[15, 28, 29] After desizing the fibers were handled only with tweezers or gloved hands. Five to six 7.5 cm length fiber tows were spread out and placed in a U-shaped SiO_2 glass boat in a 1.7 cm ID, 122 cm long SiO_2 glass tube. The tube was sealed at one end and double-distilled, deionized water was pumped into the sealed end using a peristaltic pump (Watson-Marlow 323) with 1.6 mm ID and 1.6 mm tubing wall thickness (Watson-Marlow Marprene). The pump ran at 3 rpm yielding a flow rate of 0.05 L/h. The glass tube was centered in a 71 cm long, 4.5 cm ID alumina tube. The alumina tube was centered in a 51 cm long $MoSi_2$ furnace (CMI, Inc., Bloomfield, NJ). A 6.3 cm long preheater with SiC furnace elements (Norton Model 271W) was just upstream of the main furnace along the SiO_2 tube. This pre-heater was run off a thermocouple outside the SiO_2 tube, at a temperature about 100°C hotter than the furnace set-point temperature. About 8 cm of SiO_2 wool was loosely packed in the SiO_2 tube along the preheater length, and another 8 cm of SiO_2 wool was just upstream of the SiC fibers (Fig. 1). Water evaporated as it wicked through the SiO_2 wool in the pre-heater. A type B thermocouple in an alumina sheath was used to monitor temperature just downstream of the SiC fibers. The furnace and SiO_2 tube were slightly inclined so that water pumped into the end of the tube flowed downhill. A fan cooled the upstream end of the tube at the water injection point. The furnace was temperature profiled for every temperature set-point and water flow rate used in experiments. SiC fibers were inserted in the middle of a 12 cm hot-zone with temperature within ±5°C of the set-point temperature. Heat-up and cool-down rates of 10°C/min were used.

    Experiments were done at temperatures from 500° to 1500°C in 100°C increments, for times of 1, 3, 10, 30, and 100 h. At the highest temperatures experiments could not be conducted for the longest times because the fibers would completely oxidize. The SiO_2 tube would warp during experiments run at temperatures over 1200°C, but the tube could be reused by rotating it 180° for the next high temperature experiment. Steam flow rates were calculated to be 0.2 m/s at 500°C and 0.5 m/s at 1500°C.

    Hi-Nicalon™-S scale thickness, composition, phase, and microstructure were characterized by optical microscopy, SEM, and TEM using methods described elsewhere.[15, 28-31] Average fiber diameter was 12.1 μm. Strengths of the oxidized fibers were measured by tensile testing 30 individual filaments by published methods,[32] using a loading rate of .021 mm/s and a 2.54 cm gauge length. Only data collected for fibers with clean breaks in the gauge section were used. The average ($σ_{AV}$) and Weibull characteristic value ($σ_o$) for failure stress were calculated, along with the Weibull modulus (m). Strengths were calculated using the original SiC radius (r_i)

of 6.05 μm. Fibers oxidized for long times at high temperature were often untestable because most breaks occurred at the grips.

RESULTS AND DISCUSSION

Fiber Strength

The average tensile strength (σ_{AV}) as a function of oxidation time in $Si(OH)_4$ saturated steam from 500° to 1000°C is shown in figure 2. Fibers oxidized at temperatures over 1000°C were either bonded together by thick SiO_2 scales, or too weak to be tensile tested. The same was true for fibers oxidized at 900° and 1000°C for times greater than 10 hours. σ_{AV} for as-received Hi-Nicalon™-S was 2.85 GPa.
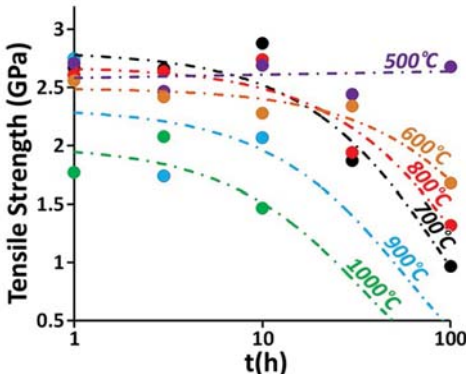
Fibers oxidized at 500°C did not show strength degradation. Strengths were degraded in fibers oxidized at 600°, 700°, and 800°C when oxidation times were greater than 10 hours. Fibers oxidized at 900° and 1000°C had degraded strengths for oxidation times of 1, 3 and 10 hours.

Figure 2. Average fiber tensile strength (σ_{AV}) of Hi-Nicalon™-S after heat-treatment in $Si(OH)_4$ s...

SiO_2 Scale Dewetting

SiO_2 scale dewetted the SiC fibers and spheroidized after steam oxidation for 30 and 100 h at 700° and 800°C (Fig. 3), and some evidence of dewetting was observed after oxidation at higher temperatures. The sizes and spacing of spheroids were not uniform from filament to filament, or along the length of a filament. Slight temperature variations and spacing between adjacent filaments may contribute to non-uniformity, but an overriding explanation was not apparent. Some of the dewetted scales formed at 800°C were facetted. TEM analysis shows crystallization to cristobalite. Crystallization of spheroidized scale was not observed at 700°C.

Much larger volumes of SiO_2 scale formed when the scale dewetted. Freshly dewetted SiC will oxidize at the fastest possible rate, defined by the linear oxidation rate constant **B/A** in Deal-Grove analysis.[28, 33] If SiO_2 wicks to a spheroid as fast as it forms, fresh surface will be available continuously and oxidation will continue to proceed at the maximum possible rate. The amount of SiO_2 that forms will be roughly proportional to the amount of that time the scale has dewetted. If scale dewets late during oxidation, scale volumes will not be much larger than those that normally form with parabolic oxidation kinetics, but if scale dewets early much larger volumes will form. This can be clearly seen in some of the examples in figure 3.
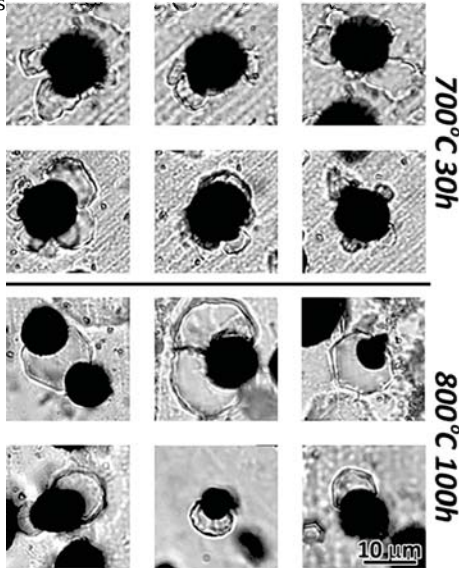

Figure 3. Optical transmitted light micrographs of SiO_2 scale dewetting after oxidation in steam at 700° and 800°C. Some scales formed at 800°C were facetted and crystallized to cristobalite.

Scale dewetting was not observed during dry air oxidation of Hi-Nicalon[1M]-S. The very large reduction in SiO_2 viscosity that accompanies incorporation of hydroxyl groups may explain dewetting. SiO_2 viscosity can be reduced by several orders of magnitude at 700° or 800°C if it is OH^{-} saturated,[34, 35] which makes dewetting and spheroidization of SiO_2 scale kinetically feasible. Rigorous analysis of SiO_2 dewetting and spheroidization conditions will be presented in a forthcoming paper.

Oxidation Kinetics

Qualitative aspects of oxidation kinetics and the relationship of kinetics to scale microstructure development are reported. Preliminary thicknesses data of (mostly) cristobalite scale formed at 700° to 1500°C measured using optical microscopy are shown in figure 4. An

average for measurements on at least 10 fibers is plotted. The standard deviations from the average are plotted as small points for each temperature/time. Gray lines showing $t^{1/2}$ time dependence expected for parabolic oxidation kinetics are shown for reference. All scales became thicker with time (Fig. 4), and did not reach a steady-state value that would be expected under conditions with only partial saturation of the steam with $Si(OH)_4$.[23, 26, 27] This inspires confidence that the experiment methods used saturate steam with the $Si(OH)_4$ volatilization product, so active oxidation is insignificant. Thin scales that formed at low temperatures and short times were not measurable by optical microscopy. They were measured by TEM, and when measurement and analysis are complete will be reported in a forthcoming publication.
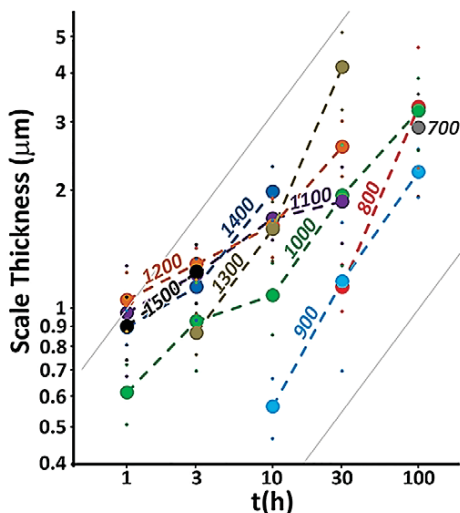
Thick scales had growth cracks from tensile stress that develops in old scale as it is pushed outward and forced to occupy a larger circumference (Fig. 5).[28, 36] This has been modeled and discussed in previous publications on SiC fiber oxidation in dry air. These scales are not hermetic. The growth cracks are short-circuit pathways for oxidation, and increase effective oxidation rates. Scale thickness measurements for these thick scales were only made on uncracked areas, which tended to be on fibers with larger diameter, which have lower tensile growth stress.[36] The scales formed in 30 h at 1300°C were anomalously thick, even in uncracked areas (Fig. 5). This positive deviation from parabolic oxidation kinetics is interpreted to be due to the effect of cylindrical geometry. When the scale thickness becomes comparable to the fiber radius, in this case around 2 μm, planar geometry no longer accurately describes Deal-Grove oxidation kinetics and there is a positive deviation from planar geometry parabolic kinetics. We have analyzed this in earlier publications.[28, 29]

Figure 4. Log-log plot of SiO_2 scale thickness on Hi-Nicalon™-S formed after oxidation in $Si(OH)_4$ saturated steam.

There are other anomalous features in the scale thickness – time plot (Fig. 4). Scales measured after 100 h oxidation at 700° and 800°C were thicker than those formed at 900°C. This may be related to the relative amount of time scales grew in the glass and crystalline states. However, as previously discussed, most scales formed at 700°C and 800°C after 100 h oxidation had spheroidized. Thickness measurements were only made on the relatively small number of scales that were continuous. These measurements may have been made on sections cut through an annular bead of dewetted SiO_2, which would account for their anomalously large thickness.

The most unusual anomaly concerns the apparent lack of significant temperature dependence on the scale growth rate from 1200° to 1500°C (Fig. 4). Transmission electron microscopy (TEM) of the scales suggests that this is related to the relative amounts of time the
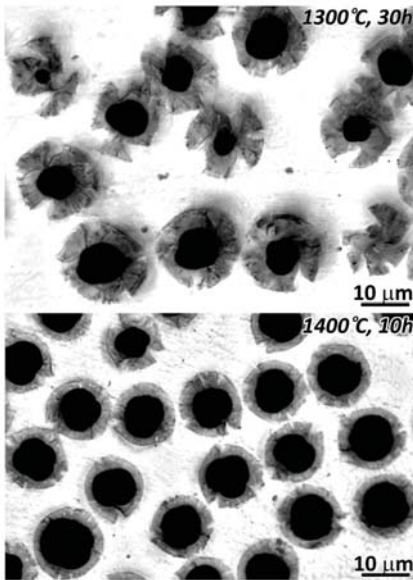
Figure 5. Optical transmitted light micrographs of SiO$_2$ scales formed on Hi-Nicalon™-S after oxidation in Si(OH)$_4$ saturated steam at 1300°C for 30 h and 1400°C for 10 h.

scale spent in the glass and crystalline state, and to the microstructure development in the scale at different temperatures. The next section will discuss TEM and the microstructure of some of these scales.

TEM of SiO$_2$ Scales Formed at 1000° to 1500°C

A TEM micrograph of a scale formed in 1 h in Si(OH)$_4$ saturated steam at 1000°C is shown in figure 6. Selected area electron diffraction patterns (SAD) for indicated areas of the scale are shown as insets. The scale is about 500 nm thick and is completely crystallized to cristobalite. It is nearly an order of magnitude thicker than glass scales that form in 1 h at 1000°C in dry air.[28] There are two distinct parts to the scale, which were previously observed after oxidation in dry air, albeit at higher temperatures. The outer part is coarse grained cristobalite. The inner part is fine, columnar grained cristobalite. They are separated by a line of pores. The outer, coarse-grained cristobalite is scale that formed as a glass and crystallized to cristobalite, in the process eliminating all the growth stress built in to the glass scale.[36] The inner, fine-grained columnar cristobalite is scale that formed as cristobalite. The enormous, GPa level growth stresses accompanying the 220% volume expansion
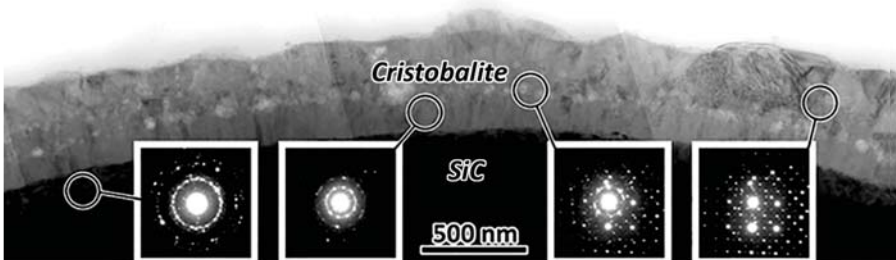
Figure 6. TEM micrograph of scale formed in 1 h on Hi-Nicalon[1M]-S in Si(OH)$_4$ saturated steam at 1000°C. SAD insets, from left to right, show: Ring pattern for β-SiC; Ring pattern for α-cristobalite; Ring pattern for α-cristobalite superimposed on a single crystal α-cristobalite pattern, and; [001] Single-crystal pattern for α-cristobalite.

to form cristobalite during SiC oxidation is relieved by dislocation slip,[16, 36] accompanied by dynamic recrystallization that forms columnar subgrains. These columnar subgrains are more obvious in a higher magnification TEM micrograph of a scale formed in 3 h in Si(OH)$_4$ saturated steam at 1000°C (Fig. 7). The width of these columnar grains was about 50 nm. Detailed, systematic measurements are underway to characterize the grain-size distributions in the scales.
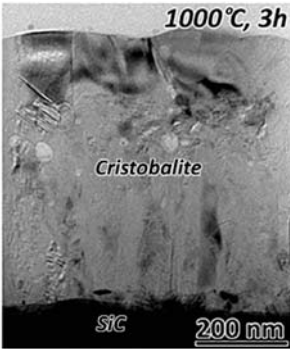
1000°C, 3h

Cristobalite

SiC   200 nm

Figure 7. TEM micrograph of scale formed in 3 h on Hi-Nicalon™-S in Si(OH)$_4$ saturated steam at 1000°C.

Scales formed at 1200°C were less well crystallized than those formed at 1000°C (Fig. 8). Some scales were completely crystallized, some were all glass, and some were partially crystallized. This erratic crystallization behavior was not observed in dry air oxidation.[28] The microstructures of some 700 nm to 1.2 μm thick scales formed in 1 h 1200°C oxidation in Si(OH)$_4$ saturated steam suggest three stages of growth: 1. Initial formation of a glass scale that eventually crystallizes to coarse-grained cristobalite; 2. Continued scale formation as fine-grained cristobalite, and; 3. Reversion to growth as a glass scale. Oxidation rates are much faster when glass scales form,[37, 38] so the prolonged presence, or reversion to, growth in the glass state at 1200°C would enhance oxidation rates. This is evident in figure 4, where the average measured scale thicknesses after oxidation for 1 h at 1200°C are slightly larger than the scales formed at any other temperature, including those at 1500°C. These scales are about 3× thicker than those formed in dry air.[28]

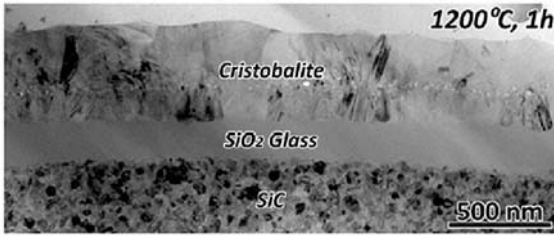Erratic crystallization continued during steam oxidation at 1400°C. After oxidation for 3 h at 1400°C in Si(OH)$_4$ saturated steam, coarse-grained cristobalite scales predominate (Fig 9a,c), but glass scales without a trace of crystallization can still be found (Fig. 9b). As expected, the glass scales are somewhat thicker than crystalline scales, but the difference is not nearly as great as that observed after oxidation at lower temperatures.

1200°C, 1h

Cristobalite

SiO$_2$ Glass

SiC   500 nm

Figure 8. TEM micrograph of scale formed in 1 h on Hi-Nicalon™-S in Si(OH)$_4$ saturated steam at 1200°C.

a   b   c

Cristobalite   SiO$_2$ Glass   Cristobalite

SiC 500 nm   SiC 500 nm   SiC 500 nm

Figure 9. TEM micrographs of scale formed in 3 h on Hi-Nicalon™-S in Si(OH)$_4$ saturated steam at 1400°C. a) Coarse-grained cristobalite scale. b) SiO$_2$ glass scale. c) Very coarse-grained cristobalite scale.

All scales formed after oxidation for 1 and 3 h at 1500°C in Si(OH)$_4$ saturated steam had crystallized to cristobalite (Fig. 10). Most were very coarse-grained, and could in some cases be described as single-crystals for dimensions smaller than the coating thickness (Fig. 10 a,c), albeit with some twinning. There were some exceptions to this microstructure (Fig. 10 b,d). Some scale microstructures show evidence of very early crystallization, with a relatively thin, coarse grained outer scale, and a relatively thick, fine-grained inner scale. Although this inner scale is described as "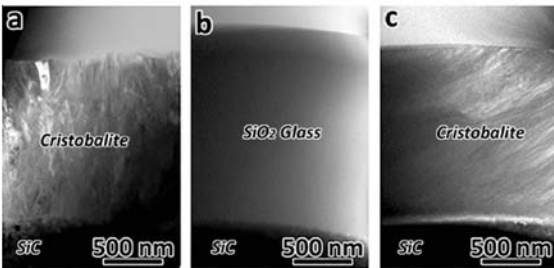fine-grained", the columnar grain width of about 200 nm is significantly larger than that observed for analogous microstructures formed at 1000°C (Fig. 6, 7).
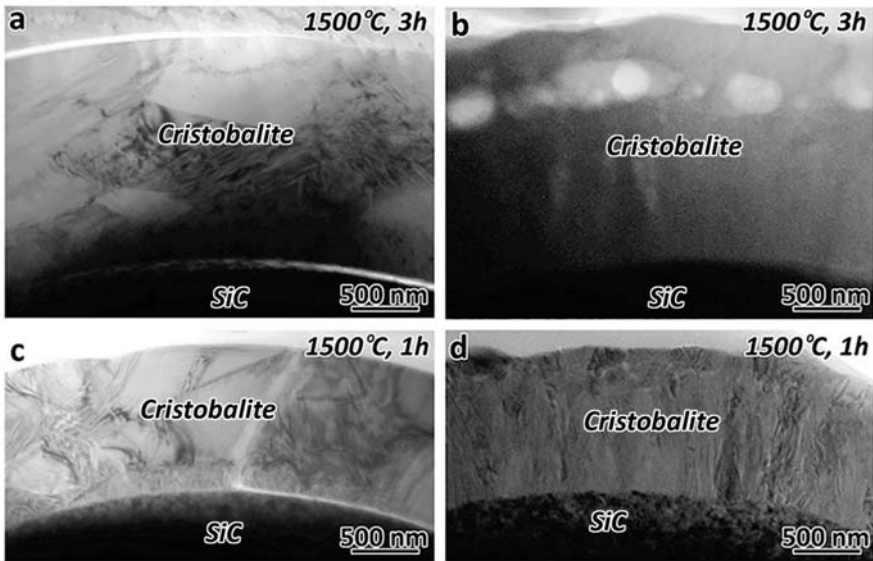
Figure 10. TEM micrographs of scale formed in 1 and 3 h on Hi-Nicalon™-S in Si(OH)$_4$ saturated steam at 1500°C. a) Very coarse-grained cristobalite scale formed after 3h at 1500°C. b) Relatively fine-grained cristobalite scale formed after 3h at 1500°C. c) Very coarse-grained cristobalite scale formed after 1h at 1500°C. d) Relatively fine columnar-grained cristobalite scale formed after 1h at 1500°C.

Stability of Fiber Microstructure

The most aggressive oxidation condition used was 3 h at 1500°C in Si(OH)$_4$ saturated steam. The glass tubes did not survive longer heat-treatments at these conditions. The effects of these conditions on the microstructure of the Hi-Nicalon™-S fiber are relevant to development of higher temperature combustion environment applications for SiC-SiC CMCs. TEM micrographs of the oxidized fiber microstructure, and one micrograph of the SiC-scale interface, are shown in figure 11. There is no obvious change in SiC grain size, or SiOC glass second-phase size. The turbostratic graphite inclusions in the SiOC glass are similar in size and morphology to those observed in as-received fiber.[28] There may be subtle microstructural changes, such as increased prevalence of faceting of SiC grains along SiC-SiOC interphases, but confirmation of these changes await detailed quantitative analysis of the microstructures.

Discussion – Fiber Strength

Hi-Nicalon™-S strengths after dry and wet (3 mol% H$_2$O) air oxidation were modeled using oxidation and scale crystallization kinetics, change in load-bearing area, and the effect of scale residual stress on SiC crack tip stress intensity factors.[16] The model predicted strength increases that accompany glass scale formation, decreases that accompany crystallization, and some of the strength differences between fibers oxidized in dry and wet air. However, fibers oxidized for long times in wet air at 800° and 900°C were ~0.5 GPa weaker than expected, implying a strength degradation mechanism associated with glass scales that was not modeled. This was suggested to be environmentally assisted subcritical crack growth (EASCG) from water-vapor related surface-active species. Despite the presence of a thin glass scale, this mechanism operates to modestly weaken SiC fibers.

After oxidation at 600° to 900°C in Si(OH)$_4$ saturated steam, Hi-Nicalon™-S strength degradation (Fig. 2) was similar in magnitude to that observed after oxidation in wet air. This
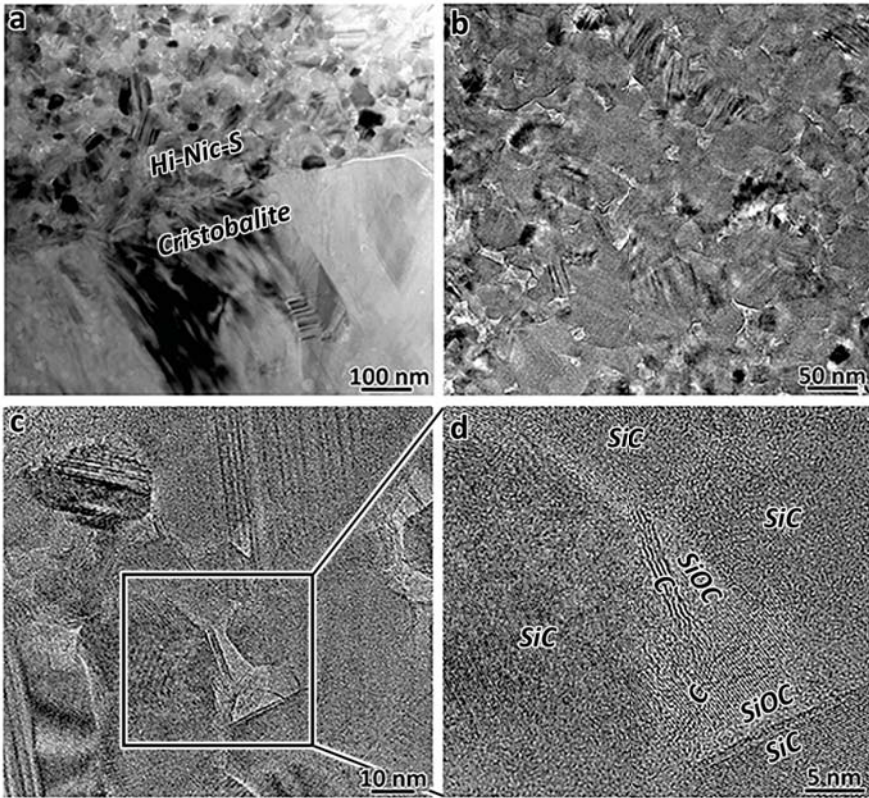
Figure 11. TEM micrographs of Hi-Nicalon[1M]-S SiC fiber microstructure after 3 h oxidation in $Si(OH)_4$ saturated steam at 1500°C. a) Low magnification image of the SiO_2 – SiC interface. b) Intermediate magnification of the SiC fiber. c) High resolution image of the SiC fiber, showing SiC grains and facetted SiOC inclusions with turbostratic graphite d) An even higher magnification image of the area in "c" showing an SiOC glass pocket with turbostratic graphite.

degradation occurred regardless of whether the SiO_2 scales were hermetic, or dewetted and spheroidized (Fig. 3). If the degradation mechanism is also EASCG, the surface-active species that promote flaw growth in the underlying SiC may not be affected by the presence or absence of a hermetic SiO_2 glass layer.

After oxidation at 1000°C for 1 to 10 h in $Si(OH)_4$ saturated steam, Hi-Nicalon™-S scales were 0.5 – 1 μm thick (Fig. 4) and had crystallized to cristobalite (Fig. 6,7). The strength degradation of these fibers (Fig. 2) is similar to that observed for dry-air oxidized fibers that had crystallized scales of similar thickness,[15, 16] although formation of 0.5 – 1 μm thick crystallized SiO_2 scales required higher temperatures and/or longer times in dry air.[28] The degradation mechanism is suggested to be the same in both dry air and steam. It is crudely analogous to reverse tempering in glass - the surface tractions imparted on strength-governing surface flaws by the tensile residual stress in the cristobalite scales increases the stress intensity factors at these

flaws, thereby degrading strength. More thorough discussion of strength degradation models for steam-oxidized SiC fibers will be presented in a later publication.

Discussion – SiO_2 Scale Microstructure Evolution

Between 1200° and 1500°C, the anomalous lack of temperature dependence for SiO_2 scale thickness formed during oxidation (Fig. 4) is attributed to the relative amounts of time the scale spends in the glass and crystalline states, and the microstructure evolution of the crystalline scale.

Scales formed at 1200°C in steam were less well crystallized than those formed at 1000°C. This is much different from the crystallization behavior of scales that formed in dry air, where crystallization rates increased systematically with temperature and kinetics were well modeled by Kolmogorov-Johnson-Mehl-Avrami (KJMA) methods.[28] Anomalously low crystallization rates at 1200°C in steam enhance oxidation rates, because O_2 diffuses faster through glass SiO_2 scales than crystalline scales.[37, 38] The SiO_2 scales that do form in the crystalline state at 1200° and 1300°C are very fine-grained from dynamic recrystallization accompanying relief of the very large growth stresses from oxidation volume expansion (Fig. 8).[36] O_2 diffusion will in this case be governed by grain boundary diffusion, and the fine grain-size of the cristobalite scale will increase diffusion rates.

At 1500°C, the relatively fine-grained scales that form as dynamically recrystallized cristobalite are more coarse-grained than those that form at lower temperatures (Fig. 10 b,d), presumably because of more rapid grain growth at higher temperatures, and more rapid dissipation of growth stress by thermally activated dislocation slip and climb-based creep mechanisms.[36] O_2 diffusion will in this case be governed by cristobalite grain boundary diffusion, and the fine grain-size of the cristobalite scale will promote rapid oxidation. However, most scales formed at 1500°C had grain-size comparable or larger than the scale thickness (Fig. 10 a,c). This is attributed to grain growth of the outer scale that formed as glass and crystallized to cristobalite, and to growth of these large grains through the fine-grained inner scale that formed as cristobalite. O_2 diffusion will in this case be governed by cristobalite lattice diffusion, which will decrease diffusion rates relative to those in fine-grained cristobalite or SiO_2 glass.[37, 38]

Future work will attempt to support this qualitative description of the relationship between scale microstructure development and oxidation kinetics. Modeling based on scale thicknesses in the glass and crystalline states, crystallization models, and cristobalite dynamic recrystallization and grain growth models based on observed grain sizes at different temperatures and times will be used to determine O_2 lattice-diffusion coefficients for OH^- saturated SiO_2 glass and cristobalite, and for cristobalite grain boundaries. Partial pressures of oxygen and H_2O will be different at various points inside a cracked or uncracked CMC. There will also be constraints on the volume expansion. SiC fiber oxidation rates, and the strength changes associated with oxidation, can be determined if partial pressures are known or modeled, the partial pressure dependence and effects of volume expansion constraint are incorporated in such models.

SUMMARY AND CONCLUSIONS

At 700° and 800°C, glass scales that form during Hi-Nicalon[TM]-S oxidation in 30 and 100 h often dewet the fiber surface and spheroidize. The scale no longer passivates the SiC surface, and oxidation proceeds at the fastest possible rate, with new SiO_2 scale wicking to the spheroidized scale as fast as it forms. The low viscosity of hydroxyl group saturated SiO_2 scales that form in steam is suggested to facilitate dewetting and spheroidization.

Oxidation rates in steam are nearly an order of magnitude faster than those in air at temperatures near 1000°C, even though scales formed in steam are crystalline and those formed in dry air are glass. However, crystallization may have a relatively small effect on scale thickness if occurs late during scale formation. The temperature – time dependence of scale crystallization in $Si(OH)_4$ saturated steam was much more erratic than that in air. Scales begin crystallization at much lower temperatures in steam than in dry air, but complete crystallization occurs at much higher temperatures. Scale thicknesses do not increase significantly with temperature from 1200° to 1500°C. This is suggested to be due to the greater amount of time scales spend growing in the glass state at temperatures near 1200°C, which increases oxidation rates at lower temperatures,

and to grain growth in crystalline scales at higher temperatures that decreases oxidation rates at higher temperatures.

Fiber strengths suffer more degradation during oxidation in $Si(OH)_4$ saturated steam than they do in dry air. Degradation becomes significant after 100 h at 600°C in $Si(OH)_4$ saturated steam. Two mechanisms for degradation are suggested. When glass scales form at 600° to 900°C, surface-active species associated with H_2O are suggested to degrade strength by environmentally assisted subcritical crack growth, regardless of whether the glass scale dewets SiC or remains hermetic. The 0.3 – 0.8 GPa strength drops observed for fibers with these types of scales was slightly larger, and occurred at lower temperatures, than similar strength drops observed previously in wet (3 mol% H_2O) air. When crystalline (cristobalite) SiO_2 scales form, strength is severely degraded by the effect of tensile residual stress in the cristobalite scale on the stress intensity factor at strength governing surface flaws in the SiC fibers. The strength drops observed for these types of scales were consistent with those observed previously for crystallized scales that formed after oxidation in dry air, albeit at higher temperatures. Heat-treatment in $Si(OH)_4$ saturated steam had no significant effect on Hi-Nicalon™-S microstructure at any temperature, including 1500°C

REFERENCES

1.   Spriet, P. CMC Applications to Gas Turbines. In *Ceramic Matrix Composites: Materials Modeling, and Technology*, Bansal, N. P.; Lamon, J., Eds.; John Wiley & Sons: Hoboken, NJ, 2015; Chapter 21, pp 593-608.
2.   Sauder, C. Ceramic Matrix Composites: Nuclear Applications. In *Ceramic Matrix Composites: Materials Modeling, and Technology*, Bansal, N. P.; Lamon, J., Eds.; John Wiley & Sons: Hoboken, NJ, 2015; Chapter 22, pp 609-646.
3.   Linebaugh, K., GE Bets on Ceramic Jet-Engine Parts. *Wall Street Journal* 2013.
4.   Curtin, W. A.; Ahn, B. K.; Takeda, N., Modeling Brittle and Tough Stress-Strain Behavior in Unidirectional Ceramic Matrix Composites. *Acta mater.* **1998**, 46, 3409-3420.
5.   Norris, G., GE Unveils CMC Production Ramp-Up Plan. *Aviation Daily* **2015**, October 27, 4.
6.   Dong, S. M.; Chollon, G.; Labruguere, C.; Lahaye, M.; Guette, A.; Bruneel, J. L.; Couzi, M.; Naslain, R.; Jiang, D. L., Characterization of Nearly Stoichiometric SiC Fibres. *J. Mater. Sci.* **2001**, 36, 2371-2381.
7.   Ichikawa, H., Development of High Performance SiC Fibers Derived from Polycarbosilane Using Electron Beam Irradiation Curing - A Review. *J. Ceram. Soc. Japan* **2006**, 114, 455-460.
8.   Sauder, C.; Lamon, J., Tensile Creep Behavior of SiC-Based Fibers With a Low Oxygen Content. *J. Am. Ceram. Soc.* **2007**, 90, 1146-1156.
9.   Lamon, J.; Mazerat, S.; R'Mili, M. Reinforcement of Ceramic Matrix Composites: Properties of SiC-Based Filaments and Tows. In *Ceramic Matrix Composites: Materials Modeling, and Technology*, Bansal, N. P.; Lamon, J., Eds.; John Wiley & Sons: Hoboken, NJ, 2015; Chapter 1, pp 3-26.
10.   Bunsell, A. R.; Piant, A., A Review of the Development of Three Generations of Small Diameter Silicon Carbide Fibres. *J. Mater. Sci.* **2006**, 41, 823-839.
11.   Ishikawa, T., Advances in Inorganic Fibers. *Adv. Polym. Sci.* **2005**, 178, 109-144.
12.   Sha, J. J.; Nozawa, T.; Park, J. S.; Katoh, Y.; Kohyaman, A., Effect of Heat-Treatment on the Tensile Strength and Creep Resistance of Advanced SiC Fibers. *J. Nucl. Mater.* **2004**, 329-333, 592-596.
13.   Tanaka, T.; Shibayama, S.; Takeda, M.; Yokoyama, A., Recent Progress of Hi-Nicalon Type S Development. *Ceram. Eng. Sci. Proc.* **2003**, 24, 217-223.
14.   Shimoo, T.; Takeuchi, H.; Okamura, K., Oxidation Kinetics and Mechanical Property of Stoichiometric SiC Fibers (Hi-Nicalon-S). *J. Ceram. Soc. Japan* **2000**, 108, 1096-1102.
15.   Hay, R. S.; Fair, G. E.; Bouffioux, R.; Urban, E.; Morrow, J.; Hart, A.; Wilson, M., Relationships between Fiber Strength, Passive oxidation and Scale Crystallization Kinetics of Hi-Nicalon™-S SiC Fibers. *Ceram. Eng. Sci. Proc.* **2011**, 32, 39-54.
16.   Hay, R. S.; Mogilevsky, P.; Krishnamurthy, R.; Chater, R. J., Strength of Hi-Nicalon™-S Fiber after Oxidation in Dry and Wet Air. *J. Am. Ceram. Soc.* **submitted**.

17.   Gauthier, W.; Pailler, F.; Lamon, J.; Pailler, R., Oxidation of Silicon Carbide Fibers During Static Fatigue in Air at Intermediate Temperatures. *J. Am. Ceram. Soc.* **2009**, 92, 2067-2073.
18.   Sha, J. J.; Hinoki, T.; Kohyama, A., Thermal and mechanical stabilities of Hi-Nicalon SiC fiber under annealing and creep in various oxygen partial pressures. *Corrosion Science* **2008**, 50, 3132-3138.
19.   Shimoo, T.; Okamura, K.; Mutoh, W., Oxidation Behavior and Mechanical Properties of Low-Oxygen SiC Fibers Prepared by Vacuum Heat-Treatment of Electron-Beam-Cured Poly(Carbosilane) Precursor. *J. Mater. Sci.* **2003**, 38, 1653-1660.
20.   Takeda, M.; Urano, A.; Sakamoto, J.; Imai, Y., Microstructure and Oxidation Behavior of Silicon Carbide Fibers Derived from Polycarbosilane. *J. Am. Ceram. Soc.* **2000**, 83, 1171-1176.
21.   Takeda, M.; Urano, A.; Sakamoto, J.; Imai, Y., Microstructure and Oxidative Degradation Behaviour of Silicon Carbide Fiber Hi-Nicalon Type S. *J. Nucl. Mater.* **1998**, 258-263, 1594-1599.
22.   Yao, R.; Feng, Z.; Chen, L.; Zhang, Y.; Zhang, B., Oxidation Behavior of Hi-Nicalon SiC Monofilament Fibres in Air and O_2-H_2O-Ar Atmospheres. *Corrosion Science* **2012**, 57, 182-191.
23.   Opila, E. J., Variation of the Oxidation Rate of Silicon Carbide with Water Vapor Pressure. *J. Am. Ceram. Soc.* **1999**, 82, 625-636.
24.   Angelici Avincola, V.; Cupid, D.; Seifert, H. J., Thermodynamic modeling of the silica volatilization in steam related to silicon carbide oxidation. *J. Eur. Ceram. Soc.* **2015**, 35, 3809-3818.
25.   Jacobson, N. S.; Eckel, A. J.; Misra, A. K.; Humphrey, D. L., Reactions of SiC with H_2/H_2O/Ar Mixtures at 1300C. *J. Am. Ceram. Soc.* **1990**, 73, 2330-2332.
26.   Opila, E. J.; Smialek, J. L.; Robinson, R. C.; Fox, D. S.; Jacobson, N. S., SiC Recession Caused by SiO_2 Scale Volatility unde Combustion Conditions: II, Thermodynamics and Gaseous Diffusion Model. *J. Am. Ceram. Soc.* **1999**, 82, 1826-1834.
27.   Opila, E. J., Oxidation and Volatilization of Silica Formers in Water Vapor. *J. Am. Ceram. Soc.* **2003**, 86, 1238-1248.
28.   Hay, R. S.; Fair, G. E.; Bouffioux, R.; Urban, E.; Morrow, J.; Somerson, J.; Hart, A.; Wilson, M., Hi-Nicalon™-S SiC Fiber Oxidation and Scale Crystallization Kinetics. *J. Am. Ceram. Soc.* **2011**, 94, 3983-3991.
29.   Hay, R. S.; Fair, G. E.; Hart, A.; Potticary, S.; Bouffioux, R., Kinetics of Passive Oxidation of Hi-Nicalon-S SiC Fibers in Wet Air: Relationships between SiO_2 Scale Thickness, Crystallization, and Fiber Strength. *Ceram. Eng. Sci. Proc.* **2012**, 33, 253-260.
30.   Cinibulk, M. K.; Welch, J. R.; Hay, R. S., Preparation of Thin Sections of Coated Fibers for Characterization by Transmission Electron Microscopy. *J. Am. Ceram. Soc.* **1996**, 79, 2481-2484.
31.   Hay, R. S.; Welch, J. R.; Cinibulk, M. K., TEM Specimen Preparation and Characterization of Ceramic Coatings on Fiber Tows. *Thin Solid Films* **1997**, 308-309, 389-392.
32.   Petry, M. D.; Mah, T.; Kerans, R. J., Validity of Using Average Diameter for Determination of Tensile Strength and Weibull Modulus of Ceramic Filaments. *J. Am. Ceram. Soc.* **1997**, 80, 2741-2744.
33.   Deal, B. E.; Grove, A. S., General Relationships for the Thermal Oxidation of Silicon. *J. Appl. Phys.* **1965**, 36, 3770-3778.
34.   Hetherington, G.; Jack, K. H., Water in Vitreous Silica Part I. Influence of Water Content on the Properties of Vitreous Silica. *Phys. Chem. Glasses* **1962**, 3, 129-133.
35.   Hetherington, G.; Jack, K. H.; Kennedy, J. C., Viscosity of Vitreous Silica. *Phys. Chem. Glasses* **1964**, 5, 130-136.
36.   Hay, R. S., Growth Stress in SiO_2 during Oxidation of SiC Fibers. *J. Appl. Phys.* **2012**, 111, 063527.
37.   Presser, V.; Loges, A.; Hemberger, Y.; Nickel, K. G., Microstructural Evolution of Silica on Single-Crystal Silicon Carbide. Part I: Devitrification and Oxidation Rates. *J. Am. Ceram. Soc.* **2009**, 92, 724-731.
38.   Rodriguez-Viejo, J.; Sibieude, F.; Clavaguera-Mora, M. T.; Monty, C., [18]O diffusion through amorphous SiO_2 and cristobalite. *Appl. Phys. Lett.* **1993**, 63, 1906-1908.

11