Enhanced oxidation resistance of SiC/SiC minicomposites via slurry infiltration of oxide layers

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SiC based composite materials commonly have protective silica surface in air. Under humid environments at high temperatures, like occur in jet engines, the silica surface layer reacts with water molecules to form volatile silicon hydroxide ($\text{Si}(\text{OH})_4$) and the protection is reduced which cause jet engine degradation. An alternative approach to protect SiC based composites would be to infiltrate the SiC matrix via slurry with an oxide material that is resistant to the high-temperature and humid environment. As proof of concept, aqueous based mullite particle slurries were infiltrated by pressurized flow and by capillarity of the wetting slurry on the external surface of the porous SiC matrix of single-fiber-tow SiC/SiC minicomposites. Minicomposites were precracked at room temperature during tensile tests then tested in tensile creep in air at 1200 °C to study the degree of protection that the infiltrated mullite provided at high temperatures. Next, fracture surfaces were examined using SEM.

1. Introduction

SiC/SiC composites are of interest for their use in next generation gas turbine engines because of their high-temperature strength, low density, high thermal conductivity and relative oxidation resistance^{1,2}. The oxidation of SiC is a critical issue which can limit use of SiC-based materials, especially SiC fiber-reinforced SiC matrix composites (SiC/SiC), in the hot section of engines. When exposed to dry air or oxygen at elevated temperatures, the SiC/SiC composite reacts with oxygen and forms a thin, dense layer of silica. The oxidation mechanism of SiC is described by the reaction equations

The thin oxidized layer of silica on the surface of the SiC material hinders oxygen transport into the interior of the material and effectively protects it from oxidation. However, in engine applications the gas phase is not dry, but contains water vapor created by the fuel combustion. This water can react with the SiO₂ layers on SiC resulting in surface recession of SiC due to the volatility of the reaction product silicon hydroxide (Si(OH)₄)^{3, 4,5,6} as described by the reaction equation

To hinder the reaction, environmental barrier coatings (EBCs)^{2,7} are applied to protect the silicon-based materials from the water vapor attack and improve their environmental durability. These coatings typically consist of Y or Yb-containing rare-earth silicates as the protective layer and mullite as a bond coat between the EBC layer and the SiC matrix and are applied via an atmospheric plasma spray approach⁸.

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4 Though plasma spray is a well-established coating technique it is limited to surface
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6 coatings. It would be advantageous for environmental barrier materials to actually infiltrate into
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8 the matrix regions of the composite in order to achieve greater protection as well as adherence.
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10 The result would be a hybrid matrix-coating which is potentially more durable to high-
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12 temperature oxidation and/or corrosion, enabling higher operating temperatures and longer use
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14 life. Therefore, the approach taken here was to incorporate to some degree the protective oxide
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16 materials as part of the matrix of the SiC-based composite. For this reason, as a proof-of-concept,
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18 a slurry-derived coating/infiltration approach was performed on porous CVI SiC matrix
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20 minicomposites to assess the slurry infiltration performance. Single-tow minicomposites
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22 consisting of a single tow of fibers with an interphase and a CVI SiC matrix were used as the
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24 substrate composite. These coating materials will be used in future studies with woven
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26 macrocomposites that are made from the same constituents that the minicomposite in this study
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28 are made from. Minicomposites offer a less expensive and quicker route to evaluate composites
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30 in the CVI SiC system. They have been investigated as a model composite for
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32 fiber/interphase/matrix interactions under various stressed-oxidation conditions since the
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34 minicomposite corresponds to the elementary scale of a macrocomposite^{9,10,11,12}. In this case, the
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36 minicomposite serves as the porous medium with the same CVI SiC matrix layer into which the
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38 oxide coatings infiltrate and bond to as in the case of a woven SiC fiber-reinforced CVI SiC
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40 matrix preform.
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50 Mullite was chosen to be the initial material infiltrated and coated for the minicomposites.
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52 Mullite^{13,14} serves as a good intermediate layer between the EBC oxide and SiC substrate since it
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54 has outstanding thermo-mechanical properties such as a thermal expansion similar to that of SiC
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56 (compared to the EBC coatings which have higher thermal expansion coefficients); low thermal
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conductivity; excellent creep resistance, good chemical stability, and oxidation resistance.

Mullite may ultimately act as a bond coat for the EBC coating¹⁵. In future studies, an outer layer of EBC coating will be added after initial mullite infiltration.

The slurry based dip/brush coating process is a simple, inexpensive and versatile non-line-of-sight coating process capable of coating complex shaped components, including complex cooling channels present in some of these components. This process enables chemical bonding between coating and substrate after sintering. It has recently been demonstrated that this slurry coating process provides a reasonably uniform coating thickness after sintering^{16,17,18}.

A variety of mullite based slurries were evaluated for effectiveness of infiltration. The slurry composition which received the best penetration with the smallest crack widths were infiltrated in Hi-Nicalon and Hi-Nicalon Type S minicomposites and tensile tested at room and elevated temperatures.

2. Materials and Experimental procedure

2.1 Materials

A series of slurries were tested for coating and infiltration. High purity sub-micron mullite powder (Baikowski Corp., Charlotte, NC) and Aluminum oxide powder (alpha phase alumina particles 40-50nm in diameter, 99.5% purity, Alfa Aesar, US), D.I. water, and ethanol (Decon Labs, Inc.) were used as the starting materials in the slurries. Tetraethyl orthosilicate (TEOS, 98%, ACROS ORGANICS, US), and tetramethylammonium silicate (16-20% water solution, Gelest, Inc.) were used in some formulations as solvent candidates. Megasol S50 (colloidal silica typically used as a glass fiber binder material, WESBOND Corp.), and corn starch (5-10 μm in size, TOPCO ASSOCIATES LCC.) were included in some slurry formulations, to enhance infiltration and coating performance.

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4 The minicomposite systems investigated in this paper were from the same batches of
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6 minicomposites that were tested and characterized thoroughly in previous studies by Almansour
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8 et al.^{9,10}. The single-tow SiC/SiC minicomposites were manufactured by Hyper-Therm Inc. (now
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10 Rolls Royce, Huntington Beach, CA) from a single tow of SiC fibers of one of the following
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12 types: Hi-Nicalon (HN) (Nippon Carbon, Tokyo, Japan), Hi-Nicalon Type S (HNS) (Nippon
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14 Carbon, Tokyo, Japan). The fibers were coated with pyrolytic boron nitride (PBN) interphase¹⁹
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16 or boron nitride (BN) interphase¹² deposited by chemical vapor infiltration (CVI). The SiC
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18 matrix was also deposited by CVI. Properties of different types of fibers that were used in this
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20 study are shown in Table 1.
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26 ***2.2 Preparation of slurry***

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28 Six candidate solvents and one blend of two solvents, listed in Table 2, were selected
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30 based on several factors including availability, cost, and ability to disperse the slurry particles.
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32 Solvent properties were considered including surface tension, viscosity, and volatility (vapor
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34 pressure)^{20, 21}. Ideally, the solvent should have low surface tension and low viscosity (for better
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36 spreading of the slurry), high enough viscosity to carry the slurry particles with flow, and low
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38 enough vapor pressure that the solvent does not evaporate too rapidly. The results column in
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40 Table 2 indicates which of the solvents were determined acceptable for testing with the slurries
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42 after initial trials. Those that had too high of vapor pressure were considered not acceptable due
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44 to rapid evaporation rate. The 60% ethanol-water solution had low enough surface tension, low
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46 vapor pressure and capable viscosity.
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53 Candidate slurries listed in Table 3 were prepared and tested. The mass amounts of solids
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55 and solvents in preparation of the slurries are indicated in the composition columns of the table.
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57 In preparation of the slurries having an ethanol and water solvent mixture, the ethanol and water
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4 were first blended in the indicated % of ethanol and were agitated with a magnetic stirrer for an
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6 hour to obtain a uniformly mixed solvent. All solid components were weighed and transferred
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8 into a container at once. The solvents were added into the container after the solids. The
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10 container was sealed and the slurries were stirred with a magnetic stirrer overnight to achieve
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12 uniform slurries.
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15 16 **2.3 Coating and infiltration process** 17

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19 Brush coating is a simple technique to apply the coating and during the brushing any
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21 excess coating materials can be brushed off of the composite surfaces. The disadvantage is the
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23 thickness of the coating is not accurately applied. As long as sufficient material is applied with
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25 the brush to fill the pores, then capillary forces take over to draw in the slurry. Once the slurry
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27 stops entering the pores, the excess material is brushed off the surface but leaving roughly a
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29 uniform outer coating thickness of about 0.1mm as estimated by eye.
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33 The minicomposites were roughly elliptic cylindrical in shape, 50 mm long and 15-7.5
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35 mm in major-minor axis diameters. The exposed (upper) side of a minicomposite sample sitting
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37 on a flat surface was brush coated on the middle 30 mm along the cylindrical axis. The samples
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39 were immediately rotated and brush coated on the opposite side to establish one coating cycle.
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41 Samples with different numbers of coating cycles were prepared and tested to study the effect of
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43 coating thickness. The two ends of the minicomposite were left uncoated for clamping in the
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45 mechanical strength tests.
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49 When coated from the outside all of the external pore openings are covered by slurry.
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51 Via capillary forces the slurry may penetrate into the pores, the extent of the penetration is
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53 limited by air that is trapped inside of the pores. Some of the samples, after coating, were placed
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55 into a vacuum chamber with an applied absolute pressure of 26.8 kPa (Vacuum pump reading
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74.5 kPa) was applied. This enabled some of the trapped air to expand as air bubbles through the slurry and to escape out of the pores, enabling the slurry to penetrate deeper into the pores.

The coated samples were dried at room temperature, and then air sintered at 1350°C for five hours. Multi-layer coatings were applied in some of the CMC samples.

2.4 Characterization

The surface tension of the slurry determines the capillary forces, controls the rate and extent of the slurry penetration into the sample. The surface tension of the SiC surface was measured by Drop Shape Analyzer (DSA) with drop weight method. The two parameters for successful infiltration are the penetration performance and minimal cracking of outside surface coating layers. These were both examined by observation of the cross sections and outside coating surface with a Scanning Electron Microscope (SEM). The crack width of coating surface was analyzed by software FibraQuant 1.3 software (nanoScaffold Technologies LLC, Chapel Hill, NC).

2.5 Minicomposites preparation and testing methodology

For room temperature tensile fast fracture specimens tested in air, the middle 40mm of the specimen was infiltrated with slurry and sintered after which the outer 31.75 mm of each side of the minicomposites were mounted inside slotted steel spring pins using high temperature thermally conductive epoxy and then cured for 4 hours at 121°C followed by 4 hours at 178°C. The length of the spring pins was 31.75 mm, to have enough area to attach acoustic emission (AE) sensors to record AE waveforms. Room temperature monotonic tensile tests were conducted at a constant crosshead displacement rate of 0.03 mm/min on an Instron 5582 equipped with a 500 N load cell. Fig. 1 shows (a) Picture and (b) Schematic of the experimental setup for room temperature fast fracture tensile testing of coated and uncoated single tow

ceramic matrix minicomposite samples where the minicomposite is mounted in steel pins in the gripping fixtures of an Instron testing machine. A Grasshopper 3 high-speed camera (Model GS3-U3-50S5C-C, Point Grey Research Inc.) was used for imaging at a rate of 4 frames per second. Modal acoustic emission (MAE) was monitored during tests using a four-channel fracture wave detector acquisition system (Digital Wave Corporation, Centennial, CO) using two wide-band sensors (Model B1025 with high sensitivity in the range 50 kHz–2.0 MHz). An Agilent multimeter (Model 34420A) with four probes was used to record electrical resistance (ER). All damage monitoring devices were concentrated on the sample gage section. Fast fracture room temperature monotonic tensile tests were performed on coated and uncoated samples up to failure to study the coating and sintering effect on the strength and mechanical behavior of SiC/SiC minicomposites. In addition, slurry coated minicomposites were subjected to tension at room temperature to induce about 1 crack/mm crack density (based on AE) in the CVI-SiC matrix, which would then be tested in creep at 1200 °C. Precracking stresses to induce the approximate 1 crack/mm in the matrix were determined from previous studies by Almansour et. al^{9,10} for the same batches of minicomposites using the acoustic emission (AE) technique.

Coated then precracked Hi-Nicalon and Hi-Nicalon type S minicomposites were also dead-weight loaded at 1200 °C in air to characterize the protection that the hybrid oxide-matrix/coating provided and compare it with uncoated minicomposites from the same batches that were previously tested in creep-rupture at 1200 °C in air¹⁰. The middle 80 mm of the minicomposite specimens was infiltrated with slurry and sintered after which the outer 31.75 mm of each side of the minicomposites were mounted inside slotted steel spring pins. The total length of the samples was 190 mm, which provided enough minicomposites surface area to allow direct attachment of the electrical resistance probes. The minicomposite stress was determined by

dividing the applied load by the calculated minicomposite cross-sectional area. Minicomposites cross-sectional areas and constituent volume fractions were calculated as previously shown in Almansour et. al^{9,10}. Displacement was measured using an AC linear variable differential transformer (LVDT, model MHR100, Measurement Specialties, Hampton, VA) with ± 0.1 inch range and $\pm 0.25\%$ linearity for the full stroke. Fig. 2 shows (a) Picture and (b) Schematic of experimental setup for creep rupture tensile testing of coated and uncoated single tow ceramic matrix minicomposite samples at high temperatures. The minicomposite is mounted vertically inside the furnace and the LVDT rod is mounted on the suspended weight frame that is attached to the bottom of the minicomposite. The LVDT core is mounted on the creep frame. Also, 4 electrical resistance probes are attached to the minicomposites to measure electrical resistance changes.

Post-testing examination

After failure, fracture surfaces were examined using a scanning electron microscope with energy dispersive spectroscopy (SEM/EDS) to determine the nature of failure crack, the amount, and location of fiber pullouts, and the oxidation location for the different minicomposite constituents. Furthermore, a region of the gage section (~ 30 mm) was extracted from tested specimens and then mounted and polished along the length to determine the number of through-thickness matrix cracks (crack density) and examine the CVI/SiC matrix/coating interphase. Average crack densities were measured over a length of at least 5 mm.

3. Results and Discussion

3.1 Optimization of slurry composition

Slurries with twenty-three different compositions listed in Table 3 were created using the acceptable solvents in Table 2 and studied for feasibility of minicomposite infiltration and coating. Slurries were first selected based upon mixing uniformity. Slurries that resulted in agglomerated particles were eliminated. The remaining slurries were coated on SiC/SiC minicomposite samples to study the resultant coating layer and slurry penetration. The thickness of each coating layer and multilayer coatings were studied and in some cases vacuum was applied to better achieve infiltration performance. The performance results are summarized in Table 3.

Thickness of each coating layer

As described in section 2.3, the brush coatings on the front and back were considered as one coating cycle. The number of coating cycles strongly affected the coating thickness, which ultimately affected shrinkage crack widths in the coating layer. Layers with different numbers of coating cycles were brushed on minicomposites to compare their performance (minimal layer cracking and good adhesion) and to determine the optimum coating thickness. For example, Figure 3 shows the surface of minicomposites coated with slurry #18 where Figure 3a was coated with ten coating cycles and Figure 3b was coated with three coating cycles. The coating thickness and shrinkage crack widths were significantly greater for the ten cycle coating layer compared to the three cycle coating layer. It was found that a two coating cycle was optimum, providing sufficient material for infiltration to form a uniform coating layer.

Multi-layer coating

Coatings having different layer properties were created by applying multiple coatings of different slurry compositions with the goal of optimizing the infiltration. Ultimately, a triple-layer coating approach was adopted. After sintering, the infiltrated coating layers were formed.

The cross-section of a triple layer coated ceramic matrix minicomposite sample is shown in Figure 4. Layer 1 of the triple coating was made from slurry #19 which has relatively lower surface tension, mixed with powders of alumina, mullite, cornstarch, and 60% ethanol-water solution. The slurry was infiltrated through the narrow pores into the interior of the minicomposite. Layers 2 and 3 were made from slurry #18, with alumina, mullite, cornstarch and water, provided better surface finish. The coating filled or at least plugged the cracks in the prior coating layer and added to the thickness of the oxide to provide a better oxidation resistance for the minicomposite.

Vacuum enhanced infiltration

The pore structure of the composite is complicated consisting of both dead-end pores and connected pores. Figure 5 shows schematically the preferential infiltration of the slurry through the main stem of the void network. Paths with small-pores are difficult to infiltrate due to the plugging by solid particles. Gas in the branches (or dead ends) can be trapped which ideally should be removed. As deduced from a simple pore-penetration model described in Appendix A, the application of a vacuum was expected to improve the penetration of the slurry into the pores. In some experiments, samples were placed into a closed chamber under an absolute pressure of 26.8 kPa to pump trapped air out of the CMC sample. Air bubbles indicated some air was pumped out and the slurry penetrated in. Figure 6a shows an image of the cross-section of a one cycle coated minicomposite sample of slurry #1 that was infiltrated without vacuum. Figure 6b shows a similar coated sample but the infiltration occurred with the applied vacuum. Inspection and comparison of Figures 6a and 6b show the penetration of the slurry was deeper and into smaller size pores when vacuum was applied.

Infiltration optimization

As indicated in Table 3, a few of the 23 slurry compositions did not mix well since the solid particles were agglomerated and were not used in the infiltration tests. Slurries of acetone, hexane, or TEOS as solvent had lower surface tension compared with other solvents, but the evaporation rate is higher and ended with large dry cracks on the coating surfaces. Slurry #18, with a composition of 0.8g Alumina, 1.6g Mullite, 4.0g Water, and 0.2g Cornstarch and slurry #19 with composition of 0.8g Alumina, 1.6g Mullite, 3.8g 60% Ethanol-water solution, and 0.2g Cornstarch had better performance than the remaining slurries. The best overall performance was obtained with two layers of mullite coating (slurry # 19) to get a good infiltration performance and a third layer of mullite coating (slurry # 18) to get a smooth surface with smallest crack width.

SEM images in Figure 7, with cross section and surface views of the best slurry coated SiC/SiC minicomposite samples, show that the slurry successfully infiltrated through pores and into the bulk of the sample. After the sintering process, the CMC sample was sealed with solid particles; and tiny cracks were found on the surface.

3.2 Minicomposites' Mechanical behavior

Mechanical behavior at room temperature

Initial room temperature mechanical behavior evaluation was performed on Hi-Nicalon fiber reinforced CVI matrix minicomposites in air. In Figure 8a, Hi-Nicalon minicomposites stress and normalized cumulative AE energy are plotted as a function of time for tensile fast fracture testing at room temperature. Also, in Figure 8b, high speed camera results are shown for the coated Hi-Nicalon fiber reinforced minicomposite before tensile loading and during the last 10 seconds prior to the final composite failure. No major cracks were observed in the surface of

the coating layer throughout the tensile fast fracture test until just prior to ultimate failure crack growth and propagation. The coating layer only cracked in the vicinity of the minicomposite fracture area.

Figure 9 shows the evolution of acoustic energy accumulation and the increase in electrical resistance plotted as a function of applied minicomposite stresses throughout representative Hi-Nicalon type S minicomposite precracking process to achieve 1 crack/mm crack density in the CVI-SiC matrix. The minicomposite stress at the onset of CVI-SiC matrix cracking was 250 MPa. The required stresses to induce 1 crack/mm in the different minicomposites were obtained from Almansour et. al^{9,10} for the different types of minicomposites. Figure 9 shows the precracked tensile condition (350 MPa) for the Hi-Nicalon type S minicomposite to induce approximately 1 crack/mm in the CVI-SiC matrix. Also, both damage monitoring techniques agree well on the onset and evolution of CVI-SiC matrix cracking where AE activity accumulation and ER increased simultaneously at the onset of matrix cracking until reaching the induced matrix cracking stress in CVI SiC matrix layer. For instance, in Figure 9, minicomposites stress at the onset ER was 255 MPa, which is approximately the same as minicomposite's stress at 1st loud event. Thus, formation of multiple through-thickness matrix cracks was confirmed in the CVI-SiC matrix.

Figure 10 compares the onset of matrix cracking and ultimate failure properties for the different minicomposite systems. Figure 10a shows the room temperature matrix cracking stress at onset of matrix cracking and the ultimate tensile strength of Hi-Nicalon fibers with Pyrolytic Boron Nitride (PBN) interphase and CVI-SiC matrix minicomposites that failed in the gage section in fast fracture tensile tests for different volume fractions. The ultimate tensile strength for uncoated minicomposites tested at room temperature in air was slightly higher than that for

1 coated minicomposites. Thus, sintering resulted in a mild reduction of the minicomposite
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6 ultimate tensile strength, presumably due to degradation of the fibers due to sintering treatment.
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8 Also, Figure 10a shows the stress on the on the CVI-SiC matrix (based on constant strain
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10 assumption and rule of mixtures¹¹) at the onset of matrix cracking associated with the first loud
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12 AE event (highest order of magnitude energy event). Matrix cracking of the infiltrated
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14 minicomposites is similar to the as-produced minicomposites. Figures 10b and 10c show matrix
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16 cracking stress at the onset of CVI-SiC matrix cracking for coated and uncoated Hi-Nicalon
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18 Type S and Hi-Nicalon with BN interphase, respectively, for different fiber volume fractions.
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20 Again, sintering the coated samples did not appear to reduce the matrix cracking stress of the SiC
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22 matrix for Hi-Nicalon Type S and Hi-Nicalon minicomposites for these minicomposite systems.
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28 ***High temperature creep behavior***

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31 An example of creep strain evolutions of coated precracked, uncoated precracked and
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33 pristine Hi-Nicalon Type S fiber reinforced minicomposites at 1200°C in air were plotted as a
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35 function of time in Figure 11. For similar stresses, the pristine specimen outperformed the
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37 precracked specimens as expected. For this condition, there was not too much difference
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41 between the coated and uncoated specimen.
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44 Figure 12 shows a micrograph of polished longitudinal region in the hot gage section of
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46 sample Hi-Nicalon Type S. The density of transverse cracks is 1 cracks per mm which was
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48 achieved by controlled precracking at room temperature post coating the sample. The coating
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50 layer did not appear to form cracks that were associated with through thickness CVI SiC matrix
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52 cracks. There appears to be good adhesion and bonding between the bond coating and CVI-SiC
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54 matrix in spite of CVI matrix cracking after the pre-crack and creep stress conditions. Also note
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that the microcracks in each mullite layer appear to be discontinuous through the thickness of the multiple layers.

The stress rupture behavior at 1200°C for coated and uncoated precracked minicomposites are shown in Figure 13. The data is plotted as stresses on the fibers if fully loaded (load divided by fiber area), i.e., the condition in a through thickness matrix crack. There was no discernable difference in time to failure for coated precracked Hi-Nicalon Type S minicomposites compared to uncoated precracked specimens. However, the stress on the fibers was very high (~ 1 GPa) and rupture performance was most likely influenced by fiber rupture properties at these stresses.

The coated precracked Hi-Nicalon minicomposites showed significant improvement in rupture life compared to uncoated precracked Hi-Nicalon minicomposites (Figure 13b). Precracked Hi-Nicalon minicomposites appear to be more sensitive to stress-oxidation than precracked Hi-Nicalon type S minicomposites at 1200°C. There is only a small increase in time to failure with reduced rupture stress for uncoated pre-cracked minicomposites. The time to failure for coated Hi-Nicalon minicomposites are far superior in time to failure for similar stresses. Presumably, the mullite layers aid in reduced oxidation-induced degradation resulting in over 300% longer rupture lives under these conditions.

3.3 Post creep fracture surface examination

The fracture surfaces (Figure 14) of Hi-Nicalon and Hi-Nicalon Type S coated composites after high temperature creep test were observed in the scanning electron microscope (SEM). For the coated Hi-Nicalon minicomposite (Figure 14a), slurry penetrated through open channels into part of the minicomposite interior; however, there were large regions of internal porosity which were not infiltrated. The outer surface of the minicomposite was covered with an approximately 100

micron mullite region which appears to have provided the additional oxidation protection for composite (Figure 14b). For the coated Hi-Nicalon Type S sample (Figure 14b), similar internal porosity with an even thicker surface layer coating was observed instead of mullite penetrating and filling pores. Tilted views of examples of fractured surfaces for the two minicomposites are shown in Figure 15. Little fiber pullout is observed for coated Hi-Nicalon Type S minicomposite (Figure 15a) compared to the pullout observed for Hi-Nicalon minicomposite (Figure 15b) crept specimens.

Hi-Nicalon and Hi-Nicalon Type S minicomposites post creep fracture surface was examined using Energy Dispersive Spectrometer (EDS). As shown in Figure 16, elemental Aluminum was dispersed around elemental Silicon, which shows the slurry coating layers covered the minicomposite. High Oxygen content was found in the BN interphase between SiC fibers and CVI-SiC matrix, which indicates high rate of oxidation of the BN interphase in the vicinity of CVI-SiC matrix cracks during the high temperature creep test of coated then precracked Hi-Nicalon and Hi-Nicalon Type S minicomposites which resulted in some stressed-oxidation embrittlement of the minicomposite. Thus, the mullite coating did not suppress stressed-oxidation, it merely slowed down the stressed-oxidation embrittlement process for this system.

4. Conclusions

23 compositions and combinations of slurries have been tested. The best performance was achieved by a three oxide layer coating infiltrated under vacuum, consisting of water, ethanol and corn starch for the inner layer and water and corn starch for the outer coatings. The coated and sintered minicomposites that were tested in tension at room temperature showed

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4 slightly lower ultimate tensile strength than the for pristine minicomposites. In addition, sintering
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6 the coated samples did not appear to affect the onset of CVI SiC matrix cracking stress based on
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8 acoustic emission. The multilayer coatings contained small microcracks which appear to have
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10 relieved the stress in the coatings and appear to result in little load being carried by the coating
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12 itself. Precracking the CVI SiC matrix of coated Hi-Nicalon and Hi-Nicalon Type S
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14 minicomposites induced through thickness CVI-SiC matrix cracks that appear to stop at the
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16 coating/matrix interphase. Moreover, the oxide layer provided some enhanced stress oxidation
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18 protection and longer creep lives to Hi-Nicalon minicomposites that were tested in creep at
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20 1200°C in air. As a result of this study, the slurry-derived mullite layer with good adhesion and
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22 beneficial oxidation enhancement will be pursued as the bond coat for environmental barrier
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24 coating schemes for woven macrocomposites.
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48 *References*

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52 1. Guan, K., Cheng, L., Zeng, Q., Li, H., Liu, S., Li, J., & Zhang, L. (2013). Prediction of
53 permeability for chemical vapor infiltration. *Journal of the American Ceramic Society*, 96(8),
54 2445-2453.
55 2. Lee, K. N., Fox, D. S., Eldridge, J. I., Zhu, D., Robinson, R. C., Bansal, N. P., & Miller, R. A.
56 (2003). Upper temperature limit of environmental barrier coatings based on mullite and BSAS.
57 *Journal of the American Ceramic Society*, 86(8), 1299-1306.
58
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64
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3. Fox, D. S., Opila, E. J., Nguyen, Q. N., Humphrey, D. L., & Lewton, S. M. (2003). Paralineer Oxidation of Silicon Nitride in a Water-Vapor/Oxygen Environment. *Journal of the American Ceramic Society*, 86(8), 1256-1261.
4. Jacobson, N. S., Opila, E. J., & Lee, K. N. (2001). Oxidation and corrosion of ceramics and ceramic matrix composites. *Current Opinion in Solid State and Materials Science*, 5(4), 301-309
5. Park, D. J., Jung, Y. I., Kim, H. G., Park, J. Y., & Koo, Y. H. (2014). Oxidation behavior of silicon carbide at 1200 C in both air and water–vapor-rich environments. *Corrosion Science*, 88, 416-422.
6. Fox, D. S., Opila, E. J., Nguyen, Q. N., Humphrey, D. L., & Lewton, S. M. (2003). Paralineer Oxidation of Silicon Nitride in a Water-Vapor/Oxygen Environment. *Journal of the American Ceramic Society*, 86(8), 1256-1261.
7. Lee, K. N., Fox, D. S., & Bansal, N. P. (2005). Rare earth silicate environmental barrier coatings for SiC/SiC composites and Si₃N₄ ceramics. *Journal of the European Ceramic Society*, 25(10), 1705-1715.
8. Harder, B.J., Zhu, D., (2011). Plasma Spray-Physical Vapor Deposition (PS-PVD) of Ceramics for Protective Coatings, *Advanced Ceramic Coatings and Materials for Extreme Environments: Ceramic Engineering and Science Proceedings, Volume 32*, 71-84
- 9 Almansour, A., Maillet, E., Ramasamy, S., & Morscher, G. N. (2015). Effect of fiber content on single tow SiC minicomposite mechanical and damage properties using acoustic emission. *Journal of the European Ceramic Society*, 35(13), 3389-3399.
- 10 Almansour, A., Maillet, E., & Morscher, G. N. (2015). Tensile Creep and Rupture Behavior of Different Fiber Content and Type Single Tow SiC/SiC Minicomposites. *Mechanical Properties and Performance of Engineering Ceramics and Composites X: Ceramic Engineering and Science Proceedings, Volume 36*, (2), 11.
- 11 Lamon, J., Rebillat, F., & Evans, A. G. (1995). Microcomposite test procedure for evaluating the interface properties of ceramic matrix composites. *Journal of the American Ceramic Society*, 78(2), 401-405.
- 12 art ne -Fernández, J., & Morscher, G. N. (2000). Room and elevated temperature tensile properties of single tow Hi-Nicalon, carbon interphase, CVI SiC matrix minicomposites. *Journal of the European Ceramic Society*, 20(14), 2627-2636.
- 13 Ohira, H., Shiga, H., Ismail, M. G. M. U., Nakai, Z., Akiba, T., & Yasuda, E. (1991). Compressive creep of mullite ceramics. *Journal of Materials Science Letters*, 10(14), 847-849.
- 14 Osendi, M. I., & Baudin, C. (1996). Mechanical properties of mullite materials. *Journal of the European Ceramic society*, 16(2), 217-224.
- 15 Lee, K. N., & Opila, E. J. (2002, January). Mullite+ CAS Bond Coat for Environmental Barrier Coatings for Si-Based Ceramics. In *High Temperature Materials: Proceedings of a Symposium in Honor of the 65th Birthday of Professor Wayne L. Worrell* (Vol. 2002, p. 263). The Electrochemical Society.
- 16 Ramasamy, S., Tewari, S. N., Lee, K. N., Bhatt, R. T., & Fox, D. S. (2010). EBC development for hot-pressed Y₂O₃/Al₂O₃ doped silicon nitride ceramics. *Materials Science and Engineering: A*, 527(21), 5492-5498.
17. Ramasamy, S., Tewari, S. N., Lee, K. N., Bhatt, R. T., & Fox, D. S. (2010). Slurry based multilayer environmental barrier coatings for silicon carbide and silicon nitride ceramics—I. Processing. *Surface and Coatings Technology*, 205(2), 258-265.

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18. Ramasamy, S., Tewari, S. N., Lee, K. N., Bhatt, R. T., & Fox, D. S. (2010). Slurry based multilayer environmental barrier coatings for silicon carbide and silicon nitride ceramics—II. Oxidation resistance. *Surface and Coatings Technology*, 205(2), 266-270.
19. Morscher, G. N., & Martinez-Fernandez, J. (1999). Fiber Effects on Minicomposite Mechanical Properties for Several Silicon Carbide Fiber-Chemically Vapor-Infiltrated Silicon Carbide Matrix Systems. *Journal of the American Ceramic Society*, 82(1), 145-155.
20. Dean, J. A. (1990). Lange's handbook of chemistry. *Material and manufacturing process*, 5(4), 687-688, p 5.90- 5.104
21. Bank, D. D. (2010). DDBST software and separation technology GmbH. *DDB Software Package Version*.

APPENDIX A

In this paper slurries were infiltrated into CVI SiC/SiC composite through pores. The pore structure of the composite can be idealized as parallel uniform cylindrical tubes of length $2h_0$, which is the sample thickness. The slurry is considered to penetrate into the pore from both sides of the composite structure. The penetration depth of the slurry can be estimated by balancing the capillary forces pulling the slurry into the pores with the pressure of the air trapped inside of the pores.

The thickness dimension of the composite is small enough and the penetration occurs from any direction so that the effect of gravity can be ignored. The slurry penetrates from the two ends symmetrically so the force balance can be applied to the capillary tube of half length, h_0 , and the end of the tube at the center of the composite is considered to be closed.

Figure 1. Model of slurry penetration into a one end open tube by capillary force

As shown in Figure 1, slurry penetrates into the capillary tube, compressing the air inside of the tube until the forces become balanced. The balanced force equation is written as

$$\pi r^2 (P_1 - P_0) = F_{Cap} \quad (\text{Eq.1})$$

in which, P_0 and P_1 are the pressure outside and inside the tube, respectively. The capillary force is due to the surface tension acting on the contact line between the slurry and the air at the tube wall, and is given by

$$F_{Cap} = 2\pi r \gamma \cos \theta \quad (\text{Eq.2})$$

Applying the idea gas law, the pressure of the air trapped in the capillary is directly related to the volume of the air in the tube.

$$PV = nRT \quad (\text{Eq.3})$$

Since the number of moles of air in the capillary are constant then the right side of Eq. (3) is constant, thus

$$P_o V_o = P_1 V_1 = \text{constant} \quad (\text{Eq.4})$$

where P_o and V_o are the initial pressure and empty capillary volume when the air occupies the whole tube length h_o . When the slurry penetrates to depth h_1 , the air occupies the capillary of length $(h_o - h_1)$ and the corresponding pressure and gas volume are P_1 and V_1 . For cylindrical tubes the expression in Eq. (4) becomes

$$P_o(\pi r^2 h_o) = P_1 \pi r^2 (h_o - h_1) \quad (\text{Eq.5})$$

With some rearrangement, the pressure difference is obtained

$$(P_1 - P_o) = P_o \left(\frac{h_o}{h_o - h_1} - 1 \right) \quad (\text{Eq.6})$$

Combining Eq. (1), (2) and (6) with algebraic rearrangement yields an expression for the slurry penetration depth as

$$h_1 = h_o \left[\frac{2\pi r \gamma \cos \theta}{2\pi r \gamma \cos \theta + \pi r^2 P_o} \right]$$

Using the experimental data

Slurry surface tension	$\gamma = 0.031 \text{ N/m}$,
Average pore size	$r = 10^{-5} \text{ m}$,
Contact angle (worst case assumption)	$\cos \theta = 1$
Atmospheric pressure	$P_o = 101325 \text{ N/m}^2$
Model thickness	$h_o = 10^{-3} \text{ m}$

the depth of penetration of the slurry is calculated to be $h_1 = 5.8 \times 10^{-5} \text{ m}$ which is a very small penetration. To enhance the penetration a two-stage process is used. In the first stage, a vacuum is applied to the composite and the slurry is allowed to penetrate, as above. This is followed by the second stage of penetration by increasing the external air pressure to 1 atm.

In first stage, when applying vacuum, the absolute pressure external to the tube, defined as P_{VAC} , is no longer atmospheric pressure. P_{VAC} is determined from the vacuum gauge reading as $P_{VAC} = \text{Atmospheric pressure} - \text{Gauge reading}$. As an example, at the highest gauge reading, 74500Pa, $P_{VAC} = 101325 - 74500 = 26825 \text{ N/m}^2$.

When the external pressure is reduced to the vacuum pressure P_{VAC} , air trapped inside of the tube flows out as a stream of bubbles through the liquid coating until the inside pressure balances the vacuum pressure and the capillary forces. We assume that the moles of gas remaining in the tube are the same as if the tube was empty of liquid and the gas pressure in the tube was P_{vac} . Then, from the ideal gas law

$$P_{vac} V_o = P_2 V_2 \quad (\text{Eq.7})$$

in which P_2, V_2 are the pressure and gas volume inside the capillary tube, respectively.

In the second stage, the external pressure is gradually increased back to P_0 . The gas pressure and gas volume inside the capillary tube are labeled P_3, V_3 . In this stage, the slurry penetration increases with increased external pressure. In the capillary tube the moles of gas are conserved. By ideal gas law

$$P_3 V_3 = P_{VAC} V_0 \quad (\text{Eq.8})$$

or upon rearrangement

$$P_3 = P_{VAC} \frac{V_0}{V_3} = P_{VAC} \left(\frac{h_0}{h_0 - h_3} \right) \quad (\text{Eq.9})$$

Applying the equilibrium force balance to the capillary tube, analogous to Eq. (1), gives

$$\pi r^2 (P_3 - P_0) = F_{Cap} \quad (\text{Eq.10})$$

from which the pressure P_3 is

$$P_3 = P_0 + \frac{F_{Cap}}{\pi r^2} \quad (\text{Eq.11})$$

Combining Eq. (9) and (11) with algebraic rearrangement yields an expression for the final slurry penetration depth as

$$h_3 = h_0 \left(1 - \frac{\pi r^2 P_{VAC}}{\pi r^2 P_0 + F_{Cap}} \right) \quad (\text{Eq.12})$$

Using the experimental data

Model thickness	$h_0 = 10^{-3} m$
Average pore size	$r = 10^{-5} m$,
Atmospheric pressure	$P_0 = 101325 \text{ N/m}^2$
Absolute vacuum pressure	$P_{VAC} = 26825 \text{ N/m}^2$
Capillary force	$F_{Cap} = 2\pi r \gamma \cos \theta = 1.95 \times 10^{-6} \text{ N}$
Contact angle (worst case assumption)	$\cos \theta = 1$
Slurry surface tension	$\gamma = 0.031 \text{ N/m}$,

$$h_3 = h_0 (1 - 0.31) = 0.00069 m$$

In conclusion, under the experimental conditions, the final penetration depth of slurry is 69% of the pore length. Compared with the tiny initial slurry penetration depth without vacuum, a significantly increase of slurry penetration was obtained. This appendix shows the advantage of applied vacuum to enhance slurry penetration into the pores.

Table 1. Properties of different types of minicomposites’ constituents that were used in this study

Fiber Type	Number of Fibers per Tow	Fiber Diameter (μm)	Fiber Volume Fractions (%)	Fiber Elastic Modulus (GPa)	Fiber Density (g/cc)	Interphase Type
Hi-Nicalon-S	500	12	16 and 25	400	3.1	Boron Nitride (BN)
Hi-Nicalon	500	14	10,16 and 25	270	2.74	Pyrolytic Boron Nitride (PBN) &(BN)

Table 2. Summarized information of candidate solvents

Liquid	Temperature (°C)	Surface Tension γ (mN/m)	Viscosity (cP)	Vapor Pressure P(kPa)	Results
Acetone	20	23.7 ²⁰	0.306 ²⁰	24.57 ²¹	Rejected
Ethanol	20	22.27 ²⁰	1.074 ²⁰	5.95 ²¹	Applied in slurries
n-Hexane	20	18.4 ²⁰	0.30 ²⁰	20.00 ²¹	Rejected
Methanol	20	22.6 ²⁰	0.544 ²⁰	13.02 ²¹	Rejected
Water	25	71.97 ²⁰	0.894 ²⁰	3.17 ²¹	Applied in slurries
Ethanol(60%)+water(40%)	25	26.25	2.32	3.29 ²¹	Applied in slurries
TEOS Solution	25	26.51	0.72	23.10	Applied in slurries

Table 3. Summarized information of candidate slurries

Slurry #	Composition			Pressure/ Vacuum	Results
	Solid components		Solvents		
1	0.8g Alumina	2.8g Mullite	4.0g Polysilicate	Atmospheric pressure 26.8 kPa	SEM
2	0.8g Alumina	2.8g Mullite	5.0g Polysilicate	Atmospheric pressure	SEM
3	0.8g Alumina	2.8g Mullite	6.0g Polysilicate	Atmospheric pressure	SEM
4	0.8g Alumina	2.8g Mullite	10g Megasol	Atmospheric pressure	SEM
5	0.8g Alumina	2.8g Mullite	12g Megasol	Atmospheric pressure	SEM
6	0.8g Alumina	2.8g Mullite	15g Megasol	Atmospheric pressure	SEM
7	0.8g Alumina	2.8g Mullite	3.0g Ethanol	Atmospheric pressure	Evaporation too rapid
8	0.8g Alumina	2.8g Mullite	3.5g Ethanol	Atmospheric pressure	Evaporation too rapid
9	0.8g Alumina	2.8g Mullite	4.0g Ethanol	Atmospheric pressure	Evaporation too rapid
10	0.8g Alumina	2.8g Mullite	4.0g Polysilicate 0.4g Ethanol	Atmospheric pressure	SEM
11	0.8g Alumina	2.8g Mullite	4.5g Polysilicate 0.4g Ethanol	Atmospheric pressure	SEM
12	0.8g Alumina	2.8g Mullite	4.0g Megasol 2.0g Ethanol	Atmospheric pressure	Particle aggregation
13	0.8g Alumina	2.8g Mullite	1.5g 3% PEO Solution 4.0g Water	Atmospheric pressure	Particle aggregation
14	0.8g Alumina	1.6g Mullite	4.0g Polysilicate	Atmospheric pressure	SEM
15	0.8g Alumina	1.6g Mullite	4.0g Megasol 1.5g Water	Atmospheric pressure	SEM
16	0.8g Alumina	1.6g Mullite	4.0g Megasol 1.5g 50% Ethanol -water solution	Atmospheric pressure	SEM
17	0.8g Alumina	1.6g Mullite	4.0g Water 0.2g Triton X-100	26.8 kPa	SEM
18	0.8g Alumina 0.2g Cornstarch	1.6g Mullite	4.0g Water	26.8 kPa	SEM
19	0.8g Alumina 0.2g Cornstarch	1.6g Mullite	3.8g 60% Ethanol -water solution	26.8 kPa	SEM
20	0.8g Alumina	1.6g Mullite	4.0g Ethanol 0.1g Dispersing Agent	26.8 kPa	SEM
21	0.8g Alumina	1.6g Mullite	4.0g TEOS	Atmospheric pressure	Safety issue
22	0.8g Alumina	1.6g Mullite	3.0g TEOS	Atmospheric pressure	SEM
23	0.8g Alumina 0.2g Corn Starch	1.6g Mullite	3.0g TEOS	Atmospheric pressure	SEM

Figure 1. (a) Picture and (b) Schematic of experimental setup for room temperature fast fracture tensile testing of coated and uncoated single tow ceramic matrix minicomposite samples where the minicomposite is mounted in steel pins in the gripping fixtures of an Instron testing machine along with 2 acoustic emission sensors and 4 electrical resistance probes.

Figure 2. (a) Picture and (b) Schematic of experimental setup for creep rupture tensile testing of coated and uncoated single tow ceramic matrix minicomposite samples at high temperatures where minicomposite is mounted vertically inside the furnace and the LVDT rod is mounted on the suspended weight frame that is attached to the bottom of the minicomposite and the LVDT core mounted on the creep frame and 4 electrical resistance probes.

Figure 3. SEM image of slurry coated minicomposite with various cycles (a. with 10 coating cycles; b. with 3 coating cycles) 10 cycles coating performed larger dry cracks and thicker coating layer compared with 3 cycles.

Figure 4. SEM image of a triple layer slurry coated minicomposite. The exterior coatings penetrated into the composite by flowing into the cracks formed during drying of the prior coating and provided a better oxidation resistance. By applying multilayered coatings, the coating slurries compositions could be altered to vary the properties of each layer.

Figure 5. Schematic diagram of slurry infiltration in porous structure having channel branches with different dimensions and dead-ends. As indicate by the dashed line of the penetration route during infiltration, slurry trend to flow through larger channels due to a smaller pressure drop. Air can be trapped in tiny pores and dead ends.

Figure 6. SEM image of slurry coated minicomposite, (a) without vacuum supply, voids can be seen in the bulk of composite (b) with vacuum supply, slurry penetrated into composite deeper and filled more pores by removed trapped air.

Figure 7. SEM images with cross section and surface views of optimized slurry coated SiC/SiC minicomposite samples. Bulk of sample has been sealed with solid particles by slurry infiltration, tiny cracks were found on the surface.

Figure 8. a) Minicomposite stress and normalized cumulative acoustic emission as a function of time, b) High speed camera results for outer surface of the coated Hi-Nicalon fiber reinforced minicomposite before tensile loading it at room temperature and during the last 10 seconds just prior to the final composite failure.

Figure 9. The evolution of acoustic energy accumulation and the increase in electrical resistance NDEs are plotted as a function of applied minicomposite stresses throughout representative Hi-Nicalon type S minicomposite precracking process to achieve 1 crack/mm crack density in the CVI-SiC matrix.

(a)

(b)

(c)

Figure 10. a) Stress on the CVI-SiC matrix at the onset of matrix cracking associated with the first AE loud event [16] and the ultimate minicomposites' strength plotted as a function of Hi-Nicalon fibers volume fraction for coated and uncoated Hi-Nicalon fibers with Pyrolytic Boron Nitride (PBN) interphase and CVI-SiC matrix minicomposites as a result of room temperature fast fracture loading until final failure. B) Plot of stress on the CVI-SiC matrix at the onset of matrix cracking as a function of Hi-Nicalon type S fibers volume fraction for coated and uncoated Hi-Nicalon type S fibers with Boron Nitride (BN) interphase and CVI-SiC matrix minicomposites. C) Plot of stress on the CVI-SiC matrix at the onset of matrix cracking as a

function of Hi-Nicalon fibers volume fraction for coated and uncoated Hi-Nicalon fibers with Boron Nitride (BN) interphase and CVI-SiC matrix minicomposites.

Figure 11. Creep strain evolutions of coated precracked, uncoated precracked and pristine Hi-Nicalon type S fibers reinforced minicomposites at 1200 °C in air as a function of creep time in air.

Figure 12. Micrograph of polished longitudinal region in the hot gage section of sample Hi-Nicalon Type S minicomposite showing intact matrix/coating interphase and uncracked coating.

Fig. 10. Fiber stress if fully loaded vs. time to rupture at 200 °C in air. (a) Coated and uncoated precracked Hi-Nicalon Type S minicomposites and (b) Coated and uncoated precracked Hi-Nicalon minicomposites.

Figure 14. SEM general and zoom-in views of slurry coated minicomposite samples at bottom side of creep test failure surface, (a) Hi-Nicalon minicomposite, as slurry penetrated through open channels into minicomposite and stopped flow at narrow points in the pores, (b) Hi-Nicalon Type S minicomposite sample, as a thick layer of matrix was formed on fiber, most of the pores were closed and the slurry tended to form an external layer instead of filling the pores

Figure 15. SEM general and zoom-in views on crept slurry coated minicomposites fracture surfaces fibers pullout of, (a) Hi-Nicalon S sample, limited fiber pullout existed, (b) Hi-Nicalon few fiber pullout existed.

Figure 16. EDS analysis of post creep fracture surface of a) coated then precracked Hi-Nicalon minicomposites, b) Coated Hi-Nicalon S.