MICROSTRUCTURAL OPTIMIZATION OF HIGH TEMPERATURE SiC/SiC COMPOSITES

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ABSTRACT

Advanced materials and process approaches are described that have allowed NASA to develop five state-of-the-art silicon carbide (SiC) fiber-reinforced hybrid-SiC matrix composite systems that can operate under mechanical loading and oxidizing conditions for hundreds of hours at upper use temperatures from 1200 to 1450°C. Key data are presented that demonstrate the ability of these materials to meet the first-level property requirements for hot-section components in advanced gas turbine engines.

INTRODUCTION

To reduce emissions and improve performance of advanced gas turbine engines for power and propulsion, the hot section components of these engines will require new structural materials that can reliably operate for long times under oxidizing conditions at temperatures greater than 1100°C, the current capability of the best metallic alloys. Today a major thrust in the United States for achieving these benefits is by the development of fiber-reinforced high-temperature ceramic matrix composites (HTCMC) in general and silicon-carbide fiber-reinforced silicon-carbide matrix (SiC/SiC) composites in particular [1]. Because of fiber-reinforcement, the SiC/SiC composites are more damage tolerant and have the capability for larger components than their SiC monolithic counterparts. Also in comparison to the best high-temperature metallic alloys, the SiC/SiC composites are lower in density (~30-50% metal density) and thermal expansion (~60% metal expansion), and have the potential for displaying temperature capability up to 1650°C based on the behavior of monolithic SiC. However, realization of this significantly greater temperature capability will depend strongly on optimization of the SiC/SiC composite microstructure, particularly in regard to the materials and processes used for the fiber, interphase, and matrix constituents.

The objective of this paper is to provide the results of recent activities at NASA aimed at developing advanced silicon carbide (SiC) fiber-reinforced hybrid-SiC matrix composite systems that can operate under mechanical loading and oxidizing conditions for hundreds of hours at 1204°C (2200°F), 1315°C (2400°F), and 1427°C (2600°F), temperatures well above current metal capability. To better understand this development, an explanation of first-level material property requirements for turbine engine hot-section components is presented. With this background, NASA approaches for microstructural optimization of each of five SiC/SiC systems are briefly discussed. Finally, key properties of each system are presented and discussed in relation to those required for the hot-section components.

HTCMC PROPERTY REQUIREMENTS

To guide SiC/SiC development, NASA has selected a short list of first-level property goals that a HTCMC system must typically display for engine hot-section component applications, such as combustor liners, turbine vanes, and turbine blades. Because detailed quantitative

property requirements for these components are engine-specific and typically engine company sensitive, these goals can only be expressed in a qualitative manner. For example, a primary need for the HTCMC system in its as-produced condition is to display as high a Proportional Limit Stress (PLS) as possible in order to allow (a) component design based on elastic mechanical behavior to a high stress, and (b) long component life since the PLS is closely related to the onset of matrix cracking. Thus *high PLS values* will allow the component to carry high combinations of mechanical, thermal, and aerodynamic tensile stresses without cracking. However, during component service, unexpectedly higher stresses may arise that can locally crack the matrix, thereby causing immediate material failure if the HTCMC does not also display a *high Ultimate Tensile Strength (UTS).* After matrix cracking, HTCMC failure could still occur in undesirably short periods of time if the fibers and fiber coatings were allowed to be degraded by the component service environment as it enters the HTCMC through the matrix cracks. Thus *long service lives at stresses above the PLS* are required for HTCMC within aggressive environments such as oxygen. For cracked Si-based HTCMC components, oxygen in engine combustion gases is especially serious at intermediate temperatures (~800°C) where it can reach the fibers before being sealed off by slow-growing silica on the matrix crack surfaces [2]. In addition, at the highest service temperatures, the fiber and matrix will tend to creep and rupture even at low stress, so that the HTCMC should also display *high resistance to creep* and *long service life at stresses below the PLS.*. Finally, because of the possibility of large thermal gradients in these components, the HTCMC should provide the *uppermost in thermal conductivity* to minimize the development of high thermal stresses within the hot-section components during service.

SiC/SiC OPTIMIZATION APPROACHES

Table I lists key constituent material and process data for five SiC fiber-reinforced HTCMC systems recently developed at NASA. For convenience, these systems have been labeled by the prefix N for NASA, followed by their approximate upper use temperature (UUT) capability in degrees Fahrenheit divided by 100; that is, N22, N24, and N26, with suffix letters A, B, and C to indicate their generation. As described later, UUT was assigned based on the approximate upper temperature at which 0/90 2D panels fabricated with each system displayed greater than 500-hour life in air without rupture at tensile stresses of ~60% of their room-temperature PLS.

The baseline processing route selected for fabricating the five systems and demonstrating their performance against the component property goals is shown schematically in Fig. 1. As indicated, it involved (1) selecting a high-strength small-diameter SiC fiber type that is commercially available as multi-fiber tows on spools, (2) textile-forming the tows into architectural preforms dictated by the CMC component shape and thermostructural service requirements, (3) using conventional chemical vapor infiltration (CVI) methods to deposit thin crack-deflecting interphases on the fiber surfaces, and (4) over-coating the interphases with a CVI SiC matrix to a controlled thickness or volume content. Besides providing environmental protection to the interfacial coating, the CVI SiC matrix functioned as a strong, creep-resistant, and thermally conductive HTCMC constituent. However its deposition was not taken to completion because this would trap pores between tows in the fiber architecture, thereby not allowing maximum matrix contribution to the thermal conductivity of the composite system. Depending on the intended HTCMC upper use temperature, the remaining open porosity in the CVI SiC matrix was then filled with ceramic-based and/or metallic-based materials. Although the filler material in the "hybrid" SiC matrix could serve a variety of functions, its composition

Table I. Key Constituent Materials / Processes for Five NASA Systems

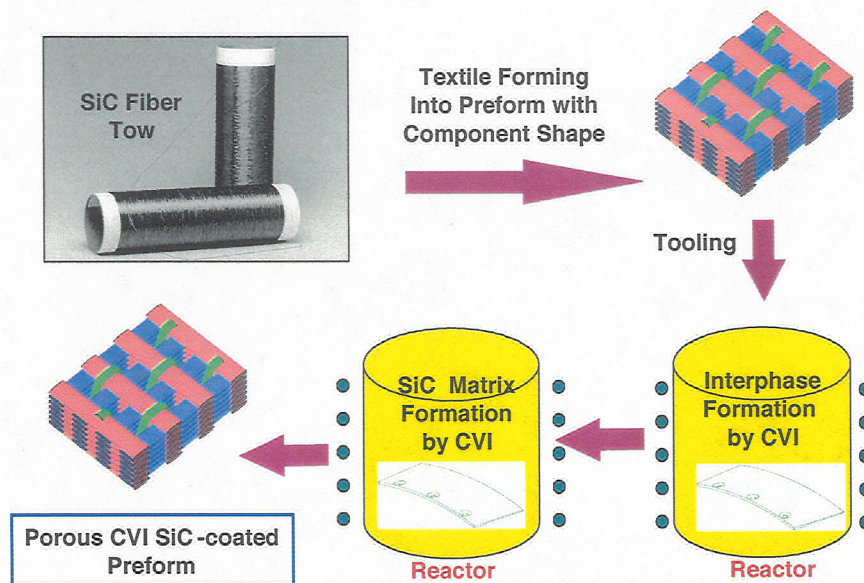| SiC/SiC System	N22	N24A	N24B	N24C	N26A
Upper Use Temperature	1204°C (2200°F)	1315°C (2400°F)	1315°C (2400°F)	1315°C (2400°F)	1427°C (2600°F)
Fiber Type	Sylramic	Syl.-iBN (N)	→	→	→
Interphase	CVI BN(Si)	→	(N)	→	→
Matrix	CVI SiC (low)	→	→	CVI SiC (med)	→
	SiC slurry	→	→	(none)	(none)
	Silicon MI	→	→	(N)	PIP SiC

(N) = NASA proprietary technologies

Figure 1. Baseline processing route for the NASA SiC/SiC systems

and content were typically selected in order to achieve as high a HTCMC thermal conductivity as possible. Another advantage of this processing route is that it could be used with any textile-formed 2D or 3D architectural preform, which is advantageous for complex-shaped components.

For the *N22* system, the selected fiber was the Sylramic SiC fiber, which is currently being produced by ATK COI Ceramics. At the time of N22 development, this nearly stoichiometric fiber offered the best combination of tensile strength, thermal conductivity, thermal stability, creep resistance, and environmental durability [3]. For the interfacial coating composition, CVI-produced silicon-doped BN as deposited by GE Power Systems Composites was selected because BN not only displays sufficient compliance for matrix crack deflection around the fibers, but also because it is more oxidatively resistant than traditional carbon-based coatings. When doped with silicon, the BN showed little loss in compliance, but an improvement in its resistance to moisture. Remaining open porosity in the CVI SiC matrix for the N22 system was filled by room-temperature infiltration of SiC particulate by slurry casting, followed by the melt-infiltration (MI) of silicon metal near 1400°C. This yielded a final composite with ~2% closed

porosity. The final composite system (often referred to as a slurry-cast MI composite) typically displayed a thermal conductivity about double that of a full CVI SiC composite system in which the CVI matrix process was carried to completion. Also the composite did not require an oxidation-protective over-coating to seal open porosity. Decreasing the porosity of the hybrid matrix also increased the N22 elastic modulus, which in turn contributed to a high PLS.

For the *N24A* system, the Sylramic fiber in the N22 system was replaced by the NASA-developed Sylramic-iBN fiber, which is produced by a thermal treatment of the Sylramic fiber in a controlled nitrogen environment. This treatment allowed mobile boron sintering aids in the Sylramic fiber bulk to diffuse out of the fiber and to form a thin in-situ grown BN layer on each fiber surface [3]. Removing boron from the bulk significantly improved the creep, rupture, and oxidation resistance of the Sylramic-iBN fiber; while the in-situ grown BN provided a buffer layer that inhibited detrimental chemical attack from inadvertent oxygen and also reduced detrimental mechanical interactions between contacting fibers. For the *N24B* system, the NASA developed "outside debonding" interphase approach was used to allow the Si-doped BN coating to remain on the fibers during matrix cracking, thereby providing additional environmental protection to the fibers [4]. It was accomplished by creating constituent and process conditions that assure that the CVI BN interphase coating was already "outside debonded" from the CVI SiC matrix during composite fabrication.

For the *N24C* system, NASA sought to minimize property limitations associated with the as-produced CVI SiC matrix. These matrix limitations relate to the fact that for best infiltration into the textile-formed fiber tows, the CVI SiC process is typically conducted at temperatures below 1100°C, which allows the SiC microstructure to contain meta-stable atomic defects and small amounts of excess silicon. These defects and silicon can exist at the matrix grain boundaries where they act as scatterers for thermal phonons and enhance matrix creep by grain-boundary sliding, thereby allowing the matrix and HTCMC to display less than optimal thermal conductivity and creep-resistance. NASA determined that by using thermal treatments above 1600°C on the CVI SiC-coated preforms prior to the N22 and N24 process steps of slurry casting and melt infiltration, excess silicon and process-related defects in the CVI SiC matrix could be removed, yielding the *N24-C* CMC system with significantly improved creep resistance and thermal conductivity [5]. Currently the Sylramic-iBN fiber is the only high-strength SiC fiber type that allows preforms to be annealed with minimal loss in fiber strength. To maximize the benefits of the CVI SiC matrix, its content in the N24-C preform was increased over that typically used in the N24-A and N24-B systems, but only to the point of avoiding significant trapped porosity. This also allowed elimination of the slurry infiltration step and its associated production costs.

For the N22 and N24 systems, it was determined that with exposures over 500 hours at 1315°C, the silicon from the melt-infiltration step was able to diffuse through the grain boundaries of the CVI SiC matrix, attack the BN coatings and SiC fibers, and severely degrade composite strength [6]. The higher CVI SiC content of the N24-C system helped to slow down this attack, but not enough to use this system for much over 1000 hours at 1315°C, or over 100 hours at 1427°C [7]. Thus for the *N26A* system, all the same constituents in the N24-C system were used, but remaining open pores in the CVI SiC matrix were filled by a SiC-yielding polymer from Starfire Inc. [8], which was then pyrolyzed at temperatures up to 1600°C. This polymer infiltration and pyrolysis (PIP) process was repeated until composite total porosity was reduced to ~15 vol. %. At this point, the HTCMC system with the hybrid CVI+PIP matrix was annealed at NASA to improve its thermal conductivity and creep-resistance. Thus, although

more porous than the other systems, the N26-A system had no free silicon in the matrix, thereby allowing long-time structural use at 1427°C and above.

SIC/SIC PROPERTY RESULTS

For the five SiC/SiC systems, Table II lists typical values for the key properties needed for hot-section components. These properties were generated at NASA using test specimens machined from thin-walled flat panels fabricated from balanced 2D-woven 0/90 orthogonal fabric. The mechanical properties were obtained in tension along the 0° fiber direction. Average total fiber content in the test specimens was ~36 vol %.

Clearly the *N24A* SiC/SiC system with the Sylramic-iBN fiber improved on temperature capability of the N22 system and showed a good combination of properties needed for hot-section engine components, particularly in regard to *proportional limit strength* and *ultimate tensile strength*, properties needed for component damage tolerance; *rupture life at high stress at 800°C,* a temperature region where oxygen attack of SiC/SiC composites is typically the greatest; *creep resistance and rupture life at 1315°C,* a temperature well above the thermal capability of metal alloys (~1100°C); and *thermal conductivity* at 20°C (and above), a property needed for reducing thermal gradients and stresses within the component.

For the *N24B* system, the high *proportional limit strength* and *ultimate tensile strength* were retained, but material damage tolerance and *rupture life at 800°C was significantly improved* with little effect on the good thermal conductivity and the high temperature structural values shown by the N24A system. Although losing some ultimate strength during the preform treatment process, the *N24C* system displayed state-of-the-art properties in terms of *thermal conductivity, and both creep resistance and rupture life at 1315°C*. Finally, for the *N26A* system, although the PIP process was insufficient in filling the CVI SiC matrix pores (resulting in reduced thermal conductivity), it did provide sufficient oxidation protection to allow this system to display *~500 hour life at 1450°C*, a temperature above its intended UUT.

Table II: Typical properties for thin-walled panels fabricated from 0/90 fabric (Total fiber ~36 vol. %; mechanical properties measured in tension in the 0° direction)

SiC/SiC System (Upper Use Temp.)	N22 (1204°C)	N24A (1315°C)	N24B (1315°C)	N24C (1315°C)	N26A (1427°C)
PLS (MPa) at 20°C	180	180	170	160	130
UTS (MPa) at 20°C	400	450	450	310	330
Rupture Life at 270 MPa, 800°C in air	~10 hr	~10 hr	~100 hr	~100 hr	~100 hr
Creep, 500 hr at 103 MPa, UUT in air	~0.4%	~0.4%	~0.4%	~0.2%	
Rupture Life at 103 MPa, UUT in air	~500 hr	~500 hr	~500 hr	>1000 hr	
Rupture Life at 69 MPa, 1450°C in air					~500 hr
Thru-Thickness Cond. at 20°C, W/m °C	23	26	20	36	23

SUMMARY AND CONCLUSIONS

With the goal of replacing metallic alloys with HTCMC in gas turbine engine hot-section components, NASA has developed a variety of SiC/SiC systems with state-of-the-art thermostructural capability from 1200°C to over 1400°C. This progression in temperature capability was related first to the development of the Sylramic-iBN SiC fiber, which displays high thermal stability, creep resistance, rupture resistance, and thermal conductivity, and possesses an in-situ grown BN surface layer for added environmental durability. Further capability was then derived by an annealing step for the CVI SiC portion of the hybrid matrix, which is a required base constituent for all the SiC/SiC systems because of its high creep resistance and thermal conductivity. Finally, for the highest temperature system, complete elimination of free silicon in the CVI SiC matrix and in the open porosity of the HTCMC was required, which was accomplished by use of a PIP SiC approach.

Although the property results presented here for the various SiC/SiC systems are limited, NASA assumes that by examining these first-level data, engine designers will be able to select the best system that meets their component performance requirements, and then initiate with commercial vendors more extensive efforts for HTCMC component evaluation. NASA research is on-going to continue to move SiC/SiC composites towards the 1650°C capability of monolithic SiC. Key optimization issues are improvement in the thermal stability and creep resistance of the fiber and matrix, and significant reduction in the HTCMC residual porosity.

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