

OVERVIEW OF NASA STUDIES ON HIGH-TEMPERATURE CERAMIC FIBERS

James A. DiCarlo and Hee Mann Yun
National Aeronautics and Space Administration
Glenn Research Center
Cleveland, Ohio

INTRODUCTION

- NASA, DOD, and DOE are currently looking to the NASA UEET Program to develop ceramic matrix composites (CMC) for hot-section components in advanced power and propulsion systems
- Success will depend strongly on developing ceramic fibers with a variety of key thermostructural properties, in particular, high as-produced tensile strength and retention of a large fraction of this strength for long times under the anticipated CMC service conditions.
- Current UEET approach centers on selecting the optimum fiber type from commercially available fibers since the costs for development of advanced fibers are high and the markets for high-temperature CMC have yet to be established.

OBJECTIVE

Present a brief overview of NASA-UEET studies aimed at

- Developing a general property base for ceramic fibers
- Selecting fibers for high-temperature structural CMC.

OUTLINE

- Key fiber property requirements for CMC components
- Commercial fibers of current CMC interest
- NASA testing for fiber strength versus time, temperature, environment
- NASA modeling of fiber results for CMC applications
- Status of fiber selection for high-temperature CMC
- Environmental issues for SiC-based CMC and fibers
- Potential for SiC fibers as seal materials

KEY FIBER AND CMC PROPERTY REQUIREMENTS FOR HOT-SECTION COMPONENTS

- ***High Capability for Complex CMC Shapes:***
will typically require 2D/3D fiber weaving/braiding and thus implies Small-diameter (<20 μm), Continuous-Length fibers which in turn implies Fine-Grained Polycrystalline fibers.
- ***High CMC Strength Retention at all temperatures after matrix cracking in oxygen and moisture-containing environments:***
implies fibers with Oxide- and Silicon-based Compositions
- ***High CMC Ultimate Tensile Strength***
- ***High CMC Strength Retention under stress up to 2400°F***
- ***High CMC Transverse and Axial Thermal Conductivity***
- ***High CMC Creep Resistance up to 2400°F***

SMALL-DIAMETER COMMERCIAL FIBERS WITH OXIDE- AND SILICON-BASED COMPOSITIONS

(Diameters 10 to 15 μm; Grain sizes ~3 to 500 nm)

FIBER TYPE	SOURCE	PROCESS	COMPOSITION
Oxide-based			
Nextel 610	3M	Sol Gel	Al ₂ O ₃
Nextel 720	3M	Sol Gel	Al ₂ O ₃ + Mullite
Silicon-based			
Nicalon	Nippon Carbon	Polymer/Pyrolysis	SiC + Si-O-C
Hi-Nicalon	Nippon Carbon	P/P (radiation cure)	SiC + C
Hi-Nicalon S	Nippon Carbon	P/P (radiation cure)	SiC + trace C
Sylramic	Dow Corning	P/P (sinter)	SiC +trace (B+ Ti)
Tyranno SA	UBE	P/P (sinter)	SiC +trace Al ₂ O ₃

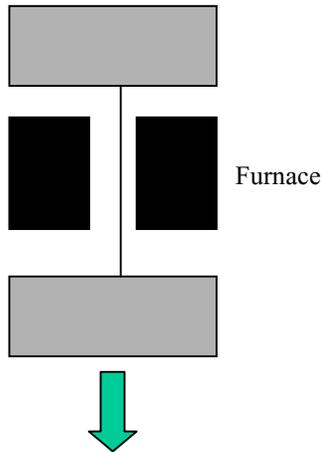
TESTS TO EVALUATE FIBER STRENGTH RETENTION DURING SIMULATED CMC SERVICE

Typical Test Variables:

stress, stress rate,
 temperature (20 to 1400°C), temperature warm-up rate,
 gauge length (~25 to 100 mm), environment (air or argon)

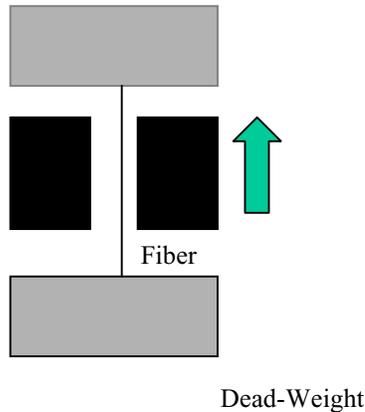
Typical Mechanical Tests

Fast-Fracture



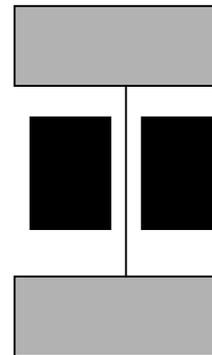
Stress Rate = Constant
 Temperature = Constant
 Measure Fracture Stress

Slow Warm-up



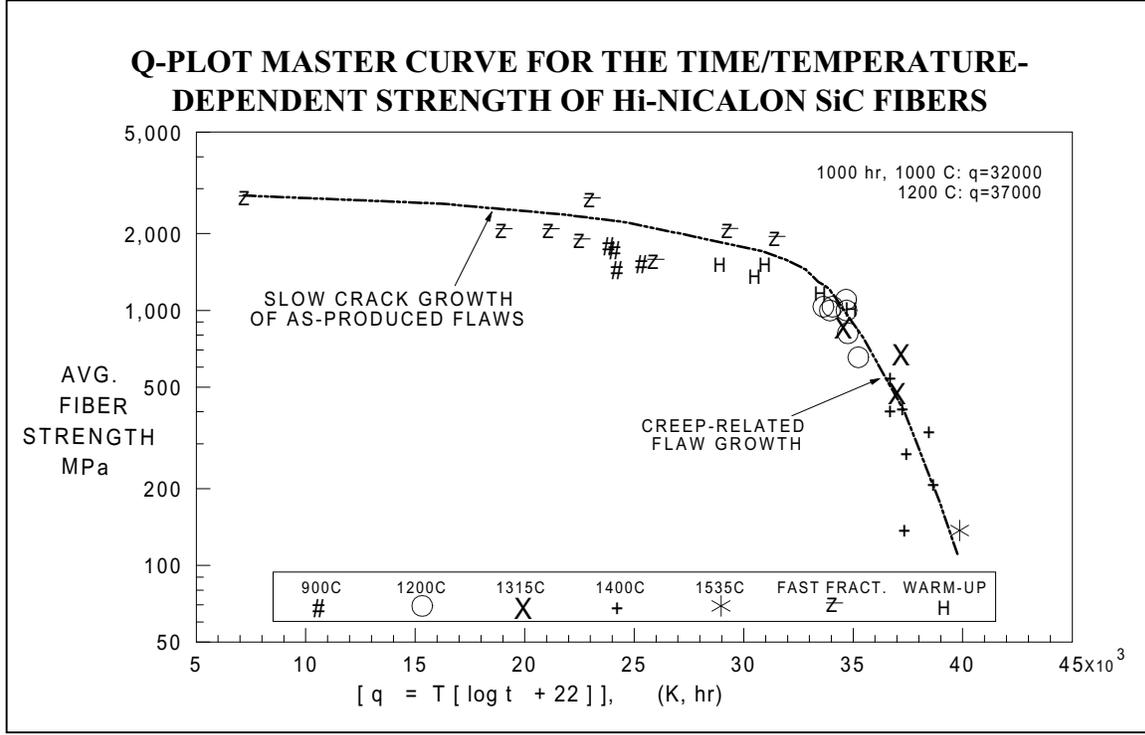
Stress = constant
 Temperature Rate = Constant
 Measure Fracture Temperature

Stress-Rupture



Stress = constant
 Temperature = Constant
 Measure Creep,
 Fracture Time

At NASA Glenn, the strength properties of a variety of oxide and SiC-based fibers have been measured from 20 to 1400°C under air and argon environmental conditions [1-7]. Air was used to simulate fiber exposure to oxidizing conditions, such as for cracked CMC in combustion environments; while argon simulated the inert conditions for fibers in an uncracked CMC. The measurements were made on single fibers across a time range from ~0.01 to over 100 hours using three types of tests: fast-fracture (constant temperature and constant rate of stress change), slow warm-up (constant stress, constant rate of temperature change), and stress rupture (constant stress and constant temperature).

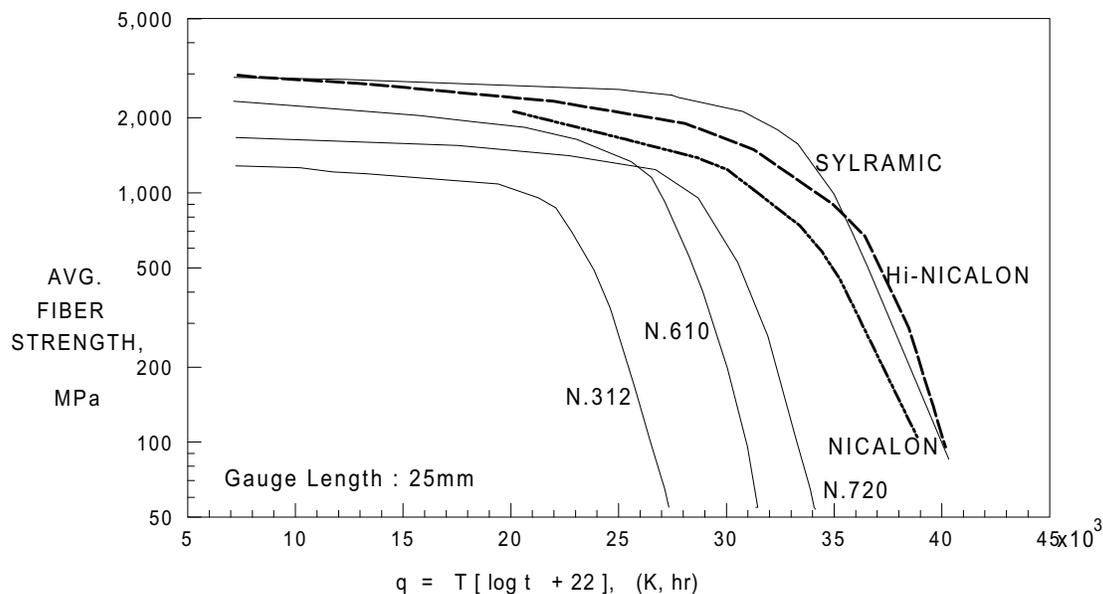


Using simple thermal-activation theory [5, 8], it was determined the single-fiber strength results from the three tests for each fiber type could be combined into a single master curve or q-plot which describes the applied stress at fracture (fiber strength) versus the time-temperature dependent parameter q given by

$$q \equiv Q / 2.3R = T (\log t + 22) .$$

Here Q is the effective activation energy for time-dependent fiber fracture, R is the universal gas constant (8.314 J/mol-K), and T (kelvin) is the absolute temperature at fiber fracture. For the stress-rupture tests, t (hours) is the fiber rupture time. By applying slow crack growth theory for the time conditions of the other tests [5], $q = 18.3 T$ for the fast-fracture tests and $q = 20.2 T$ for the slow warm-up tests.

Q-PLOT MASTER CURVES FOR THE TIME/TEMPERATURE-DEPENDENT STRENGTH OF OXIDE AND SiC-BASED FIBERS



The q-plots, shown here and the previous slide, for ceramic fiber tensile strength versus time and temperature have many important basic and practical implications. First, on the basic level, all curves have the same shape with increasing q ; that is, an initial section with a small negative slope (Region I), and a remaining section with a much larger negative slope (Region II). This behavior is typical of the rupture of monolithic ceramics in which at low temperatures, as-produced flaws grow slowly in size (slow crack growth); whereas at high temperatures, creep mechanisms aid in the more rapid growth of the same flaws or in the nucleation and growth of new micro-cracks and cavities.

On the practical side, the q- plots indicate that fiber strength values throughout Region I depend directly on the fiber's as-fabricated strength at room temperature ($q \approx 7000$). That is, the entire Region I section moves up in strength when as-produced flaws are reduced in size or frequency. Alternatively, the Region I curves would move up or down if the test gauge lengths were smaller or greater, respectively, than the ~ 25 mm length used to generate the curves. In addition, the q-plots clearly indicate the greater thermostructural capability of the SiC fibers over the oxide-based fibers both in Regions I and II. The Region I advantage is related to the higher fracture toughness of SiC; while the Region II advantage is primarily due to slower diffusion processes in the SiC-based fibers. Finally, the curves allow the prediction of fiber strength behavior if any four of the following five application variables are known: stress, stress rate, temperature, temperature rate, and time [5].

APPLICATION OF CERAMIC FIBER q-PLOTS FOR MODELING MAXIMUM CMC STRENGTH

- Assume a **cracked** CMC under constant uniaxial stress σ_c at a constant temperature T in an air environment. If V_f^* is the effective fiber volume fraction bridging the through-thickness cracks in the stress direction, CMC strength can be predicted from:

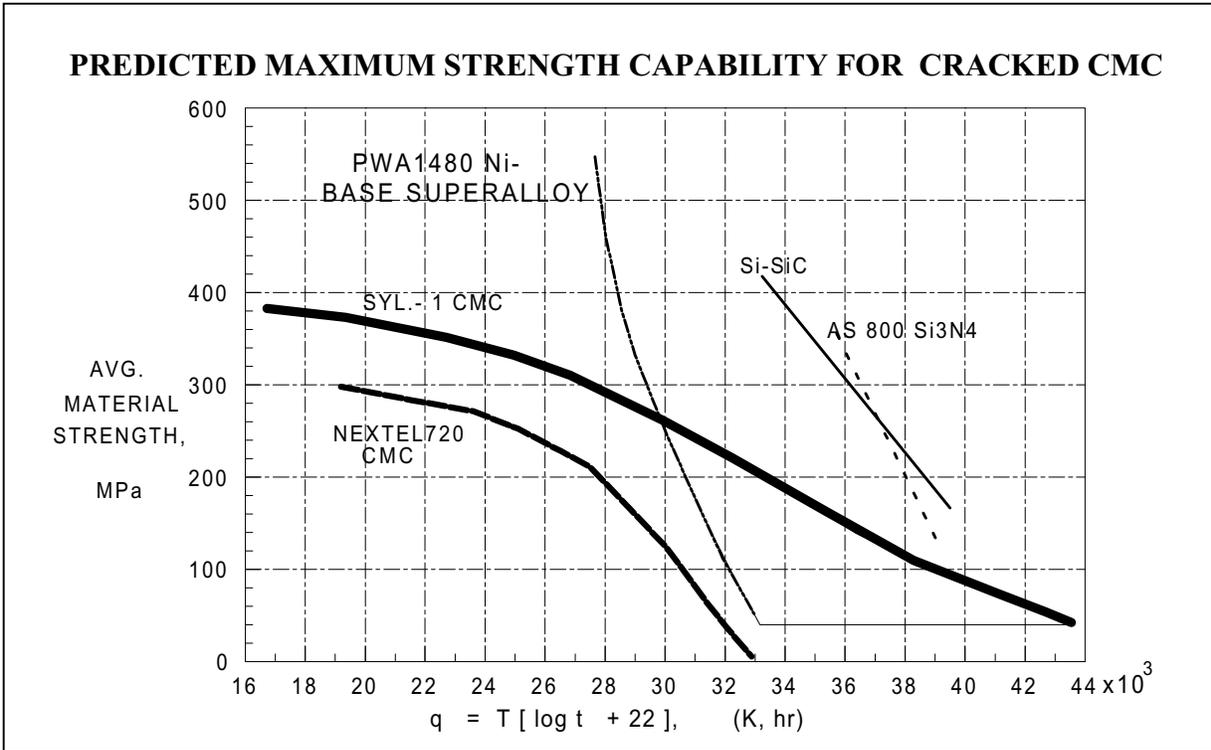
$$\sigma_c = V_f^* \sigma_B(t, T, L_e)$$

Here σ_B is the average strength of the fiber bundles within the cracks, and L_e is the effective bundle gauge length within the cracks.

- When interfacial conditions and bundle fracture statistics are taken into account, a good approximation for $\sigma_B(L_e)$ is the average strength of individual fibers measured at ~25 mm gauge length; so that

$$\sigma_c \approx V_f^* \sigma_f(q, 25 \text{ mm})$$

One very important CMC application condition is that in which the composite contains through-thickness matrix cracks that are bridged by the fiber reinforcement. These cracks could have developed during CMC fabrication due to a thermal expansion mismatch between the fibers and matrix, or during CMC service due to some random overstress or the need for a high design stress. For a simple CMC strength model, one might assume that the application requires the cracked CMC to experience a relatively constant uniaxial stress σ_c at a constant temperature T in an air environment. Then as described above, one can use the fiber q-plots, $\sigma_f(q, 25 \text{ mm})$, and the effective fiber volume fraction V_f^* within a cracked CMC to predict its maximum tensile strength capability as a function of application time and temperature. A variety of recent CMC studies have confirmed the validity of this modeling approach for cracked CMC under simple test conditions [9].



An important advantage of CMC strength modeling using fiber q-plots is that it gives insight into how CMC will perform at high temperatures in comparison to competing structural materials. For example, the above slide displays maximum strength behavior predicted for cracked CMC reinforced by Nextel 720 and Sylramic(1) fibers, the most creep and rupture resistant oxide- and SiC-based fibers examined to date at NASA. For this slide, 0/90 woven composites were assumed with a typical total volume fraction of 40% so that $V_f^* = 20\%$. Also shown are the measured strength behavior for one of the highest-temperature nickel-based superalloys currently available and for SiC and Si₃N₄ monolithic ceramics. It can be seen that the CMC with the best oxide-based fiber barely competes with the superalloy in the creep-rupture regime; whereas the CMC with the SiC-based fiber has the potential for much better thermostructural performance than both materials (hatched area). On the other hand, the SiC-reinforced CMC does not outperform the Si-based monolithics, which follows simply from a reduced volume fraction (i.e., 20 versus 100%). However, in contrast to CMC, the monolithics suffer from catastrophic failure upon local material fracture and also cannot be reliably fabricated into large and complex-shaped components .

**KEY PROPERTIES OF NEAR-STOICHIOMETRIC SiC FIBERS FOR
HIGH-TEMPERATURE CMC APPLICATIONS**

Trade Name	Hi-Nicalon S	Tyranno SA (1,2,3)	Sylramic	Sylramic (1,2)
Max. Process Temperature	~ 1600°C	> 1700°C	> 1700°C	> 1700°C
Average Diam., μm	13	8-10	10	10
Second Phases	trace O + C	trace Al ₂ O ₃	trace B + Ti	Reduced B, trace Ti
Average Grain Size, nm	< 100	≥ 150	~ 100	> 100
Avg. Surface Roughness, nm	< 10	~ 10	~ 10	~ 27
Thermal Cond. W/m ² .°C at R.T	18	65	46	> 46

Given the goals of the UEET Program to develop CMC hot-section components with as high a thermostructural capability as possible, the results of the fiber testing and modeling studies have clearly pointed to the use of SiC fibers in general and pure stoichiometric SiC fibers ($C/Si = 1$) in particular. This is based primarily on observations that impurities such as oxides degrade SiC fiber creep resistance and result in fiber strength degradation upon their decomposition and reaction with SiC at high temperatures; while excess carbon in the SiC fiber can reduce its oxidation resistance and thermal conductivity. Thus current UEET focus is centered on down-selection from the commercial near-stoichiometric SiC fibers listed in the above slide. As indicated in Slide 2, these fibers are produced by three different manufacturers primarily from the pyrolysis and sintering of polymer-derived precursor fibers. As shown in the above slide, the polymer, pyrolysis, and sintering routes are different enough to affect the impurity content and grain size within the final fiber microstructures. These two factors are critical to high-temperature fiber performance because they significantly affect fiber strength retention, creep resistance, and thermal conductivity [6]. Generally the best structural and conductivity performance is obtained for high purity SiC fibers with grain sizes between 100 and 500 nm. At the present time, in lieu of complete property data from SiC/SiC composites, the Sylramic(1) fiber with reduced boron is displaying the best combination of desirable properties. This fiber type was developed at NASA Glenn by treating the commercial Sylramic fiber in such a manner so as to reduce the creep-prone boron sintering aid in the fiber grain boundaries, while at the same time forming an in-situ boron nitride layer on the fiber surface [7]. As explained on the next slide, approaches such as these will be required to achieve and maintain the high thermostructural performance available in the stoichiometric SiC fibers, particularly in oxidizing environments.

POTENTIAL STRENGTH DEGRADING MECHANISMS FOR SiC/SiC CMC AND SiC FIBERS IN COMBUSTION ENVIRONMENTS

- Above ~2000°F, silica rapidly forms on SiC surfaces, which then vaporizes due to moisture-induced volatilization of silicon hydroxides. The SiC surface recesses and the material loses cross-sectional area and load-bearing capability [10].

Current solution: Oxide environmental barrier coatings (EBC) such as aluminum silicates, which minimize silicon exposure and reactivity with combustion environments.

- From ~1000 to 2000°F, oxygen penetrates into CMC through matrix cracks, which then attacks the fiber interfacial coating and forms thin silica layers on internal SiC fiber surfaces. Silica bonds the fibers to the matrix and to each other, so that when the matrix or one weak fiber in a tow breaks, neighboring fibers fracture at low stress.

Current solution: Interfacial coatings such as silicon-doped BN, which rapidly form oxide glasses that inhibit oxygen penetration away from the matrix cracks.

POTENTIAL FOR SiC FIBER TOWS AS SEAL MATERIALS

Key Benefits in Relation to Oxide-based Fibers:

- Intrinsic strength and elasticity retention to above 2000°F

Key Performance Issues:

- Above ~1000°F, silica formation on fiber surfaces and fiber-fiber bonding, resulting in loss of tow flexibility and strength
- Above ~2000°F, surface recession and dimensional reduction in moisture-containing combustion environments

Possible Solutions:

Protective fiber coatings (deposited or in-situ formed) that are high-temperature oxides or convert to high-temperature oxides which

- display low surface diffusion and intrinsic bonding and/or
- slowly ablate in combustion environments

References

1. DiCarlo, J.A., "Property Goals and Test Methods for High Temperature Ceramic Fibre Reinforcement", *Ceramics International*, Vol. **23**, 1997, pp. 283-289.
2. Yun, H.M., Goldsby, J.C., and DiCarlo, J.A., "Tensile Creep and Stress-Rupture Behavior of Polymer Derived SiC Fibers", *Ceramic Transactions*, Vol. 46, 1994, pp. 17-28.
3. DiCarlo, J.A., Yun, H.M., and Goldsby, J.C., "Creep and Rupture Behavior of Advanced SiC Fibers", *Proceedings of ICCM-10*, 1995, Vol. VI: Microstructure, Degradation, and Design, Poursartip, A. and Street, K.N., Eds, pp. 315-322.
4. Yun, H.M., Goldsby, J.C., and DiCarlo, J.A., "Environmental Effects on Creep and Stress-Rupture Properties of Advanced SiC Fibers", *Proceedings For HTCMC-2, II*, Evans, A.G. and Naslain, R., Eds., *Ceramic Transactions*, Vol. 57, 1995, pp. 331-336.
5. Yun, H.M. and DiCarlo, J.A., "Time/Temperature Dependent Tensile Strength of SiC and Al₂O₃-Based Fibers", *Ceramic Transactions*, Vol. 74, 1996, pp. 17-26.
6. DiCarlo, J.A. and Yun, H.M., "Microstructural Factors Affecting Creep-Rupture Failure of Ceramic Fibers", *Ceramic Transactions*, Vol. 99, 1998, pp. 119-134.
7. Yun, H.M. and DiCarlo, J.A., "Comparison of the Tensile, Creep, and Rupture Strength Properties of Stoichiometric SiC Fibers", NASA/TM – 1999-209284.
8. DiCarlo, J.A., Yun, H.M., and Morscher, G.N., "Models for the Thermostructural Properties of SiC Fibers", *Proceedings for HTCMC-2*, *Ceramic Transactions* **57**, 1995, pp. 343-348.
9. DiCarlo, J.A. and Yun, H.M., "Factors Controlling Stress-Rupture of Fiber-Reinforced Ceramic Composites", *Proceedings of ICCM-12*, Paris, France, 1999.
10. Smialek, J.L., Robinson, R.C., Opila, E.J., Fox, D.S., and Jacobson, N.S., "SiC and Si₃N₄ Recession Due to SiO₂ Scale Volatility under Combustor Conditions", *Adv. Composite Mater.*, Vol. 8, No. 1, 1999, pp. 33-45.