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SYLRAMIC™ SiC fibers for CMC reinforcement

Richard E. Jones [a,*], Dan Petrak [a,1], Jim Rabe [a], Andy Szweda [b]

[a] *Dow Corning Corporation, P.O. Box 995, Mailstop 500, Midland, MI 48686, USA*

[b] *Engineered Ceramics, Inc., San Diego, CA, USA*

Abstract

Dow Corning researchers developed *SYLRAMIC* SiC fiber specifically for use in ceramic–matrix composite (CMC) components for use in turbine engine hot sections where excellent thermal stability, high strength and high thermal conductivity are required. This is a stoichiometric SiC fiber with a high degree of crystallinity, high tensile strength, high tensile modulus and good thermal conductivity. Owing to the small diameter, this textile-grade fiber can be woven into 2-D and 3-D structures for CMC fabrication. These properties are also of high interest to the nuclear community. Some initial studies have shown that *SYLRAMIC* fiber shows very good dimensional stability in a neutron flux environment, which offers further encouragement. This paper will review the properties of *SYLRAMIC* SiC fiber and then present the properties of polymer impregnation and pyrolysis (PIP) processed CMC made with this fiber at Dow Corning. While these composites may not be directly applicable to applications of interest to this audience, we believe that the properties shown will give good evidence that the fiber should be suitable for high temperature structural applications in the nuclear arena.

1. Introduction

Small-diameter ceramic fibers, which are sufficiently flexible to permit weaving and braiding, provide many desirable properties for use in continuous-fiber ceramic-matrix composites (CMC) [1]. These fibers have generally been prepared by polymer precursor routes. Products which have reached commercial status include: NICALON™ ceramic grade fiber, an Si–C–O composition [2] from Nippon Carbon, Japan, and TYRANNO™ Lox M, an Si–C–O–Ti composition [3] from Ube Industries, Japan. The oxygen content and amorphous phases in these fibers significantly reduce thermal stability [4] and mechanical properties relative to crystalline SiC.

More recently, both Nippon Carbon (Hi-Nicalon) and Ube (Tyranno SA) have introduced fibers with much lower levels of oxygen, which leads to improved modulus and thermal stability [5–7]. Dow Corning, with considerable NASA support, developed *SYLRAMIC*™ SiC fiber [8,9]. Although the development was clearly targeted toward turbine engine hot section components, this fiber may find utility in other areas such as nuclear power, conventional power generation and waste incineration. This paper outlines the properties and structure of *SYLRAMIC* SiC fiber and illustrates the properties of preceramic polymer (PCP) derived CMCs reinforced with this fiber.

2. Experimental

Fiber tensile strength and elastic modulus measurements were obtained on single filaments using a Model 1122 Universal Testing Instrument (Instron) according to a modified ASTM-D3379-75 [10]. Density values were obtained with a Model MPY-2 helium pycnometer (Quantachrome). Carbon, hydrogen, nitrogen and silicon analyses were made using a Model 240XA CHN analyzer (Control Equipment) and sodium peroxide fusion followed by silicon analysis with a Model ARL 3580 ICP (ARL/FISONS Instruments) analyzer respectively. Oxygen content was measured with a Model RO-316 oxygen analyzer (Leco).

* Corresponding author. Tel.: +1-517 496 4041; fax: +1-517 496 6278.

E-mail address: rick.jones@dowcorning.com (R.E. Jones).

[1] Retired.

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Composites were fabricated using 5HS cloth laid up in a symmetrical warp-aligned architecture as 10 ply laminates. Prior to CMC fabrication, the cloth was given a chemical vapor deposition (CVD) coating of BN to enhance interface debonding between the fiber and the matrix. Due to the excellent thermal stability of the fiber, CVD coating temperatures at least as high as 1550°C can be used to achieve a refractory coating.

The coated cloth was initially impregnated with a silazane preceramic polymer (PCP/filler/solvent) mixture to form a flexible, tacky prepreg for lay-up. Si_3N_4 filler was used in this work. The 10-ply stack was vacuum bagged using conventional materials and techniques prior to an autoclave cycle to consolidate and cure the laminate. The cured laminate was pyrolyzed, yielding a composite with >20% open porosity. Subsequent vacuum impregnation steps (PCP and solvent) and pyrolysis cycles were used to reduce porosity to typically <5% in the finished panel. This polymer impregnation and pyrolysis (PIP) process is similar to the polymer route to carbon/carbon composites practiced for many years. Again, because of the thermal stability of the fiber, pyrolysis temperatures can be used that are sufficiently high to crystallize the polymer-derived matrix.

3. Fiber properties

SYLRAMIC SiC fiber contains silicon (66.6% by weight), carbon (28.5%), boron (2.3%), titanium (2.1%) and traces of nitrogen and oxygen. This can best be represented by the phases present. Essentially, the fiber is stoichiometric SiC (95 wt.%) with TiB_2 grains (3 wt.%) at the triple points and small amounts of B_4C (1 wt.%) and BN. Transmission electron microscopy (TEM) shows the grain boundaries to be very clean, with no evidence of amorphous phases [11].

Typical properties (Table 1) are as expected from the composition and structure. The high degree of crystallinity and high density yield high elastic modulus and thermal conductivity. The small diameter and fine grain size allow high strength to be achieved. Because the diameter is small and the strength is high, this fiber can be readily woven into 2-D fabrics or 3-D structures using conventional techniques.

Table 1
Typical *SYLRAMIC* SiC fiber properties

Tensile strength, ksi (MPa)	450 (3.2)
Elastic modulus, msi (GPa)	55 (380)
Diameter, μm	10
Density, g/cm^3	3.0–3.1
Fils/tow	800
C/Si ratio	1.0
Specific heat, J/kg K (50°C)	613–753
Denier, g/9000 m	1600
Thermal Conductivity (W/m K)	40–46

A scanning Auger microprobe depth profile of *SYLRAMIC* SiC fiber shows the composition to be virtually constant through the entire analyzed depth (up to 1–2 mm) except for a very thin carbon-rich surface layer and perhaps some slight enrichment of boron and titanium near the surface. No oxygen is found either at the surface or within the internal structure of the fiber. One important characteristic of a ceramic fiber is thermal and chemical stability under CMC processing conditions. To determine *SYLRAMIC* SiC fiber stability a 1550°C, argon atmosphere heat treatment was selected for 10 h. Numerous tests on many lots of fibers have shown negligible effect of this treatment on fiber strength. This clearly indicates (Table 2), that the fiber can be processed at temperatures needed to achieve good quality refractory interface coatings and dense, crystalline matrices.

4. CMC properties

The impact of higher processing temperatures was examined by treating composites at a series of temperatures. For temperatures of 1300°C, 1500°C and 1600°C, ultimate tensile strengths ranged from 300 to 342 MPa, with failure strains of 0.28–0.31%. At 1700°C, strength began to drop (250 MPa at 0.23% strain), indicating the beginning of degradation. Based on these results, 1600°C was selected as the pyrolysis temperature for the rest of this study.

The high-temperature pyrolysis conditions used to prepare the CMC result in a matrix that is a unique combination of phases. Crystalline beta-SiC and Si_3N_4 (both alpha and beta) derived from the PCP surround larger Si_3N_4 grains used as the filler in the initial prepreg.

The most notable effect of the increased process temperature and resulting crystallinity was the increase in the thermal conductivity of the CMC. Fig. 1 illustrates three types of CMCs. Typical CG NICALON reinforced PIP CMC has a largely amorphous matrix. This, combined with the largely amorphous fiber, results in a low thermal conductivity of about 2 W/m K. Switching to high conductivity *SYLRAMIC* SiC fiber raises conductivity significantly. The fiber-dominated in-plane property increases $5x$ while the matrix dominated through thickness property increases only $2x$. However, when a crystalline matrix is combined with the crystalline fiber, conductivity increases to 20 W/m K at room temperatures and is still 15 W/m K at 1400°C. As expected, in this case, the in-plane and through thickness conductivity are both high and nearly equal.

Fig. 2 shows a typical tensile stress–strain curve for *SYLRAMIC* SiC fiber reinforced composites. In these composites, the matrix is an amorphous Si–N–C glass

Table 2
SYLRAMIC™ SiC fiber strength retention

Lot identification	As-made strength		Stength after 10 h, 1550°C, argon treatment	
	MPa	S.D.	MPa	S.D.
A	2740	±710	3080	±550
B	3210	±650	3020	±690
C	3310	±650	2860	±750
D	3000	±820	2670	±760
E	3490	±590	2815	±560

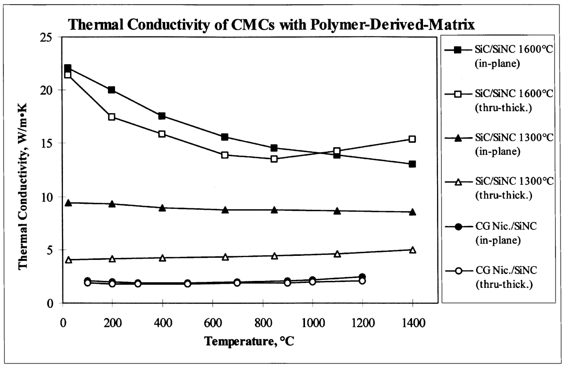

Fig. 1. Thermal conductivity of CMCs with polymer-derived matrix.

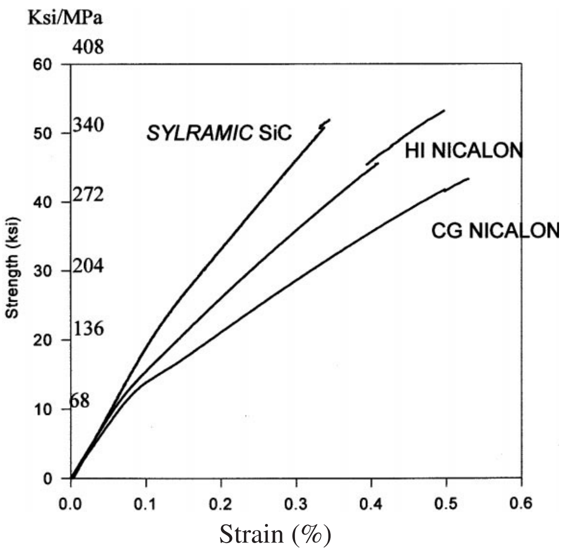

Fig. 2. Stress vs. strain curves for SiNC composites.

(low temperature processing) to illustrate the impact of fiber selection. Note that *SYLRAMIC* SiC fiber yields a CMC with higher initial modulus and a higher proportional limit (130–150 MPa) than either the HI-NICALON or CG NICALON containing CMCs.

In previous studies, we have shown that PIP CMCs behave much like other non-oxide CMCs in fatigue, where the fatigue limit is approximately equal to the proportional limit. Thus, CG NICALON CMCs will typically show a fatigue run-out at 10^6 cycles at 1100°C at stresses of $\leqslant$70 MPa. Above this stress-level fatigue, life is significantly less. Our hypothesis is that the higher proportional limit for *SYLRAMIC* SiC fiber reinforced CMC would translate to fatigue run-outs at higher stress levels. Our results demonstrate that *SYLRAMIC* fiber reinforced CMC does survive >10^6 cycles at 1200°C up to 136–150 MPa.

Previous work has shown that CG NICALON reinforced PIP composites show significant creep at temperatures above 1000°C (Fig. 3). Initial results with *SYLRAMIC* SiC fiber reinforcement have shown significantly reduced creep strain. Simple substitution of *SYLRAMIC* fiber into a PIP composite processed at 1300°C (amorphous matrix) reduces total creep strain (after 200 h) to a level about 30% of that for CG NICALON reinforced material. A further reduction is then

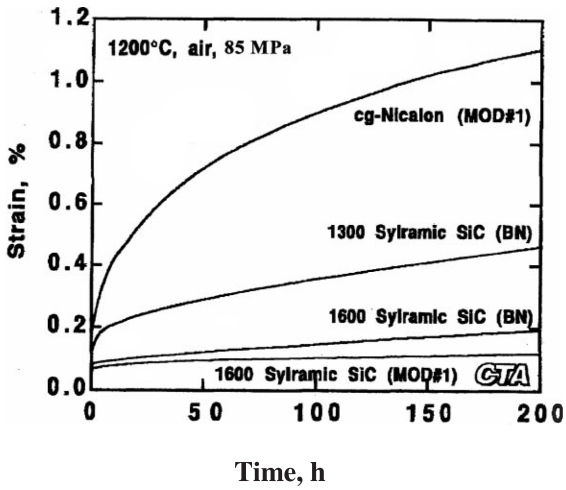

Fig. 3. Creep behavior of polymer-derived matrix composites.

seen when the matrix is crystallized using higher processing temperatures.

5. Summary

SYLRAMIC SiC fiber is a stoichiometric SiC composition that demonstrates high strength and the thermal and physical properties that should be expected for dense polycrystalline SiC. It is shown here that these properties translate well into PIP-derived CMC to show increased modulus, proportional limit and fatigue resistance as well as reduced creep. The authors believe that other composite systems will also benefit from the use of this fiber.

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