Nonoxide polymer-derived CMCs for "super" turbines

By Zhongkan Ren and Gurpreet Singh

The melting point of single-crystal blades limits further advancement in operating temperature of gas turbines with metallic materials. Ceramics, which have much higher melting points, hold the promise for future "super" turbines.

Superalloy turbine blades for gas turbines may have been the most significant energy and transportation technology development in the last century. It empowered our military prowess, made it possible for civilian aircraft to fly halfway around the world, and now single-crystal blades are employed in gas turbines for energy conversion because of their superior creep resistance over traditional polycrystal alloys.

The single-crystal technology evolved over 50 years, through an intimate coupling between materials science, mechanical engineering, and manufacturing research. These single-crystal blades, coated with low thermal conductivity ceramics, now perform close to their melting points for thousands of hours (Figure 1). However, the melting point limits further advancement in the operating temperature of gas turbines with metallic materials.

Ceramics, which have much higher melting points than metals, hold the promise for "super" turbines in the future (Figure 2). But while ceramics have high strength at high temperatures, ceramics also suffer from thermal shock. Structural ceramics are of two kinds: oxides, like aluminum oxide (think sapphire), and nonoxides, mainly silicon carbide (SiC). Oxides generally have a high coefficient of expansion that renders them prone to thermal shock, but they also have better oxidation resistance than SiC in extreme environments (Figure 1b). The current ceramics technology is therefore based upon structures made from SiC with environmental barrier coatings made from oxides.

Work from the 1980s to 1990s on ceramics for high-temperature structures demonstrated that fibrous composites would be able to avoid brittle behavior because single-fiber fractures in fiber-bundles would be rendered harmless by displacement between the broken ends. Specifically, the ends were being accommodated by neighboring fibers through interfacial sliding, thereby spreading strain across the composite.

Critical Components to a CMC

There are three critical components to a ceramic matrix composite (Figure 3)[4]: reinforcement, interface coating, and ceramic matrix. Reinforcement provides strength and structural foundation or shape for the composite, generally in the form of a complex 3D woven structure

Capsule summary

END OF AN ERA

Single-crystal technology empowered our military prowess, increased civilian aircraft flight distance, and served in gas turbines for energy conversion. However, this technology has reached its limit—the melting point limits further advancement in operating temperature.

CERAMIC POSSIBILITIES

Ceramics, which have much higher melting points than metals, hold the promise for "super" turbines. Three critical components—reinforcement, interface coating, and ceramic matrix—play a role in ceramic matrix composite performance.

MULTIPLE WAYS FORWARD

New preceramic polymers, reinforcement fiber materials, failure prediction methods, and additive manufacturing methods all offer ways to increase performance of nonoxide polymer-derived ceramic matrix composites in the future.

designed to closely match the final shape of the component. Interface coating is a thin coating on the fiber that provides a low-strength interface between hard ceramic matrix and high-strength fiber. Ceramic matrix provides the load transfer between fibers and majority of chemo-thermophysical properties of the composite—in some cases, the whole CMC is coated with an environmental barrier coating to further improve performance under harsh conditions.

Reinforcement in a CMC is added mainly to improve toughness. It is typically in the form of either a carbon/graphite fiber or an oxide or nonoxide ceramic fiber that can withstand high-application temperatures. Carbon fibers are generally the least expensive while nonoxide fibers are the most expensive. Although oxide-based fibers like alumina show better oxidation resistance than nonoxide fibers, oxide-based fibers' strength retention and creep resistance at high temperatures is compromised due to grain growth at elevated temperatures. In some cases, creep rates for oxide fiber can be two orders of magnitude greater than those of nonoxide fibers. Because of light weight, good oxidation resistance, good thermal shock resistance, and relatively high modulus and strength values, only silicon-based nonoxide ceramic fibers (tending toward SiC composition) are preferred for ultrahigh temperature aerospace applications. Oxide CMCs are perhaps more suitable for relatively less demanding applications.[4-7]

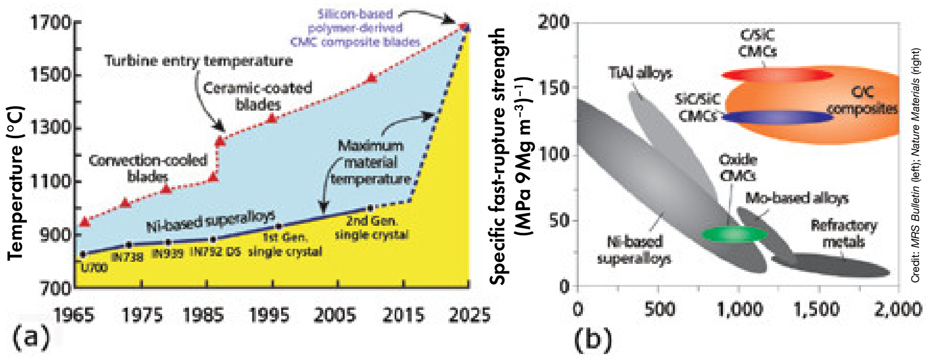


Figure 1 (a): Firing temperature trend and material capability over time [Reproduced with permission from *MRS Bulletin*[1]]. (b): A comparison of high temperature mechanical property of SiC/SiC ceramic matrix composites (CMCs) with oxide CMCs and aeroengine materials like the nickel-based super-alloy Inconel [Reproduced with permission from *Nature Materials*[2]]. The current genesis of multi-component silicon-based polymer-derived ceramic (PDC)-CMC technology will continue to evolve over the next decade.

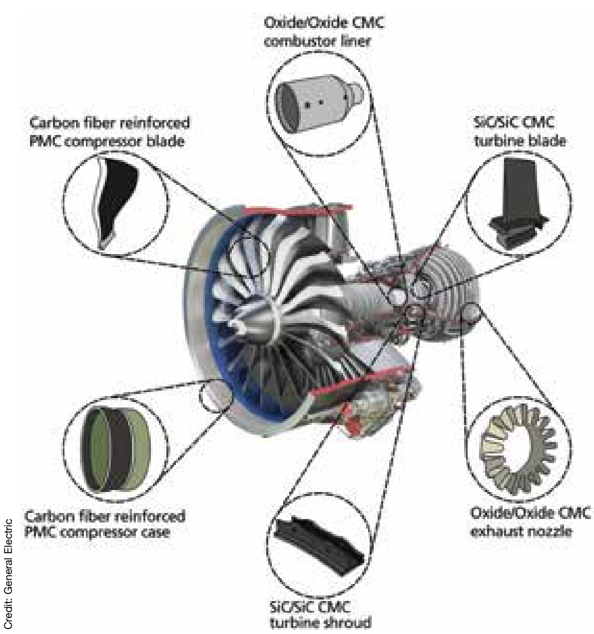


Figure 2: Schematic (cross-section) of a GE gas turbine engine. Polymer matrix composites (PMCs) are preferred for low temperature applications while polymer-derived ceramics (PDCs) are attractive materials for the engine hot section, for example, turbine blade and shroud. Image courtesy General Electric.[3]

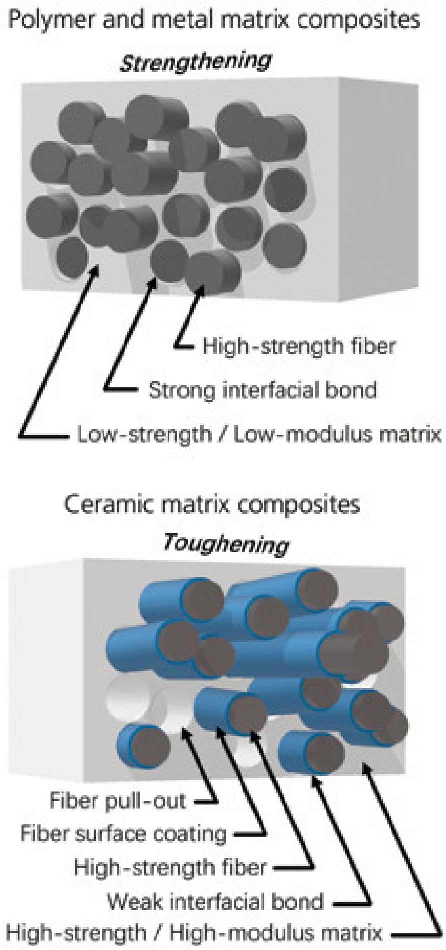
Manufacturing nonoxide ceramic fibers

Three different approaches to manufacturing nonoxide ceramic fibers exist—chemical vapor deposition (CVD), extrusion/sintering of powder slurries, and polymer precursor route.

CVD is the oldest method for production of SiC fibers. In this method, SiC is generally deposited on a heated amorphous carbon or tungsten wire ("core") resulting in a high-strength fiber.[5,8,9] Such fibers are monofilaments with minimum diameter in the range of 75 to 100 microns, which limits their minimum bend radius and renders them unsuitable for weaving into textile or making complex-shaped ceramic parts. Such high-strength fibers, however, could be used as reinforcement in a metal matrix composite.

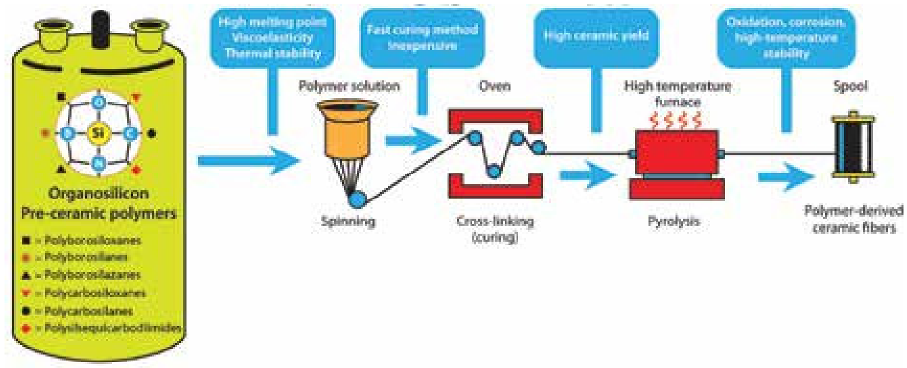
The extrusion/sintering to make SiC fiber involves spinning SiC powder in a polymeric binder, followed by sintering. These fibers are generally thicker than 30 microns, have surface defects, and never fully densify due to difficulty in sintering a nonoxide ceramic.[5,9]

Because high-temperature CMCs would require high-strength flexible ceramic fibers (diameters less than 20 microns), research on alternate routes to obtain continuous and flexible fibers had been ongoing when a discovery by Yajima et al.[10] in late 1970s showed how



Credit: Koshy et al., ASM International

Figure 3: Polymer versus ceramic matrix composites. Unlike PMCs, the fiber-reinforced CMCs require weak interphases to deflect cracks in the matrix around the fibers, thereby avoiding catastrophic failure during service. Reproduced with permission from ASM International.[4]



Credit: Gurpreet Singh

Figure 4: Schematic showing various steps involved in PDC fiber processing.

high-temperature ceramic fibers could be made from certain organometallic oligomers or silicon-based polymers using a combination of polymer and ceramic processing methods. This process was later developed into a commercial technology in Japan. These fine fibers show good mechanical properties, thermal properties, and oxidation resistance, and can be woven in textile to make complex-shaped ceramic parts. These SiC fibers are the backbone of the ceramic-fiber ceramic-matrix technology that is heralding the next-generation turbine engines,[6] as discussed below.

The production of these fibers involves steps (Figure 4) that are somewhat similar to those used for manufacturing carbon fibers from polyacrylonitrile (PAN):[5,9–12]

1. Synthesis of preceramic polymer with desired rheological properties for spinning processes;
2. Melt or dry spinning of precursor into green fibers;
3. Curing (thermally, chemically, or radiation) of green fiber to cross-link molecular chains into duroplastic-like state, rendering it infusible during pyrolysis; and
4. Pyrolysis of green fiber under argon at high temperature to obtain ceramic fiber.

The first generation SiC fibers based on Yajima et al.[10] were spun in inert environments but required curing in air to make them infusible during the pyrolysis at high temperatures. As a result, such fibers had oxygen in the ceramic upon pyrolysis and the fibers were amorphous, non-stoichiometric Si-O-C instead of crystalline SiC. The poor thermal and mechanical properties of the fiber were attributed to high oxygen content of these fibers. The second generation SiC fibers focused on reducing oxygen content by curing the green fibers under gamma or electron irradiation in inert environment. As a result, these fibers had larger SiC grains along with the graphene-like carbon.[5]

The third-generation fibers were manufactured at even higher pyrolysis temperatures with addition of trace amounts of aluminum, titanium, or boron to sintering of SiC. Such fibers are essentially polycrystalline SiC with

Table 1: Cost, availability, and properties of bulk PDC ceramics.

Preceramic Polymer*	Cost	Availability	PDC*	Density (g/cm^3)	Modulus (GPa)	Fracture Strength (MPa)	Fracture Toughness (MPa·√m)	CTE (×10^6/K)	Oxidation temp. (°C)	Decomposition temp. (°C)
Polysilazane	Low-medium	Commercially available (medium availability)	SiCN	2.3	80 to 155	<1200	<3.5	3	~1300	~1600
Polycarbosilane	High	Commercially available (limited availability)	SiC	3.1	405	418	4 to 8	3.8	~1200	–
Polysiloxane	Low	Commercially available (large availability)	SiOC	2.3	<113	< 900	<1.8	3.2	–	–
Polyborosilazane	Very high	Laboratory synthesis (very limited availability)	SiBCN	2.3	–	–	–	–	~1600	~2300

*Physical state of preceramic polymer and engineering properties of the pyrolyzed ceramic are strongly influenced by the molecular structure and composition of pre-ceramic polymer and processing conditions used. Data from *Journal of the American Ceramic Society* and *American Ceramic Society Bulletin*.[12-14]

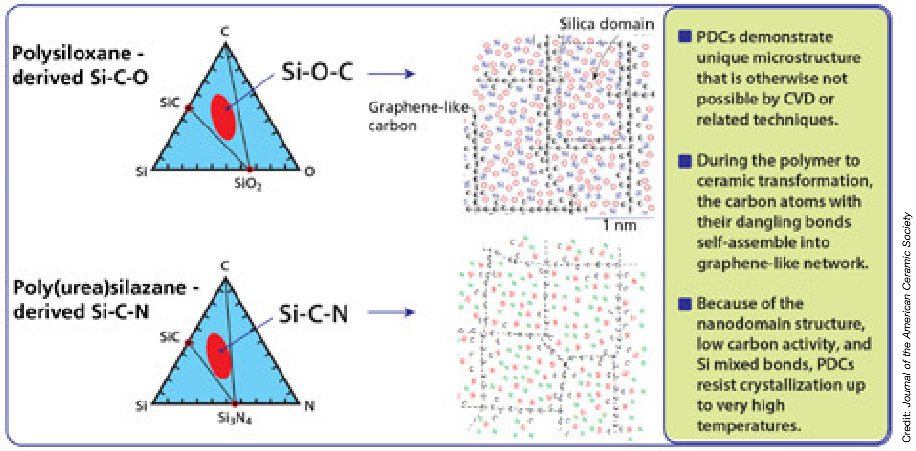


Figure 5: Amorphous nanodomain structure is the hallmark of PDC materials—such microstructure has been shown to improve chemo-thermo-mechanical properties at high temperatures.[16]

small amounts of sp2 carbon phase at grain boundaries. Higher sintering temperature generally leads to larger SiC grain size, elastic modulus, strength, and creep resistance over a wide temperature range. Such fibers, however, are exorbitantly expensive, costing over €18,000/kg.[5] The high cost of manufacturing SiC fibers is apparently related to the control of oxygen content—costly autoclave techniques are needed for synthesis of the preceramic polymer while additional pyrolysis steps are required to drive out oxygen from the ceramic fiber.

The General Electric Company recently introduced CMC components into its LEAP engines. This innovation is expected to generate tens of billions in new revenue for GE. The development of CMC-turbine blades is rumored. GE Aviation expects that increased jet engine production will increase demand for SiC fibers and tapes as much as tenfold over the next decade.[15] The high cost of these fibers is a major barrier to future growth.

Engineering new compounds

Over the last 25 years, fundamental research in Si-C-O-N compounds yielded new results that show how their nanostructure relates to mechanical properties and thereby provides the insights needed to engineer new compounds for turbine engine applications (Figure 5):

- *Stability of the amorphous structure*: While the binary Si-C crystallizes at 1,200°C, the ternary and quaternary compounds are intrinsically amorphous, with a negative enthalpy of formation relative to the crystalline state.
- *The nanodomain network of graphene*: The SiCNO materials contain a network of graphene or sp2 carbon with a domain size of 1–5 nanometers. The domain boundaries consist of mixed bonds of Si-C- (N,O) while the tetrahedral of Si-(O,N) occupy the space within the domains.
- *Zero creep behavior*: The carbon network imparts unusual mechanical properties such as zero creep in the steady state at temperatures up to 1,500°C, while the interlaced Si-O-N protects the carbon from oxidation.

Polycarbosilane-derived nanocrystalline SiC fibers contain grain boundaries. Although such fibers are known for their ultra-high-temperature stability, presence of grain boundaries and some low melting phases/impurities at grain boundaries may make them susceptible

CMC MATRIX manufacturing

Infiltration is the most common technique for creating aerospace grade SiC/SiC ceramic matrix. Fiber preform could be infiltrated with matrix material in gaseous (CVD) or liquid (melt infiltration and polymer infiltration) form.[6] The fiber preform preparation requires a rather complex approach—the preform is generally a hollow 3D replica of the final component (e.g., combustion liner or vane) designed computationally based on function of the component, expected mechanical and thermal loadings at the site, and topology/materials properties of the fiber, matrix, and interface coating.[2]

CVD or CVI: CVD processing involves introduction of vapors of silicon-based metal organic compounds (generally methyltricholorosilane) along with a carrier gas, such as hydrogen, into a chamber containing heated fiber preform substrate. The silicon-based precursor decomposes at a high temperature to yield high purity SiC, which fills the preform to form the continuous matrix phase. This process is slow due to lower ceramic yields and deposition rates. Large amounts of highly corrosive vapors are produced during the deposition process, which increases the capital equipment cost and downtime. Large-size, thick CMC parts are prone to nonuniform coating and density gradients.[9]

Melt infiltration: Molten silicon at 1,500°C is introduced into a carbon fiber preform, and SiC is formed at the interface as molten silicon reacts with carbon. Silicon oxide and carbon oxide are the byproducts released during carbothermal reduction. The process is expensive due to high temperatures required for melting of silicon. In addition, the byproducts may react with furnace elements, causing damage or significant downtime.[9] Excess or unreacted silicon could be present in the final part, which significantly degrades mechanical properties at high temperatures.

Polymer infiltration and pyrolysis: This technique is similar to those employed for fabrication of polymer matrix composites. The fiber preform is infused with liquid preceramic polymer that transforms into ceramic matrix upon pyrolysis (PDC route). Because of its simplicity, relatively lower processing temperatures, and shorter cycle times and ability to produce complex CMCs, this technique is the most cost effective and efficient. Preceramic polymers with high ceramic yield and improved stability against moisture and air (long shelf life) are preferred; carbosilane-based preceramic polymers that yield stoichiometric SiC composition are most desired.

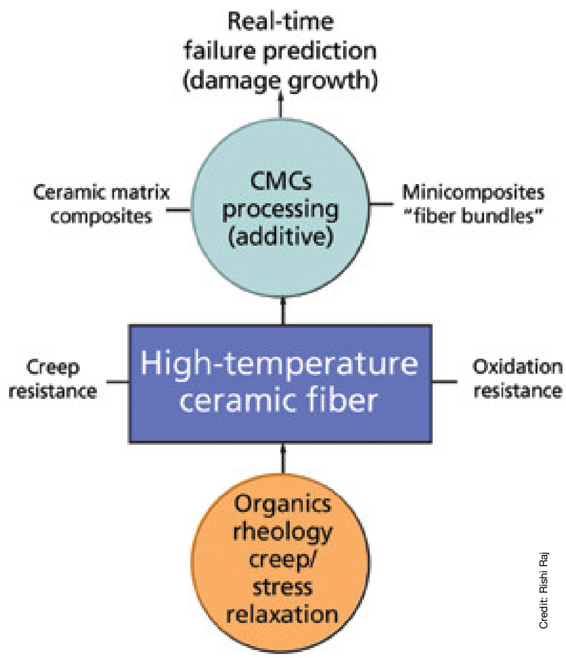


Figure 6: High-temperature ceramic fibers are the bridge between basic research on synthesis of preceramic polymers with desired properties and CMC processing based on real time failure predictions.

to deformation and creep at temperatures as low as 900°C. For example, the SiC grains may slide relative to one another due to softening at grain boundaries, leading to creep cracks and the eventual deformation of fiber.[8] In addition, the role of small amounts of oxygen in commercial SiC fibers is poorly understood. In contrast, multi-component amorphous fibers such as SiCN, SiOC, and SiBNC could be produced by suitable selection of preceramic polymer (Table 1). Such ternary and quaternary systems are shown to improve chemical and thermal stability.[9,12,17,18] The SiCNO ceramics are amorphous and contain significant amounts of oxygen, which is rendered harmless by its nanodomain structure of graphene. The synergy between the carbon network and the silicon-oxygen-carbon matrix within which it is embedded imparts thermodynamic stability to the amorphous structure, creep resistance, and, most importantly, the opportunity to manufacture fibers at low cost (polysiloxanes and polysilazanes are significantly more abundant and cheaper than polycarbosilanes—Table 1).

Ceramic fibers also generally require an interface-compliant coating (100 nanometers to 1 micron thick) and a SiC overcoating to provide a weak fiber/matrix bond in order to realize high toughness in CMCs and to protect the fiber from harsh oxidation environments, respectively.[19,20] The coating, generally composed of pyrocarbon or hexagonal boron nitride (or a combination of both) has low shear strength and is applied directly to the fibers via CVD techniques.[4,7] CVD of interface boron nitride and overcoat SiC is expensive, time consuming, and requires use of hazardous chemicals; as a result, the costs associated with such coatings could be 10 to 50 times on a square-meter basis than a fabric of carbon or graphitic fiber.[9]

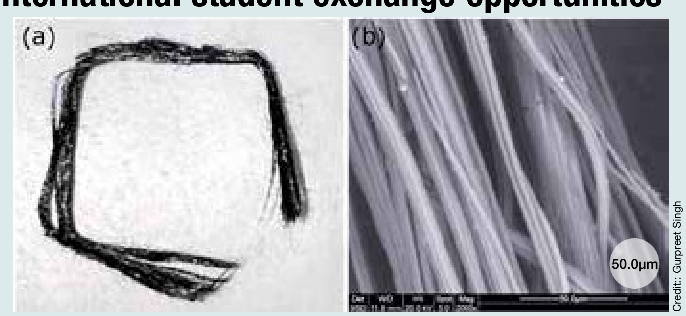
Future directions for nonoxide CMC materials and manufacturing processes

1. *New preceramic polymers based on ternary and quaternary systems for CMC matrices:* Liquid-phase high-purity, low-cost, high-yield polymers that are nontoxic and noncorrosive are being researched at both university and industry levels. Preceramic polymers that can produce amorphous ceramics with Si-X-C-N/O, where X is boron, hafnium, or zirconium, composition are of particular interest due to improved thermal stability and corrosion resistant of the resulting ceramic. Likewise, preceramic polymers that are photocurable (for example, via chemical interfacing with photo polymers) at room temperature are being studied. Polymers that contain simpler side (hydrocarbon) groups with high ceramic yield at increased heating rates are desired in order to minimize release of volatile components during pyrolysis stages and lower processing costs, respectively—larger hydrocarbons, which diffuse out during pyrolysis, could lead to increased porosity in the matrix. This task is not trivial considering that thermal stability and rheological properties of preceramic polymer are tied to the composition and molecular weight of the side groups.

2. *New reinforcement fiber materials:* As stated earlier, oxygen-containing amorphous PDC fibers based on ternary and quaternary systems composed of combinations of elements that form strong covalent bonds (such as silicon, carbon,

Developing negligible creep resistance and international student exchange opportunities

The challenge is to develop ceramic fibers constituted from silicon, boron, carbon, nitrogen, or oxygen that exhibit negligible creep resistance at temperatures up to 1,600°C in oxidizing environments, with a target production cost of approximately $1,000/kg (Figure 4). To address this technical challenge and create international student exchange opportunities in PDC science, the National Science Foundation awarded a five-year $4.7 million Partnerships for International Research and Education (PIRE) grant to Gurpreet Singh and co-workers (Alexandra Navrotsky—University of California Davis, Himanshu Jain—Lehigh University, Rishi Raj and David Marshall—University of Colorado Boulder, Elsa Olivetti—MIT, and Peter Kroll—University of Texas at Arlington). So far, Singh et al. have demonstrated the feasibilty of drawing such low-coat fibers. ■



PDC SiCNO fibers being investigated in Singh's lab. (a): digital camera picture and (b): SEM image. Foot-long fibers of preceramic polymer could be drawn by hand using a glass rod. The challenge, however, is to maintain structural integrity of the fiber during the pyrolysis process.

nitrogen, boron, oxygen) and show resistance to crystallization and high temperature creep should be the focus of future research. Such ceramics could be prepared from preceramic polymers based on polysiloxane and polysilzanes, which are relatively cheaper and easy to mass produce compared with carbosilanes. As for fiber processing, preceramic polymers that can be melt-spun or electro-spun are preferred over traditional dry spinning techniques, to keep costs lower due to reduced number of processing steps. Likewise, polymers that allow rapid in-line curing (cross-linking) and pyrolysis with high ceramic yields (greater than 85 percent) are expected to be significantly cheaper and hold low porosity and surface defects.

3. *CMC failure prediction:* Experimental approaches to understanding ultrahigh temperature thermo-chemo-mechanical behavior of a CMC material could be cost prohibiting. To ensure rapid commercialization of CMCs would require guidance regarding material development and design of fiber preform (Figure 6).[21] This could be achieved to some extent by developing and employing analytical fiber and CMC material models for time-temperature deformation and rupture behavior. These models may involve computing responses under conditions that induce severe thermomechanical gradients and be able to capture progressive failure of CMCs[22]—multi-scale length CMC material models that accommodate effects of high strain rate and fatigue would be needed for design of high-speed rotating components inside turbine engines.

4. *Additive manufacturing of PDC CMCs:* Like PMCs, a variety of additive manufacturing or 3D printing technologies could potentially be employed to manufacture CMCs from silicon-based preceramic polymers. Opportunities exist in use of preceramic polymers to produce ceramic components in a range of compositions using either conventional stereolithography printing (via chemical interfacing with photopolymers) or direct extrusion-based fused deposition modeling of composite slurries followed by pyrolysis at high temperatures.[13] Challenge lies in the ability to produce uniform, large-area, defect-free components with desired thermomechanical properties in an economical manner. Very limited data has been reported in literature on such composites—some new reports from the Air Force Research Laboratory, HR Lab, and university researchers in Italy and the United States have started to emerge.[13]

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