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Status quo and future trend on R&D for high temperature and high performance ceramic fibers derived from polymers

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Abstract—Several kinds of SiC-based ceramic fibers are presently fabricated on an industrial scale using precursor polymers. The Si-C-O ceramic fiber that was first developed in 1975, has high tensile strength and relatively high heat resistance. The Si-Ti-C-O fibers emerged after the Si-C-O fiber was developed. These fibers have been applied as reinforcement for aluminum wire, glass-ceramics, or silicon carbide matrix composite materials. Through the research work on these fiber reinforced metal or ceramic matrix composites, these fibers have increased heat resistance. In the past ten years, a new fabrication process of the fiber, a radiation curing method, has been developed. In addition, the conversion process of polymer precursors to ceramics and the thermal stability of the fibers have been widely studied at high-temperatures ranging above 1500 K. These research works have successfully produced excellent SiC-based ceramic fibers with high-temperature resistance. These fibers are mainly prepared from polycarbosilane family polymers. In the future, in order to strengthen the ceramic fibers and to establish a low-cost fabrication process, more effective precursor polymers will need to be developed.

Keywords: SiC fiber; polymer precursor; composite; pyrolysis; tensile strength; heat resistance.

1. INTRODUCTION

In the 1970s, non-sinterable ceramics such as silicon carbide and silicon nitride have been actively synthesized with advanced sintering technology. They are high density and high strength molds, and they are superior to metallic materials in their heat resistance and oxidation resistance. The ceramics began with applications to such practical parts as turbo rotors, bearings and machine tools. We expected strongly the development of engineering ceramics as the materials used for thermal engines of high efficiency. However, it has been pointed out that the fracture toughness and the thermal shock resistance of the ceramics are poor and their reliability is also low. In order to solve these problems, extensive research on ceramic

matrix composite (CMC) has been made. CMC is roughly classified into the fiber reinforcement type, such as continuous fibers and whiskers and the particle dispersion type by nano-structure control. The fracture toughness can be extensively improved by reinforcement using continuous ceramic fibers. Research and development of continuous-fiber-reinforced CMC (CFR-CMC) were significantly advanced because of the development and commercialization of continuous Si-C-O ceramic fiber (Nicalon) [1, 2] which has high tensile strength and relatively high heat resistance. Major research works in the 1980s in the CFR-CMC were the lithium aluminosilicate glass or glass-ceramics composite reinforced by Nicalon (Compglas^{TM}) [3] and Nicalon-reinforced SiC composite (Ceracep SiC/SiC) [4–6] fabricated by using the CVI method. In the 1990s, in order to improve mechanical and thermal stability properties of CFR-CMC, it became necessary to create ceramic continuous fibers that possessed high performance properties at high temperature. The target properties for R&D of continuous ceramic fibers were as follows:

- Fiber diameter: below 15 μm.
- Tensile modulus: above 350 GPa.
- Tensile strength: above 2.1 GPa (at 25.4 mm gauge length).
- Tensile strength: above 1.4 GPa (at 1673 K in Ar and air at 57.4 mm gauge length).
- Maintenance of tensile strength: above 80% after holding 12 h at 1673 K in air and 12 h at 1873 K in Ar.

2. IMPROVEMENT OF HIGH TEMPERATURE STRENGTH FOR SiC-BASED CERAMIC FIBERS

Nicalon (NL-200) and Si-Ti-C-O fibers (Tyranno, Lox-M), that were developed after Nicalon, are flexible ceramic fibers and have been fabricated using the thermal oxidation curing process from polycarbosilane (PCS) and polytitanocarbosilane of organosilicon polymers, respectively. Its preparation method is roughly shown in Fig. 1.

NL-200 and/or Lox-M fibers have high tensile strength at room temperature, but its strength is generally degraded above 1473 K. We can explain the improvement of the ceramic fibers by using Nicalon as an example. This fiber is amorphous-like phase of SiC_xO_y composed of Si, C and O, and the following thermal decomposition reaction occurs at high temperatures:

$$SiC_xO_y \rightarrow SiC\ (S) + SiO\ (g) + CO\ (g). \quad (1)$$

By the generation of SiO (g) and CO (g) gases, the fiber morphology undergoes an extreme change, and the tensile strength rapidly decreases. The degradation of strength is due to the above thermal decomposition [7–9]. In order to improve the degradation of the fiber at high temperature, it is necessary to reduce the oxygen content introduced in the thermal oxidation curing process. As a result of research

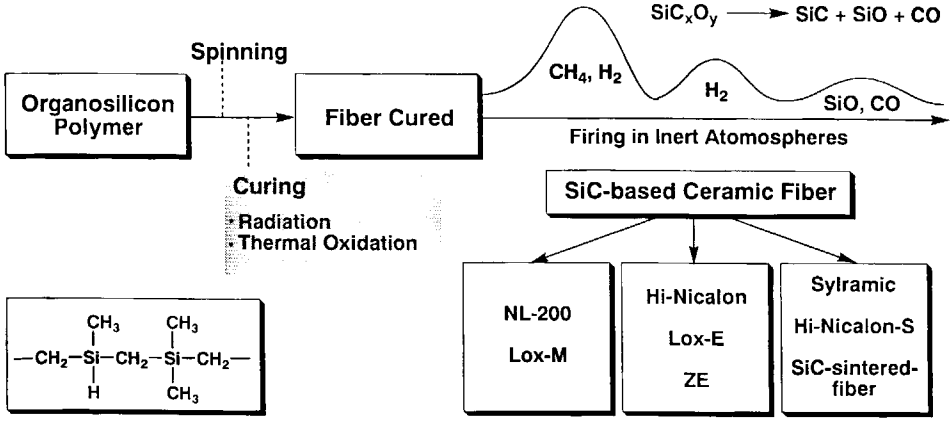

Figure 1. Fabrication process of SiC-based ceramic fibers: NL-200, HI-Nicalon and HI-Nicxalon-S: Nippon Carbon Co., Ltd.; Lox-M, Lox-E, ZE and SiC-sintered-fiber (SA): UBE Industries, Ltd.; Sylramic: Dow Corning Corporation.

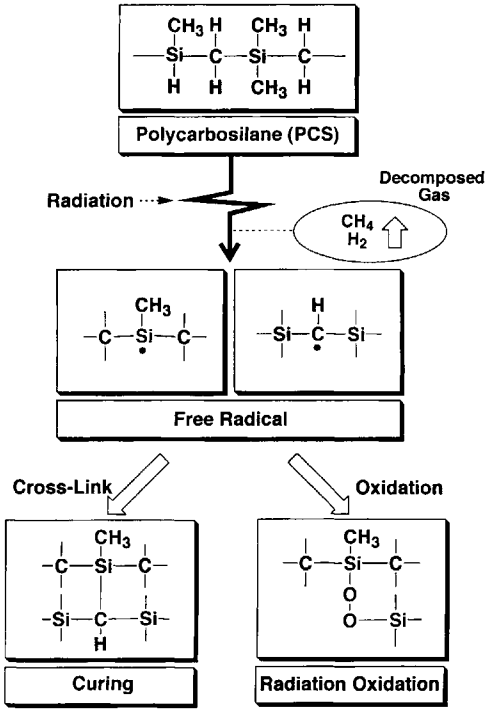

Figure 2. The model for radiation curing of polycarbosilane fiber.

works, the crosslinked PCS fiber by the radiation curing process [10, 11] has been developed under the national project of AIST, MITI and JSTC. The radiation curing mechanisms are simply shown in Fig. 2. At the initial stage of the irradiation, the active sites as free radicals and gaseous products are produced by the scission of

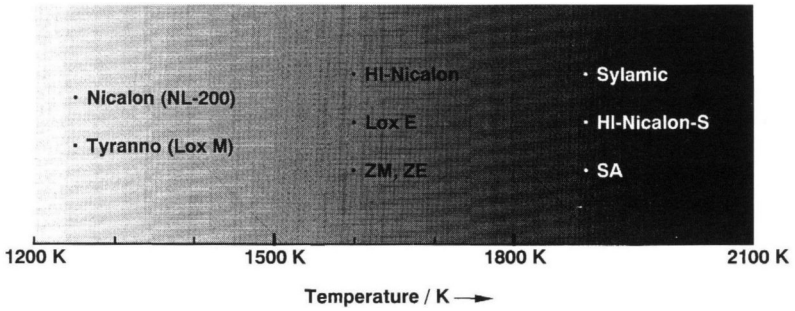

Figure 3. The heat resistance of SiC-based ceramic fibers.

chemical bonds of Si-CH_3, Si-H, and C-H. These active sites react with each other to form crosslinks between molecular chains. The oxidation can easily occur in these processes by the presence of oxygen during irradiation. The ceramic fiber (HI-Nicalon) obtained using this radiation curing process possesses less oxygen, higher strength and higher modulus than Nicalon at high temperature. For Tyranno (Lox E and ZE), its high temperature strength is also improved, and the previous targets are gradually being achieved.

On the other hand, the conversion process of polymer to SiC ceramics, for example gas evolution process [12, 13] in Fig. 1 and the thermal decomposition (equation (1)) of the Nicalon or Tyranno have been actively studied at high temperature ranging above 1473 K. Especially, the thermal decomposition rate is found to be determined by the diffusion-controlled nucleus formation and three-dimensional grain growth process of SiC involving the diffusion of carbon in the fiber. By applying this mechanism, most recently new SiC-sintered fibers (Sylramic, HI-Nicalon-S and SA etc.) were developed [14–17]. The properties of a series of SiC-based ceramic fibers are shown in Table 1. These commercialized ceramic fibers is roughly classified by the heat resistance as shown in Fig. 3.

3. APPLICATION OF POLYMER-DERIVED SiC-BASED FIBERS TO CMC

In the middle of the 1990s, high-temperature strength for Nicalon type and Tyranno type ceramic fibers has been improved, and CFR-CMC [20] using the fiber, HI-Nicalon, has been prepared. Its main properties are shown in Table 2 with those of other CFR-CMCs. The properties of SiC-based ceramic fibers at high temperatures were improved, but it becomes a problem that the cost of these fibers is high. Now, these polymer-derived fibers are flexible and 2D or 3D fabrics are industrially made of the fibers. With 2D [21] or 3D [22, 23] fabric, CMCs have been fabricated. In the CMCs, the fabrication method is the polymer-infiltration-pyrolysis (PIP), CVI method, or the method combining PIP and CVI. The 3D composites are better with their capability for complicated shaping and shaping as one mold, and high shock resistance [22, 23]. In these composites, it is important to design a polymer that has a high ceramic yield.

Table 1.
Typical properties of polymer-derived SiC-based fibers

SiC fibers	Nicalon [15]			Tyranno				Sylramic [14]	UF-HM [18]	Sintered fiber [19]
	NL-200	HI-Nicalon	HI-Nicalon-S	Lox M [16]	Lox E [16]	ZE [16]	SA [17]			
Atomic composition	$SiC_{1.34}O_{0.36}$	$SiC_{1.39}O_{0.01}$	$SiC_{1.05}$	$SiTi_{0.02}C_{1.37}O_{0.32}$	$SiTi_{0.02}C_{1.59}O_{0.16}$	$SiZr_{<0.01}C_{1.52}O_{0.05}$	SiC*	$SiCTi_{0.02}B_{0.09}O_{0.02}$	SiC	SiC
Tensile strength (GPa)	3.0	2.8	2.6	3.3	3.4	3.5	> 2.5	2.8	2.1–3.4	1.65–2.07
Tensile modulus (GPa)	220	270	420	187	206	233	> 300	400	—	—
Elongation (%)	1.4	1.0	0.6	1.8	1.7	1.5	~ 0.8	0.7	—	—
Density ($g\,cm^{-3}$)	2.55	2.74	3.10	2.48	2.55	2.55	—	> 3.1	3.1–3.2	—
Diameter (μm)	14	14	12	11	11	11	10	10	10–15	20
Specific resistivity ($\Omega\,cm$)	10^3–10^4	1.4	0.1	30	0.8	0.3	—	—	—	—
Thermal expansion coeff. ($10^{-6}/K$)	—	3.5 (298–773 K)	—	—	—	—	—	5.4 (293–1593 K)	—	—

*The composition of O and Al for the impurity is less than 0.008.

Table 2.
Some properties of typical SiC/SiC materials

Method	Fiber	V_f (%)	Density (g/cm^3)	Heat resistant temperature (K)	Tensile strength (MPa)	Work of fracture (kJ/m^2)	K_{IC} ($MPa\,m^{1/2}$)	Thermal conductivity (W/mK)
Reaction sintering	HI-Nicalon UD [20]	30	3.0	1623	500	6.4		50 (room temperature) 30 (1273 K)
PIP	Tyranno 3D [22, 23]	35–39	2.4	1473	400 (bending strength)	4.3–8	11.5–16	
	HI-Nicalon 2D [21] (Nicalo-ceram™)	35	2.3	1693	260–460 (bending strength)			
CVI	Nicalon 2D [4–6]	36	2.3	1473	215–280		27–29	~ 7 (room temperature–1273 K
Fiber-bonded ceramics	Tyranno UD, 2D [24–26] (Tyrannohex)	90	2.54	1773	450–550, UD 190–210, 2D	8.9	46.2	4.5 (room temperature)

On the other hand, CMC (Tyrannohex) made of fiber-bonded ceramics is attractive as a future CMC. Tyrannohex is prepared by sintering Tyranno fiber tow itself [24–26]. During sintering, the morphology of the fibers changes from a columnar shape to a hexagonal shape. The cross-section of Tyrannohex shows perfectly hexagonal closed-packed structure. Its structure and properties are affected by the sintering process with the high temperature pyrolysis of Tyranno. By using a new type of fiber prepared from a newly designed polymer and by the detailed examination of the high temperature pyrolysis mechanism, the properties of Tyrannohex type composites will be improved step by step.

4. CONCLUSION

In the development process of the SiC-based ceramic fibers prepared from organosilicon polymers, first, amorphous fibers are fabricated; next, low-oxygen contained fibers are developed; and finally, sintered fibers are created. The precursor polymers of these fibers or matrix of CMC are mainly PCS-type polymers obtained by the thermal decomposition of polydimethylsilane (PDMS). The SiC-based ceramic fibers or their related materials are prepared by the process of PDMS → PCS → SiC as shown in Fig. 4. In the near future, in order to strengthen the properties of the ceramic fibers and to establish a low-cost fabrication process, for example, the

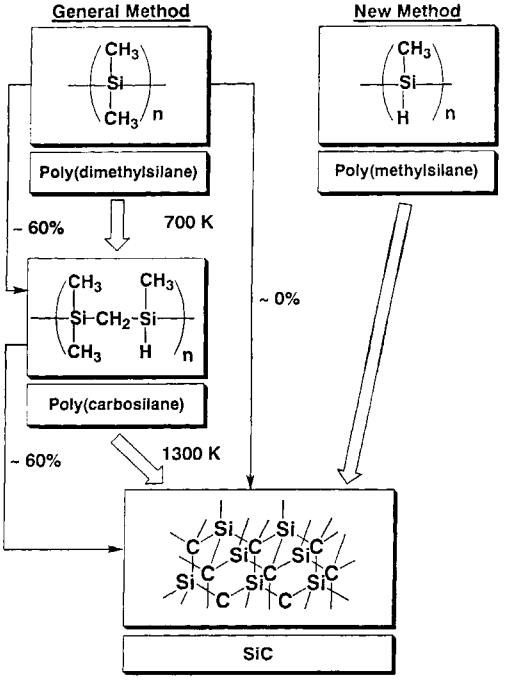

Figure 4. Schematic process of polysilanes into SiC: ~ 60%: the yield of PCS obtained from PDMS, the SiC ceramic yield obtained from PCS; ~ 0%: the SiC ceramic yield obtained directly from PCMS.

process of Polysilane → SiC, more effective polymers for the starting materials of the fibers or the matrix will be developed.

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