Reinforced SiC Composites

Development of Silicon Carbide Fibre through Preceramic Polymer route

J. N. Sharma*, P. K. Mollick, Ramani Venugopalan, Ashok K. Arya and Vivekanand Kain

Glass & Advanced Materials Division, Materials Group, Bhabha Atomic Research Centre, Mumbai 400085, INDIA



Melt-spun (green) fibre

ABSTRACT

Silicon carbide fibres derived from polycarbosilane (PCS), a precursor polymer to SiC, offer exceptional opportunities for fabrication of SiC fibre reinforced SiC matrix composites. These composites are proposed as high temperature nuclear materials due to their excellent high-temperature fracture, creep, corrosion and thermal shock resistance and safety advantages arising from low induced radioactivity. PCS was synthesized at kilogram scale by pressure pyrolysis of polydimethylsilane (PDMS) in a gas induction autoclave in the temperature and pressure range of 480-500°C and 90-100 bar respectively. PDMS was synthesised from Wurtz-type reductive dehalogenation of dimethyldichlorosilane with molten sodium. PCS of different molecular weight fractions were obtained by fractional distillation. The molecular weight, structure, softening temperature, creamic yield and properties of PCS were characterized by measurements of GPC, FT-IR, ¹H-NMR, TG-DTA-DSC, Raman and XRD. SiC ceramic fibre was obtained from PCS by melt spinning, cross-linking of melt-spun fibre by oxidative curing followed by heat treatment of cured-fibre in argon atmosphere up to a temperature of 1250°C. XRD of SiC fibre indicated presence of β -SiC nanocrystallite as main phase and SEM showed a smooth surface with no visible defects.

KEYWORDS: Polydimethylsilane, Polycarbosilane, Melt spinning, Curing, Pyrolysis, Silicon carbide fibre

Introduction

SiC fibres offer high strength-to-weight ratios and exceptional thermal stability in harsh environmental conditions. Such fibres are one of the best candidates as reinforcement for highperformance ceramic matrix composites due to their high mechanical properties, oxidation and creep resistance at elevated temperatures [1-3]. The ceramic derived from polymer enabled significant technological breakthroughs in development of ceramic fibres, coatings and ceramics stable at ultrahigh temperatures (up to 2000°C)[4]. Polymer precursors represent organo-silicon polymeric systems that provide ceramics with a tailored chemical compositions and a crystalline nanostructured organization when subjected to proper thermal treatment under an inert atmosphere. Yajima et al. first reported the pioneering work on preparation of SiC fibre from PCS precursor, PCS, a polymer having silicon and carbon atoms repeated alternately, was melt spun to obtain precursor fibre, then cross-linked to render the fibres infusible, and finally pyrolyzed under inert atmosphere to produce SiC fibre. The SiC fibre obtained was continuous, having β-SiC nano-crystallite structure, high tensile strength and young's modulus[5,6]. Nippon Carbon Company, Japan made the first commercial SiC fibres under the trade name Nicalon[™]. These fibres have excellent stability up to a temperature of 1200°C, resistance to acid/base corrosion and oxidation, high tensile strength and Young's modulus of 2.5-3.2 GPa and 180-300 GPa respectively[7]. Nippon Carbon in collaboration with Japan Atomic Energy Research Institute, carried further modifications in fibre processing parameters and developed SiC fibre which retained its high tensile strength and Young's modulus up to a temperature of 1800 °C. This remarkable heat resistance fibre was named as Hi-Nicalon[8]. SiC fibre is an outstanding reinforcement for various composites, because of their excellent compatibility with resins, metals and ceramics. The SiC fibre reinforced SiC composite (SiC,/SiC) is a class of ceramic matrix composites in which a SiC fibre preform phase is imbedded in a SiC matrix phase[8]. SiC_f/SiC matrix composites are fabricated from fibre wound preforms or fibre fabric preforms through processes such as, chemical vapour infiltration (CVI process), preceramic polymer infiltration pyrolysis (PIP process), reaction sintering process and SiC nanoparticle slurry infiltration transient eutectic (NITE process)[9-12]. These composites can be engineered for specific stress, temperature, life and environmental conditions. NASA patented SiC_t/SiC composites, which can withstand adverse structural and environmental conditions for a very long time at temperatures up to 2500°C[13]. Several fusion power reactor design studies have mentioned the use of SiC₄/SiC composites as structural material[14-15]. These composites offer significant benefits over metallic superalloys, monolithic ceramics, carbon fibre and oxide/non-oxide ceramic composites[16-17].

Worldwide, the development and availability of these composites have been restricted to a few countries only, which either have the technology to manufacture SiC fibre through the preceramic polymer route or have free access to it. The key challenges in the manufacturing technology of SiC fibre is the large scale production of PCS and PDMS, the melt spinning of PCS to continuous PCS fibre, curing of PCS fibres by oxidative activation or electron beam irradiation and pyrolysis of the cured fibre to SiC fibre. In relevance to the DAE reactor programme, SiC_t/SiC matrix composites are the most promising material for Accident Tolerant Fuel Cladding and for high temperature structural applications, while the PCS itself is important for SiC coatings on various structural components of high temperature reactors. In defence and space sector, C_t/SiC and SiC_t/SiC composites are used as light weight-high temperature stable structural materials. Recently, DRDO approached us for their large scale requirements of PCS for fabrication of C_t/SiC components through hybrid process consisting of PIP, CVI & CVD for hypersonic applications.

In this article, the on-going work on development of continuous SiC fibre through large scale synthesis of PCS, melt spinning of PCS to green fibre, oxidative curing and pyrolysis of cured fibre to SiC fibre and their characterization are reported.

Preparation of PCS

Yajima method for synthesis of PCS using PDMS is followed. Details of synthesis are given as under.

Synthesis of PDMS

PDMS is composed of a Si-Si backbone structure with methyl substituents attached to the silicon atoms. It is synthesised by Wurtz-like reductive dehalogenation of dimethyl dichlorosilane with molten sodium. The synthesis was carried out in a 10 L round bottom flask fitted with mechanical stirrer, reflux condenser and addition funnel. 1 kg of sodium was added with 5 L of xylene and heated up to 110 °C under N₂ atmosphere, then added 2.45 L of dimethyldichlorosilane drop-wise by maintaining the temperature in the range of 110-120°C. The reaction mixture was refluxed for 10-12 h. The product was separated after necessary work-up. PDMS obtained was 1 kg with a yield of 85%. It is a white powder and was found to be insoluble in almost all paraffinic and aromatic solvents. It was characterized by FTIR. IR spectra show absorptions at 2900, 1400 cm⁻¹ for C-H and 1250, 835,750, 690, 635 cm⁻¹ for Si-CH₃.

Synthesis of PCS

1 kg of PDMS was charged in a gas induction autoclave in argon atmosphere and raised the temperature to 480° C at the rate of 200° C/h. The temperature was maintained between $480-500^{\circ}$ C for 6-10 h. The autogenic pressure at this temperature was about 100 bar. After completion of reaction, the reaction mass was fractionated under vacuum to obtain different molecular weight fractions of PCS. Autoclave for synthesis and fractionation is shown in Fig.1.



Fig.1: Autoclave for synthesis of PCS.

The rearrangement polymerization reaction is written as:







Fig. 2 &3: Liquid/gel and solid fractions of PCS.

Characterization of PCS

The formation of PCS is confirmed by presence of characteristic peaks, Si-H & Si-CH₂-Si by FTIR and ¹H-NMR (CDCl₃) measurements. IR absorptions, as shown in Fig.4, at 2098 cm⁻¹ contributed to Si-H, 1016 & 1356 cm⁻¹ to Si-CH₂-Si, and 600 to 920 cm⁻¹ to Si-CH₃. ¹H-NMR spectra (Fig.5) shows chemical shift at 4.26 for Si-H and 0.1695 for Si-CH₃.

Molecular weight distribution of PCS is measured by Gel Permeation Chromatography (GPC) using Agilant system, model: 1260 Infinity, fitted with refractive index detector. THF was used as eluent and polystyrene as calibration standard. PCS of number average molecular (M_n) in the range of 400 to 500 are low viscous liquid, $M_n \sim 500$ to 700 are viscous liquid (gel) and M_n above 700-800 are solid. Melting points, M_n and weight average molecular (M_w) of solid PCS fractions are given in Table 1.

Ceramic yield of PCS is obtained by measurement of weight loss due to thermal decomposition using Mettler Toledo



Fig.4: FT-IR spectra of PCS.



Fig.5: ¹H-NMR of PCS.

Table 1: Melting point and molecular weight information of PCS fractions.

PCS fractions Melting points (°C)	M _" g/mol	M _w g/mol
<15 (liquid/gel)	400-700	800-1020
118-124	1230	2279
135-141	1300	2619
148-154	1457	2914
174-184	1550	4693
237-250	1647	9000
285-290	1746	9650
>350	1912	11059

TGA/DSC 3+ star system. PCS sample of 285-290 °C melting point fraction was heated up to a temperature of 1250 °C at a heating rate of 10 °C/min and argon flow rate of 40 cm³/min. Polymer to ceramic conversion is completed up to 1250 °C and ceramic yield obtained was about 75%.

SiC ceramic powder obtained on pyrolysis of PCS was analysed by XRD (Cu K α) and Raman spectroscopy. The XRD pattern shows formation of β -SiC crystallite as major phase (Fig.6). The peaks at 2 θ = 36°, 60°, 72° corresponds to (111), (220), and (311) diffraction planes of face centered cubic β -SiC polymorph of SiC. The crystallite size of SiC was found to be 12 nm. Raman spectra (Fig.7) also shows cubic (3C) β -type crystal structure of SiC powder.



Fig.6: XRD pattern of SiC obtained on pyrolysis of PCS at 1250 °C in argon atmosphere.



Fig.7: Raman spectra of SiC obtained on pyrolysis of PCS at 1250 °C in argon atmosphere.

Processing of PCS to SiC Fibre

It mainly consists of three steps: (a) Melt spinning of PCS to green fibre (b) Curing of PCS fibre by heating in an oxidising atmosphere to make it infusible (antimelt) fibre and (c) Pyrolysis of cured fibre in an inert atmosphere to obtain SiC fibre.

Melt Spinning of PCS

Solid PCS was converted to fibre by extruding the molten PCS under nitrogen pressure through a ten-hole spinneret of a melt spinning unit. For winding of fibre, a large diameter rotating bobbin was placed just below the spinneret. Prior to spinning, the PCS was heated just above its melt temperature under nitrogen gas pressure and kept for 1 h for obtaining uniform molten mass. The temperature was then reduced to near melting point and fibre spinning started by increasing the N_2 gas pressure and by adjusting the winding speed of bobbin. About 5 m continuous fibre without any surface defect was obtained. Image of the melt-spun fibre is shown in Fig.8. Different range of fibre diameter, nitrogen pressure, winding speed and melt viscosity. Details of spinning conditions of a typical run are given in Table 2.

Table 2: Spinning parameters of PCS of melting point 237-250 °C.

PCS	Spinning Temperature	Spinneret hole diameter	N ₂ pressure	Winding speed
Melting point 237-250°C	270-280°C	0.2 mm	5-7 bar	300m/min



Fig.8: ¹H-NMR of PCS.



Fig.9: Cured PCS fibres.

Oxidative Curing of Green Fibre

Curing step is necessary to make the green fibre infusible so that it retains the fibrous shape during pyrolysis. Here curing is carried by slow heating of fibre in a flow of dry air in an oven. The as-spun fibre was cut into a length of 20 cm and placed in an air-oven and heated at a rate of $0.5 \,^{\circ}$ C/min up to a temperature of 200 °C. Curing results in surface oxidation of fibre infusible. Extent of curing is determined by the gel fraction of the cured fibre. Gel fraction is the insoluble portion during Soxhlet extraction of the cured fibre with xylene as eluent at 150 °C for 8 h. The gel fraction obtained in the present curing condition is about 70%. A gel fraction above 50% is sufficient to make fibre infusible and to retain the fibre shape on further heat treatment. Image of cured fibre is shown in Fig.9.

Pyrolysis of Cured Fibre

The cured PCS fibre was kept in an alumina boat and placed into a tubular furnace connected with a high purity argon gas cylinder and mass flow meter. The temperature of the furnace was raised to 1250 °C at a ramp rate of 5 °C/min and argon flow rate of 100 mL/min. The soaking time at set temperature was 1 h. The pyrolysis converted the yellowish



Fig.10: Typical SiC fibre of 10 cm length obtained on pyrolysis of cured fibre.



Fig.11: Micrograph of SiC fibre.



Detector = SE2 EHT = 5.00 kV WD = 4.6 mm Mag = 10.00 K X 2 µm

Fig.12: A SiC fibre of diameter 15 μ .

cured fibre to lustrous black SiC ceramic fibre (Fig.10). XRD of SiC fibre shows major phase as β -SiC with peaks at $2\theta = 36^{\circ}$, 60°, 70° for (111), (220) and (311) diffraction lines. SEM image indicated a smooth surface with no visible surface defects (Fig.11). Diameter of fibres obtained was in the range of 14 to 16μ (Fig.12). Measurement of mechanical properties of the fibres is in progress.

Conclusions

Kilogram scale synthesis of PDMS, PCS and fractionation of PCS to different molecular weight fractions and along with their characterizations has been well established. Processing parameters for conversion of PCS to SiC fibre through, melt spinning of PCS to green fibre, oxidative thermal curing (crosslinking) of green fibre and finally pyrolysis of cured fibre to SiC fibre have been optimized. Here, it is to be noted that, technology for manufacture of continuous SiC fibre is associated with numerous challenges. Some of the difficulties encountered during the experiments are: (a) Spinning of continuous green fibre with uniform diameter and smooth surface, (b) Spinning of very low diameter (< 20μ) continuous green fibre, (c) Control of oxygen content during thermal curing of green fibre, (d) Avoiding defects due to shrinkage of fibre during pyrolysis. All these challenges are being addressed methodically to realise the goal of making continuous SiC fibre and SiCf/SiC composites.

References

[1] A. Kohyama, M. Singh, Hua-Tay Lin, Y. Katoh (Eds.), Advanced SiC/SiC Ceramic Composites: Ceramics Transactions, American Ceramic Society, 2002, 144.

[2] Y. Katoh, S.M. Dong and A. Kohyama, Thermo-mechanical properties and microstructure of silicon carbide composites fabricated by nano-infiltrated transient eutectoid process, Fusion Eng. Des., 2002, 61-62, 723-731.

[3] A. Kohyama, Joon-Soo Park, Hun-Chea Jung, Advanced SiC fibres and SiC/SiC composites toward industrialization, J. Nuclear Mater., 2011, 417 (1-3), 340-343.

[4] Paolo Colombo, Polymer-Derived Ceramics: 40 Years of Research and Innovation in Advanced Ceramics, J. Am. Ceram. Soc., 2010, 93(7), 1805-1837.

[5] S. Yajima, Y. Hasegawa, J. Hayashi, M. limura, Synthesis of continuous silicon carbide fibre with high tensile strength and high Young's modulus, Part 1: Synthesis of polycarbosilane as precursor, J. Mater. Sci., 1978, 13, 2569-2576.

[6] Y. Hasegawa, M. limura, S. Yajima, Synthesis of continuous silicon carbide fibre, Part 2: Conversion of polycarbosilane fibre into silicon carbide fibres, J. Mater. Sci., 1980, 15, 720-728.

[7] Richard M. Laine, Florence Babonneau, Preceramic Polymer Routes to Silicon Carbide, Chem. Mater., 1993, 5, 260-279.

[8] Toshikatsu Ishikawa, Recent development of the SiC fibre Nicalon and its composites, including properties of the SiC fibre Hi-Nicalon for ultra-high temperature, Composies Science and Technology, 1994, 51, 135-144.

[9] W. Yang, H. Araki, A. Kohyama, S. Thaveethavorn, H. Suzuki, T. Noda, Fabrication in-situ SiC nanowires/SiC matrix composite by chemical vapour infiltration process, Materials Letters, 2004, 58, 25-32.

[10] C.A. Nannetti, A. Ortona, D.A. de Pinto, and B. Riccardi, Manufacturing SiC-Fibre-Reinforced SiC Matrix Composites by Improved CVI/Slurry Infiltration/Polymer Impregnation and Pyrolysis. Journal of the American Ceramic Society, 2004, 87, 1205-1209.

[11] Kazuya Shimoda, Akira Kohyama, Tatsuya Hinoki, High mechanical performance SiC/SiC composites by NITE process with tailoring of appropriate fabrication temperature to fibre volume fraction, Composite Science and Technology, 2009, 69, 10, 1623-1628.

[12] William B. Hillig, Melt Infiltration Approach to Ceramic Matrix Composites. Journal of the American Ceramic Society, 1988, 71, 2, 96-99.

[13] https://technology.nasa.gov/patent/LEW-TOPS-25

[14] R.H. Jones, L. Giancarli, A. Hasegawa, Y. Katoh, A. Kohyama, B. Riccardi, L.L. Snead, W.J. Weber, Promise and challenges of SiCf/SiC composites for fusion energy applications, Journal of Nuclear Materials, 2002, 307-311, 1057-1072.

[15] T. Noda, Advanced SiC-SiC Composites for Nuclear Application. In: Y.R. Mahajan, R. Johnson (eds) Handbook of Advanced Ceramics and Composites, Springer, Cham., <u>https://doi.org/10.1007/978-3-030-16347-1 20(2020).</u>

[16] J. Lamon, Chemical vapour infiltrated SiC/SiC composites (CVI SiC/SiC), Handbook of Ceramic Composites, 2005, Springer.

[17] Masaki Kotani, Akira Kohyama, Yutai Katoh, Development of SiC/SiC composites by PIP an combination with RS, Journal of nuclear Materials, 2001, 289, 37-41.