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Silicon carbide wires of nano to sub-micron size from phenol-furfuraldehyde resin

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Abstract Phenol-furfuraldehyde (PFu) resin synthesized in our laboratory was characterized for its thermal properties and mixed with elemental silicon and the mixture was evaluated as precursor for SiC ceramics. The mix on sintering at 1,500 °C gave nano-SiC powder. The sintering experiment carried out in flowing argon has also resulted in the formation of SiC wires/fibers having diameter in nano to sub-micron range.

Introduction

Silicon carbide possesses many favorable properties making it suitable for advanced applications such as high-temperature structural materials, reinforcement in composites and filters for molten metals or hot gases and also as grinding materials, polishing paste, wear resistant materials, and catalyst supports [1–4]. The high values for properties such as melting point, hardness, and abrasion resistance combined with good chemical, radiation and thermal shock resistance, and low-thermal expansion coefficient make it a candidate material for such diverse applications.

Several methods have been used for the synthesis of SiC such as carbothermal reduction of silica [5], sol gel process [6], chemical vapor deposition [7], and direct combustion [8]. Carbonaceous polymers when mixed with the required additives or ceramic powders followed by firing at high temperatures are reported to give densified ceramic bodies [9]. The significant advantage of this route is that objects of choice of any shape can be molded. Phenol-formaldehyde resin fits into this category with its thermosetting property [10–12] and high carbon yield on pyrolysis.

Phenolic resins-silicon powder mix has been explored as a simple and economical precursor for obtaining SiC shaped objects and composites [13]. In place of silicon powder various silicon containing chemical precursors like silica [14], fumed silica powder [15], tetraethoxysilane [16], etc. are also used with phenolic resin for obtaining SiC ceramics [17, 18]. Phenolic resin-silicon mix is also used as binder for sintering commercially available SiC powder [13]. The syntheses using phenolic resin as one of the starting materials along with some silicon containing compounds with or without carbon as external additive are cited in many research publications [19–23].

Phenol-furfuraldehyde (PFu) resin has been widely used as basic resin for grinding wheels [24] and organic aerogels [25, 26]. But apart from its use as a thermosetting resin for plastic molding applications, it has not been explored as a precursor resin for the preparation of SiC. The presence of double bond in furfural is expected to facilitate polymerization producing additional cross linking sites. Thus it is expected to influence the char residue and thereby control the final SiC ceramic composition.

In the present study, PFu resin synthesized in our laboratory and silicon powder mix is evaluated as precursor for SiC ceramics.

Experimental

Phenol-formaldehyde (PFu) resin was prepared from phenol and furfural as per the procedure described else where

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[27]. Silicon powder (MEPCO, Madurai, India, particle size 17 µm, purity >99.5%) was used as such.

Stoichiometric quantity of silicon powder equivalent to the char residue of the PFu resin was mixed thoroughly and cured at 175 °C. The cured mix was charged in a furnace under an argon flow of 5 ml/min and pyrolyzed at 900 °C for 120 min. The pyrolyzed PFu + Si mix was charged in a tubular sintering furnace and heated to 1,500 °C at a heating rate of 1 °C/min and kept at this temperature for 240 min. After the reaction, the greenish gray powder was analyzed and characterized. The same experiment when carried out at 1,500 °C skipping the pyrolysis step gave a greenish gray ceramic growth on the walls of the furnace and the material was also characterized.

TGA analysis of the PFu resin was carried out in a TA instrument SDT 2960 at a heating rate of 10 °C/min under nitrogen atmosphere. The SiC powder and the ceramic growth obtained were characterized by elemental, FTIR (Perkin-Elmer Spectrum GX spectrometer) and XRD (Philips 1729) analysis. The morphology of SiC growth was analyzed by SEM (Hitachi S-2400). The SiC assay of the ceramic samples was done by wet analysis.

Results and discussion

Phenol-furfuraldehyde resin was characterized by FTIR, ^{1}H and ^{13}C NMR analysis for confirming the chemical structure. The curing characteristics of PFu were also studied by using DSC and it showed that the resin starts curing at 100 °C by methylene crosslinking followed by crosslinking of double bond which starts at 200 °C.

Thermal analysis of the resin was carried out in an inert atmosphere. During dynamic heating, it is expected that the resin would undergo curing followed by thermal decomposition of the cured product. The TG, DTA and DTG curves of PFu resin are given in Fig. 1.

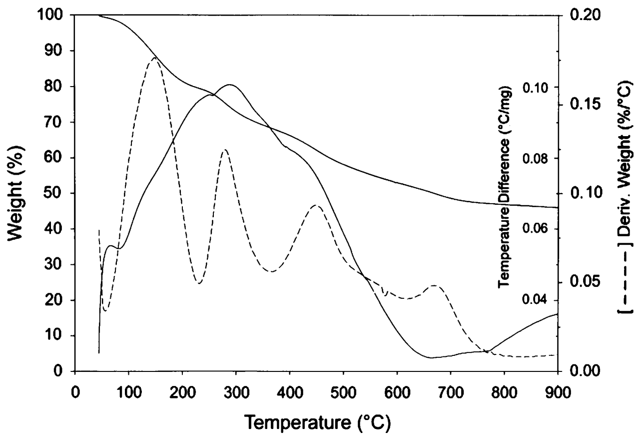

Fig. 1 TGA, DTA, and DTG curves of PFu (10 °C/min)

The weight loss in the region 100–350 °C is caused by the loss of water and low molecular weight products due to curing and unreacted phenol and furfural. The second major weight loss happens in the 350–750 °C range, where cross linked PFu starts degrading to low molecular weight products resulting in the formation of pyrolytic carbon. DTA curve shows a broad exotherm in the temperature region 100–650 °C with maximum peak temperature at 290 °C. In this temperature region, PFu undergoes curing followed by degradation. DTG curve indicates that the weight loss takes place in four stages. The reason for this is not clearly understood. TG studies indicate that PFu gives a char residue of 46% at 900 °C.

Conversion of PFu resin-silicon mix to nano-silicon carbide powder

The quantity of silicon required for complete conversion of carbon to SiC was arrived at, based on the char residue obtained in the pyrolysis of PFu at 900 °C. The analysis of the char residue at 900 °C resulted in 98% pure carbon. The cured PFu + Si slurry was converted to ceramic by subjecting to heat treatment (heating and cooling rate: 2 °C, soaking at 1,500 °C for 4 h). The ceramic powder obtained was characterized by IR (Fig. 2) and XRD (Fig. 3). The peaks at 835 cm^{-1} and 1,093 cm^{-1} in the IR spectrum are due to SiC and SiO$_2$, respectively. The X-ray diffraction pattern (Table 1) shows peaks corresponding to *β*-SiC. The SiC assay obtained by chemical analysis is 98%. Elemental composition of the powder was found to be 68.8% Si and 29.0% C by weight. The particle size of SiC powder calculated from XRD data using Bragg's Equation is 79.5 nm. This suggests that the SiC obtained from PFu + Si mix is nano in size.

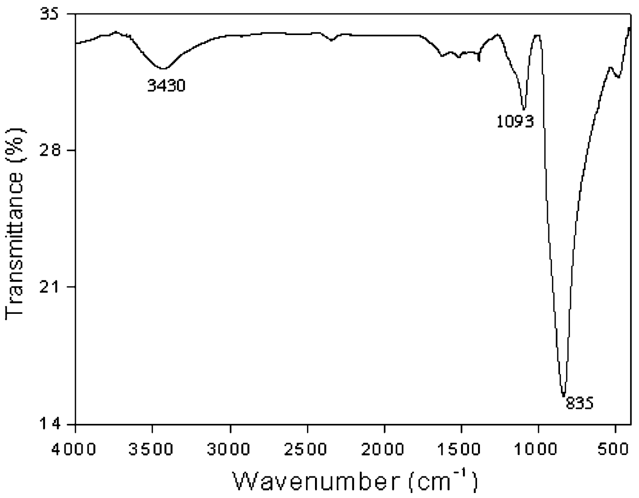

Fig. 2 FTIR spectrum of silicon carbide obtained from PFu + Si

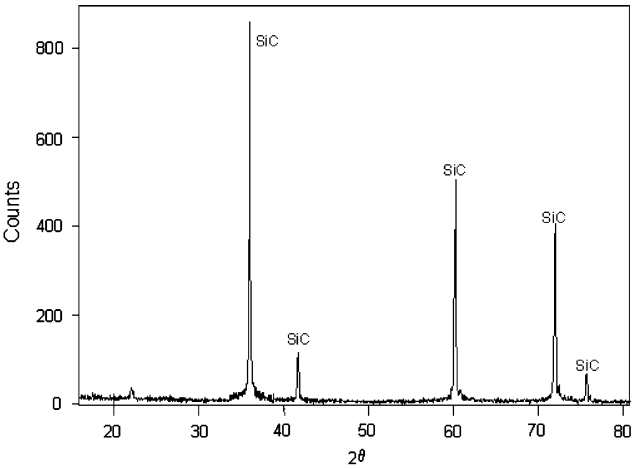

Fig. 3 XRD pattern of reaction sintered sample of PFu + Si

Table 1 XRD characteristics of β-SiC formed from PFu + Si

Angle (2θ)	d value (Å)	Intensity (%)	Diffraction plane
35.96	2.50	100.00	(111)
41.68	2.16	13.60	(200)
60.24	1.54	54.42	(220)
72.00	1.31	41.29	(311)
75.69	1.26	4.83	(222)

SiC wires from PFu

During the preparation of SiC from PFu + Si by heat treatment, a ceramic material growth (CMG) was observed. CMG was characterized by IR, XRD and SEM. In the IR spectrum (Fig. 4) peaks corresponding to SiC is observed at 786 cm^{-1} and the peaks corresponding to silica are observed at 1,111 and 483 cm^{-1}. XRD studies (Fig. 5) indicate the presence of β-SiC. The XRD characteristics of β-SiC present in CMG are given in Table 2.

It is noticed that in the case of CMG, the diffraction line corresponding to (220) plane at $2\theta = 59.95$ has the highest relative intensity and it differs from the standard powder diffraction pattern of β-SiC. (In the standard β-SiC, multi oriented random crystals with (111) plane at $2\theta = 35.96$ showed the highest intensity). This is attributed to the fact that single crystalline SiC is formed with orientation along (111) plane [28] in the case of CMG. Yet another interesting feature is that multiple diffraction (two) lines are observed for (220) planes in the XRD pattern of CMG system. The reason for this observation is not clearly understood. The particle size of β-SiC as calculated from XRD is 60.9 nm for the CMG.

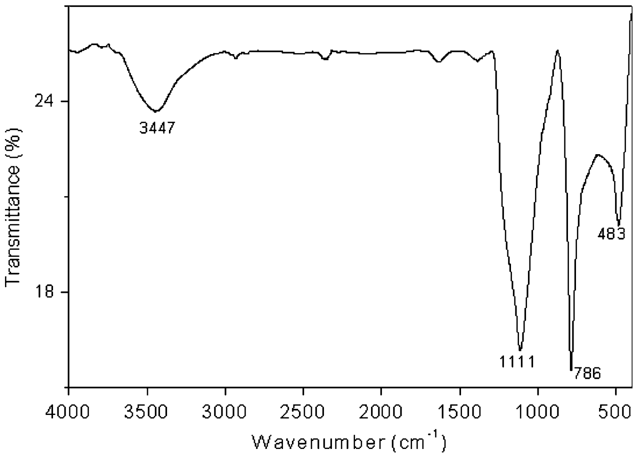

Fig. 4 FTIR spectra of ceramic material growth (CMG) from PFu + Si

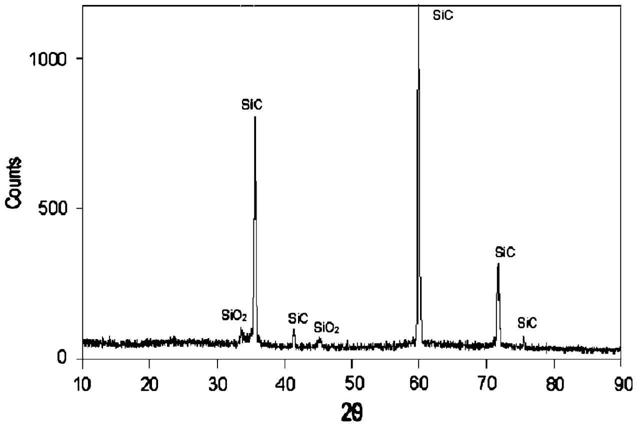

Fig. 5 XRD pattern of ceramic material growth (CMG) from PFu + Si

Table 2 XRD characteristics of β-SiC of CMG

Angle (2θ)	d value (Å)	Intensity (%)	Diffraction plane
35.56	2.52	59.96	(111)
41.34	2.18	4.98	(200)
59.79	1.55	58.70	(220)
59.95	1.54	100.00	(220)
71.63	1.32	21.26	(311)
75.44	1.26	3.39	(222)

The morphology of CMG was studied by SEM (Fig. 6a–f). Wires and rods, wires and rods with nodes at regular intervals, and wires and rods with nodes of different size and shape at irregular intervals are the main features of CMG. In addition, it is noticed that the diameter of the wires and rods is in the range of 459 nm to 1,060 nm, respectively.

Mechanism of growth

There exist several models to explain the vapor phase growth of crystalline fibers/whiskers including vapor–solid

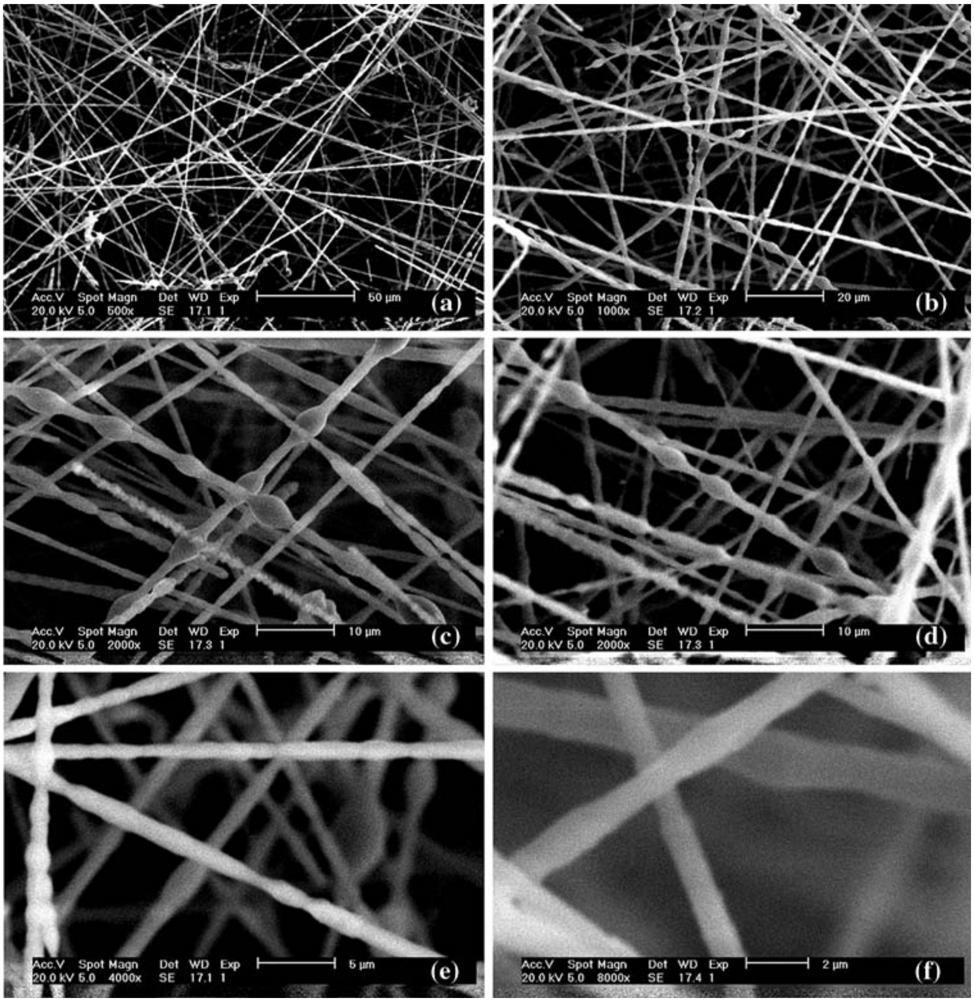

Fig. 6 **a**–**f** SEM of ceramic material growth (CMG) from PFu + Si

(VS) [29] and vapor–liquid–solid (VLS) mechanisms [30]. The main feature of the VLS mechanism is the presence of intermediates that serve as catalyst between the vapor feed and the solid growth at elevated temperatures and the morphology feature is the presence of nano-particles located at the end of the nano wire. SEM studies indicate that the diameter of wire/fiber is in the range of 459 nm to 1.06 µm. Formation of wire/fiber of such dimensions from nano-SiC particles with size of 60.9 nm would have taken place through the reaction with SiO vapors (VS mechanism) and Si vapor (VLS mechanism) with carbon. As SiO_2 is present as impurity on the surface of Si particles, at high temperature (in the temperature region of 1,200–1,300 °C) it can react with Si metal forming SiO. SiO reacts with carbon to give SiC. With further increase in temperature, silicon vapors would be formed, which would react with carbon resulting in the formation of SiC wire/fiber of larger diameter. This growth follows VLS mechanism. As the temperature increases, VLS mechanism involving Si can shift to VS mechanism. In PFu + Si system it appears that the nano to sub-micron wires and rods are directly formed by VS and VLS mechanisms.

Some of the important features observed in CMG system are discussed below with representative figures highlighting the features:

(i) A few rods with nodes at regular intervals are seen (Fig. 7a). The distance between the nodes in rod 1 is in the range of 10–13 µm and in rod 2 it is in the range of 11–16 µm. The formation of such nodes at regular intervals is due to the deposition of Si followed by its conversion to SiC. It is also noticed that the size (3–4 µm) and shape of the nodes are uniform in Fig. 7a, whereas in Fig 7b they differ in shape and size. This type of feature probably results from variation in the concentration of reactive species at different locations.

(ii) In CMG, branching and joining are very uncommon. Two such locations where the rods got joined when they crossed over each other are shown in Fig. 8. At the crossover location, deposition of nano-SiC particles or deposition of Si followed by its conversion to SiC probably takes place resulting in the formation of such joints as seen in the pictures in Fig. 8.

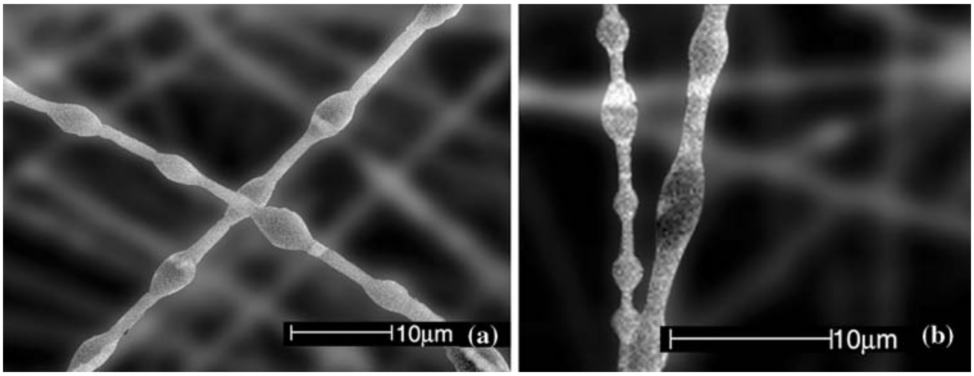

Fig. 7 SEM of CMG showing different types of nodes

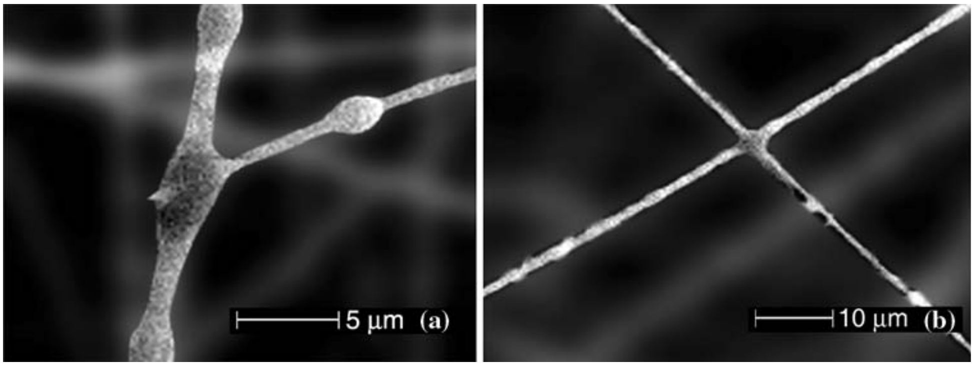

Fig. 8 SEM of CMG showing joined over branches

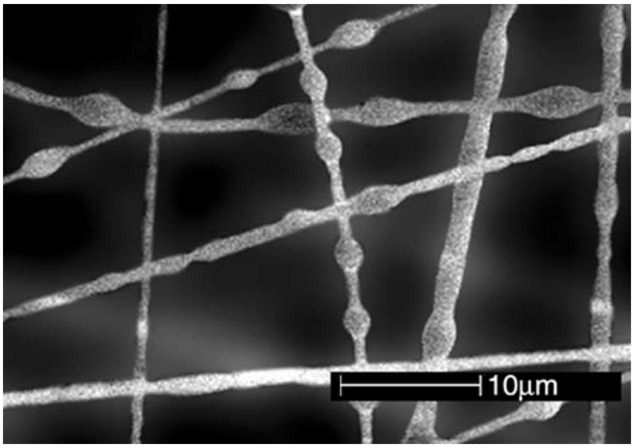

Fig. 9 SEM of CMG showing variation in diameter

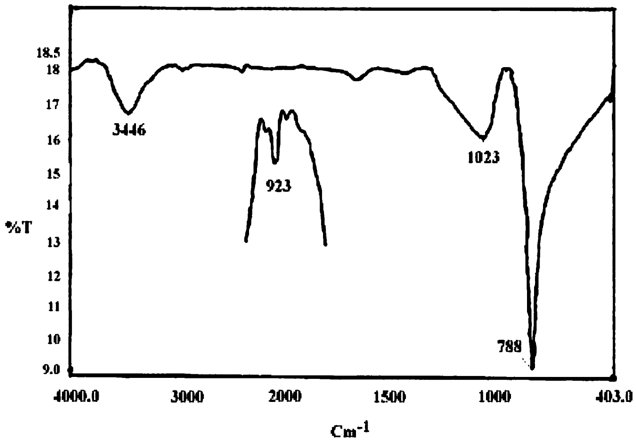

Fig. 10 FTIR spectrum of CMG after treatment with hydrofluoric acid (insert shows 923 cm^{-1} peak)

(iii) Magnified pictures indicate that there is a wide variation in the diameter of the wires and rods present in CMG. Neck formation and generation of rods and wires varying in their diameter at different locations are the common features observed Fig. 9.

Presence of SiO_2 in CMG is evidenced by IR and XRD analyses. The broad peak at 1,111 cm^{-1} is due to SiO_2 in the IR spectrum (Fig. 4). Chen et al. [31] reported hollow SiC tube and the IR spectrum of this tube showed a peak at 923 cm^{-1}. In order to find out the possibility of SiC tube formation, CMG was etched with hydrofluoric acid, to remove the silica present, at 100 °C for 2 h and the IR spectrum of this sample is given in Fig. 10. It is seen that the intensity of the peak due to SiO_2 has diminished. The picture given as insert shows a small peak at 923 cm^{-1}, which implies that hollow SiC tube is present in very less concentration.

Conclusions

Phenol-furfural (PFu) resin synthesized in the present study was converted into SiC ceramic by blending the resin with stoichiometric quantity (based on char residue) of elemental silicon followed by curing, pyrolysis and sintering. The ceramics obtained were characterized by IR, XRD and elemental analyses. A ceramic growth was observed during the heat treatment of preceramic blend. The ceramic growth was characterized by IR, XRD and SEM methods. Based on the above studies, the following conclusions were drawn:

(i) PFu with elemental silicon on sintering gives β-SiC. The particle size of β-SiC obtained is 79.5 nm. Chemical assay of SiC indicates that the purity is 98%.

(ii) During direct sintering of PFu + Si (skipping the pyrolysis step) results in the formation of ceramic material growth. IR and XRD studies indicate that the ceramic is β-SiC. The particle size as calculated from XRD is 60.9 nm.

(iii) SEM analysis of the above ceramic material growth suggests that the SiC growth resembles wires/fibers with nodes at regular intervals. A suitable mechanism, vapor–solid (VS) and vapor–solid–liquid (VLS) has been proposed for the growth of SiC wires/fibers. A suitable mechanism has been proposed for the growth of these nodes too.

(iv) A comparison of the XRD pattern of the ceramic material growth with that of the corresponding ceramic powder obtained from the same system reveals that (111) plane has 100% intensity in the case of SiC powder, whereas (220) plane has 100% intensity for the SiC growth. This is attributed to the orientation of single crystalline β-SiC along (111) plane, which results in increase in intensity of (220) plane in ceramic growth.

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