

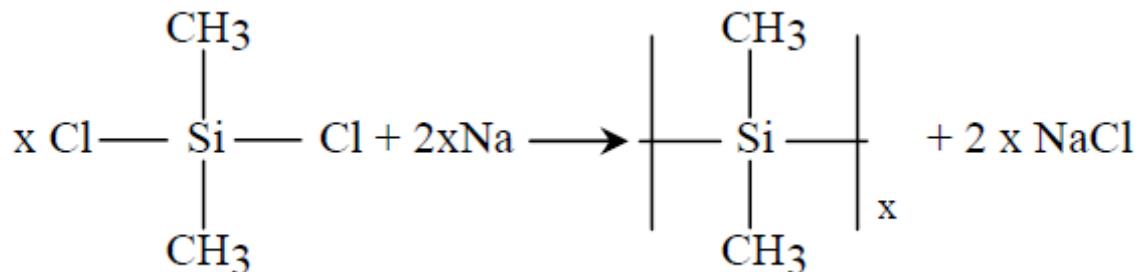
1-2.2 Fibers

The oldest method used to manufacture non-oxide fibers is a decomposition of precursors ($\text{Cl}_3\text{SiCH}_3/\text{H}_2$, BCl_3/CH_4) on a filament substrate (C, W) heated by the Joule effect. This method presents the disadvantage of yielding fibers with large diameters (80–150 μm) at a high cost.

In the last two decades, a new process has been developed, very similar to one used for carbon fibers. It consists of a thermal decomposition or pyrolysis of organometallic polymer fibers containing silicon or boron. This method is used to manufacture long weavable fibers with low diameter (8–15 μm), controlled composition and state of crystallization. This process generally includes five stages summarized below for silicon carbide fiber, which is currently the most developed.

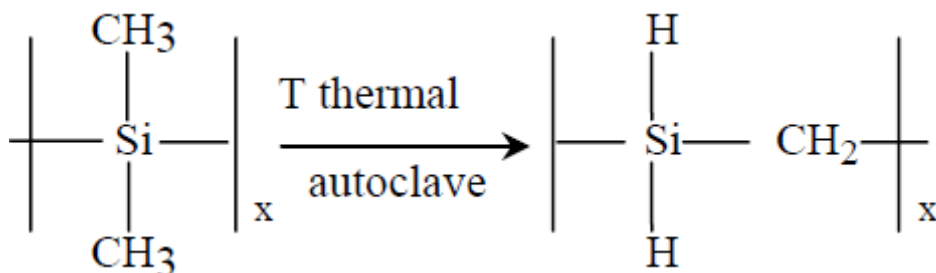
•Synthesis

Polydimethylsilane (PDMS) is synthesized by reaction in an organic solvent between dimethylchlorosilane and sodium:



•Polymerization

The polymerization of liquid PDMS can be done in an autoclave ($T = 450^\circ\text{C}$, $P = 1\text{--}5 \text{ MPa}$) and yields polycarbosilane (PCS) which is a fusible solid:



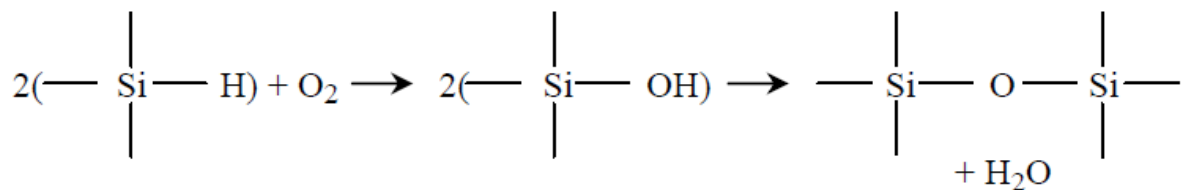
PCS has a very complex connected structure with a very broad molar mass distribution. It is then treated by dissolution-filtration to eliminate the infusible macromolecules which could cause structural defects in the ceramic fiber.

● Extrusion

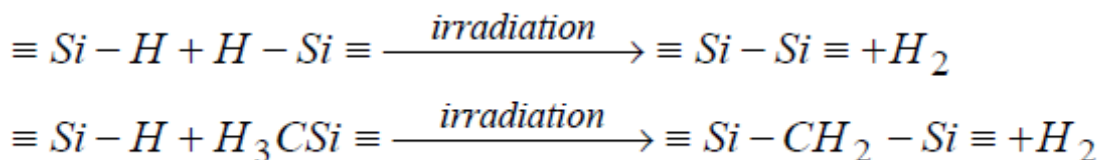
The purified precursor is then molten in a die in inert atmosphere at 300°C to manufacture organometallic fibers by mechanical extrusion (diameter Ø 20 µm).

Cross-linking-infusibility

As PCS fibers are fusible, they must be cross-linked to make them infusible before the ceramization stage. During this treatment, chemical reactions are developed to considerably increase the size of the macromolecules. The most widely used processes consist of a controlled oxidation in air of fibers between 175 and 200°C with formation of Si-O-Si and Si-O-C bridges:



or by electronic bombardment, during which hydrogen is eliminated and Si-Si or Si-C bonds are created:



● Pyrolysis

The ceramization heat treatment is carried out under mechanical tension in neutral atmosphere (vacuum/N₂) up to temperatures of 1,400°C, according to the desired state of crystallization. During this stage, the polycarbosilane precursor undergoes many structural transformations with ruptures of chemical bonds that are accompanied by variations in composition, mass and gaseous releases (see Figure 1.6). First of all, up to 500 –550°C we observe a release of matter corresponding to the elimination of volatile oligomers, then, thermal decomposition occurs with the rupture of Si-H, C-H, Si-CH₂, and Si-CH₃ bonds.

This transformation of polycarbosilane starts with deshydrogeno-carbonation and dehydrogenation reactions. With the departure of hydrogen and alkanes, a three-dimensional lattice of Si-C bonds develops, the C/Si ratio tends towards 1 and C = C bonds appear in the structure. At 1,200°C, mineralization is practically completed (Figure 1.7).

Figure 1.6 Structural evolutions and gaseous releases

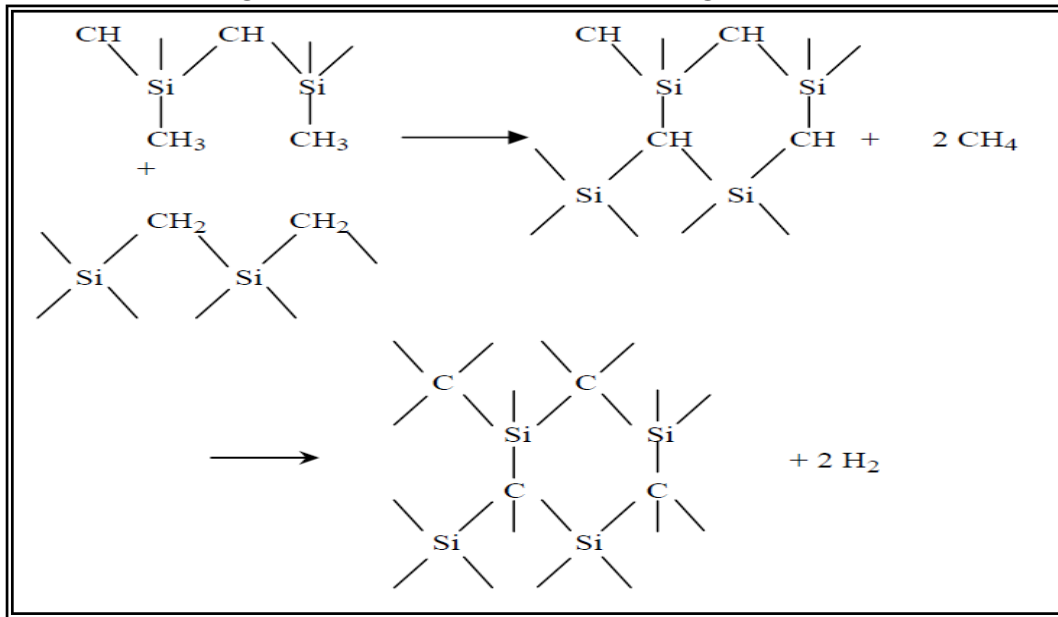


Figure 1.7 Schematic representation of the mineralization of PCS

The fibers are then formed from β -SiC nanocrystals, carbon nanoparticles and amorphous phase of $\text{SiO}_x\text{C}_{4-x}$ type if the cross-linking has been carried out by controlled oxidation (Figure 1.8).

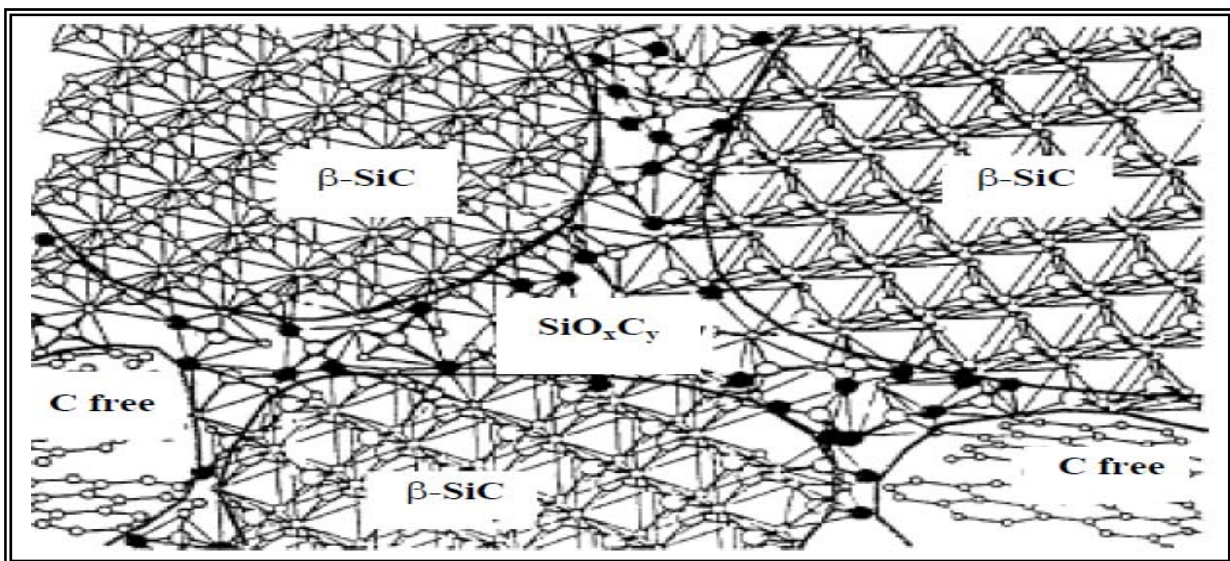
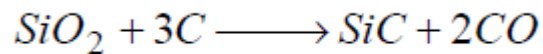


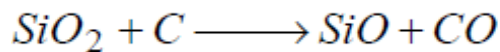
Figure 1.8 Structural model of the fiber

1-2.3 Monocrystals

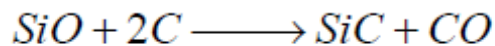
Monocrystals (β -SiC, β -Si₃N₄, B₄C) in the form of filaments ($\varnothing < 10 \mu\text{m}$, $L < \text{qcq mm}$) or plates ($L < 200 \mu\text{m}$) can be prepared by crystalline growth along a simple crystallographic axis. Several methods have been developed, but the purity of the raw materials strongly influences the characteristics and morphology of the monocrystals obtained. The manufacture of β -SiC whiskers is the most developed. SiC monocrystals can be synthesized by coking at 700–800°C and pyrolysis at 1,500–1,800°C in inert atmosphere of organic matters, like rice, which contains a large quantity of silica and carbon:



The final product consists of a mixture of silicon carbide particles and monocrystals of low dimensions (\varnothing : 0.2–0.5 μm , $L < 100 \mu\text{m}$). The growth of monocrystals that results from a gas phase matter transport is controlled much better in the VLS method (vapor-liquid-solid). The synthesis is done in a heated reactor at 1,400°C. At this temperature and in the presence of gas mixtures CH₄/H₂, CO, silicon monoxide is generated by the reduction of silica by carbon:



On the internal walls of the reactor small particles containing iron are deposited, which at the temperature of 1,400°C are liquid. Silicon monoxide and carbon coming from the decomposition of methane dissolve in the liquid droplets until saturation and precipitation of SiC:



As the droplets are constantly fed by the gas phase transfer, precipitation continues with the growth of SiC monocrystals along the crystallographic direction (111). The morphology varies with the composition of the gas phase. For low pressures of SiO, whiskers with circular cross-section ($\varnothing < 5 \mu\text{m}$ – $L \approx \text{mm}$) with a perfectly smooth surface can be manufactured.