Chemical Vapor-Deposited (CVD) SiC Fibers CVD was the first approach used for the 2.3.2.1 production of SiC fiber core-shell composite filaments.The production capacity reached an annual output of 12 kg. The dispersion coefficient of the tensile strength was less than 10%, and the continuous length was longer than 1000 m. 2.3.2.2 Pre-ceramic Polymer-Derived (PPD) SiC Fibers The precursor approach of transferring organic materials into inorganic materials by high-temperature treatment under oxygen-free atmospheres has been used since ancient times.The process includes four steps: (1) synthesis of pre-ceramic polymers (precursors); (2) melt spinning of polymers into green fibers; (3) curing of green fibers by oxidation or EB radiation, and (4) pyrolysis of the cured fibers under an inert atmosphere at high temperatures.Additionally, B-containing SiC fibers with improved mechanical properties can also be obtained by mixing a polycarbosilane precursor with polyborosilazane or polyborazine, or by curing polycarbosilane fibers in a B-containing atmosphere, such as BCl3.In 1987, Si3N4 fibers were prepared by Dow Corning by the synthesis of polymers from chlorosilane and hexamethyldisilazane (HMDS), melt spinning, curing in a chlorosilane atmosphere and pyrolysis at up to 1200 ?C under an inert atmosphere.Similar to the method to obtain carbon fibers wherein PAN or other organic fibers are carbonized in an inert atmosphere at high temperatures, this kind of precursor method has been applied to the commercial production of ceramic fibers [23].Ti and Zr only increase the thermal stability of SiC fibers to a limited extent, and more stable fibers are obtained upon the incorporation of Al and B. These elements act as sintering agents at higher temperatures.The Tyranno SA fibers by Ube Industries and the Sylramic fibers by Dow Corning have been produced by the sintering effect of Al and B near-stoichiometric SiC fibers, as listed in Table 2.25.Three typical Si3N4 fibers are available from the Dow Corning Corporation in the USA, Toa Nenryo Kogyo K. K. (TNK) in Japan and Domaine University in France, and these represent three different preparation technologies.(4) Functional SiC Fibers Based on their high strength, high modulus, low coefficient of thermal expansion and adjustable electrical resistivity, SiC fibers are not only good reinforcements for structural composites but are also good high-temperature radar-absorbing reinforcements for functional composites.Fortunately, precursor varieties, processing parameters and ultimate microstructures (cross section of the fibers) can all be used to achieve this target, and radar-absorbing fibers with the best absorption capacities in the range of 10- 12 GHz can be obtained [39-42].The tensile strength of the fibers was 2.6 GPa, and the continuous length reached 900 m. The radio-frequency heating method was then successfully applied to produce CVD SiC (W core) fibers.Newer silicon-based ceramic fibers have also produced such as M-containing SiC fibers (M = Ti, Zr, Al, etc.), near-stoichiometric SiC fibers, silicon nitride (Si3N4) and Si-B-C-N fibers [23, 25, 30-41].These fibers were applied, respectively, to reinforce polymers, aluminum, titanium, intermetallic compounds and ceramic matrixes.In addition, PPD SiC fibers are very good heat-resistant materials and can be used as insulation materials, high-temperature conveying belts, melt filters, etc.Polycarbosilane-derived Nicalon fibers (NL-200, for example) are not pure SiC fibers as they contain oxygen (14.0 wt%) and a trace of hydrogen (0.15 wt%) in addition to silicon (55.5 wt%) and carbon (28.4 wt%).The high-temperature mechanical properties of Nicalon fibers are limited because of the unstable SiCxOy phase, which will undergo decomposition upon an increase in the grain size of b-SiC at temperatures higher than 1200 ?C.(2) M-Containing SiC Fibers (M = Ti, Zr, Al, B) Another effective method to improve

Nicalon fibers is the introduction of metal or other nonmetallic elements such as Ti, Zr, Al and B [32–39]. Upon heating to 1400 ?C for 1 h under argon, their retained tensile strengths are both over 95% of the original value, confirming that their thermal stabilities are better than that of the Nicalon NL201 fibers. The precursor can be cross-linked by heating giving an infusible but still soluble fiber, and therefore, it is suitable for the preparation of high-purity Si3N4 fibers without other elements. Because of the limited thermal stability of Si–C–N fibers, B was introduced and an amorphous Si–B–N–C fiber, SiBN3C, is currently being developed by Bayer HG in Germany. China entered this field in the early 1980s, and a variety of SiC fibers have been studied including carbon-rich SiC fibers, magnetic particle-containing SiC fibers and non-circular SiC fibers. The improvement in mechanical properties upon titanium introduction is due to a generation of TiC microcrystals preventing the growth of b-SiC crystals. Another type of Nicalon fiber is the high-volume-resistivity (HVR) type such as NL-400, which has an electrical resistance of 106–107 X_cm, and can be used as an excellent radar transmission fiber. Continuous SiC (W core) fibers with surface protection coatings were successfully manufactured with properties close to the similar US and UK products in the 1990s (see Table 2.27). Compared with CVD SiC fibers, the biggest advantage of PPD SiC fibers is their much smaller diameter, which allows easy weaving into a variety of fabrics. After several years of research, important progress was made such as the synthesis of polycarbosilane at normal pressure, multi-spinneret melt spinning, continuous curing and continuous pyrolysis. The tensile strength of the continuous fibers ranged from 2.6 to 3.0 GPa with Young's moduli of 150–190 GPa and diameters of 12–15 lm, which are close to those of the Nicalon fibers. Ti-, Zr- andAl-containing SiC fibers have been developed by Ube Industries in Japan. Compared with the Nicalon fibers, the obvious advantages of Tyranno fibers are their higher thermal stability and good compatibility with aluminum and aluminum alloys. China has also developed Al- and B-doped SiC fibers from polyaluminocarbosilane or a hybrid precursor of polyborazine and polycarbosilane [34, 35]. They are mainly used in metal matrix composites (MMC), ceramic matrix composites (CMC) and heatproof composite materials. These Si3N4 fibers are good reinforcing candidates for CMCs and MMCs because of their high thermal stabilities and oxidation resistance. Domaine University used polycarbosilazane as the precursor for Si3N4–SiC fibers, and this was synthesized from chlorosilanes by ammonolysis and polymerization. Low oxygen content Si3N4 fibers were also obtained by electron beam irradiation, but their mechanical properties need to be improved. For example, the electrical resistance of Nicalon fibers of low-volume-resistivity (LVR) type, NL-500, is 0.5–5.0 X_cm. Systematic studies were carried out on non-circular fibers by changing the shapes of the spinnerets upon melt-spinning polycarbosilanes [38]. The results showed that at the same equivalent diameters, the tensile strength of the fibers with a trilobal cross section is about 30% higher than that with a circular cross section, and the rate of tensile strength reduction upon increasing the diameter is also lower. The electromagnetic parameters of trilobal SiC fibers measured using a rectangular waveguide approach in the X-band are listed in Table 2.30. The electromagnetic parameters of the trilobal SiC fibers are similar to those of the circular fibers (NL202) at lower pyrolysis temperatures. In 1961, Gareis and coworkers applied for a patent using ultra-fine W silk as the deposition support to produce SiC (W core) fibers [28]. Meanwhile, detailed studies on the reaction mechanism revealed characteristics such as microstructure and optimal

parameters.Nippon Carbon Co. first realized the industrial production of a series of continuous SiC fibers under the trademark Nicalon.(1) Continuous SiC fibers In the 1970s, Professor Yajima first obtained SiC fibers from a silicon-based polymer, polycarbosilane.Based on this modification, oxygen-free Hi-Nicalon and Hi-Nicalon type S fibers have been produced by Nippon Carbon, and these fibers can withstand temperatures up to 1500-2000 ?C.China started to synthesize polycarbosilane from polysilane according to a modified Yajiam route at normal pressure using domestic raw materials.China also developed Ti-containing SiC fibers and obtained continuous fibers longer than 300 m with a filament count of 400-600 [33].The composition, microstructure and properties of the Si3N4 fibers differ greatly depending on the polymers.If their green fibers are cured by c-ray irradiation, oxygen-free Si-C-N fibers can be obtained with a tensile strength and Young's modulus of 2.4 and 214 GPa, respectively.However, when the pyrolysis temperature was increased to 1100 ?C or 1250 ?C, the imaginary part of the permittivity (e?) of the trilobal SiC fibers is about 30-60 times that of circular fibers.Recently, the US company Textron (formerly AVCO Corporation) was allowed to produce a series of SCS-2, SCS-6 and SCS-8 SiC (C core) fibers.Research has been carried out in China on mercury electrode-heated CVD SiC (W core) fibers as early as 1975 [29].Fine-diameter continuous SiC fibers are finally obtained from polycarbosilane precursors.Therefore, Nicalon fibers are not good enough to be used as heat-resistant materials or as advanced composite reinforcements.One effective method is to reduce oxygen incorporation using oxygen-free approaches such as electron beam curing [31, 32].Furthermore, they have a low coefficient of thermal expansion, low thermal conductivity, good thermal shock resistance, good oxidation resistance and good insulation.The processing of Si3N4 fibers is similar to that of SiC fibers in terms of synthesis, spinning, curing and pyrolysis.Their pre-ceramic polymers are polysilazanes or polycarbosilazanes, which can be synthesized in various strategies.This fiber has high room-temperature strength and stiffness and is reported to have remarkable strength retention and creep resistance at elevated temperatures.(1) Non-circular SiC fibers A reason to change the cross section of SiC fibers from circular to non-circular can be explained using carbon fibers, which are radar reflection fibers with an electric resistance of about 10-2 X_cm.In 1972, US company AVCO Corporation produced large-diameter C-wire, and as a result, SiC (C core) fibers were produced with better performance and lower cost.Subsequently, from 1981 to 1984, SiC (C core) fibers were successfully commercialized by AVCO.The successful development of SiC fibers by the PPD method resulted in a large amount of interest from material scientists.Recently, plenty of research has been carried out on Nicalon fibers and their composites resulting in an understanding of their advantages and disadvantages.These elements are in the b-SiC (1-5 nm), SiCxOy and free carbon forms, respectively.However, this precursor is unstable in air, and the SiC fibers obtained had low tensile strength.The fiber diameter range is 14-16 lm, the tensile strength range is 2.20-2.80 GPa and the Young's moduli range is 160-180 GPa.Their tensile strengths are 2.8 and 2.2 GPa, respectively, with diameters of 12 lm and 13 lm, respectively.(3) Silicon Nitride (Si3N4) and Si-B-C-N Fibers As another type of important Si-based ceramic fibers, silicon nitride (Si3N4) fibers also have excellent mechanical properties [25].They synthesized a hydropolysilazane precursor via ammonalysis of dichlorosilane.The precursor only contains Si, N and H, resulting in plenty of Si-H bonds and N-H bonds and thus a very reactive material.Their diameter,

tensile strength and Young's modulus are 20 lm, 1.85 and 186 GPa, respectively. It produced a series of fibers referred to as SM1040, SM1140 and SM1240 with different surface coatings. This is the first ceramic fiber obtained using polymer techniques. Subsequently, Nippon Carbon procured the patent and started scale-up production. A series of fibers were then commercialized and trademarked as Nicalon, as listed in Table 2.28. They are thus more suitable for reinforcing aluminum matrixes. In addition, the creep resistance of the Al-containing SiC fibers is better than that of the Nicalon fibers. There are thus two strategies for the preparation of target Si3N4 fibers, pure Si3N4 fibers and Si3N4-SiC fibers. Their diameter is 10- 15 lm, their tensile strength is 3.1 GPa and their Young's modulus is 260 GPa. China has also carried out a series of similar studies and obtained Si-C-N-O fibers from chlorosilane. Pure SiC is a semiconducting material with an electrical resistance lies in the range of 104-106 X_cm. The properties of Nicalon serial fibers are listed in Table 2.28. These SiC fibers have been commercialized and have the trade name Tyranno. They can withstand temperatures up to 2000 ?C just like the Hi-Nicalon type S fibers. TNK began research into Si3N4 fibers slightly later than Dow Corning. Because Si3N4 and SiC coexist in the Si-C-N-O fibers, they are expected to have new features. After 1600 ?C treatment, their tensile strength and Young's modulus are still as high at 2.1 and 220 GPa, respectively. For use as good radar absorbents, their electrical resistance should be in the range of 101-103 X_cm. Therefore, measures are required to adjust their electrical resistance. They are all reinforcements with functional properties, as listed in Table 2.28. British company BP bought the original German technology for the production of SiC (W core) fibers. This lay the foundation for further enhancements of fiber performance and a reduction in production costs. Recently, a kind of carbon-free Si-B-N fiber has been developed in China [36]. It can then be easily used as reinforcements in complicated composites. In addition, the fiber surface is oxygen-rich in the form of SiO2. However, more oxygen was also introduced, which has negative influence on their thermal stabilities. The ultimate fibers are stoichiometric Si3N4. Their properties are listed in Table 2.29. They have good radar-absorbing properties. They can also absorb .microwaves if the shape and size of the cross section are changed