Development of polymer-derived SiC fiber

Jun Dong\textsuperscript{1,a}, Weicheng Bai\textsuperscript{1}, Guiliang Huang\textsuperscript{3}, Liang Han\textsuperscript{1} and Guangjun Zhang\textsuperscript{2*}

\textsuperscript{1}Aeronautical Repair Engineering Department, Aviation Maintenance Sergeant College, Air Force Engineering University, Xinyang, Henan, 464000
\textsuperscript{2}Military and Political Foundation Department, Air Force Engineering University, Xi’an, Shanxi, 710000
\textsuperscript{3}Aviation University Air Force, Changchun, Jilin, 130000
\textsuperscript{a}sbliu@nuaa.edu.cn
\textsuperscript{*}Corresponding author’s e-mail: zhanggj3@126.com

Abstract. The polymer—derived SiC fiber is one of the most important reinforcing materials for high performance ceramic matrix composites (CMC). Three generations of SiC fibers have been developed over the past thirty years. In this article, the preparing methods, compositions, microstructures and performances of three generation fibers are reviewed. Furthermore, the relationships are discussed between microstructure and the main properties of the fibers, such as high temperature-resistance and creep resistance. As a summary, some improving methods for the properties of SiC fibers derived from precursor are summarized.

1. Introduction

Ceramic matrix composites with high specific strength, high specific modulus, high temperature resistance, oxidation resistance and corrosion resistance are needed urgently to replace high temperature alloy and single-phase ceramics in many fields such as aviation, aerospace, atomic energy, high-property weaponry and high temperature engineering. SiC fiber has excellent properties high strength, high modulus, high temperature resistance, corrosion resistance, oxidation resistance, low density and adjustable resistivity, etc. that are incomparable to other inorganic fibers, which is mainly used for high temperature resistant ceramic matrix composites and has a wide range of applications in industries such as aviation, aerospace, metallurgy, weaponry and electronics. Specific application fields include: advanced aviation and aerospace vehicle structural components, high temperature engines, turbines, atomic reactor walls, structural radar absorbing materials, catalyst heat exchangers and combustion systems, gas filters in high pressure boiling combustion beds, thermal insulation materials in high temperature equipment and microelectromechanical system high temperature sensors, etc.

The high temperature property of SiC fiber is incomparable to other inorganic fibers: Glass fiber is not suitable to be used as ceramic matrix composite for its low modulus (<100GPa) and sharp decline in strength at 600°C; Carbon fiber is also very limited by its low oxidation resistance; although the oxidation resistance property of oxide ceramic fiber is excellent, it is not suitable to be used as high temperature reinforcement material due to the rapid growth of grain and the decrease of strength and strong creep caused by grain boundary diffusion. As SiC fiber has functions that cannot be replaced by other fibers, developed countries have invested a lot of money in the research and development of such ceramic fibers, with a view to achieving wide application in aviation, aerospace, automobile,
sporting goods and environmental protection. SiC fiber is an extremely important strategic material in the field of high technology of national defense, and it has great commercial value at the same time. At present, only Japan and the United States have mastered the commercial-scale production technology, and they have imposed strict technical blockade and product export restrictions on China. China must develop and study SiC fiber independently, especially SiC fiber with ultra-high temperature resistance, so as to promote the development of advanced composite materials and the research of weaponry in China, and improve China’s military strength and comprehensive national strength simultaneously.

At present, the main methods for producing continuous SiC fiber include: polymer-derived conversion method, chemical vapor deposition method and activated carbon fiber conversion method, etc. Among them, the polymer-derived conversion method is a mature and industrialized production method, which is the main direction of SiC fiber production and research.

2. Foreign development process of three generations of polymer-derived SiC fibers

2.1. First generation SiC fiber

In the 1970s, the research group of Professor Yajima in Japan adopted polycarbosilane (PCS) as the polymer-derived continuous SiC fiber with small diameter, namely Nicalon200. PCS remains the most successful and representative SiC fiber precursor up to now. Condense and polymerize dichlorodimethylsilane to synthesize polydimethylsilane (PDMS), and then further crack and rearrange PDMS to obtain PCS\[1,2\]. With a molecular weight of only 1,000 to 10,000, the protofilament of PCS obtained by spinning is very fragile, soluble and fusible. It needs to be oxidized in air or cross-linked to become insoluble and infusible fiber by other means, so as to retain the fiber shape at high temperature firing. Infusible fibers are generally fired in an inert atmosphere of 1,200 to 1,400°C, converting the fibers from organic polymers to inorganic SiC fibers. The resulting SiC fibers have a relatively low density and can be used at high temperature around 1,000°C. However, the oxygen mass fraction in the final fiber is 10% to 15% due to the introduction of air oxygen when having the infusible treatment of the air. Therefore, when the temperature is higher than 1,200°C, SiCxOy phase will have decomposition reaction to release SiO and Co gases and nano-SiC crystal will grow up, resulting in a large number of defects such as pores and cracks, etc. As a result, the strength and elastic modulus of the fiber decrease significantly \[3, 4\].

Japanese UBE Industries Ltd. grafted alkoxide Ti (OR) 4 of titanium to the main chain of PCS to generate titanium carbosilane precursor, which was used to produce Tyranno LOX-M fiber by utilizing air crosslinking with this precursor. The properties are shown in table 1 and 2.

Table 1. Comparison on manufacturers, element compositions and costs of three generations of SiC fibers

| Generation | Name       | Manufacturer                          | Crosslinking Method | Approximate Maximum Production Temperature / °C | Elementary Composition Mass Fraction /% | Density / (g/cm³) | Average Diameter /μm | Appraisal / USD. kg⁻¹ |
|------------|------------|---------------------------------------|---------------------|-----------------------------------------------|----------------------------------------|-------------------|----------------------|------------------------|
| First      | Nicalon200 | Japanese Carbon Company                | Oxidation           | 1,200                                        | 56Si+32C+12O                           | 2.55              | 14                   | 2,500                  |
|            | Tyranno LOX-M | Japanese UBE Industries Ltd.            | Oxidation           | 1,200                                        | 54Si+32C+12O+2Ti                       | 2.48              | 11                   | 1,500                  |
| Second     | Hi-Nicalon | Japanese Carbon Company                | Electron Beam       | 1,300                                        | 62.5Si+37C+0.5O                       | 2.74              | 12                   | 9,000                  |
| Generation | Name | Manufacturer | Treatment | Electron Beam Crosslinking | Chemical Composition | Thermal Expansion Coefficient Below 1,000°C (10^-6 /°C) | Axial Thermal Conductivity at Room Temperature (W/m.K) | Tensile Strength at Room Temperature (GPa) | Young Modulus at Room Temperature (GPa) |
|------------|------|--------------|-----------|---------------------------|---------------------|--------------------------------------------------------|-------------------------------------------|----------------------------------------|----------------------------------------|
| First Generation | Nicalon200 | Japanese Carbon Company |   | 3.2 | 3.0 | 3.0 | 200 |
| | Tyranno LOX-M | Japanese UBE Industries Ltd. | Oxidation Crosslinking | 3.1 | 1.5 | 3.3 | 285 |
| Second Generation | Hi-Nicalon | Japanese Carbon Company |   | 3.5 | 8.0 | 2.8 | 270 |
| | Tyranno LOX-E | Japanese UBE Industries Ltd. | Oxidation Crosslinking | N/A | N/A | 2.9 | 200 |
| | Tyranno ZM | Japanese UBE Industries Ltd. | Oxidation Crosslinking | N/A | 2.5 | 3.4 | 200 |
| | Tyranno ZE | Japanese UBE Industries Ltd. | Oxidation Crosslinking | N/A | N/A | 3.5 | 233 |
| Third Generation | Tyranno SA 1 | Japanese UBE Industries Ltd. | Oxidation Crosslinking | N/A | 6.5 | 2.8 | 375 |
| | Tyranno SA 3 | Japanese UBE Industries Ltd. | Oxidation Crosslinking | N/A | 6.5 | 2.9 | 375 |
| | Sylramic | American Dow Corning | Oxidation Crosslinking | 5.4 | 4.6 | 3.2 | 400 |
| | Sylramic iBN | American Dow Corning | Oxidation Crosslinking | 5.4 | >4.6 | 3.5 | 400 |
| | Hi-Nicalon Type-S | Japanese Carbon Company | Electron Beam Crosslinking | N/A | 1.8 | 2.5 | 400 |

Table 2. Comparison on properties of three generations of SiC fibers.
2.2. Second generation SiC fiber

Nicalon fiber, the first generation SiC Fiber, has relatively high oxygen content (13%), and a large number of thermal decomposition occurs in SiCxOy phase, resulting in the porous structure, and then oxygen diffuses easily to promote active oxidation. Hence, the second generation SiC fiber has specially taken some measures to reduce the oxygen mass fraction of the fiber and improve the high temperature property of the fiber. There have been methods such as plasma source infusible method, UV light irradiation crosslinking method, chemical vapor phase infusible method, NO2 and unsaturated hydrocarbon gas infusible method and electron irradiation infusible method, etc., reducing the oxygen mass fraction of the infusible fiber to different degrees. The second generation SiC fiber, including Hi-Nicalon and Tyranno LOX-E, of Tyranno ZM and Tyranno ZE of UBE Industries Ltd. Among them, a Japanese carbon company obtained Hi-NicalonSiC fiber by applying electron irradiation infusible method in 1995, and realized industrialization. The oxygen content of the fiber is reduced to be 0.5%, which determines that SiCxOy has less decomposition and compact structure, and is not conducive to oxygen diffusion, so that the degree of active oxidation is reduced. Moreover, the mass fraction of free carbon is relatively high, the preferential oxidation of free carbon has the effect of inhibiting the active oxidation of SiC, the grain size is larger than that of the first generation, the heat resistance and creep resistance are improved to a certain extent, and the temperature maintaining the maximum tensile strength increases from 1,200℃ of the first generation to 1,300℃. Hi-Nicalon in the air begins to oxidize when the temperature is higher than 800℃[5]. It may be the result of the free carbon of the fiber being more sensitive to the oxidizing atmosphere. However, when the temperature is lower than 1,400℃, the inactive oxidation of Hi-Nicalon still occurs; When the temperature is higher, the oxide layer is destroyed, failing to protect its interior from oxidation and producing bubbles. Bubbles arise because the excess carbon in Hi-Nicalon forms CO in a high-temperature oxidizing atmosphere.

Although the electron irradiation infusible method reduces the oxygen content effectively, the cost of electron beam equipment incurred is relatively high. UBE Industries Ltd. uses Zr to replace Ti to produce ZrSiC fiber (Tyranno ZM) through air infusible method, and the oxygen content of the fiber is 10%, which is lower than that of the fiber containing Ti. However, Tyranno LOX-E and Tyranno ZE are SiC fibers produced through electron beam irradiation infusible method, and it has no industrialization for the high oxygen content and high cost.

2.3. Third generation SiC fiber

It can be seen from the above that the high temperature resistance and creep resistance of the second generation fiber are improved, but the oxidation resistance is still not ideal. CMC, which is applied in many fields such as aviation and aerospace, requires its reinforced fibers to be used stably in air not lower than 1,300℃ and inert atmosphere not lower than 1,600℃. Therefore, it is necessary to further upgrade SiC fiber and the polycrystalline SiC fiber with close chemical ratio has been developed.

2.3.1. Hi-Nicalon type S fiber

Production of Hi-Nicalon type S: Adopt ordinary PCS precursor production technology, ordinary spinning technology, electron irradiation crosslinking process and pyrolysis in the hydrogen atmosphere. Since the production technology firstly contains pyrolysis in the special hydrogen atmosphere at 1,000℃, it is conducive to the removal of surplus carbon, and be fired at a high temperature finally to further increase the grain size. Therefore, the fiber consists of submicron β-SiC grains, a small amount of carbon and trace oxygen ultimately. This fiber has high Young modulus, high creep resistance, high oxidation resistance and good thermal stability below 1,600℃.

The Nicalon, Hi-Nicalon and Hi-Nicalon Type S fibers that the three fibers change significantly from amorphous to microcrystalline structure, and the heat resistance of SiC fiber also improves gradually.
2.3.2. Tyranno SA and SA-Tyrannohex fibers
Polyaluminocarbosilane (PACS), the precursor of Tyranno SA fiber is produced by the reaction of PCS and aluminum acetylacetonate, and the technological process: In a nitrogen atmosphere of 300°C, the condensation reaction between Si-H bond of PCS and the dentate of aluminum acetylacetonate occurs. Meanwhile, aluminum acetylacetone vaporizes, introducing Si-Al-Si and Si-O-Al bonds, thus the relative molecular weight of the polymer increases and the polyaluminocarbosilane is generated. The amorphous Si-Al-C-O fiber is obtained after the polyaluminocarbosilane going through 220°C melt spinning and 160°C air crosslinking and being fired in 1,300°C inert atmosphere. This fiber intermediate contains 12% carbon and oxygen. Si-Al-C-O fiber emits CO gas at 1,500 to 1,700°C, and then is sintered at a temperature higher than 1,800°C in argon. Aluminum plays the role of sintering aid in the sintering process, and finally Tyranno SA fiber is produced.

The production process of SA-Tyrannohex fiber precursor and the production process of Si-Al-C-O fiber are the same as that of Tyranno SA fiber. However, SA-Tyrannohex fiber adopts the hot-pressing sintering technology of the ceramic technology, that is, CO is released by hot pressing at 1,700°C to form Si-Al-C-O fiber one-way slice with a thickness of about 100μm, and then have hot pressing and sintering at 1,800°C (50MPa). In general, SiC materials are prone to have inactive oxidation at high temperature to form SiO2 protective layer, which can prevent oxygen from further reaction through the oxide layer effectively. However, when the temperature is below 1,600°C, the oxide layer is destroyed or volatile SiO is generated, that is, the active oxidation occurs, leading to a sharp decline in SiC quality. It seems that there is not protective layer, and its corresponding mechanical properties also decline sharply. SA-Tyrannohex fiber does not change in argon at 1,900°C, has no significant loss of mass in air at 1,600°C and maintains the initial strength. Therefore, SA-Tyrannohex fiber shows good heat resistance in air.

2.3.3. Sylramic fiber
For Sylramic fiber, Dow Coming of the United States used methyl polydisilazane and hydrogenated polysilazane as the precursors to produce silicon-carbon-nitrogen fiber in 1980. The highlight lied in the introduction of boron sintering aid in the sintering process, and sintered at 1,800°C to get the polycrystalline SiC fiber containing boron. The fiber has high strength and modulus and good heat resistance, and the continuous long fiber has been produced (the trade name is Sylramic)[6, 7]. Compared to Sylramic fiber, Sylramic-iBN generates BN in situ on the fiber surface and removes boron at grain boundary, which further improving its creep property.

Besides the above several foreign companies have made progress in the industrial development of polymer-derived SiC fiber, foreign institutions studying polymer-derived SiC fiber also include Bayer AG in Germany, Tohoku University in Japan, Institute of Special Inorganic Materials in Ibaraki-ken, Atomic Energy Laboratory in Takasaki, Florida State University and the University of Michigan in the United States and Domaine University in France, etc.

3. Domestic research progress of polymer-derived SiC fiber
SiC is a strategic national defense science and technology material and widely used in weaponry, so China also attaches great importance to the independent research and development of the technology and capability of SiC fiber. In recent years, China’s National University of Defense Technology and Xiamen University, etc. follow the international forefront closely, having done a lot of fruitful work in SiC fiber, precursor polyaluminocarbosilane and polymethylsilane synthesis.

National University of Defense Technology is the earliest unit of researching polymer-derived SiC fiber in China, which has experienced the process from experimental production of short fiber to the production of continuous fiber and industrial development. Corresponding to foreign three generations of SiC fibers, National University of Defense Technology also has developed KD-I, KD-II and KD-SA SiC fibers. It also has produced SiC fiber containing boron, aluminum, iron and nickel, and has made many innovations and improvements in links such as synthesis of polycarbosilane, melt spinning of polycarbosilane, infusible treatment and high temperature sintering, etc. Among them,
different from the synthesis of polycarbosilane at high temperature and high pressure of Japan, National University of Defense Technology has realized the synthesis method at room temperature and pressure and has realized mass production. Besides, it also applies the airflow yarn collecting method to solve the yarn collecting problem of fragile fibers. Meanwhile, it also has developed the structure-function integrated fiber for stealth, wave transmission and wave absorption, etc.

Under the leadership of Academician Zhang Li of the Chinese Academy of Engineering, Xiamen University has formed a manufacturing platform for high-property continuous ceramic fiber that is advanced internationally and the only one in China through independent research and development and international cooperative development. The property of the produced SiC fiber is close to that of similar Japanese products, and the technology of small batch is being perfected. The characteristic of Xiamen University lies in obtaining SiC fiber with low oxygen content and few defects through the infusible treatment by electron beam irradiation and thermochemical crosslinking and having high temperature firing.

4. Key technologies
In order to produce SiC fiber resistant to high temperature and oxidation, it is crucial to reduce the content of oxygen and free carbon in SiC fiber to produce SiC fiber with near chemical ratio and high density. There are the following main measures at present:

(1) Improve the production technology to minimize or avoid the introduction of oxygen. For example, non-oxygen infusible method is adopted: electron beam radiation crosslinking method, thermal crosslinking method, chemical gas crosslinking method or changing the spinning method. The precursor with high relative molecular weight is directly sintered to obtain low-oxygen SiC fiber after dry spinning without infusible treatment.

(2) Introduce heterogeneous elements. The main effects of introducing heterogeneous elements into ceramic precursor to improve the comprehensive properties of SiC fiber are as follows[8-13]: Improve the heat resistance of SiC fiber; Add sintering aids and adopt high temperature sintering; Inhibit the grain coarsening of ceramics at high temperature.

(3) Change the firing atmosphere: The firing of SiC fiber is usually completed in an inert atmosphere at about 1,300℃. The surplus carbon content in SiC fiber can be reduced by changing the firing atmosphere. Some alkyl groups in PCS can become alkanes and olefins in small molecules by firing gases such as H2, etc., so as to achieve the purpose of removing surplus carbon and generating SiC fiber with near chemical ratio.

5. Summary and prospect
SiC crystal is a covalent compound dominated by covalent bond. In the crystal, carbon and silicon are arranged in sp3 hybridization to form SiC crystal with diamond structure. Therefore, the ideal β-SiC can withstand high temperature up to 2,600℃. However, SiC fiber produced by polymer-derived conversion method is still far from this ideal level.

Nicalon fiber with high oxygen and carbon contents → Nicalon fiber with low oxygen and high carbon contents → Hi-Nicalon Type S fiber of stoichiometric ratio → Tyrannohex fiber adopting sintering aid densification → Syllramic fiber, amorphous SiBN3C fiber → SA-Tyrannohex fiber with hot pressed sintering, it is not difficult to find that researchers creatively used ceramic sintering technology to improve the density and properties of fibrous ceramics and produce high-property SiC fiber. Therefore, it has great significance for the improvement of fiber properties by studying SiC fiber from the perspective of ceramics, adopting appropriate sintering technology and optimizing and adjusting sintering technology.

The amorphous SiBN3C fiber produced by new polyborazine precursor by German Bayer A G is also an innovative initiative and angle, and we can obtain high temperature ceramic fiber from other high temperature ceramic angles. In addition, it also has profound significance on the promotion and application of SiC fiber by reducing the production cost and improving the spinning property of the fiber.
At present, the properties of the third generation of SiC fiber has basically met the needs of practical application. The CMC research on the third generation SiC fiber as the reinforcement has been widely carried out. It is not only applied in heat resistant parts of aviation and aerospace engines, thermal protection material systems of reusable vehicles and hypersonic transport propulsion systems, etc.[14-17], and also has extensive application potential in nuclear energy, high-speed brakes, hot-end components of gas turbines, high temperature gas filtration and heat exchangers, etc[18].

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