Effect of Intrinsic Structure on Stability of Domestic SiC Fiber

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Abstract. The morphology, structure and composition of three different SiC fibers were studied by SEM, XRD and elemental analysis techniques in this paper. The high temperature stability of SiC fiber bundles was also characterized. The results show that the intrinsic structure of domestic first, second, and third generation silicon carbide fibers possesses large differences. The above three fibers can be classified into high oxygen high carbon, low oxygen high carbon and near stoichiometric ratio according to the composition, and classified into amorphous, low crystallinity and high crystallinity according to the structure. The difference in composition and structural characteristics of the above fibers has a great influence on the comprehensive properties of SiC fibers, especially the oxidation resistance. The high temperature oxidation resistance of the first, second and third generation SiC fibers increases gradually, which provides material basis and technical support for the preparation of ceramic matrix composites suitable for hot end components of aero-engines with different thrust-weight ratios.

1. Introduction

SiC/SiC composites have the advantages of light weight, oxidation resistance, high temperature resistance and excellent environmental performance which have wide application prospects in aero engine the hot end components, aerospace vehicle thermal protection system and so on [1-3].

As the reinforcing phase and dispersed phase, SiC fiber is the main bearing structure of SiC/SiC composites, which determines the mechanical properties of SiC/SiC composites, especially the strength of materials. Currently, commercialized SiC fibers can be divided into three generations. The first generation is the high oxygen and high carbon SiC fiber, represented by the Nicalon 200 fiber of Nippon Carbon and the Tyranno Lox-M fiber of Ube Industries. The second generation is the high oxygen and low carbon SiC fiber, represented by the Hi-Nicalon fiber of Nippon Carbon and the Tyranno Lox-E, Tyranno ZM and Tyranno ZE fibers of Ube Industries. And the third generation of SiC fibers is near stoichiometric ratio fiber represented by Hi-Nicalon Type S fiber of Nippon Carbon, Tyranno SA fiber of Ube Industries and Sylramic fiber of Dow Corning. With the support of our country and the efforts of scientific researchers, the first and second generation SiC fibers have been commercialized, and the key technologies for the third generation SiC fiber preparation have been broken [4-7].

This paper aims to explore the evolution of mechanical properties evolution of SiC fiber bundles by studying the intrinsic structures of the domestic first, second and third generation SiC fiber, such as
morphology, structure and composition which will provide technical support and theoretical support for the environmental performance analysis of SiC/SiC composites and failure mechanism research of hot end components.

2. Experimental

2.1. Preparation of SiC fiber test samples.

The domestic first, second and third generation SiC fibers were cut to a specific length and placed in a muffle furnace for static oxidation test in the temperature range of 800°C~1400°C.

2.2. Testing of intrinsic properties and structural stability of SiC fibers.

The morphology was measured by SEM (Hitech S-4800) and the phase structure of SiC fibers was tested by XRD on PANalytical X’Pert PRO. The composition of fiber was detected using an elemental analyzer. The mechanical properties of SiC fibers were tested on a universal material tensile tester (Instron 5567).

3. Results and analysis

3.1. Characterization of intrinsic properties of SiC fibers

The intrinsic properties such as density, tensile strength and oxygen content of domestic first generation, domestic second generation and domestic third generation SiC fibers are shown in Table 1. The density, tensile strength of the domestic first, second and third generation SiC fibers increased gradually. It's remarkable that oxygen content of the domestic second and third generation SiC fibers decreased significantly to less than 1.00%. The test results show that the density and increases gradually and the oxygen content decreases greatly of SiC fibers with the improvement of the preparation process, which is of great significance for improving the high temperature stability of SiC fibers.

| Fiber type          | Density (g/cm³) | Tensile strength (MPa) | Oxygen content (wt%) |
|---------------------|----------------|------------------------|----------------------|
| First generation SiC fiber | 2.44          | 2291                   | 10.48                |
| Second generation SiC fibers     | 2.65          | 2458                   | < 1.00               |
| Third generation SiC fibers       | 2.95          | 3517                   | < 1.00               |

3.2. Morphology analysis of SiC fibers

The domestic first, second and third generation SiC fibers were put into muffle furnaces and static oxidation tests were carried out at 800°C, 1200°C and 1400 °C. Figures 1 to 3 are the SEM photos of the three generation SiC fibers mentioned above after oxidation.

Results show the domestic first, second and third generation SiC fibers all show smooth surface and compact structure at room temperature, which lays a good foundation for the subsequent preparation of interface layer or fiber preforms. When the oxidation temperature rises to 800 °C, the three kinds of fibers still show good structural stability in morphology, without cracks, peeling and other defects. However, when the oxidation temperature rises to 1200 °C, the three kinds of fibers show different morphology. Especially the first generation SiC fibers become rough with a small amount of small particle impurities attached to the surface, and a small amount of cracks begin to appear. No obvious defects have been found on the surface of the domestic second and third generation SiC fibers. The above phenomena are mainly attributed to the high oxygen content of the first generation SiC fibers, which contains a large amount of amorphous and easily decomposable SiC₆O₇ phase at high temperature.
When the oxidation temperature rises to 1400 °C, cracks appear on the surface of most of the first domestic generation SiC fibers, resulting in serious damage to the fiber structure stability. Partial surface cracks and material stability of the second-generation SiC fiber in China were also seriously affected. The surface of the domestic third-generation SiC fiber was not found to change significantly, and it still showed the characteristics of smooth surface and compact structure. Cracks appear on the
surface of some domestic second-generation SiC fibers, which may cause serious structural stability. Unlike other SiC fibers, the surface of domestic third generation SiC fiber shows no obvious change, and it still expose the characteristics of smooth surface and compact structure.

![Figure 3. Morphology of domestic third generation SiC fibers after oxidation.](image)

### 3.3. Phase analysis of SiC fiber

In order to further study the evolution mechanism of structural and components of different SiC fibers in high temperature oxidation environment, XRD test technology was used to analyze the structural and components of SiC fibers after oxidation at different temperatures in this study.

The experimental results show that the intrinsic phase structure at room temperature shows a typical amorphous phase for the domestic first generation SiC fibers. When the oxidation temperature was raised to 800 °C, a distinct diffraction peak of SiO₂ appears at 2θ=22.30°, indicating that SiC fibers undergo oxidation reaction, which is disadvantageous to the high temperature stability of the fibers. As the oxidation reaction continues, the diffraction peaks of the oxidation products were still maintained in the XRD spectrum under the oxidation conditions of 1200 °C and 1400 °C. For the domestic second generation SiC fibers, the room temperature intrinsic phase structure exhibits a distinct structurally ordered crystal structure, and a distinct SiC diffraction peak appears at 2θ=35.8°. Moreover, the oxidation reaction starts at 800 ° C and a distinct diffraction peak of SiO₂ still exists between 800 °C and 1400°C. It is worth noting that for the domestic first and second generation SiC fibers, the diffraction peaks of SiO₂ appearing near 2θ=22.30° in the oxidation products at 800°C are significantly stronger than those at 1200 °C. This may be mainly attributed to the fact that the oxidation product SiO₂ is loose in structure which is difficult to form a dense oxide film to prevent the aggravation of oxidation reaction. The intensity of SiO₂ diffraction peak increases obviously When the oxidation temperature up to 1400°C, which may lead to the instability of the structure for the domestic first and second generation SiC fibers [8,9].
For the domestic third generation SiC fibers, the intrinsic phase structure at room temperature is similar to that of the domestic second generation SiC fibers, and both exhibited obvious ordered $\beta$-sic crystal structure. More importantly, the domestic third-generation SiC fiber did not show the diffraction peak of SiO$_2$ at the oxidation temperature of 800°C and 1200°C, indicating that the oxidation SiO$_2$ film is very thin and dense and it was difficult to detect by XRD technology. The oxidation film mentioned above was conducive to inhibiting the continuous oxidation reaction, indicating that the oxidation resistance of the domestic third generation SiC fiber is significantly improved compared with the domestic first generation and second generation SiC fibers. When the oxidation temperature up to 1400 °C, obvious SiO2 diffraction peak appears in the XRD spectrum which is not conducive to the high temperature stability of the SiC fibers and even the even ceramic matrix composites for the obvious oxidation reaction.

**Figure 4.** XRD Spectra of the domestic first generation fibers.

**Figure 5.** XRD Spectra of the domestic second generation fibers.
3.4. Mechanical properties of SiC fibers

The domestic first, second, and third generation SiC fibers oxidized at different temperatures are tested on an Instron 5567 universal material tensile machine, and the tensile strength test results are shown in figure 7, figure 8 and figure 9, respectively. The test results show that the tensile strength of the domestic first generation SiC fibers at room temperature is 2291 MPa, and the retention rates of mechanical properties are 72.02%, 60.28% and 51.72% respectively when the oxidation temperature rises to 800 °C, 1000 °C and 1200 °C. At an oxidation temperature of 1400 °C, the bundle fibers become particularly brittle and can't be tested, so the tensile strength and strength retention were marked as zero.

The mechanical properties of the domestic second generation SiC fibers are better than those of the domestic first generation SiC fibers from room temperature to 1200°C. The tensile strength reaches
1987 MPa with the retention rate of 74.89%, in the oxidation environment at 1200 °C. However, the fibers become very brittle in the oxidation environment at 1400 °C which was similar to the domestic first generation SiC fiber. All the mechanical strength test results of the domestic first and second generation SiC fibers are in good agreement with those of the fibers tested by SEM and XRD analysis [10,11].

![Second generation](image1.png)

**Figure 8.** Tensile strength of second generation fibers at different oxidation temperatures.

![Third generation](image2.png)

**Figure 9.** Tensile strength of third generation fibers at different oxidation temperatures.

The mechanical properties of the domestic third generation SiC fiber have been greatly improved. The tensile strength of the room temperature bundle filaments is up to 3517 MPa, which is 1.54 times and 1.33 times of the domestic first and second generation SiC fibers respectively. More importantly, the tensile strength of the bundle wire is as high as 2619 MPa at the oxidation temperature of 1200 °C, which is equivalent to the tensile strength of the domestic second generation SiC fibers at room temperature. In particular, the tensile strength of the fibers was 1969 MPa, and the strength retention ratio was 56.04% when the oxidation temperature was raised to 1400 °C. On the contrary, the
domestic first generation and second generation SiC fibers were particularly brittle and their mechanical strength fails at this temperature.

In summary, the domestic third generation SiC fiber overcomes the defects of poor stability and low strength of the first generation and second generation SiC fibers above 1400 °C, and lays a good technical foundation for the preparation of SiC/SiC composites as high thrust-to-weight ratio aeroengine hot end components.

4. Conclusion
(1) The oxidation reactions of domestic first generation and second generation SiC fibers start at 800 °C with obvious SiO₂ diffraction peaks existing in the phase, and the tensile strength decreased to 1185 MPa and 1987 MPa respectively in the oxidation medium at 1200 °C. Crack defects occurring in both fibers in the oxidation medium at 1400 °C cause in significant instability structure and decrease in mechanical properties, resulting in fibers not being used as reinforcing phases.

(2) The domestic third generation fibers have excellent comprehensive properties, such as high densification, high tensile strength and low oxygen content. In the range of room temperature to 1400 °C, the SiC fibers always maintain smooth surface and compact structure. The tensile strength of the fiber is 3517MPa at room temperature, and the strength retention rate is as high as 74.47% and 56.04% at oxidation temperatures of 1200°C and 1400°C respectively, which is significantly better than the domestic first and second generation SiC fibers. So, the excellent comprehensive performance of domestic third generation fibers, especially good oxidation resistance and high temperature structural stability, lays good material basis and technical support for the preparation of SiC/SiC composites suitable for hot end components of aero-engines with different thrust-weight ratios.

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