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Effects of Oxidation Behavior on the Strength and Thermal Resistance of Continuous Silicon Nitride Fibers

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Abstract: This study evaluates the oxidation resistance and the thermal stability in inert atmosphere of silicon nitride fibers. Results show that when the silicon nitride fibers are oxidized at 1000 ℃ for 1 h, they possess the highest tensile strength (1.53 GPa) because of the surface defect healing effect of the glassy phase, whereas those oxidized at higher temperatures exhibit lower strength than the non-oxidized fibers. After treatment at 1200 ℃ in air, they retain 63% of strength, which indicates that the fiber may possess high serving life at the temperature lower than 1200 ℃. Besides, the strength retention of the fibers after treatment at 1450 ℃ for 1 h in nitrogen remains 57%, showing good thermal stability. However, surface oxidation adversely affected the thermal stability of the fibers at high temperatures in nitrogen because of the predominant oxygen-containing phase. Above 1500 ℃, crystallization of Si_3N_4 along with decomposition of SiN_xO_y occurs, resulting in a considerable decrease in mass and a catastrophic decrease in strength for the oxidized fibers.

Key words: silicon nitride fibers; surface oxidation; strength improvement; thermal resistance

Silicon nitride materials have been intensively studied for several decades because of their intriguing structural properties, including high tolerance to mechanical stress, good thermal stability, and excellent oxidation resistance. Owing to their low dielectric constant and high electrical resistivity, silicon nitride ceramics are considered superior wave-transparent and electrical insulating materials that can be used in high-temperature applications[1,2]. Continuous silicon nitride ceramic fibers are optimal candidates for the reinforcement of wave-transparent ceramic-matrix composites (CMCs)[3-5]. However, very few studies have been conducted on continuous silicon nitride fibers, because of the difficulty in the preparation of these fibers[6].

The oxidative resistance of silicon nitride fibers is of great importance for application as reinforcements of CMCs in extreme environments. To the best of our knowledge, however, there is scarce information in the literature concerning their oxidation behavior or effects. In the present work, the influence of oxidation on the fiber tensile strength was investigated. Moreover, the thermal stability of the oxidized fibers was assessed at temperatures up to 1500 ℃ and compared with that of the original fibers.

1 Experiment

The as-prepared silicon nitride fibers produced in our laboratory were strands of 1000 single filaments, with a molar composition of $SiN_{1.21}C_{0.03}O_{0.03}$. To determine their oxidation resistance, the fibers were oxidized by heating at temperatures from 1000 ℃ to 1300 ℃ under a normal atmosphere in a muffle furnace for 1 h at a heating rate of 10 ℃·min^{-1}. Then, the fibers were cooled to room temperature in the furnace.

For high-temperature treatment experiments, the fibers were placed in graphite boats and heated at a rate of 5 ℃·min^{-1} in a carbon-resistant furnace. They were maintained at the annealing temperature (1450 or 1500 ℃) for 1 h under N_2 flow (99.9999%, Xiangfeng Co. Ltd, China).

The tensile strength and Young's modulus of the fibers were measured using an Instron-type test machine (Micro-350, Testometrix), with a gauge length of 25 mm and a crosshead speed of 5 mm·min^{-1}. The average value was obtained from the measured results for 24 filaments. X-ray photoelectron spectra (ESCALAB 250Xi, Thermo Fisher) were recorded using an Al Kα excitation source to detect

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the surface compositions and chemical bonding states in a few atomic layers. Prior to X-ray photoelectron spectroscopy (XPS) analysis, the fibers were cleaned by argon ion bombardment. The depth profile of the fiber surfaces was obtained by Ar^+ etching for 15, 85 and 225 s, with a sputtering rate of 7.2 nm·s^{-1}, using Ta_2O_5 as a reference. The phases of the fibers were characterized by X-ray diffraction (XRD, D8 Advance, Bruker), using Cu Kα irradiation (λ=0.154 nm) at a scanning rate of 2θ=0.15 ° per step. The microstructure of the samples was observed by scanning electron microscopy (SEM, S-4800, Hitachi). The quantitative analysis of nitrogen and oxygen was carried out using a N/O analyzer (EMGA-820, Horiba), and the carbon was measured using a C/S analyzer (EMIA-320V2, Horiba). Atomic force microscopy (AFM) experiments were performed on a Bruker Dimension Fastscan system with a silicon probe in non-contact mode. The roughness was determined by treating and analyzing the images using nanoscope analysis software.

2 Results and Discussion

2.1 Characterization of as-prepared and oxidized fibers

According to Table 1, the tensile strength of silicon nitride fibers retains a higher value (1.53 GPa) after heat treatment at 1000 ℃ for 1 h in air. However, when the oxidizing temperature increases to 1100 ℃ and 1200 ℃ (for 1 h in air), the tensile strength decreases to 1.21 GPa and 0.83 GPa, respectively. As indicated in Fig.1, the morphology of the fractured surface of a single fiber after heat treatment (up to 1200 ℃ for 1 h in air) is very similar to that of the fresh fibers[7]. No additional flaws are observed, but the failure strength has decreased. After oxidation at 1300 ℃, the fiber loses its strength and the crystals are formed on the fiber surface, resulting in adhesion of the filaments to one another.

Below 1000 ℃, the oxygen increment is not conspicuous, indicating that the silicon nitride system exhibits excellent oxidation resistance. As the oxidizing temperature is increased to above 1000 ℃, SiO_2 structures begin to form on the fiber surfaces (Reaction (1)), according to the Si 2p XPS spectra shown in Fig.2.

$$Si_3N_4\ (s) + O_2\ (g) \rightarrow SiO_2\ (s) + N_2\ (g) \quad (1)$$

As shown in Fig.2 and Table 2, the Si 2p peak of the fibers oxidized above 1100 ℃ could be attributable to the SiO_2 phase[8]. Furthermore, the peaks at 102.2 and 101.3 eV are assigned to the SiN_xO_y phase and Si_3N_4 structure[9,10], respectively. Based on the bulk oxygen increment described in Table 1, thicker SiO_2 layers are formed at higher oxidizing temperatures, consequently decreasing the strength.

The crystalline structures of the oxidized fibers were investigated by XRD analysis, as shown in Fig.3. It can be seen that the fibers remain almost amorphous in the temperature range of room temperature to 1200 ℃. Since the degree of oxidation increases with heat-treatment temperature, α-cristobalite phase can be found when the heat-treat temperature is 1300 ℃, confirming that the crystals formed on the fiber surface in Fig.1 are SiO_2 grains.

2.2 Increase in fiber strength after oxidation

The surface morphology of the as-prepared fibers and oxidized fibers was analyzed using AFM. Both images are presented at the same scales to facilitate their direct comparison.

Table 1 Elemental composition (bulk analysis) and mechanical properties of the fibers

Fiber	O content/ wt%	N content/ wt%	C content/ wt%	Tensile strength/ MPa	Young's modulus/ GPa	Diameter/ μm
As-prepared	0.95	37.05	0.85	1.31	152	12.6
1000 ℃	1.91	36.56	0.83	1.53	152	12.7
1100 ℃	2.60	36.16	0.82	1.21	152	12.9
1200 ℃	2.95	35.98	0.82	0.83	136	12.9
1300 ℃	11.80	32.11	0.70	-	-	-

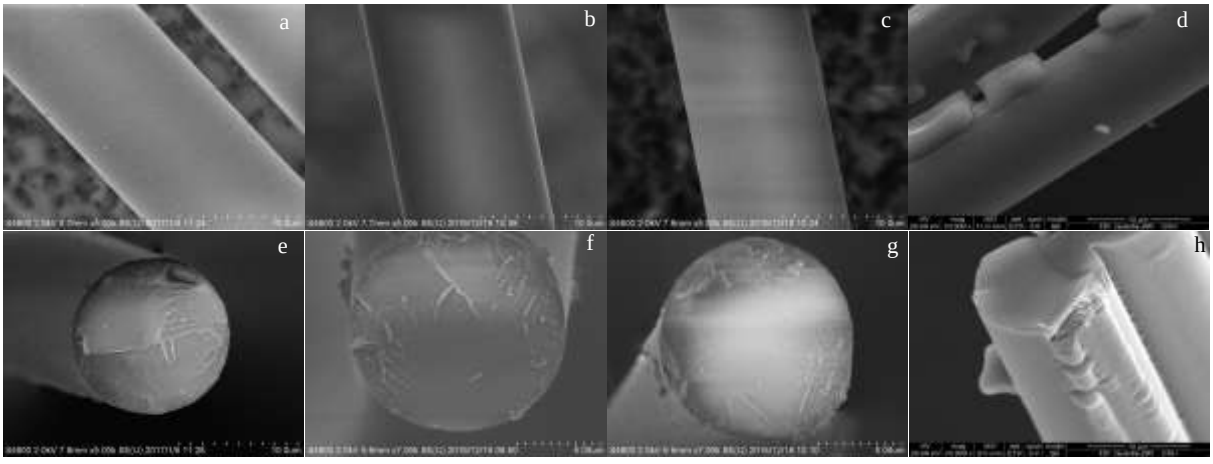

Fig.1 SEM images of silicon nitride fibers after oxidation at 1000 ℃ (a, e), 1100 ℃ (b, f), 1200 ℃ (c, g) and 1300 ℃ (d, h)

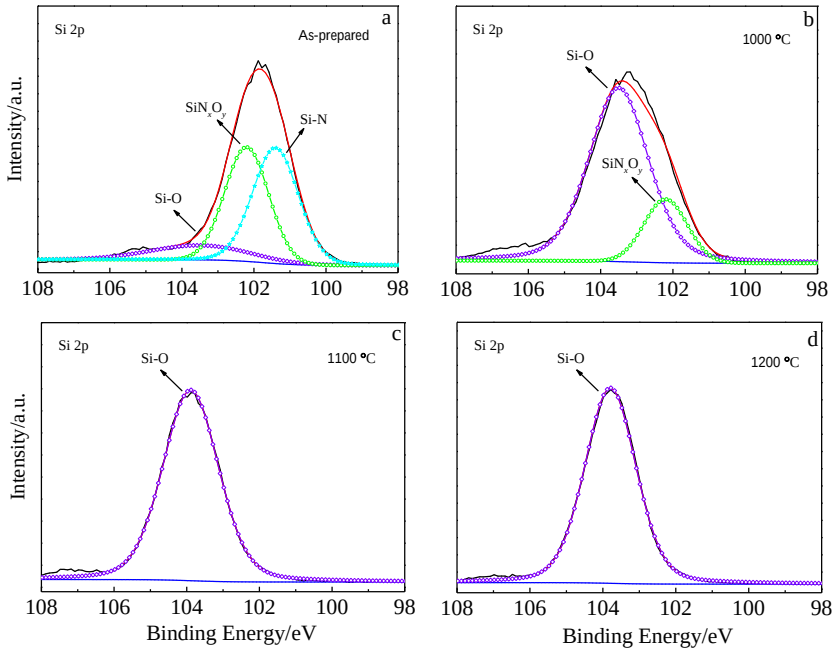

Fig.2 High-resolution XPS spectra of silicon nitride fibers after oxidation at different temperatures: (a) as-prepared, (b) 1000 °C, (c) 1100 °C, and (d) 1200 °C

Table 2 Surface composition of the fibers (by XPS analysis)

Fiber	Surface composition/at%				Si 2p/%		
	Si 2p	C 1s	N 1s	O 1s	SiO_2	SiN_xO_y	S_3N_4
As-prepared	38.07	8.36	43.86	9.71	11.9	42.0	46.1
1000 ℃	34.84	5.58	11.36	48.22	81.0	19.0	-
1100 ℃	33.86	4.1	0.52	61.52	100	-	-
1200 ℃	31.46	4.74	0.51	63.27	100	-	-

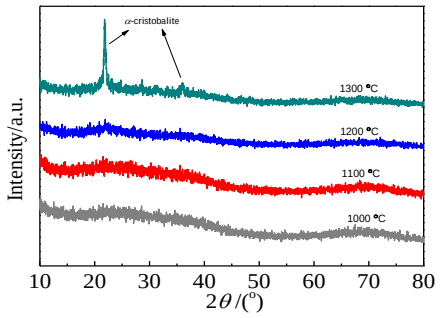

Fig.3 XRD patterns of silicon nitride fibers after oxidation

The surface roughness in the AFM images was also characterized based on the arithmetic average roughness (R_a) and root mean square roughness (R_q). As seen in Fig.4a, the original fibers present a rather rough surface with pits and bulges. However, it is difficult to observe these minor defects solely by SEM. Structural defects such as pores are usually generated owing to the release of gases and backbone breakage during nitridation[11]. In comparison, the oxidized fiber surface has a broader depth distribution and higher maximum depth, with lower frequency of peaks, possibly due to the inhomogenous

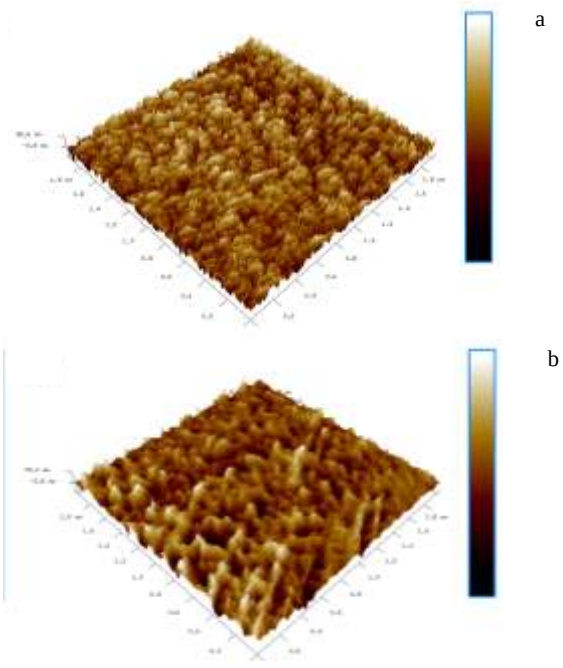

Fig.4 AFM images (3D height representation) of the as-prepared fibers (a) and 1000 ℃-oxidized fibers (b)

growth of SiO_2 and the flaw-repairing effect. AFM analysis (Table 3) shows that the roughness values of oxidized fibers are higher than those of the original fibers, which indicates that the extra roughness caused by oxidation does not adversely affect the mechanical properties of the fibers. Léon[12] stated that the higher the roughness in the phase angle contrast, the better the mechanical properties will be for the corresponding carbon fibers prepared through controlled stretch in an oxidizing atmosphere. It could be concluded that when the fibers are oxidized at 1000 ℃, a glassy phase is formed for repairing the surface nanopores despite the increased roughness, thus resulting in higher strength.

The depth profile in Fig.5 confirms that oxidization occurs primarily at the fiber surface. As the surface etching thickness increases, the degree of oxidation decreases.

2.3 High-temperature behavior of as-prepared and 1000 ℃-oxidized fibers

Although the strength of the oxidized fibers increases as compared to that of the original fibers, their thermal stability in nitrogen decreases considerably. From our experience, the tensile strength of silicon nitride fibers decreases drastically when annealed above 1400 ℃. Specifically, as shown in Table 4, the as-prepared fibers treated in N_2 at 1450 ℃ retain 57% of their original strength, while the oxidized fibers lose their strength after annealing at the same temperature. Comparison of the SEM images of the fibers (Fig.6) explains the difference in strength. The fibers exposed at 1450 ℃ have a smooth and glassy appearance in the as-prepared state, while the oxidized fibers have a slightly rough surface with visible

Table 3 Roughness of the as-prepared fibers and 1000 ℃-oxidized fibers

Fiber	R_a/nm	R_{ms}/nm
As-prepared	8.71	10.9
1000 ℃	14.4	19.1

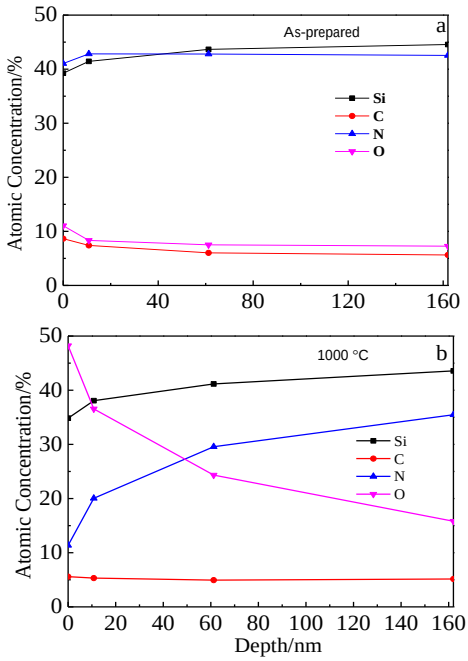

Fig.5 XPS depth profiles of as-prepared fibers (a) and 1000 ℃-oxidized fibers (b)

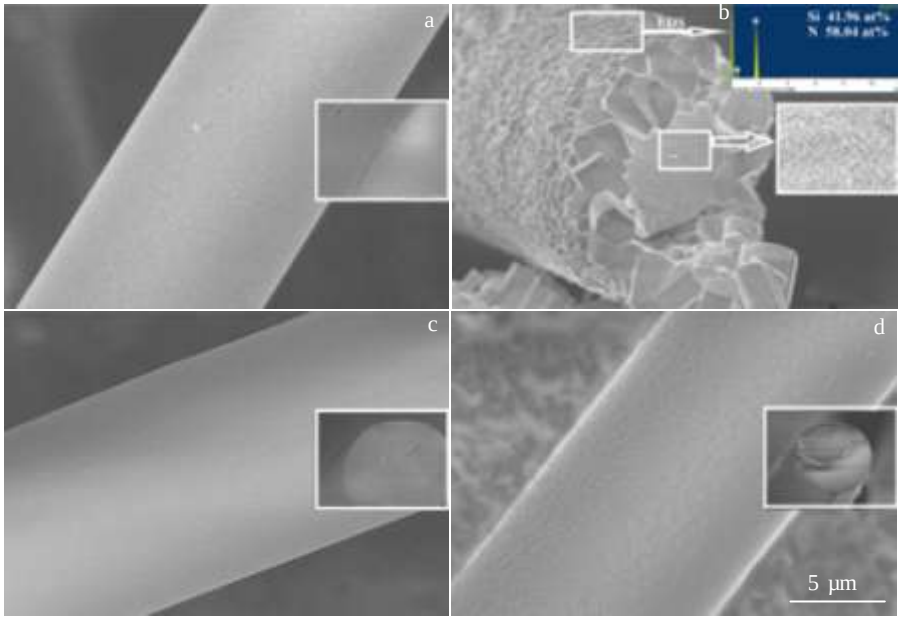

Fig.6 SEM micrographs of the 1000 ℃-oxidized fibers (a, b) and the as-prepared fibers (c, d) annealed in N_2 at 1450 ℃ (a, c) and 1500 ℃ (b, d)

Table 4 Chemical composition, mechanical properties, and residual mass of fibers at high temperatures

Fiber	O content/wt%	N content/wt%	C content/wt%	Tensile strength/MPa	Young's modulus/GPa	Residual mass/%
As-prepared	0.95	37.05	0.85	1.31	152	100
1450 ℃	1.09	37.28	0.85	0.75	142	98.6
1500 ℃	1.11	37.78	0.86	-	-	98.3
Oxidized	1.91	36.56	0.83	1.53	152	100
Oxidized-1450 ℃	1.46	37.50	0.80	-	-	97.4
Oxidized-1500 ℃	1.03	37.69	0.80	-	-	89.6

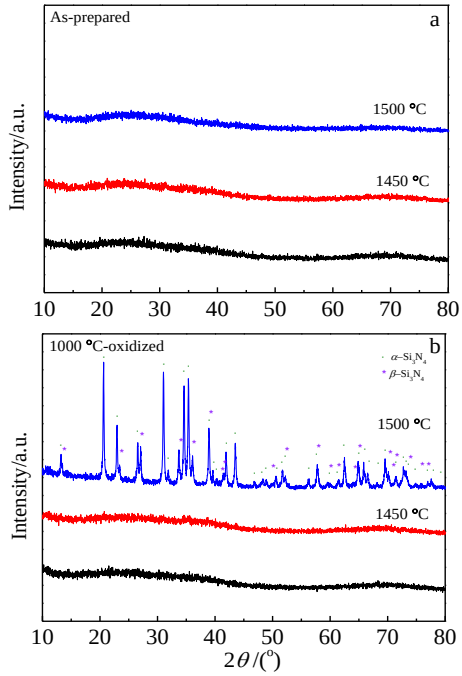

Fig.7 XRD patterns of the as-prepared fibers (a) and the 1000 ℃-oxidized fibers (b) annealed in N_2

defects. After exposure at 1500 ℃, pores begin to form on the surface of the as-prepared fibers. Nevertheless, large Si_3N_4 crystals are formed on the surface of the oxidized fibers, as confirmed by Fig.7. Moreover, the single-fiber core is no longer smooth, but rather rough with pores.

The results of bulk elemental chemical analysis, combined with the residual mass measurements of the various fibers, are shown in Table 4. The mass loss is extremely small for the as-prepared fibers annealed up to 1500 ℃. Conversely, this value dramatically increases up to 10.4% at 1500 ℃ for the oxidized fibers. The oxygen, nitrogen, and silicon contents are maintained at the same level for the original fibers annealed up to 1500 ℃ in N_2, while an obvious decrease in oxygen content is observed for the oxidized fibers that were heat-treated at high temperatures.

The negligible decrease in residual mass, along with the stable elemental composition, suggests that the thermal decomposition of SiN_xO_y occurs here to a minor extent via Reaction (2)[13]. However, crystallization is observed for the oxidized fibers treated at 1500 ℃. This phenomenon indicates that the decomposition of large amounts of SiN_xO_y not only yield SiO and N_2, but also produce crystalline Si_3N_4 above 1500 ℃ according to Reaction (3), as previously reported by Chollon et al[14]. Reaction (4), as reported by Mocaer et al[15], may also occur. This assumption is supported by the homogeneous distribution of crystals on the fiber surface and the decreased weight percentage of oxygen, which implies additional oxygen loss. The release of oxygen may cause the formation of pores inside the fibers, as shown in the inset of Fig.6b. The occurrence of Reactions (3) and (4) consequently leads to mass loss, which is dependent on the amount of the SiN_xO_y phase and the rates of these reactions[13].

$$SiN_xO_y\ (s) \rightarrow SiO\ (g) + N_2\ (g) \quad (2)$$

$$SiN_xO_y\ (s) \rightarrow SiO\ (g) + N_2\ (g) + Si_3N_4\ (s) \quad (3)$$

$$SiO\ (g) + N_2\ (g) \rightarrow Si_3N_4\ (s) + O_2\ (g) \quad (4)$$

3 Conclusions

1) Oxidation treatment has both favorable and unfavorable effects on the strength of silicon nitride fibers. Surface oxidation increases the fiber strength due to the surface flaw healing effect; however, the strength of the fibers is degraded probably because of the brittle nature of the SiO_2 layer and the easy formation of crystals which cause adhesion of the filaments to one another.

2) The 1000 ℃-oxidized fibers show a higher tensile strength while the elastic modulus remains unchanged.

3) After exposure at 1450 ℃ in N_2, the strength of the oxidized fibers is greatly diminished, while the as-prepared fibers retain 57% of their original strength. Above 1500 ℃, crystallization of Si_3N_4 along with decomposition of SiN_xO_y occurs, resulting in a considerable decrease in mass for the oxidized fibers.

4) The appropriate surface oxidation improves the strength of silicon nitride fibers but degrades their thermal resistance.

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连续氮化硅纤维的氧化行为与高温影响研究

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摘　要：连续氮化硅陶瓷纤维是透波/承载一体化陶瓷基复合材料的关键原材料，也是制约复合材料耐高温性能与力学性能的关键因素。系统研究了国防科技大学研制的连续氮化硅纤维的抗氧化性能，分析了高温处理后纤维的组成结构与力学性能变化规律。结果表明：1000 ℃氧化 1 h 后纤维强度高于原始纤维强度，主要是形成的玻璃相能减少和弥补纤维的表面缺陷。随着空气中处理温度提高，氧含量增加，纤维表面形成的 SiO_2 层逐渐变厚，纤维强度明显降低。纤维在 1200 ℃氧化 1 h 后强度保留率为 63%，表明在此温度以下纤维有较好的服役性能。另一方面，氮化硅纤维在 1450 ℃ N_2 中处理 1 h 的强度保留率为 57%，表现出良好的耐高温性能。纤维表面氧化对其在 N_2 下的耐高温性能具有不利影响，1000 ℃氧化的纤维在 1450 ℃处理后丧失强度，1500 ℃处理后形成氮化硅结晶，失重明显增长，纤维内部也开始产生缺陷。

关键词：氮化硅纤维；表面氧化；强度提升；高温性能

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