Fabrication of Silicon Nitride Fiber Materials by Organic Foam Impregnation Method

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Abstract. In this paper, porous silicon was prepared by organic foam impregnation, and silicon nitride fibers were prepared by direct in-situ nitridation of porous silicon. The effect of pore structure of porous silicon on material properties was studied. The results show that the silicon nitride fiber material with low density, high strength and low thermal conductivity can be obtained by using organic foam impregnation method. The pore size of template has a certain effect on the growth of silicon nitride fibers. The smaller the pore size of the template, the higher the content of silicon nitride in silicon nitride fiber material. This is due to the concentration of gas phase reactants in pore.

1. Introduction

Silicon nitride is widely used as high temperature structural materials, transmissive materials and semiconductor materials because of its high strength, good toughness, thermal chemical corrosion resistance, good thermal shock resistance and good transmissibility. However, the thermal conductivity of silicon nitride is very high, which has gradually become a disadvantageous factor restricting its wider application. For example, the new energy-saving aluminum electrolyzer requires good thermal insulation and cryolite vapor corrosion resistance, while the microwave sintering furnace requires good thermal insulation and wave transmission performance of lining materials. If silicon nitride is made into porous or fibrous structural materials with low density, low thermal conductivity and low thermal capacity, it will have excellent thermal insulation performance [1]. It can not only meet the high requirements of thermal insulation in the new technology field, but also be expected to be used for filtering corrosive flue gas and wastewater. The mature preparation method of silicon nitride fiber is precursor conversion method. The prepared silicon nitride fiber has excellent properties and can be used as reinforcement of cermet matrix composites and preparation of heat-proof functional composites [2]. It is used in aerospace and military fields, but the disadvantage is that the preparation cost is expensive. Silicon nitride fibers can also be grown by gas-solid-liquid (VLS) and gas-solid (VS) mechanisms. The specific preparation methods include direct nitriding, carbothermal reduction [3], Precursor Pyrolysis, amorphous silicon nitride conversion [4], chemical vapor deposition, etc. Silicon nitride nanofibers prepared by direct nitridation have many problems, such as low yield, difficult collection and separation from impurities. Therefore, the cost of synthesizing silicon nitride fiber products by traditional two-step method will be very high, which limits its application in the industrial field.

From the growth mechanism of silicon nitride fibers, enough silicon, nitrogen sources and fiber growth space are the necessary conditions to ensure the full growth of silicon nitride fibers. In the
preparation of silicon nitride fibers mentioned above, the growth raw materials are nitrided in the form of natural accumulation or pressing, and the growth of silicon nitride nanofibers is limited. If the raw metal silicon is nitrided in a porous and uniformly distributed form, it will be very beneficial for the growth of silicon nitride fibers. Many pores provide space for the growth of silicon nitride fibers, and facilitate the penetration and circulation of N\textsubscript{2}, NH\textsubscript{3} and other gases to provide adequate nitrogen sources.

In this paper, an innovative preparation method of silicon nitride fiber material is proposed. The silicon foam was designed and made into porous billets by organic foam impregnation method, and the pore structure was controlled. The silicon nitride fiber material was directly prepared by in-situ nitridation reaction. The effects of foaming agent and pore structure on the microstructure and the properties of Si\textsubscript{3}N\textsubscript{4} fiber materials were studied.

2. Experimental

2.1. Raw materials and preparation process
Polyurethane sponges with specifications of 40 ppi and 10 ppi were selected as templates. Silicon powder (99 wt\%) was used as raw material, ammonium polyacrylate (NH\textsubscript{4}-PAA, active content 60\%) as dispersant, and resin as binder.

First, binder and NH\textsubscript{4}-PAA were dissolved into deionized water by mechanical stirring. Then, silicon powders were dispersed into the premix solution. In order to ensure good affinity between slurry and sponge, slurry should maintain high viscosity. The surface of polyurethane sponge was pre-treated with acid-based solution. The pre-treated sponge was impregnated, and the excess slurry was discharged by twice extrusion hanging slurry, which was made into green body and dried. Finally, porous green bodies were nitrided at 1400 °C with a slow heating rate under a constant static pressure (0.15MPa) of high purity nitrogen.

2.2. Heating system
Figure 1 is the TG curve of the heating rate of polyurethane sponge in N\textsubscript{2} atmosphere at 5°C/min. It can be seen from the graph that when the temperature rises to 300°C, the weight loss of polyurethane sponge begins, and when the temperature rises to 600°C, the thermogravimetric loss of polyurethane sponge basically ends. In order to avoid the collapse of the billet in the process of heating, the rate of heating up at the temperature range of heavy weight loss of polyurethane foam is as slow as possible. Therefore, the heating system of porous foam prepared by impregnation of organic foam is shown in Figure 2.
2.3. Materials tested
Bulk density and porosity of the sintered samples was measured based on the Archimedes method. The microstructures of the samples were observed by scanning electron microscope (PHILPS-XL30). Phase identifications of the samples were determined by X-ray diffraction (XRD, D8 advance, Bruker, Germany). The compressive strength was examined by style pressure test machine (WHY-5) with the specimen size of 25mm×25mm×25mm. Thermal conductivity was tested by the plate method with the specimen size of Φ180mm×20mm.

3. Results and discussion

3.1. Physical properties
Figure 3 is a macroscopic digital photograph of porous Si green body before and after nitriding. Among them, a (40ppi) and b (10ppi) impregnated porous green body digital photographs, c (40ppi) and d (10ppi) is the green body after nitriding firing photographs. It can be seen from figs. the holes of prefabricated body are clear, there is no phenomenon of blocking holes, and the holes and ribs are obvious, which indicates that the impregnation process is suitable. Nitrided sample have obvious holes and ribs, and cotton flocculent substances are formed in holes.

Table 1 shows the physical properties of sample a and b after nitriding firing. The bulk density of sample a is 0.97g/cm³, the compressive strength at room temperature is 6.4Mpa, the thermal conductivity is 0.541 (w/m·k) at 1000°C, the bulk density of sample b is 0.83g/cm³, the compressive strength at room temperature is 5.9Mpa, and the thermal conductivity is 0.422 (w/m·k) at 1000 °C. It can be seen from the table that the prepared silicon nitride fiber material has low bulk density, high strength and good thermal insulation performance. The bulk density, strength and thermal conductivity of sample a are higher than that of sample b, which is due to the smaller porosity of sample a.
### Table 1. Physical properties of sample a and b after nitriding firing.

| Pore size | Bulk density (g/cm³) | Compressive strength (MPa) | Thermal conductivity (W/m·K) (1000 °C) |
|-----------|----------------------|---------------------------|----------------------------------------|
| a: 40ppi  | 0.97                 | 6.4                       | 0.541                                  |
| b: 10ppi  | 0.83                 | 5.9                       | 0.422                                  |

#### 3.2 Phase analysis

The XRD results of nitrided samples are shown in Figure 4. Table 2 calculates the relative content of each phase by Rietveld full spectrum fitting. The nitrided phases of sample a and b are the same. They all contain alpha-Si₃N₄, beta-Si₃N₄, SiO₂ and some residual Si. The content of Si₃N₄ in sample a is higher than that in sample b, and the content of SiO₂ in sample a is lower than that in sample b.

![Figure 4. The XRD of samples after nitridation.](image)

### Table 2. Relative contents of crystalline phases after nitridation.

| Content (wt%) | α-Si₃N₄ | β-Si₃N₄ | SiO₂ | Si |
|---------------|---------|---------|------|----|
| Sample a      | 40.9    | 57.9    | 1.1  | 0.1|
| Sample b      | 36      | 53.4    | 10.1 | 0.5|

#### 3.3 Thermodynamic analysis

Figure 5 is the volatile phase diagram of Si-O-N system at 1400°C. The nitrogen used in the experiment is high purity nitrogen, in which P(O₂) = 1 Pa. If the partial pressure of oxygen in the atmosphere is less than the partial pressure of oxygen at point A in Figure 6, the initial stage of reaction is the stage of SiO formation [5]. The raw material used in the experiment is silicon, so the following reactions occur at the beginning of the reaction.

\[
Si(s) + \frac{1}{2}O_2(g) = SiO(g) \tag{1}
\]

\[
Si(s) + SiO_2(s) = 2SiO(g) \tag{2}
\]

With the consumption of Si and the continuous formation of SiO, the partial pressure of SiO increases gradually, but the partial pressure of oxygen decreases gradually. When the partial pressure of SiO and oxygen reaches the Si₃N₄ region in Figure 5, the reaction will take place reaction (3).
Figure 5. The volatile phase diagram of Si-O-N system at 1400°C.

Figure 6. The relationship between $\Delta G_m^0$ and temperature of reaction (5) and (6).

$$3SiO(g) + 2N_2(g) = Si_3N_4(s) + \frac{3}{2}O_2(g)$$

(3)

Silicon nitride fibers are formed. If the partial pressure of oxygen in the atmosphere is greater than that at point A in Figure 5, the reaction will take place at the beginning of the reaction (4).

$$Si(s) + O_2(g) = SiO_2(s)$$

(4)

Because the pore of sample b is much larger than that of sample a, sample b is much more permeable than that of sample a, and the experiment is carried out in the circulating N2 atmosphere, so the content of Si$_3$N$_4$ formed in sample b is lower and the content of SiO$_2$ is higher [6].
The raw material used in the experiment is Si powder, which is easy to volatilize. At higher temperatures, Si vapor can be produced, and the fibers can also be formed by reacting with N\(_2\). Figure 6 is the relationship between \(\Delta rG^\circ\) and temperature of reaction (5) and (6). It can be seen from the graph that the standard Mole Gibbs generating function of reaction (5) is lower than the standard Mole Gibbs generating function of reaction (6) when the temperature is higher than 554°C. Therefore, even if there is Si vapor in the reaction process, the reaction temperature of Si vapor will give priority to the reaction of oxygen to produce SiO [7]. So Si\(_3\)N\(_4\) nanofibers grow by gas-solid (VS) mechanism from SiO.

\[
\begin{align*}
Si(g) + \frac{1}{2}O_2(g) &= SiO(g) \\
Si(g) + \frac{2}{3}N_2(g) &= \frac{1}{3}Si_3N_4(s)
\end{align*}
\]

3.4. Microstructure analysis

Figure 7 is the microstructure of sample a (40 pii) and sample b (10 pii) after nitriding. It can be seen from the figure that the fiber output of sample a is more, its distribution is uniform, its surface is smooth, and its length is longer, its length is more than 10 microns. Sample b has less fiber output, more granular morphology, shorter fiber length, uneven fiber distribution and smaller diameter than sample a. When the number of impregnated polyurethane sponges is small, the pore size is larger and the green body is more permeable. In the nitriding process, the oxygen partial pressure on the green body surface decreases less obviously, so the output of silicon nitride fiber will be very small and the length will be shorter[8].

![Figure 7](image_url)

**Figure 7**. The microstructure of sample a (40 pii) and sample b (10 pii) after nitriding

4. Conclusions

Si\(_3\)N\(_4\) fiber materials with relatively low thermal conductivity were prepared by organic foam impregnation method. Si\(_3\)N\(_4\) fibers with different mechanical properties and thermal properties could
be prepared by selecting templates with different pore sizes. The smaller the pore size of the template, the higher the content of silicon nitride in silicon nitride fiber material. This is due to the different concentration of gas phase reactants in the pore.

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