

FABRICATION AND PROPERTIES OF Si₃N₄ FIBER MATERIALS

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ABSTRACT

In this paper, porous Si green bodies were firstly prepared by foaming method combined with gel-casting. Si₃N₄ fiber materials were fabricated by nitridation of porous Si green bodies at 1400 °C for 5h. Silicon powders converted to Si₃N₄ fiber during the nitridation process, and the main phase was α-Si₃N₄. The properties of the fiber materials were also studied. As the addition of foaming agent increased from 1 wt % to 4 wt %, the bulk density of fiber materials reduced from 0.76 g/cm³ to 0.37 g/cm³, the compressive strength decreased from 6.1 MPa to 1.6 MPa and the thermal conductivity at 1000 °C decreased from 0.494 W m⁻¹ K⁻¹ to 0.216 W m⁻¹ K⁻¹. It was indicated that Si₃N₄ fiber materials had excellent heat insulation performance and enough strength.

Keywords: Si₃N₄ fiber materials; nitridation; foaming method combined with gel-casting; thermal insulation

INTRODUCTION

Si₃N₄ fiber materials have some outstanding properties including high strength, high temperature resistance, good wave transmissivity, good thermal shock resistance and electrical insulation. It can be used widely in fiber-reinforced composites, wave-transmitting materials, thermal insulation materials, and so on [1-3].

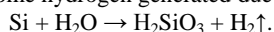
Si₃N₄ fiber materials can be obtained by two steps. First, Si₃N₄ fibers are prepared and then Si₃N₄ fiber materials are fabricated with the fibers via weaving or needling process. There are two types of Si₃N₄ fibers: one is continuous Si₃N₄ fibers and the other is Si₃N₄ nanowires. Continuous Si₃N₄ fibers are usually prepared by precursor (e. g., polysilazane, polycarbosilazane and perhydropolysilazane) infiltration pyrolysis method. Continuous Si₃N₄ fiber materials have been applied in aerospace and military fields [4, 5]. But the application in industrial fields was limited for its ultra-high cost. Si₃N₄ nanowires are the fibers with diameter between tens of nanometers to hundreds of nanometers. They can also be synthesized through the vapor-liquid-solid (VLS) or vapor-solid (VS) mechanism [6, 7]. Si₃N₄ nanowires are still in the stage of investigation, without actual production and application.

In this paper, a novel method was proposed to prepare Si₃N₄ fiber materials. Direct foaming method was used to design and prepare porous Si green bodies. Then Si₃N₄ fiber materials were fabricated via nitridation. The effects of foaming agent on the microstructure and the properties of Si₃N₄ fiber materials were studied.

EXPERIMENTAL

A commercial silicon powders (99 wt%, 9.1 μm, Jinan yinfeng silicon products co., LTD) were used as raw material; polyacrylic acid ammonium salt (NH₄-PAA, 60% active content) was selected as dispersant. Triethanolamine lauryl sulfate (TLS, 20% active content) was used as foaming agent. An epoxy compound sorbitol polyglycidyl ether (SPGE, epoxy equivalent weight is 173 g/epoxy equivalent), and a polyamine hardener polyethyleneimine (PEI, 30% in water) were employed to consolidate liquid foams.

The silicon powders in the slurry reacted with the water and some hydrogen generated due to the following chemical reaction:



The H₂ could accumulate in the slurry and make some big pores in the green body or even break the body. Therefore, silicon powders were treated in air at 600~800 °C for 2h and the oxide layers were formed on the surface of Si particles. The raw silicon powders and oxidation at 600 °C, 700 °C and 800 °C were named

as S0, S6, S7 and S8, respectively.

Fig. 1 is the flowchart for fabricating Si₃N₄ fiber materials. First, NH₄-PAA and PEI were dissolved into deionized water by mechanical stirring. Then silicon powders were dispersed into the premix solution. After adding foaming agent, vigorous stirring about 5min was applied to generate foams. For setting the foamed slurry, SPGE was added with further stirring about 2min. The slurry was cast immediately into a suitable mold.

The porous green bodies with mold were left in air for 3 days, then demolded and dried at 80 °C for 6h in an oven. Finally, porous Si green bodies were nitrided at 1400 °C with a slow heating rate under a constant static pressure (0.15MPa) of high purity nitrogen.

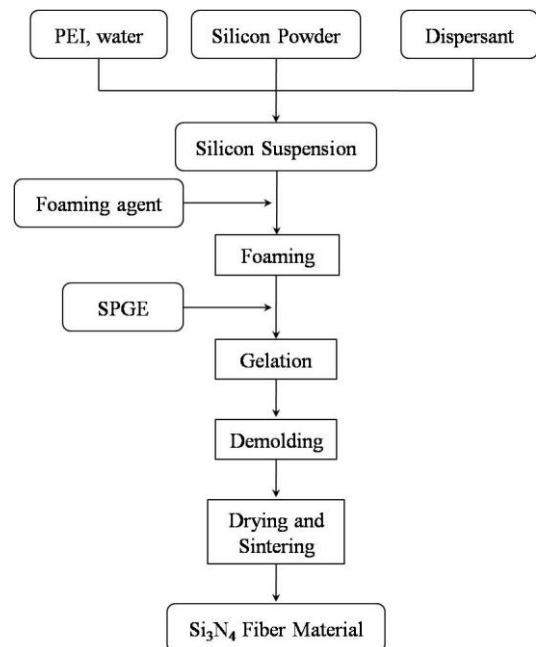


Fig. 1: Flow-chart for preparation of Si₃N₄ fiber materials

The viscosity and rheological behaviour of 40 vol% silicon suspensions were also studied by a Brookfield R/S Rheometer as a function of shear rates. The zeta potential values of silicon powders were characterised by a zeta potential analyser (Colloidal Dynamics, US) as a function of pH for 20wt% suspensions. Bulk density of the sintered samples was measured based on the Archimedes method. The microstructures of the samples were observed by scanning electron microscope (PHILIPS-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.

RESULTS AND DISCUSSION

Slurry characterisation

Tab. 1 shows the effect of silicon powders preoxidation temperature on the emitting H₂ while silicon powders in the water at pH value of 12. The raw silicon powders reacted fast with water, and reacted slow after oxidation process. Especially

after preoxidizing above 700 °C, there was no H₂ releasing for a long time, which helps to obtain good green bodies.

Tab. 1: The status of H₂ bubbles emitting while silicon powders in the water at pH=12

Time/min	S0	S6	S7	S8
≤60	Very small	Little, very small	None	None
60~120	Small	Very small	None	None
120~150	Small	Small	None	None
150~180	Large	Large	Little, very small	None

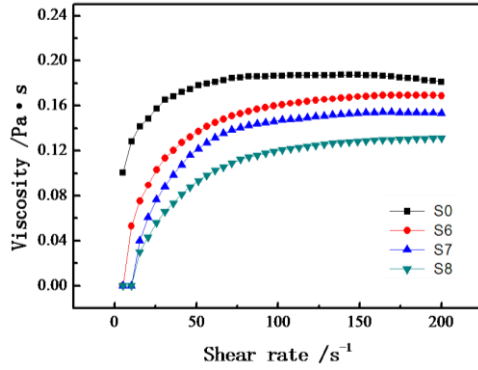


Fig. 2: Viscosity versus shear rate for silicon suspensions with 0.6% NH₄-PAA

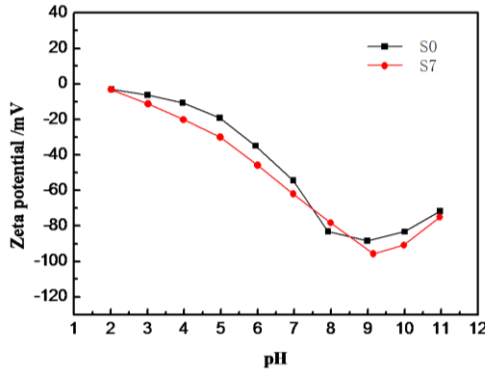


Fig. 3: Zeta potential versus pH for S0 and S7

The rheological behavior of silicon powders was studied by measuring the viscosity and zeta potential. The viscosity values measured for S0~S7 with the solid loading 40 vol% are presented in Fig. 2. The higher oxidation temperature of silicon powders was the lower in viscosity of the slurry. This would help to preparation silicon suspension with high solid content.

Another property with which the condition of the dispersability could be discerned is their zeta potential. The flow curves obtained by plotting zeta potential versus pH for S0 and S7 are presented in Fig. 3. Zeta potential of S7 was larger than that of S0 which indicated that S7 developed higher surface charges and got better dispersion.

In order to obtain higher solid content, the viscosity values of S7 suspension of plotted as a function of addition of dispersant with different solid content at shear rate of 100/s are presented in Fig. 4. Dispersant had little effect on the viscosity when the solid loading of suspension was low. But when the solid loading rose to 48 vol%, S7 suspension showed a minimum viscosity at the addition of 0.6 wt% which attributed to the state of good dispersion.

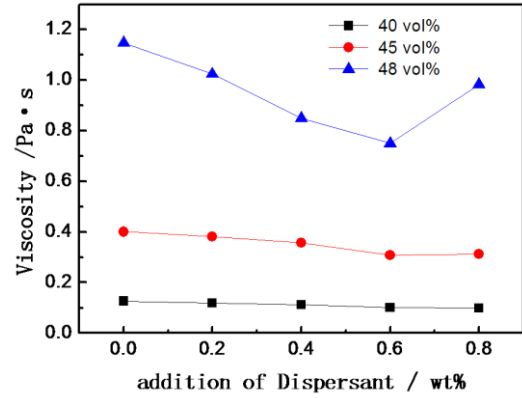


Fig. 4: Viscosity versus addition of dispersant (D=100/s)

Foaming and gelling of the suspension

Fig. 5 shows the effects of foaming agent on foaming volume ratio (F_{VR}) of the suspension with 45% solid loading and the green bulk density. Foaming volume ratio (F_{VR}) was equal to the volume ratio of foamed suspension to the original one and used to evaluate foaming capacity of foamed suspension. As the foaming agent was added from 1 wt% to 4 wt%, F_{VR} increased from 1.8 to 4.2 and the green bulk density decreased from 0.54 g/cm³ to 0.27 g/cm³. It was explained that the addition of foaming agent favors the adsorption at the gas/liquid interface and decrease of the surface tension^[8].

After adding SPGE and mixing for about 5min, the foamed suspensions should be cast as soon as possible. A three-dimensional network was formed continuously, and the suspensions consolidated at about 30min.

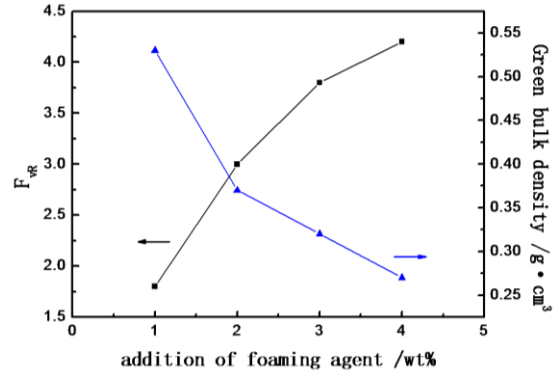
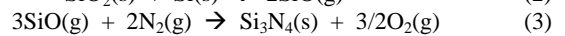
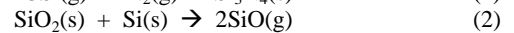
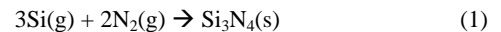


Fig. 5: Effects of foaming agent on foaming volume ratio (F_{VR}) and the green bulk density

Nitridation of porous Si green bodies

Nitridation schedule of porous Si green bodies is shown in Fig. 6. High porosity of porous Si green bodies favors the volatilization of Si which participates in reaction (1) to form Si₃N₄. Besides, the SiO₂ layer on Si particles was reduced to SiO(g) vapor based on reactions (2). SiO vapor then reacted with N₂ to form Si₃N₄ fibers based on reaction (3). It was concluded that Si₃N₄ fibers were formed through a vapor-solid (VS) mechanism^[6, 7]. The reaction between SiO and N₂ was dominating. It was different from nitriding of a dense green body.



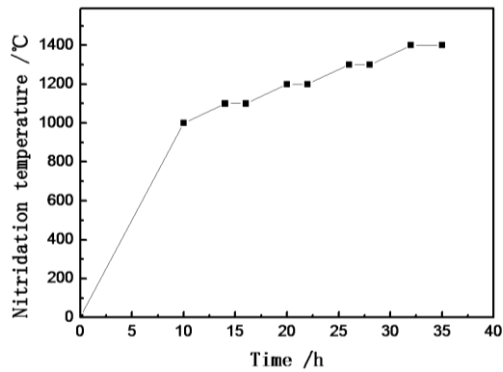


Fig. 6: Flow curve of nitridation schedule

Phase, microstructure and properties

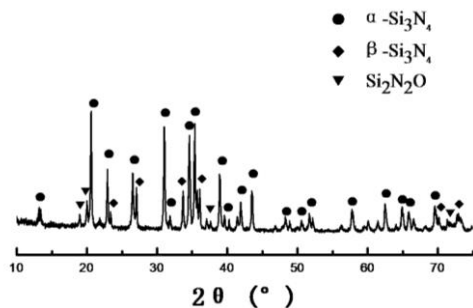


Fig. 7: XRD pattern of Si_3N_4 fiber materials

Fig. 7 shows the XRD result of a sintered sample. The major phase was α - Si_3N_4 and there was little β - Si_3N_4 and $\text{Si}_2\text{N}_2\text{O}$. No residual silicon was found, due to the porous structure which made it easy for nitrogen to get inside and react with silicon.

Fig. 8 (A) shows the microstructure of porous silicon green body. It had typical cell structure formed by foaming. The pores were spherical and with pore diameter 50~200 μm . Fig. 8 (B) and (C) show the microstructures of the sintered sample. The pores all disappeared and only silicon nitride fibers remained in the sample. The fiber diameters varied from less than 1 μm to a few microns.

Tab. 2 shows the relationship between addition of foaming agent and properties. With the addition of foaming agent increasing from 1% to 4%, the bulk density of Si_3N_4 fiber material reduced from 0.76 g/cm^3 to 0.37 g/cm^3 , the compressive strength decreased from 6.1 MPa to 1.6 MPa and the thermal conductivity at 1000 $^\circ\text{C}$ fell to 0.216 $\text{W}/(\text{m K})$ from 0.494 $\text{W}/(\text{m K})$. More foaming agents provided more pores in the green body, so the bulk density decreased. More space in the sample could provide greater thermal barrier, and ultra-low conductivity was obtained.

Tab. 2: Properties of Si_3N_4 fiber materials

Addition of foaming agent (wt %)	Bulk density (g/cm^3)	Compressive strength (MPa)	Thermal conductivity ($\text{W}/\text{m K}$)
1	0.76	6.1	0.494
2	0.52	3.2	0.288
3	0.45	2.1	0.242
4	0.37	1.6	0.216

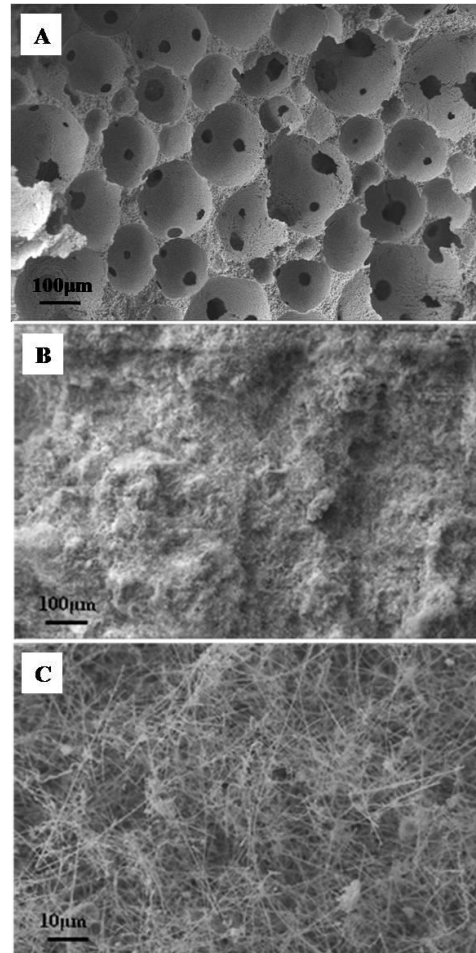


Fig. 8: (A) the microstructure of porous Si green body; (B) and (C) the microstructures of Si_3N_4 fiber materials

CONCLUSIONS

Si_3N_4 fiber materials were fabricated by direct nitridation process of porous silicon green body which prepared by foaming-gelcasting of Si suspensions. It mainly consists of α - Si_3N_4 fibers and has excellent properties. silicon nitride fiber material with different bulk density can be prepared by adjusting the addition of foaming agent. When foaming agent added 4 wt%, its compressive strength was 1.6MPa and its thermal conductivity at 1000 $^\circ\text{C}$ was 0.216 $\text{W}/(\text{m K})$.

ACKNOWLEDGEMENT

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