Formation of hierarchical Si₃N₄ foams by protein-based gelcasting and chemical vapor infiltration

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Abstract: Silicon nitride foams with a hierarchical porous structure was formed by the combination of protein-based gelcasting, chemical vapor infiltration, and *in-situ* growth of silicon nitride nanowires. The porosity of the foams can be controlled at 76.3–83.8 vol% with an open porosity of 70.2–82.8 vol%. The pore size distribution was presented in three levels: < 2 μm (voids among grains and cross overlapping of silicon nitride nanowires (SNNWs)), 10–50 μm (cell windows), and >100 μm (cells). The resulted compressive strength of the porous bodies at room temperature can achieve up to 18.0±1.0 MPa (porosity = 76.3 vol%) while the corresponding retention rate at 800 °C was 58.3%. Gas permeability value was measured to be 5.16 (cm³·cm)/(cm²·s·kPa). The good strength, high permeability together with the pore structure in multiple scales enabled the foam materials for microparticle infiltration applications.

Keywords: ceramics; sintering; porosity; mechanical properties; permeability

1 Introduction

Porous silicon nitride ceramics are widely used in high-temperature dust filtration, sensors, antenna windows, catalyst carrier, and membrane separation due to their good thermal stability, high mechanical strength, corrosion resistance, and wide bandgap [1–3]. Particulate matter (PM) pollutant particles containing complex components like sulfur dioxide, nitrogen oxides, toxic metals, and bacteria normally have a diameter of < 10 μm, which display tremendous harmfulness to human health [4,5]. It has been proved that these microparticles mainly come from industrial dust, vehicular emission, as well as biomass burning,

etc. [5]. For industrial dust filtration purpose, ceramic foams play an important role as they possess better high-temperature resistance compared with organic materials and lighter weight compared with metallic materials. Meanwhile, a hierarchical porous structure is often required for the efficient capture of dust particles with a wide size distribution [4–6].

How to construct the adjustable pore architecture is a tricky problem. Currently, the main manufacture approaches for porous ceramics include partial sintering, direct foaming, template method, freeze-casting, and gelcasting, etc. [7–10]. Among them, gelcasting process can realize controlling of pore profile as well as nearly net-shape molding of complex components, which has been of particular concerns during the last decade [10–14]. For gelcasting process, the foaming agent is a key material for obtaining desired porosity and pore size distribution. Recently, protein has been selected

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acting as both gelling and foaming material due to its good performance and low cost [15]. Other techniques like chemical vapor infiltration (CVI) were reported for tuning the pore profiles [3,16,17]. Compared with the sintering method, the CVI route can take place at a relatively low temperature and the amount of infiltrated phases can be well regulated. It can also be used to effectively adjust the density of porous materials and improve their mechanical property [16]. In addition, recent CVI approaches including low-pressure chemical vapor infiltration (LPCVI) and laser assisted-chemical vapor infiltration (LA-CVI) were also reported [18].

In this paper, we attempted to employ protein-based gelcasting together with the CVI technique for making Si_3N_4 foams with a hierarchical architecture. A three-level pore size distribution of $< 2 \mu\text{m}$, $5\text{--}50 \mu\text{m}$, and $> 100 \mu\text{m}$ was designed. The pore profile, mechanical property, and permeability of the obtained ceramic bulks were evaluated and discussed eventually.

2 Materials and method

2.1 Raw materials

Si_3N_4 powder (α -phase content $> 94 \text{ wt}\%$, particle size $1.0 \mu\text{m}$; purity $> 99.9 \text{ wt}\%$, Xing Rong Yuan Technology Co., Ltd., Beijing, China) was used as raw material. Al_2O_3 (particle size $1 \mu\text{m}$, purity $\geq 99.9 \text{ wt}\%$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China), and Y_2O_3 (particle size 50 nm , purity $\geq 99.9 \text{ wt}\%$, Sinopharm Chemical Reagent Co., Ltd., Shanghai, China) powders were chosen as sintering additives. SiO (purity $\geq 99.9 \text{ wt}\%$, Shanghai Chemical Reagent Co., Ltd., Shanghai, China) was employed as one of the silicon sources for the growth of silicon nitride nanowires (SNNWs). The mixing mass ratio of the aforementioned powders was $94:3:31.8:1.2$ ($\text{Si}_3\text{N}_4:\text{SiO}:\text{Y}_2\text{O}_3:\text{Al}_2\text{O}_3$). The egg white powder (Wuhan Bing De Biotechnology Co. Ltd., Wuhan, China) was selected as both gelling and foaming agent. Gaseous SiCl_4 and NH_3 were introduced into the CVI process as inorganic precursors.

2.2 Gelcasting, CVI, and pressureless sintering processes

Preparation of hierarchical Si_3N_4 foams mainly included three steps: protein-based gelcasting, CVI, and pressureless sintering. The first step aimed at obtaining

a porous Si_3N_4 green body and the procedure was as follows: The powder mixture was well mixed with $10 \text{ wt}\%$ (relative to the powder mixtures) egg white powder, and then it was added to deionized water in batches for ball milling. During this step, the solid content was controlled to $55\text{--}65 \text{ wt}\%$ and the pH value was kept at $10.0\text{--}11.0$. Subsequently, the mixtures were milled for 6 h with a rotation speed of 300 r/min to form the ceramic suspension. Then the suspension was poured into moulds and maintained at $80 \text{ }^\circ\text{C}$ for 30 min to form the ceramic gel. Complete drying of the gel was conducted in a confined space for 36 h at room temperature and then it was transferred to the oven ($60 \text{ }^\circ\text{C}$) for 72 h . At last, binder burning-out was carried out at $600 \text{ }^\circ\text{C}$ for 1 h in air with a heating rate of $1 \text{ }^\circ\text{C/min}$.

The CVI process took place in a CVI furnace by using SiCl_4 and NH_3 as inorganic precursors. The temperature was firstly raised to $750 \text{ }^\circ\text{C}$ with a heating rate of $8 \text{ }^\circ\text{C/min}$, and then it was continuously heated up to the target temperatures. The gas pressure of the system was maintained at 1.0 kPa for $60\text{--}300 \text{ h}$.

Pressureless sintering was finally carried out in a graphite furnace under an N_2 atmosphere. The infiltrated Si_3N_4 foams were placed in the corundum crucible with SiO located at the bottom. The sintering temperature was set to $1500 \text{ }^\circ\text{C}$ for 2 h with a heating rate of $5 \text{ }^\circ\text{C/min}$, followed by natural cooling.

2.3 Characterization

Density, open porosity, and total porosity of porous Si_3N_4 were measured by Archimedes' method in distilled water. The microstructure of the pore profile was examined by a scanning electron microscope (SEM, MIRA 3 LMH, Tescan Ltd., Czech Republic) and a transmission electron microscope (TEM, Technai G2 F20 S-TWIN 200kV , FEI Corp., USA) equipped with an energy-dispersive spectroscopy (EDS) detector. The pore size distribution of the porous bulks was analyzed by direct measurement from the SEM images (at least 300 counts) as well as a mercury intrusion porosimeter (Micromeritics AutoPore IV9510, McPrettyk, USA). The compressive strength was evaluated in a mechanical test machine (CTM 9100, Xieqiang Co., Ltd., China) using a load speed of 0.5 mm/min . The samples (S1–S5) were cut into cubes with a dimension of $10 \text{ mm} \times 10 \text{ mm} \times 10 \text{ mm}$. At least three values were measured for obtaining the average. For the high-temperature mechanical test, the samples were heated to $800 \text{ }^\circ\text{C}$

with a dwell of 600 s in air. Gas permeability test was conducted in a permeability tester (DTQ, Xiangtan Xiangyi Instrument Co., Ltd., China) using sample S2 with a cylindrical geometry of $\phi 30$ mm $\times$ 10 mm (GB/T 1968-1980) at room temperature. Three samples were tested for averaging.

3 Results and discussion

Table 1 lists the thickness, density, and porosity of porous Si_3N_4 ceramic samples with different CVI durations. The total porosity can be tuned between 76.3 and 83.8 vol%. It was found that increasing CVI duration can improve CVI thickness and density but decrease porosity. Meanwhile, the decreasing rate of porosity became lower as infiltration time increased. This is because that the pores were gradually filled during the CVI process which enhanced the entrance

resistance of gaseous precursors and depressed the deposition rate. As can be seen, the open porosity can keep at 70.2 ± 0.3 vol% after CVI for 300 h.

Figure 1 shows the optical, SEM, and TEM images of the Si_3N_4 foam sample S2 at different synthesis stages. Before the CVI process, the gelcasted green foam displayed large pores that were visible to the naked eyes (Fig. 1(a)). A further check by SEM suggested a

Table 1 Density and porosity of porous Si_3N_4 ceramic samples with different CVI durations

Sample	CVI duration (h)	CVI thickness (μm)	Density (g/cm^3)	Open porosity (vol%)	Total porosity (vol%)
S1	60	3.1 ± 0.4	0.59 ± 0.01	82.8 ± 1.1	83.8 ± 0.9
S2	120	5.4 ± 0.2	0.62 ± 0.02	76.7 ± 1.3	80.8 ± 0.7
S3	180	6.5 ± 0.2	0.72 ± 0.01	72.6 ± 1.5	77.4 ± 0.5
S4	240	7.4 ± 0.1	0.74 ± 0.01	71.6 ± 1.1	76.9 ± 0.3
S5	300	8.2 ± 0.3	0.76 ± 0.01	70.2 ± 0.3	76.3 ± 0.2

Fig. 1 Optical, SEM, and TEM images of the Si_3N_4 foam sample S2: (a–d) before CVI; (e–h) after CVI; and (i–k) after pressureless sintering. Figure 1(l) displays the sample S5 with a longer CVI duration for comparison.

cell-window microstructure with a cell size distribution of 50–500 μm (Fig. 1(b)). Using a higher magnification in Figs. 1(c) and 1(d), Si_3N_4 particles and voids among them ($< 2 \mu\text{m}$) were observed. After CVI for 120 h, the cell size encountered shrinkage to 50–400 μm , and the cell structures became thicker (Figs. 1(e) and 1(f)). It is also found that some of the cell windows were covered by the infiltrated Si_3N_4 from the comparison of Fig. 1(f) with Fig. 1(b). The thickness of the coated Si_3N_4 layers was estimated to be 5 μm (Fig. 1(g)), while the grain voids ($< 2 \mu\text{m}$) still existed as observed from the inset in Fig. 1(g). The pressureless sintering led to the densification of the ceramic foams, which can be proved by Fig. 1(i) that the sample was much stiffer than that as shown in Figs. 1(a) and 1(e). Another evident change is the narrowing of the cells (Fig. 1(j)). This is not only because of the consolidation of the foams but also due to the formation of enormous nanowires on the cell walls. From the high-resolution TEM images in Fig. 1(k), the length and diameter of the nanowires can be measured to be several tens of microns and 50–100 nm, respectively. The cross overlapping of the NWs splitted the space into abundant small meshes having a dimension of $< 2 \mu\text{m}$. In addition, there was no spherical droplet at the tip of the nanowire body (see the red circle in Fig. 1(k) inset). Further analysis results by TEM were given in the Fig. 1(k) inset. The electron diffraction pattern and semi-quantitative EDS data (at%: Si/N = 47.05/52.95) suggested the composition of Si_3N_4 . This can be also verified by the high-resolution image that the lattice fringes exhibited (110) plane of $\alpha\text{-Si}_3\text{N}_4$ ($d_{110} = 0.388 \text{ nm}$). These features indicated the vapor–solid (VS) growth of SNNWs [19]. Ref. [20] has demonstrated that the *in-situ* VS growth of SNNWs rendered SiO as silicon sources, and the final formation of one-

dimensional (1D) nanostructure resulted from the depletion of Si element reacting with N_2 . Figure 1(l) discloses the comparison of samples with different CVI durations. It can be seen that the extension of processing time to 300 h (sample S5) led to a thicker appearance (the inset in Fig. 1(l)) and much coarser grains than 120 h (sample S2). Thus, the CVI thickness was enhanced but the porosity was reduced (Table 1).

Figure 2 illustrates the pore size distribution of sample S2 by both direct counting and intrusion methods. Statistics displayed in Fig. 2(a) has implied the major size of cells was between 50 and 400 μm and the range of 200–300 μm was dominant. This is in accordance with the results from Fig. 1. As direct measurement of the cell window size was difficult, the intrusion method was also employed and the corresponding results are shown in Fig. 2(b). There are three peak regions in the curve: $< 2 \mu\text{m}$, 5–50 μm , and 100–400 μm . The 100–400 μm region can be ascribed to the cell size, which is consistent with Fig. 2(a). Accordingly, the peaks located at 5–50 μm can belong to the cell windows. It seems that the micropores with a size distribution of $< 2 \mu\text{m}$ originated from the meshes created by SNNWs (Fig. 1(i)). However, considering the basic principle of the mercury intrusion method, these meshes were pseudo pores which can hardly be reflected by the intrusion curve. These micropores were evolved from the packing voids between Si_3N_4 particle (Figs. 1(c) and 1(f)).

The formation mechanism of the hierarchical pore structure is revealed in Fig. 3. The primary pore structure with a size of $> 100 \mu\text{m}$ was formed by partial infiltration of the gelcasted process. The secondary pore size range is 5–50 μm and these pores originated from the residual cell windows after the CVI process. Finally, the voids among Si_3N_4 grains together with the

Fig. 2 Pore size distribution of the Si_3N_4 foam sample S2: (a) computational results based on SEM micrographs and (b) tested results by mercury intrusion method.

meshes constructed by the SNNWs constituted the tertiary pore architecture ($< 2 \mu\text{m}$). Because most of the secondary and tertiary pores were interconnected, the ceramic foams had a large open porosity as depicted in Table 1. Furthermore, the configuration that the cell chambers are filled with a large number of NWs is similar to the nasal cavity of higher animals. Such a structure is helpful for infiltration and retardation of the microparticles.

Investigations on the mechanical properties of the ceramic foams were performed and the corresponding data is shown in Fig. 4. Figure 4(a) indicates that the compressive strength suffers degradation with increasing porosity. The maximal strength value obtained at room

temperature was $18.0 \pm 1.0 \text{ MPa}$ when the open porosity was $70.2 \pm 0.3 \text{ vol}\%$. In other investigations, de Moraes *et al.* [2] employed direct foaming methods to obtain Si_3N_4 foams with a porosity of 79–86 vol% and a corresponding compressive strength of 1.0–9.9 MPa. Yu *et al.* [21] used colloidal particles for stabilization of Si_3N_4 foams and they got a strength value of 3.8 MPa (porosity = 82.1 vol%). Ren *et al.* [22] reported a facile method for fabricating SiC nanofibrous network reinforced hierarchical structured porous Si_3N_4 based ceramics, and the resulted compressive strength was 10.8 MPa with 76.7 vol% porosity. It can be seen that the strength value obtained in our study is comparable to the above-mentioned studies. The main reason for

Fig. 3 Schematic diagram for the formation mechanism of the hierarchical pore structure.

Fig. 4 Compressive strength of the samples S1–S5: (a) the compressive strength values with varying open porosity and the TEM inset illustrates the formation of grain necks after pressureless sintering for sample S5; (b) the corresponding load-displacement curves.

the high strength is the generation of Si_3N_4 grain necks (see the inset in Fig. 4(a)) which brought densification to the end of the initial sintering stage (neck formation) based on the conventional sintering theory [23,24]. The load-displacement curves of the samples with different CVI durations are shown in Fig. 4(b). Overall, it appeared a brittle fracture mode for all the samples. A more careful view of sample S5 curve exhibited that the load reached the highest value and then suffered a ladder-like drop. This indicated that the gradual propagation of cracks along cell structures can be somewhat hindered by the cell-window-NWs structure. Furthermore, the compressive strength of sample S5 at 800 °C was measured to be 10.5 ± 0.7 MPa, which was 58.3% retention of the original one at room temperature. Wu *et al.* [25] reported porous anorthite ceramics which possessed a compressive strength of < 3 MPa at 800 °C with a total porosity of 82.3 vol%. Deng *et al.* [26] fabricated self-reinforced porous mullite ceramics (0 wt% $\text{AlF}_3 \cdot 3\text{H}_2\text{O}$ addition) with a compressive strength of 11–12 MPa at 800 °C (67% porosity). It is suggested that the high-temperature mechanical performance of our samples is competitive.

Gas permeability of the hierarchical pore structure was tested according to the method and device described in Ref. [27]. The average value was obtained to be $5.16 (\text{cm}^3 \cdot \text{cm})/(\text{cm}^2 \cdot \text{s} \cdot \text{kPa})$. In comparison, Si_3N_4 -SiCN ceramic foam with a 79.3% porosity displayed a permeability value of $3.27 (\text{cm}^3 \cdot \text{cm})/(\text{cm}^2 \cdot \text{s} \cdot \text{kPa})$ [27]. Obviously, pure Si_3N_4 foams prepared in this study have much higher gas permeability. The reason lies in the high open porosity and good interconnectivity of the hierarchical architecture, which is also beneficial for efficient microparticle filtration.

4 Conclusions

1) Increasing CVI duration can improve CVI thickness and density with decreasing porosity. Meanwhile, the decrease rate of porosity became lower as infiltration time increased. The open porosity of Si_3N_4 foam can keep at 70.2 ± 0.3 vol% after CVI for 300 h.

2) The total porosity can be tuned between 76.3 and 83.8 vol% with an open porosity of 70.2–82.8 vol%. A hierarchical structure was generated with a pore size distribution of < 2 μm , 5–50 μm , and > 100 μm .

3) The compressive strength of the foams at room temperature can achieve up to 18.0 ± 1.0 MPa (porosity = 76.3 vol%) while the corresponding retention rate at

800 °C was 58.3%.

4) The Si_3N_4 foams possessed a gas permeability value of $5.16 (\text{cm}^3 \cdot \text{cm})/(\text{cm}^2 \cdot \text{s} \cdot \text{kPa})$. The good strength, high permeability together with hierarchical pore structure make the porous materials promising for microparticle infiltration.

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