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Short communication

Microstructure characterization of in situ synthesized porous Si_2N_2O ceramics using spodumene additive

Xue Dong, Jiachen Liu, Haiyan Du*, Anran Guo, Mengxia Liu

School of Materials Science and Engineering of Tianjin University, Key Lab of Advanced Ceramics and Machining Technology of Ministry of Education, Tianjin 300072, China

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Abstract

Porous Si_2N_2O ceramics was synthesized by the tert-butyl alcohol-based gel-casting method at a relatively low temperature using Si_3N_4 and SiO_2 powders as the starting materials and spodumene ($LiAl(SiO_3)_2$) as the sintering additive. Porous Si_2N_2O ceramics with relative high compressive strength (10.80 MPa) and high porosity (65.5%) were successfully fabricated. The microstructure of porous Si_2N_2O after sintering at different sintering regimes was studied. The fibers observed in the pores can increase the compressive strength and the specific surface area of the sample.

Keywords: A. Sintering; Ceramics; Fibers; TBA-based gel-casting

1. Introduction

Silicon oxynitride (Si_2N_2O) is a unique compound in the Si_3N_4–SiO_2 system and shows an excellent oxidation resistance at severe conditions for high temperature engineering purposes [1–6]. Si_2N_2O has been considered as an industrial material because of its superior properties such as high hardness (Hv: 17–22 GPa), low thermal expansion coefficient ($3.5 \times 10^{-6}\ K^{-1}$) and high thermodynamic stability temperature (about 1800 °C). [2,3] However, the sintering temperature of Si_2N_2O is too high due to its strong covalent bonds and low diffusion coefficient. Recently, Tong prepared dense Si_2N_2O by a hot-pressing method at a relatively low temperature by introducing a Li_2O additive. [7] They also found that increasing Li_2O content has no apparent influence on the mechanical and dielectric properties of dense Si_2N_2O, which is due to the easy evaporation of Li_2O at sintering temperature. The as-prepared bulk Si_2N_2O exhibits both low dielectric constant (6.17 at 1 MHz) and loss tangent (0.0008 at 1 MHz) and combines good mechanical performance.

Furthermore, the porous ceramics have been reported as candidate materials as environmental adsorbent for the purification systems of polluted air and water. The adsorption efficiency can be adjusted by the microstructure control of the sintered bodies such as porosity, pore size, pore shape and morphology of the pore surface. Moreover, an introduction of whiskers or fibers on the pore surface is also an effective method to increase the adsorption efficiency due to their high surface area [8].

As a new method, TBA-based gel-casting process is a recently developed method for fabrication porous ceramics [9]. Compared with water, TBA can evaporate easily under relatively low temperatures (40 °C) and cause small shrinkage during drying process [10]. Furthermore, the physical, mechanical, thermal and electrical properties of the porous ceramics produced by this technique could be adjusted directly by changing the solid loading in the slurry and the sintering temperature. Porous ceramics such as YSZ, SiO_2, PZT and Al_2O_3 with ultra-high porosity, relative high strength and excellent properties have been successfully fabricated by this method [11–14].

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*Corresponding author. Tel.: +86 13682032861;
fax: +86 022 27408244.
E-mail address: hydu2010@gmail.com (H. Du).

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In this work, using the spodumene ($LiAl(SiO_3)_2$) as the sintering additive, the continuously porous in-situ Si_2N_2O ceramics were fabricated by a TBA-based gel-casting method at a relatively low temperature (1500 °C). It should be noted that the synthesis of Si_2N_2O and the forming of the porous structure were completed in one step. The morphology of the fibers observed in the porous Si_2N_2O ceramics was investigated by changing the sintering regime. The compressive strength and the specific surface area were measured. The results obtained in this paper are beneficial for the understanding of the synthesis, sintering and properties of porous Si_2N_2O and for the promotion of porous Si_2N_2O material as a candidate for high-temperature structural and functional material.

2. Experimental

Si_3N_4 powders (average particle size <300 nm), nano-silica powder (about 50 nm) and spodumene ($LiAl(SiO_3)_2$) were used as the starting materials. The weight ratio is Si_3N_4:SiO_2: $LiAl(SiO_3)_2$ = 14:6:1. Tert-butyl alcohol was used as shaping solvent and pore forming agent in gel casting process. A premix solution was prepared in TBA with monomer (acrylamide, AM, $C_2H_3CONH_2$), and cross linker (N, N-methylenebisacrylamide, MBAM, $(C_2H_3CONH)_2CH_2$), and the weight ratio is AM: MBAM: TBA = 12:1:50. Ammonium persulfate (APS) and N, N, N, N-tetramethylethylenediamine (TEMED) was selected as initiator and catalyst for gelation reaction, respectively. Citric acid was used as dispersant (1 wt% of the Si_3N_4 powders and nano-silica powders) to form stable mixed suspensions in TBA.

The slurry mixture including Si_3N_4 powders, silica powders, spodumene, premix solution and citric acid solution was prepared by ball milling for 10 h. The prepared slurries with 20 wt% solid loading were found to be stable. The suspension was then poured into polyethylene molds after adding the initiator solution (20 wt% in water) and catalyst. Green bodies were removed from molds and dried at a temperature of 40 °C for 12 h. Three different sintering regimes (regime A, B and C) were adopted during the sintering process. The sintering regime A entailed heating the samples at 1 °C/min up to 600 °C followed by 1 h of dwell time at an air atmosphere, and then heated at 4 °C/min from room temperature to final sintering temperature (1500 and 1550 °C) at a nitrogen atmosphere for 2 h. With sintering regime B, the samples were heated to 1550 °C at 4 °C/min followed by 2 h of dwell time at a nitrogen atmosphere. Sintering regime C was to heat the sample to 1550 °C at 4 °C/min followed by 4 h of dwell time at a nitrogen atmosphere.

The phases of the samples were analyzed via X-ray diffraction (XRD, D/Max-2500 Rigaku, Japan). Microstructure of the sintered samples was observed by scanning electron microscope (S-4800, Hitachi Ltd, Japan). Open porosities of the sintered samples were determined by the water-immersion technique using the Archimedes method. The compressive strength was measured by a universal testing machine (XWW, Beijing Shengxin detecting instrument, China) with a loading speed of 0.5 mm/min. The dimensions of measured samples were 30 mm in diameter and 5 mm in height. Each value represented an average of five measurements of five different specimens. The pore size distribution was measured by an automatic mercury injection apparatus (IV9500, Micromeritics Instrument Corporation, USA). The specific surface area was measured by BET capacity method (3H-2000BET-M, Beijing, China).

3. Results and discussion

The pore forming schematic diagram of porous Si_2N_2O ceramics by the TBA-based gel-casting method is shown in Fig. 1. The polymerization of AM occurred in a few minutes after adding appropriate amount of initiator and catalyst solution into the stable mixture slurry (Fig. 1(a)). In Fig. 1(b), the formed strong macromolecular gel network trapped mixture particles among its branches, and the green body with high strength was obtained. Then the TBA vaporized leaving the pores in the ceramics bodies during the drying process at 40 °C. The pores connected with each other and distributed homogeneously throughout the dried body which was shown in Fig. 1(c). After sintering, the polymer was removed completely. The mixture particles (Si_3N_4 powders and nano-silica powders) reacted into Si_2N_2O with the assistance of spodumene and formed a loose skeleton structure (Fig. 1(d)). The linear shrinkage of the specimens after drying was about 10%, which was mainly due to the ultra-low solid loading. In addition, there were no obvious cracks observed on the surface of green bodies. Some fibers also grew in the pores of the sample after sintering.

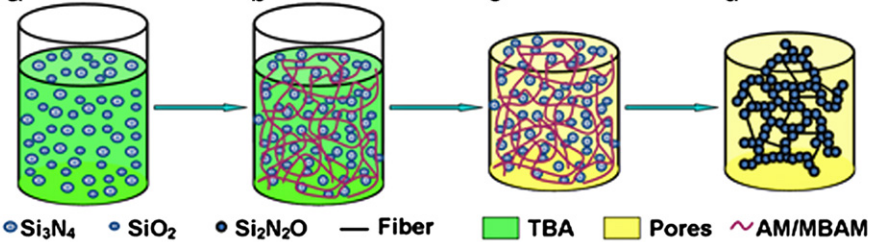

Fig. 1. The pore forming schematic diagram of porous Si_2N_2O ceramics by the TBA-based gel-casting method. (a) Slurry, (b) Green body, (c) After evaporating and (d) After sintering.

Fig. 2(a) reveals the SEM image of the green body after drying. It can be concluded from Fig. 2(a) that the pores connected with each other and distributed homogeneously. Fig. 2(b) and (c) shows the green body sintered under sintering regime A at 1500 and 1550 °C, respectively. AM polymerized forming a strong polyacrylamide network at room temperature, and after sintering the polyacrylamide was removed completely. So the Si_3N_4 and silica particles reacted into Si_2N_2O and lapped with each other forming the looser skeleton structure at high temperature. Moreover, the skeleton structures of the sample sintered at 1500 and 1550 °C did not show any apparent differences with each other. The XRD patterns of the green bodies sintered 1500 and 1550 °C under the sintering regime A are illustrated in Fig. 2(d). All characteristic peaks corresponding to Si_2N_2O (JCPDS card # 47-1627) were confirmed to be present. This result demonstrated that the reaction between Si_3N_4 and SiO_2 was sufficient. The synthesis process of the Si_2N_2O involves a liquid phase sintering mechanism. A liquid phase Al_2O_3–Li_2O–SiO_2 is formed by the reaction of spodumene additives and SiO_2. And then Si_2N_2O is formed through a process whereby Si_3N_4 dissolved and reacted with the SiO_2 component of the liquid phase. The heights of diffraction peaks of Si_2N_2O sintered at 1550 °C were apparently greater than that of sintered at 1500 °C. It indicated that the crystallization of Si_2N_2O sintered at 1550 °Cwas higher than that of Si_2N_2O sintered at 1500 °C. Besides, because of the low content of spodumene additives and the easy evaporation of Li element, the diffraction peaks of spodumene cannot be observed.

Fig. 3 shows SEM image of the porous Si_2N_2O bodies sintered at 1550 °C under different sintering regimes. Fig. 3(a and b) shows the microstructure of the sample sintered under sintering regime A. The pore size distribution of the samples was uniform and few fibers can be observed in the pores. In Fig. 3(c and d), many short fibers with 20–50 nm in diameter were observed in the pores of the sample sintered under sintering regime B and all grew unidirectional. Fig. 3(e and f) shows the image of porous Si_2N_2O bodies sintered under sintering regime C. Long fibers which grew anisotropic from the pore can be observed. The reaction process of the Si_2N_2O fiber generated as follows:

$$SiO_2(s)+C(s)=SiO(g)+CO(g) \quad (1)$$

$$3SiO(g)+Si_3N_4(s)+N_2(g)=3Si_2N_2O(s) \quad (2)$$

The carbon source in this experiment which came from the organic (premix solution) during the gel casting process prompted more silica to react into SiO and the formation of Si_2N_2O fiber was due to the existence of the vapor phase SiO during the synthesis reaction of Si_2N_2O [15]. Under sintering regime A, there was no carbon source for the formation of whiskers, which is because that the samples sintered at an air atmosphere made the carbon source in

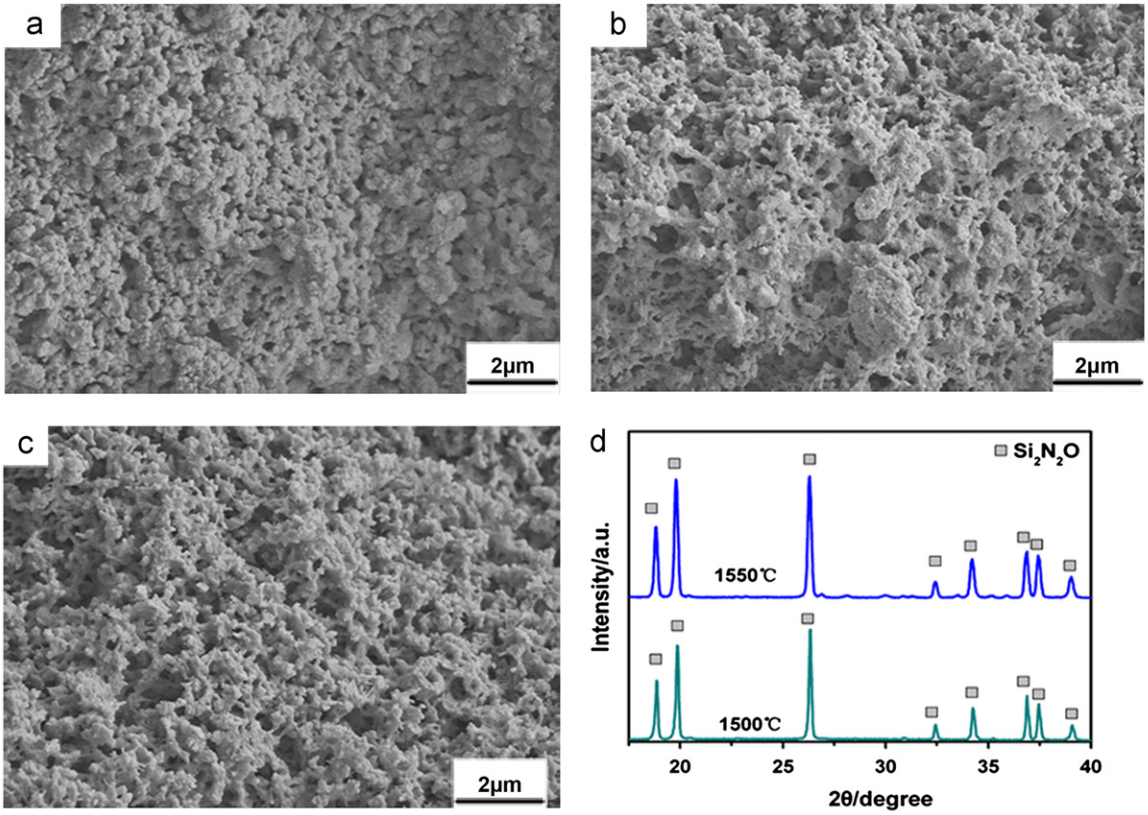

Fig. 2. SEM images of (a) the green body and the sample sintered at (b) 1500, (c) 1550 °C under sintering regime A and (d) XRD patterns of Si_2N_2O synthesized at different temperatures under sintering regime A.

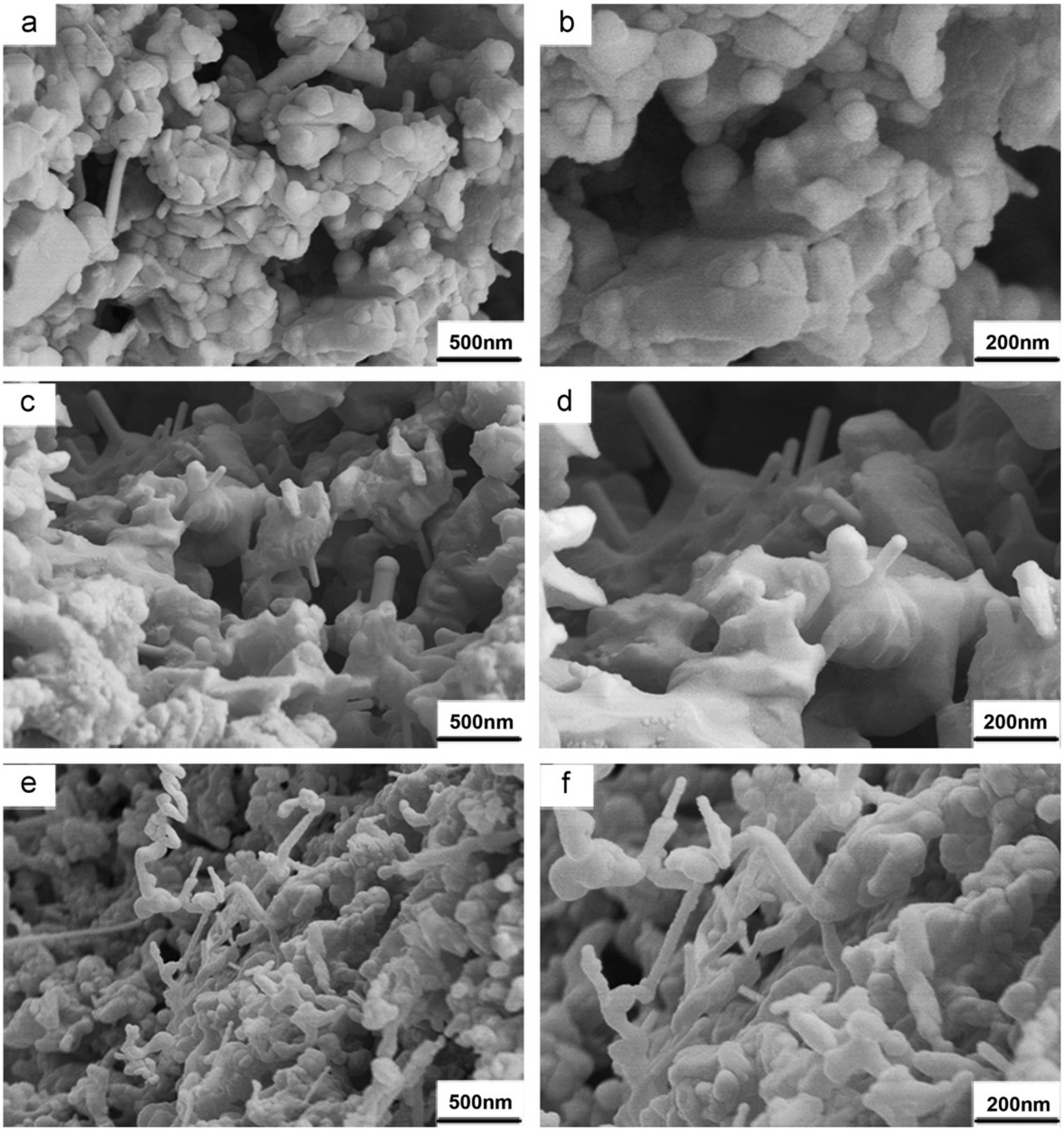

Fig. 3. The details of 3D-interconnection of pores in the samples sintered at 1550 °C under (a and b) sintering regime A, (c and d) sintering regime B and (e and f) sintering regime C.

the porous body deplete. Under sintering regime B, due to an inert atmosphere (nitrogen atmosphere) compared with that of sintering regime A, the carbon in the sample could be maintained during the sintering process and reacted with SiO_2 forming a certain amount of SiO. When the dwell time increased, the fibers did not grow unidirectional but anisotropic, which can be seen from Fig. 3(e and f).

Fig. 4(a) shows the pore size distribution of the sample which were sintered at 1550 °C under different sintering regimes. The pore sizes of the sample under sintering regime B were 0.11 and 0.23 μm, respectively. And the pore sizes of the sample under sintering regime C were 0.12 and 0.20 μm, respectively. From Fig. 4(a), it can be seen that the pore size distribution was not concentrated in one area under both sintering regime B and C. The reason was that the fibers which grew in the pores caused the singularity of the pore. Conversely, there were few fibers in the pores of porous Si_2N_2O under sintering regime A. Consequently, the pore size distribution of porous Si_2N_2O under sintering regime A was relatively uniform (about 0.20 μm).

Fig. 4(b) shows the specific surface area of the sample sintered at 1550 °C under different sintering regimes. It can be seen that by changing the sintering regime from A to C, the specific surface area increased from 35.4 to 63.7 m^2/g. Fig. 4(c) shows the compressive strength and porosity of the samples under different sintering regimes. The compressive strength increased from 7.34 to 10.80 MPa by changing the sintering regime from A to C, as the porosity decreased from 68.6 to 65.5%. It meant that the growing of the fibers in the pores of the porous Si_2N_2O increased the compressive strength and the specific surface area.

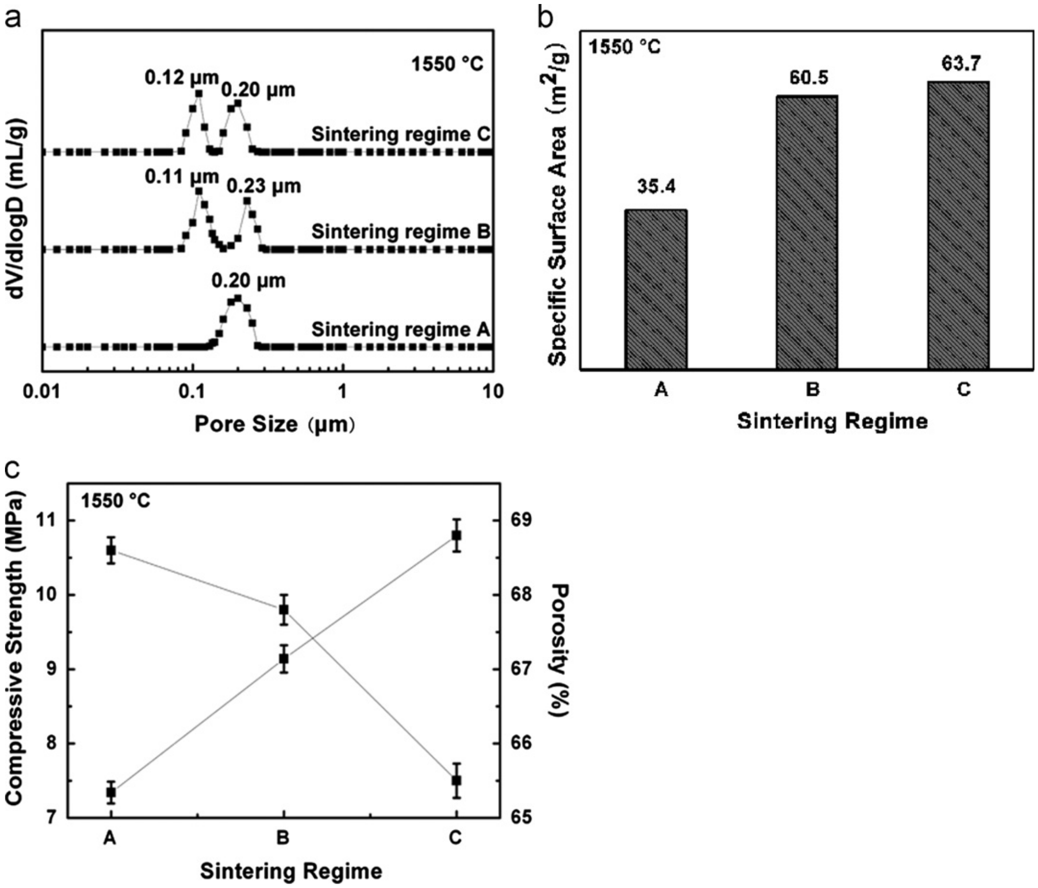

Fig. 4. (a) Pore size distribution, (b) specific surface area and (c) compressive strength and porosity of the samples sintered at 1550 °C under different sintering regimes.

4. Conclusions

(1) Porous Si_2N_2O ceramics was synthesized by sintering Si_3N_4 and spherical SiO_2 powder mixtures at 1500 °C for 2 h using spodumene ($LiAl(SiO_3)_2$) as an additive. The relatively low sintering temperature of Si_2N_2O is ascribed to the lower melting point of the Al_2O_3–Li_2O–SiO_2 glass phase.

(2) Porous Si_2N_2O ceramics with relative high compressive strength (10.80 MPa) and high porosity (65.5%) were successfully fabricated by tert-butyl alcohol (TBA)-based gel-casting method. The diameter of the pores was about 200 nm.

(3) Si_2N_2O fibers having 20–50 nm in diameter were observed in the pores and the formation of Si_2N_2O fibers was due to the vapor phase of SiO during the synthesis reaction of Si_2N_2O. The fibers observed in the pores can increase the compressive strength and the specific surface area of the sample.

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