

Effect of Diatomite Additive on the Mechanical and Dielectric Properties of Porous SiO₂-Si₃N₄ Composite Ceramics

YOU Guanglei^{1,2}, BI Jianqiang^{1,2*}, CHEN Yafei^{1,2}, YIN Chonglong^{1,2}, WANG Chang'an³

(1. Key Laboratory for Liquid-Solid Structure Evolution and Processing of Materials, Ministry of Education, Shandong University, Jinan 250061, China; 2. School of Material Science and Engineering, Shandong University, Jinan 250061, China; 3. State Key Laboratory of New Ceramic and Fine Processing, Tsinghua University, Beijing 100084, China)

Abstract: Porous SiO₂-Si₃N₄ composite ceramics with high porosity and excellent mechanical properties were fabricated by pressureless-sintering at relatively low temperature of 1 500 °C using diatomite as pore forming agent. The effects of diatomite on flexural strength, fracture toughness, shrinkage, porosity and phase transformation of the porous ceramics were investigated in detail. Compared with that of the ceramic without adding diatomite, the porosity of the ceramic with 10% diatomite is increased by about 27.4%, the flexural strength and fracture toughness reaches 78.04 MPa and 1.25 MPa·m^{1/2}, respectively. As the porosity increases, the dielectric constant of porous SiO₂-Si₃N₄ ceramic decreases obviously from 3.65 to 2.95.

Key words: silicon nitride; diatomite; porosity; mechanical property; dielectric constant

1 Introduction

Silicon nitride (Si₃N₄) ceramics are of great promise for radome and antenna window applications due to insulation and wave-transmissivity^[1]. On the basis of excellent mechanical properties of Si₃N₄, porous silicon nitride ceramics have been prepared by various methods to enhance their dielectric property, the common ones include combustion synthesis^[2], freeze-drying^[3], gel casting^[4], foaming^[5] and pyrolysis of various organic additives^[6]. However, it is difficult to obtain both perfect mechanical and dielectric performance simultaneously via these routes in spite of energy consumption and pollution creation. For example, Zhang *et al* fabricated porous Si₃N₄ ceramics with high porosity of 66.4%-76.8% by freeze-casting, while the flexural strength was only 33.5-14.3 MPa^[7]. Some research demonstrates that increasing the

porosity and compositing with the additives with low dielectric constant are effective ways to enhance the dielectric performance of porous Si₃N₄ ceramics. As has been known, SiO₂ is an attractive additive due to its prominent performances, such as high chemical stability, low dielectric constant and dielectric loss, low thermal expansion coefficient and thermal conductivity^[8-10]. Nevertheless, monolithic silica is intrinsically brittle with only low flexural strength and poor fracture toughness, so SiO₂-Si₃N₄ composite ceramic is an ideal candidate^[11]. Li *et al*, prepared a porous SiO₂-Si₃N₄ composite ceramic with porosity of 23.9% through combining oxidation-bonding with sol-gel infiltration-sintering, and attained a flexural strength of 120 MPa and fracture toughness of 1.4 MPa·m^{1/2}^[11]. The interconnected pores were divided into separate pores, and sharp angles were blunted effectively owing to the oxidation-bonding. As a result, the flexural strength and fracture toughness were improved to some extent.

Pore design is generally believed to be a feasible way to balance porosity and mechanical property^[12]. Diatomite is an abundant biological mineral material remaining the skeleton of aquatic diatom. It has a complex structure with numerous fine microscopic pores arranged orderly, high porosity and large pore volume^[13-15], as shown in Fig.1. It is possible to use diatomite as pore-forming skeleton to increase the

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YOU Guanglei(油光磊): E-mail: youguanglei2008 @126.com

*Corresponding author:BI Jianqiang(毕见强): Prof.; Ph D;

E-mail: bjq1969@163.com

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porosity and to modify the pore structure. The porous smooth structure of diatomite, amorphous SiO_2 essentially, can exert more beneficial effects on strength than granulated SiO_2 . Lu *et al* reported a method that porous Si_3N_4 ceramics were fabricated by carbothermal reduction between carbon black and diatomite. The porous Si_3N_4 ceramics exhibited a porosity of 70.1%-79.5% and a flexural strength of 2.3-14.5 MPa^[14]. However, the carbon impurity in the ceramics cannot be removed thoroughly.

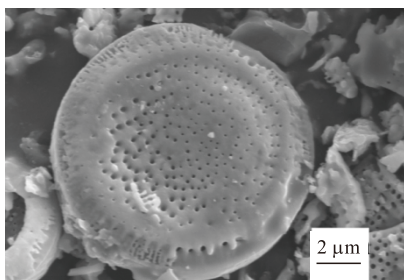


Fig.1 SEM image of diatomite powder

In this work, porous Si_3N_4 - SiO_2 ceramics were prepared using diatomite as pore-forming skeleton by pressureless sintering at 1 500 °C. The effect of diatomite on microstructure, porosity, mechanical property and dielectric properties was investigated.

2 Experimental

α - Si_3N_4 ($\alpha > 93$ wt%), sintering additives Al_2O_3 and Y_2O_3 (chemical pure reagent), BN (99 wt%), and diatomite ($\text{SiO}_2 > 90$ wt%) were used as starting materials for the fabrication of SiO_2 - Si_3N_4 composite ceramics. The samples were prepared according to the compositions shown in Table 1 (6 wt% Al_2O_3 and 4 wt% Y_2O_3 were constant in all the samples). The mixture was wet-milled in ethanol for 6 h. The slurry was dried at 100 °C for 12 h and sifted out by crushing with a 200 mesh sieve. Then the resultant mixtures bonded with polyvinyl alcohol were directionally pressed into rectangular shape of 40 mm × 40 mm × 40 mm under a pressure of 40 MPa. The green compacts were firstly preheated in air at 700 °C for 1 h with a heating rate of 3 °C/min. Then the specimens were sintered in a multi-purpose high temperature furnace (High-Multi 5000, Fijidenpa Co. Ltd., Osaka, Japan) to final temperature 1 500 °C under protecting atmosphere of N_2 for 1 h, followed by natural cooling to room temperature.

All samples were measured before and after the sintering to estimate the shrinkage degree of ceramics. The specimens were machined to the dimension of

3 mm × 4 mm × 4 mm for the flexural strength (σ_f) test, 2 mm × 4 mm × 40 mm bars with a notch in the depth of about 2 mm for fracture toughness (K_{IC}) test. The σ_f and K_{IC} tests were measured via a three-point bending method (Shenzhen SANS Testing Machine Co. Ltd, Shenzhen, China) with a support distance of 20 mm, cross-head speeds of 0.5 and 0.05 mm/min, respectively. Generally, five specimens of each sample were tested for each test.

Table 1 Compositions of the starting powder mixture

Samples no.	Compositions/wt%		
	$\text{Si}_3\text{N}_4 + \text{Al}_2\text{O}_3 + \text{Y}_2\text{O}_3$	BN	Diatomite
CA1	95	5	0
CA2	90	5	5
CA3	85	5	10
CA4	75	5	20
CA5	65	5	30

Both bulk density (D) and open porosity (P_o) of the sintered products were determined by Archimedes displacement method using distilled water according to ASTM C-20 standard. The theoretical density (D_{th}) of the composite ceramic was calculated by the rule of mixture:

$$D_{th} = V_i D_i \quad (1)$$

where D_i and V_i represent the theoretical density and volume fraction of different components in the specimens, respectively.

The total porosity was calculated according to the following formula^[11]:

$$P_t = 1 - D/D_{th} \quad (2)$$

Crystalline phases were identified by X-ray diffraction (XRD) analysis (Dmax-rc, Rigaku Co, Tykyo, Japan). The microstructure was characterized by a scanning electron microscope (SEM, Quanta FEG 250, FEI, USA). The dielectric constant was measured by a vector network analyzer (Agilent-E8363B, Agilent).

3 Results and discussion

3.1 Porosity and mechanical properties

The porosity and mechanical properties of the samples are listed in Table 2. The total porosity is calculated according to Eq.(2). The porosity increases from 39.8% to 50.7% (increased by about 27.4%) when the diatomite ratio increases from zero to 10%, but then decreases to 39.8% when the diatomite ratio is 30%. The micro-pore is developed by the shrinkage of diatomite piece at high temperature, as the diatomite

Table 2 Porosity and mechanical properties of samples

Sample no.	Pt/%	PO/%	Linear shrinkage/%	σ_f /MPa	K_{IC} /(MPa·m ^{1/2})
CA1	39.8	34.0	28.0	100.27±9.28	1.90±0.054
CA2	48.9	41.7	24.1	86.46±2.90	1.41±0.051
CA3	50.7	44.6	17.8	78.04±0.209	1.25±0.054
CA4	47.7	40.1	21.6	77.62±2.06	1.33±0.046
CA5	39.8	32.2	26.5	103.56±4.65	1.62±0.063

is loose and has numerous microscopic pores. It is obvious that the addition of diatomite influences the porosity significantly. Compared with the sample without diatomite, the closed pores in the samples with diatomite increase slightly due to the bonding of Si₃N₄ particles with the liquid phase formed from diatomite at grain boundaries. The flexural strength and fracture toughness of the samples are shown in Table 2. The shrinkage ratio of ceramics is estimated by measuring the samples before and after the sintering. The regularity of the shrinkage ratio is contrary to the change of porosity. The main reason is that a small quantity of dispersed diatomite could prevent the mass transporting and acts as the pore-forming agent during shrinking. The particles of BN also retard the liquid diffusion rate and increase the porosity.

The dependence of bending strength and fracture toughness on the porosity has been extensively investigated and a simple expression can be described as follows:

$$\sigma_f = \sigma_0 \exp(-b p) \quad (3)$$

where σ_0 is the bending strength with nonporous structure, b is the material constant related with the pore characteristics and σ_f is the strength at porosity V_p . The increase in porosity will generate micro-crack easily and inevitably deteriorate the flexural strength and fracture toughness. The experimental results indicate that the variations of flexural strength and fracture toughness are almost in consistent with the regularity of porosity, and the relationship between strength and porosity is almost in good agreement with that from Eq.(3). The ceramic with the maximum porosity of 50.1% attains σ_f of 78.04 MPa, and K_{IC} of 1.25 MPa·m^{1/2} when the diatomite ratio increases to 10%.

3.2 Phase transformation and microstructures

The XRD patterns of the porous Si₃N₄ ceramics with different contents of diatomite are shown in Fig.2. The main α -Si₃N₄ phase and minor β -Si₃N₄ phase can be detected by XRD analysis in all samples. It is shown that a slight α/β phase transformation happened by

comparing the peak intensity of α -Si₃N₄ and β -Si₃N₄. The grain boundary phases such as Si₂N₂O, Y₂Si₂O₇, and Sialon phase Si₂AlON, can be identified, which formed by the reaction of Si₃N₄ with Al₂O₃, Y₂O₃, and SiO₂, respectively. The peaks from h-BN are not obvious because of its low content in the samples. With increasing diatomite content, the SiO₂ and grain boundary phases grow in quantity. The appearance of liquid phase at grain boundaries can accelerate the particle rearrangement and promote the particle bonding. So the effect of retarding phase rearrangement by diatomite is counterbalanced partially, and the porosity increases and then decreases. When the weight ratio of diatomite reaches 30%, the boundary phase increases obviously, resulting in increased linear shrinkage and decreased porosity. Tridymite phase was also detected in the sample with 30% diatomite, and it may be transformed from the excess diatomite. The presence of tridymite phase will induce microcracks easily, worsening the flexural strength and fracture toughness^[16].

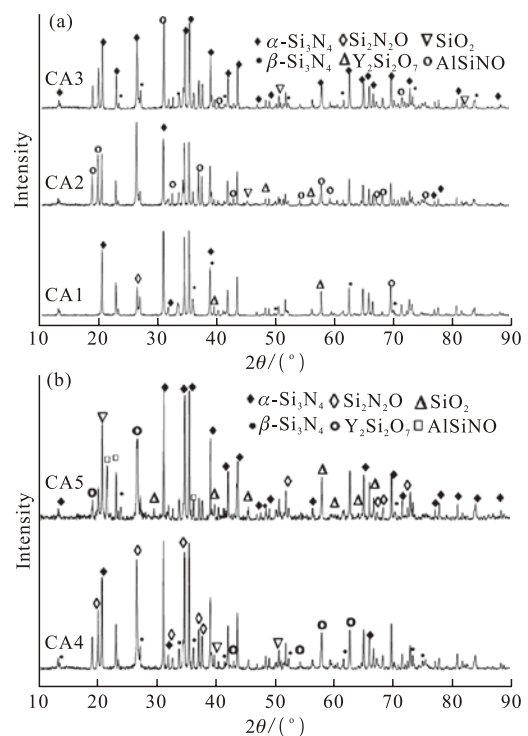


Fig.2 XRD patterns of porous SiO₂-Si₃N₄ composite ceramics: (a) CA1, CA2, CA3; (b) CA4, CA5

Figs.3(a-e) give the SEM images of the fractured porous Si_3N_4 ceramics with different diatomite contents. It is observed that all the samples show a typical microstructure consisting of bonded particles and slightly elongated $\beta\text{-Si}_3\text{N}_4$ grains, in consistent with the XRD analysis. The diatomite microstructure after mixed by ball-milling is given in Fig.3(f), which still maintains the microstructure partially. This microstructure could block powder movement during extrusion forming, and lessen the shrinkage during sintering. So the porosity of the samples with less diatomite increases. Compared to the samples with 0-20% diatomite, the sample with 30% diatomite exhibits high densification with large grains bonded with each other, and so its porosity declines hard. It is observed that minor columnar grains with high aspect ratio exist in Fig.3(e) due to the increase of liquid phase at grain boundaries. The elongated $\beta\text{-Si}_3\text{N}_4$ grains are helpful to enhance the flexural strength by pull-out and bridge of rod-like grains^[17]. However, the bending strength and fracture toughness of the sample increase slightly, because it is bad that cracks propagate into matrix with larger grains transgranularly.

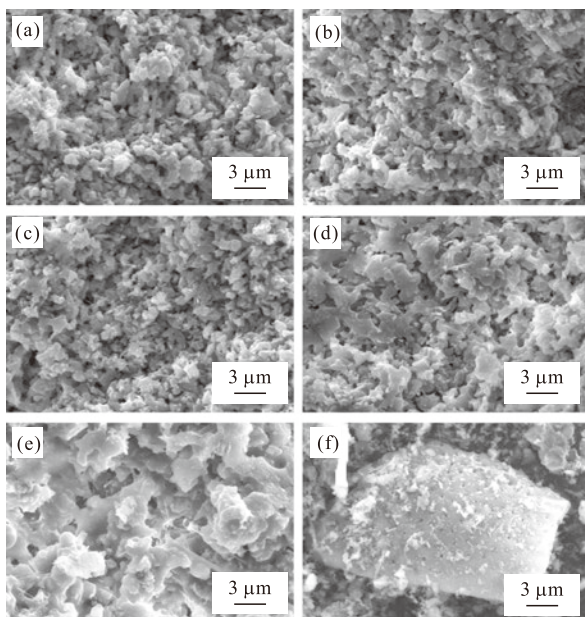


Fig.3 SEM images of fractured porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics with: (a) 0% diatomite; (b) 5% diatomite; (c) 10% diatomite; (d) 20% diatomite; (e) 30% diatomite; and (f) mixed material

Figs.3(a-d) show that there is no obvious difference in grain size, and the pores distribute uniformly in the matrix. Compared to the sample without diatomite, the samples with 5%-10% diatomite still maintain grain size of 0.5-2 μm , and a small quantity of open pores which are surrounded by

stacking particles. The degree of particle packing in Figs.3(b-c) is declined relative to the sample without diatomite, which indicates that large discoid diatomite does not increase the grain size and fine grains are in favor of enhancing the bending strength and fracture toughness, because the large discoid diatomite has been shrunk and fused with sintering additives. The microstructure and matrix morphology of the sintered samples are affected to a large extent by characterization of starting powder, such as grain size, morphology of particles and so on. The pores are produced when diatomite with numerous microscopic pores and low density shrink during sintering, and the porosity increases obviously. A small quantity of pure crystal of SiO_2 is detected by XRD analysis in the samples with 5%-20% diatomite, demonstrating that the diatomite has partially reacted with the sintering additives and the Si_3N_4 matrix. So the diatomite powder with the large discoid microstructure is not the impact factor for the degradation of flexural strength of the samples, and it is excellent pore-forming agent.

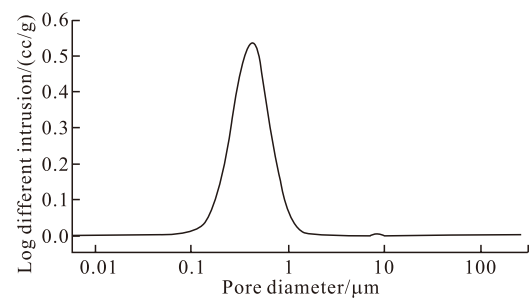


Fig.4 Pore size distribution of porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics sample no. CA3

The pore size distributions were measured by a mercury porosimeter (Poremaster 33, Quantachrome Instruments Co., Boynton Beach, FL, USA). Fig.4 shows the pore size distribution of the sample CA3, the mean pore size of porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ ceramic distributes from 0.1 to 1 μm . The pore size distribution shown in Fig.4 is consistent with the SEM images shown in Fig.3(c). The uniform distributed pores further confirm the diatomite to be good for microstructure of the porous ceramic.

3.3 Dielectric properties

The dielectric properties of porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics strongly depend on their porosity and phase components. Compared to Si_3N_4 , SiO_2 shows better dielectric property, whose ϵ is 4 at room temperature than that of $\alpha\text{-Si}_3\text{N}_4$ ($\epsilon=5.6$). Fig.5 shows the relationship between dielectric constant (at range of 26.5-32.0 GHz) of porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics with different diatomite content, respectively.

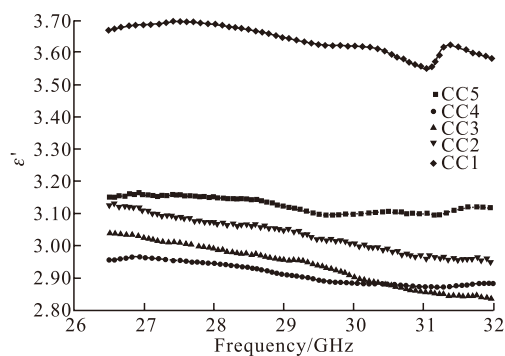


Fig.5 Dielectric constant of porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics

The results show that the dielectric constant decreases from 3.65 to 2.95 with the increase of diatomite content from 0 to 10%, which fits well with the mixture law. High porosity and diatomite content together contribute to the decrease of the ϵ value, which is the reason why the dielectric constant of sample CA4 is the lowest and the dielectric constant of sample CA5 increases slightly.

4 Conclusions

Porous $\text{SiO}_2\text{-Si}_3\text{N}_4$ composite ceramics with high porosity and excellent mechanical properties were fabricated by pressureless-sintering at 1500 °C using diatomite as the pore-forming agent. The ceramic with a maximum porosity of 50.1% attains σ_f of 78.04 MPa, K_{IC} of 1.25 $\text{MPa}\cdot\text{m}^{1/2}$ and ϵ of 2.95 when the ratio of diatomite increases to 10%. Compared with the sample without diatomite, the porosity of the ceramic with 10% diatomite is increased by about 27.4%. Numerous pores were produced by the shrink of diatomite and the degree of particle packing of samples with 5%-10% of diatomite was declined relative to the sample without diatomite. Even the microscopic pores of sample with 30% of diatomite was bad as shown by image of SEM, however, diatomite is also one excellent pore-forming agent.

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