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High performance porous Si_3N_4 ceramics prepared by coated pore-forming agent method

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Abstract

Coated pore-forming agent method (CPFAM) was introduced to improve the pore-forming agent method (PFAM) for the preparation of porous silicon nitride ceramics. Using SEM in combination with measurements of porosity and flexural strength, it has been found that the flexural strength of the porous silicon nitride ceramics produced with the CPFAM method is significantly higher than those without the coating process: a 100% increase in flexural strength for samples with a porosity of 50%. The porous silicon nitride ceramics also have a very low dielectric constant, which is ideal for applications in wave-transmitting systems. The enhanced mechanical strength of the silicon nitride made by the CPFAM method is a result of a more uniform distribution of the spherical pores and the formation of a dense layer of rod-like microstructures near the surface of the pores.

Keywords: CPFAM; Porous Si_3N_4 ceramic; Flexural strength; Dielectric properties; Microstructure

1. Introduction

Due to its important application as structural and functional ceramic materials, silicon nitride (Si_3N_4) matrix ceramic has been studied intensively because of its superior properties, such as high-temperature strength, superior oxidation resistance, low thermal expansion coefficient, dielectric constant stability at high temperatures and its good corrosion resistant against rain [1–7]. Si_3N_4 is also an important material for the wave-transmitting industry [8]. For wave-transmitting materials, there is the need to reduce the material's dielectric constant when the dielectric loss is very low (10^{-3}). There are two ways to make low dielectric constant silicon nitride materials. One is the preparation of porous α-Si_3N_4 ceramics (it is reported that α-Si_3N_4 intrinsically has lower dielectric constant than β-Si_3N_4 [9,10]). However, porous α-Si_3N_4 ceramics have too low a mechanical strength to be practically useful. The other approach is the production of porous β-Si_3N_4 ceramics which have a high flexural strength. The introduction of pores to the β-Si_3N_4 gives rise to an effectively reduced dielectric constant, but the mechanical strength of such porous β-Si_3N_4 decreases with porosity. The degrading flexural strength is in most cases associated with defects around the pores, or due to overlapping of pores which is a source of local stress concentration. In order to prevent pore overlapping and thus improve the flexural strength of porous β-Si_3N_4, we have introduced a coating step where the pore-forming agent (urea balls) is pre-coated with a uniform layer of α-Si_3N_4 before mixing with the α-Si_3N_4 powder. This pre-coating step has been found to improve the distribution of the pores in the final β-Si_3N_4 matrix after sintering. Moreover, a dense layer of rod-like β-Si_3N_4 network has been observed to form at the boundaries of the pores. The resulting β-Si_3N_4 material has a much higher flexural strength than those prepared without the pre-coating step, whilst its dielectric constant remains low.

2. Experimental procedure

2.1. Raw materials

The starting powder mixture contains α-Si_3N_4 (Shanghai Ansaimei Co., China, $\alpha \geq 95\%$, $D50 \leq 1.0\ \mu m$), with 5 wt%

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Table 1
Experiment prescription.

N	Coated pore-forming agent, content/wt%	Pore-forming agent, content/wt%
	50	20
2	70	30
3	90	40
4	100	50

CeO_2 (A.R., Chemical Co. of National Medicine, China) and 5 wt% MgO (98.5%, Chemical Co. of National Medicine, China) as sintering additives. The raw materials were milled by agate balls in a Teflon jar for 10 h with absolute ethanol used as the medium, and the slurry obtained from the milling process was dried in an oven at 70 °C for 8 h, and passed through a 60 mesh sieve. The pore-forming agent is urea ball (Sichuan Meifeng Chemical Industry Co., Ltd., $D \approx 800\ \mu m$).

2.2. The CPFAM process

Special oil was added into a glass containing a suitable numbers of urea balls such that all the urea balls were covered with a thin film of the oil. Then a small amount of α-Si_3N_4 powder was added and the mixture stirred. This process leads to the coating of each urea ball with a layer of α-Si_3N_4. Due to the variation in the thickness of the α-Si_3N_4 coating on different balls, the final diameters of the balls are thus different. To select a uniform size, the coated balls are sieved so that only those with a coating thickness in between 100 and 200 μm are selected for the next step. The coated urea balls as PFA were mixed with α-Si_3N_4 powder according to the proportions listed in Table 1, and then shaped into a disc of $\phi 70\ mm \times 5\ mm$ under a pressure of 50 MPa. The disk was heated to 130 °C to allow the urea to be released, and then the temperature was increased to 700 °C to eliminate all carbon containing species from the pores. Finally the porous disk was heated under 0.6 MPa N_2 atmosphere at 1750 °C for 2 h for sintering.

2.3. Characterization

The porosity of the samples was measured by Archimedes method after processed for 0.5 h in boiling water. The flexural strength was tested by the three-point bending method. A scanning electric microscope (SEM, Model S-570, Hitachi) was used to characterize the microstructures of the sintered sample. The sample was cut into small blocks, with dimensions of $22.9\ mm \times 10.2\ mm \times (2.0 \pm 0.1)\ mm$ for the measurement of dielectric properties at 10 GHz on an Agilent E8326B PNA series network analyzer. Three samples per each porosity content were prepared for the strength measurements.

3. Results and discussion

Due to the highly covalent nature of the Si–N bond and low diffusivity, the porous Si_3N_4 bodies were all sintered at 1750 °C for 2 h with sintering additives (MgO and CeO_2) under the conditions of liquid sintering mechanism [11,12]. During the

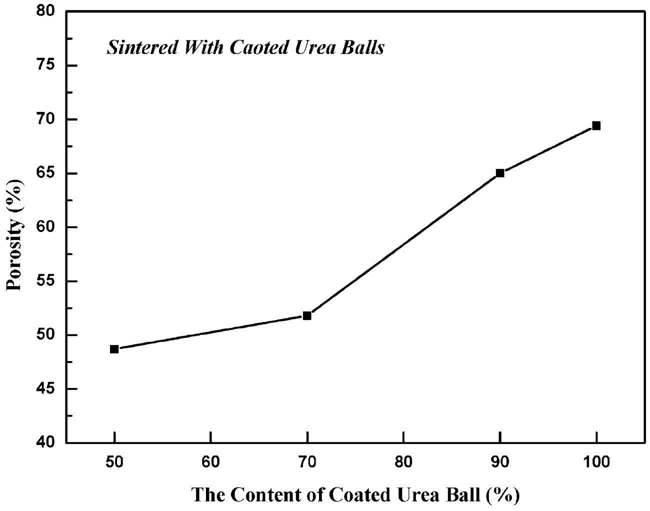

Fig. 1. The porosity of sintered porous Si_3N_4 ceramics as a function of content of coated urea balls.

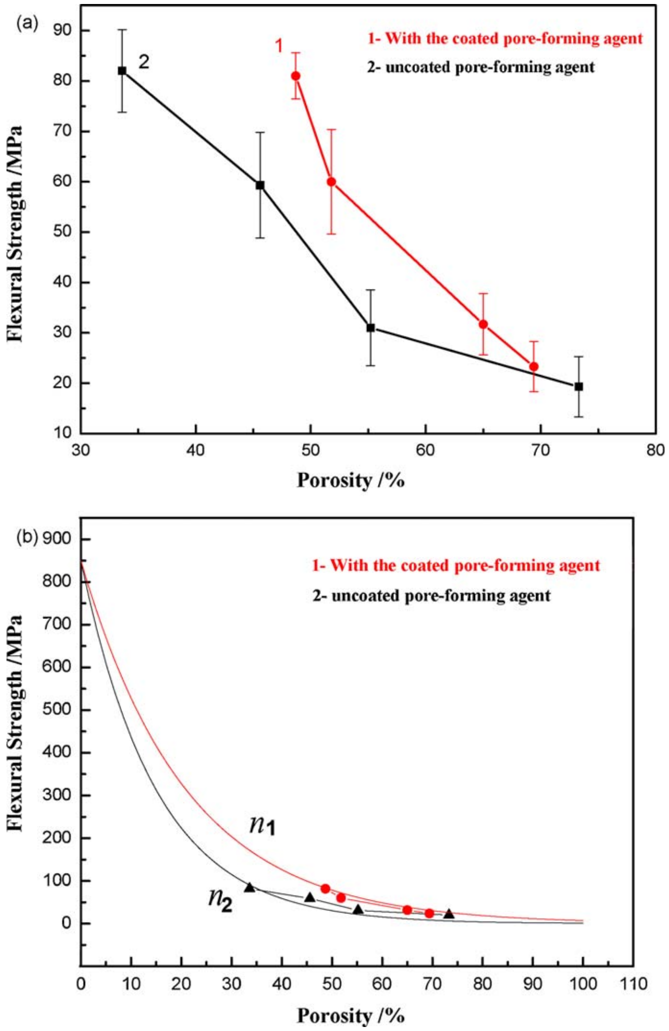

Fig. 2. (a) and (b) The flexural strength of sintered porous Si_3N_4 ceramics.

sintering process the microcavities were filled with liquid the phase and then disappeared during cooling, but the macropores produced by the pore-forming agent (coated urea balls) were retained. Fig. 1 shows the ceramic porosity as a function of the percentage of the added pore-forming agent. The maximum porosity of the sintered sample can be adjusted by using balls coated with a different thickness of α-Si_3N_4: thicker coatings result in lower porosity. For the coated balls in this particular experiment, the maxim porosity can be achieved is 70%, and this maximum porosity is obtained by using the coated balls without any further addition of α-Si_3N_4 powder.

3.1. The mechanical property of sintered porous Si_3N_4 ceramics

The flexural strength of porous ceramics is very strongly dependent on the porosity, as shown by the Ryshkewitch in the following formula [13]:

$$\sigma = \sigma_0 \exp(-nP) \qquad (3\text{-}1)$$

where σ_0 is flexural strength when the total porosity P is 0%. And n is the structure parameter of porous ceramics.

Fig. 2 shows the flexural strength for porous β-Si_3N_4 as a function of porosity for two samples. Curve (1) is obtained from a sample where pre-coating of the urea balls was performed before sintering, whereas curve (2) was obtained from a sample without the pre-coating step. It can be seen that the flexural strength for the sample with the CPFAM method is significantly higher. For instance, at a porosity of 50%, the CPFAM treated sample has a flexural strength of 75 MPa, which is almost twice of that the sample without CPFAM. Since the porosity is the same for the two samples, thus according to Eq. (3-1), there must be a large difference in the structure parameters due to differences in the shape of the pores and the distribution of the pores inside the ceramic [13].

Fig. 3(a) schematically summarizes the procedural of CPFAM method. Since the minimum distance between the surfaces of two adjacent pores is more or less determined by the thickness of the pre-coating on the urea balls, overlapping and direct contact between pores are not possible with samples

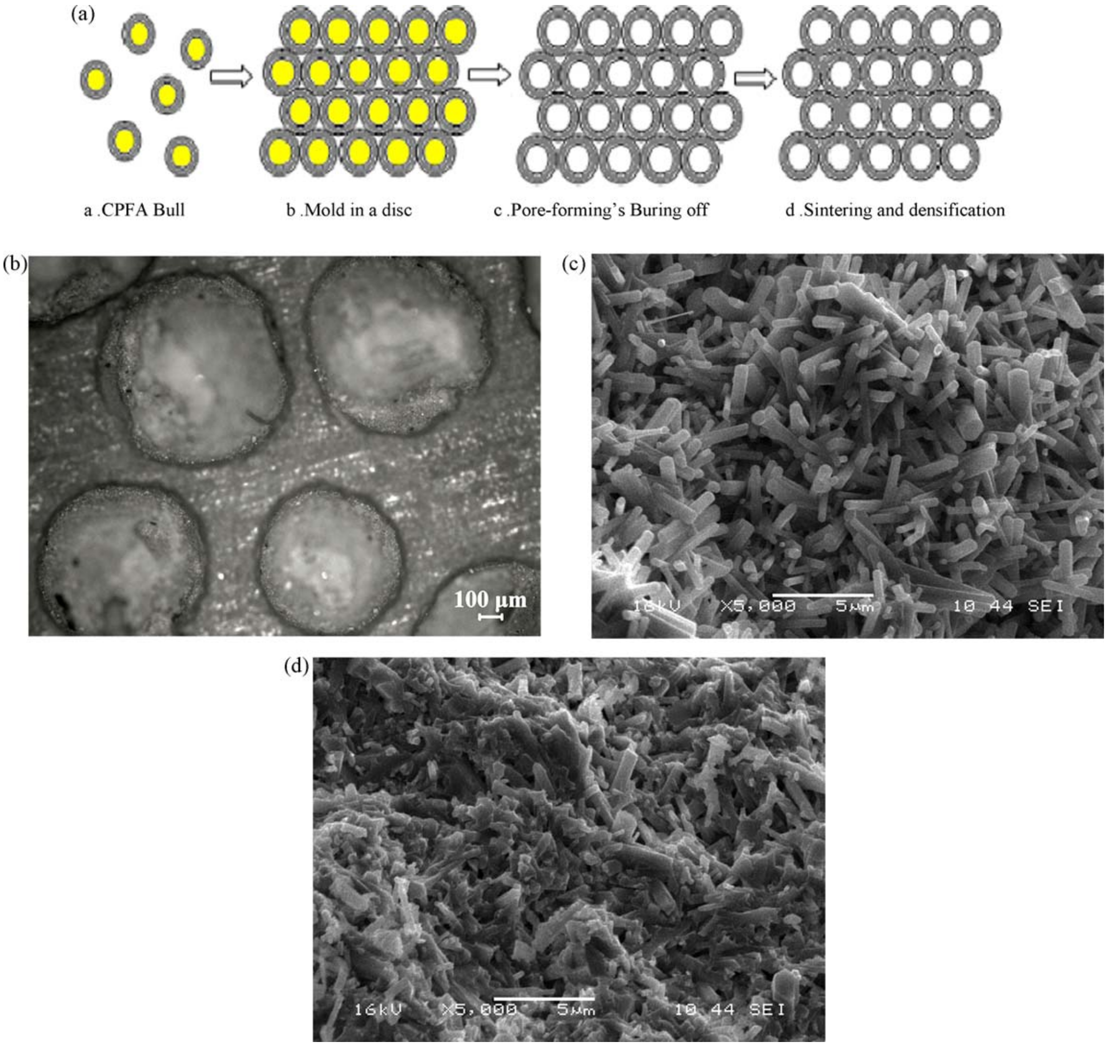

Fig. 3. The surface structure of porous Si_3N_4 ceramics with 70% coated pore-forming agent: (a) the schematic diagram for the procedure of coated pore-forming agent method; (b) the surface structures by the optical microscopy; (c) the SEM figure of the fracture matrix structure; (d) the SEM figure of the fracture pore inner surface.

prepared using the CPFAM method, Fig. 3(b). It is also noticed that pore distribution is more uniform and interconnectedness of pores does not occur following the CPFAM method. The sticky oil coating on the urea balls assists in obtaining a better distribution of silicon nitride powder around the balls, therefore making them more homogeneously embedded within the ceramic matrix and also making there is a lay of silicon nitride powder between two pore, which makes the pores less clustered and interconnected. Interconnectedness of pores is a macro-fracture source in porous ceramics which are fatal to the mechanical strength. This is the main idea of the CPFAM method.

Fig. 3(c) shows the structure of the ceramic in regions between the pores. The material in these regions appears to consist of β-Si_3N_4 and amorphous phase of silicon nitride. The structure at the boundaries of the pores as shown in Fig. 3(d) is much more uniform. It consists of regular rod-shaped β-Si_3N_4 with a relatively high aspect ratio. XRD data (not shown) confirms that the rods are crystalline β-Si_3N_4. The rods point in nearly every direction, with each rod in direct contact with a number of other rods giving rise to a woven fabric type of structure. It is possible that these inter-penetrating rods have contributed to an increased strength of the pore surfaces, and thus the observed increase in the flexural strength.

3.2. The dielectric property of sintered porous Si_3N_4 ceramics

In the green bodies the added pore-forming agents disappeared when we put them into a shaft furnace at 700 °C and resulted in spherical pores. The micropores vanished during the sintering process, but the macrospherical pores remained. These pores, as a low dielectric constant phase, distribute rather uniformly in the porous Si_3N_4 ceramic matrix.

The porous ceramic's dielectric property depends on the β-Si_3N_4 main phase, the structure of the grain boundaries, and pores in the ceramics bodies [10]. The mixture principle can explain this as follows:

$$\log \varepsilon = \sum\nolimits_i \nu_i \log \varepsilon_i \tag{3-2}$$

where ν_i is volume fraction of the i phase, and ε_i is the corresponding dielectric constant.

Fig. 4 shows the dielectric constant of the porous Si_3N_4 ceramic as function of porosity. The dielectric constant decreases with porosity as expected. For porosity higher than ~60%, the sample prepared using the CPFAM method is lower than that prepared without the pre-coating step. It is known that using ordinary pore-forming agent without the pre-coating procedure, the pores in the ceramics are usually connected with each other creating many sharp edges. This causes more reflections in the ceramics and low permeate flux through the samples causing an increase in the dielectric constant. When the porosity is low, the probability of pore connecting is small and thus the difference between pre-coating and non-coating is minimal.

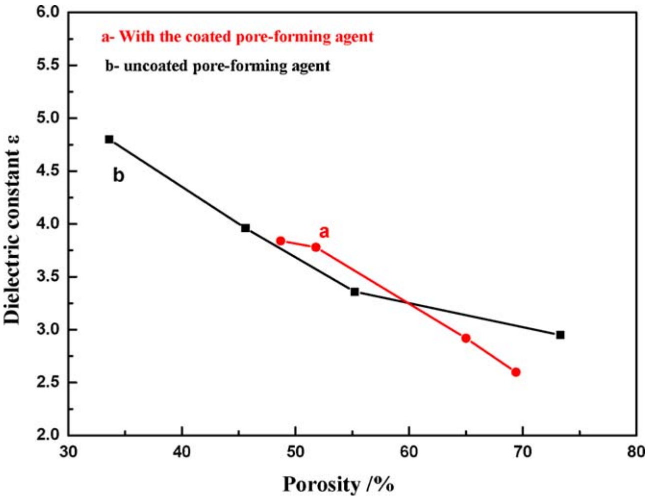

Fig. 4. The dielectric constant of sintered porous Si_3N_4 ceramics.

4. Conclusions

Porous Si_3N_4 ceramics, as a potential candidate for wave-transmitting materials, Si_3N_4 matrix has a relatively high dielectric constant. The pores in the ceramic matrix can decrease the dielectric constant. When the porosity is high, the pores' distribution will be a main factor affecting both the flexural strength and the overall dielectric constant. By coating the pore-forming balls before sintering, we have developed a CPFAM procedure which is able to produce porous β-Si_3N_4 ceramics with high porosity (nearly 70%) and high flexural strength. For a porosity of 50%, the flexural strength can reach 75 MPa, which is almost twice that of the β-Si_3N_4 ceramics produced using the ordinary (no pre-coating) pore-forming agent method. The major effects of pre-coating the balls are: a more uniform distribution of the pores, a more uniform wall thickness between the pores, and the formation of an interacting β-Si_3N_4 rods at the inner surface of the pores. Therefore the coated pore-forming agent method has proven to be a very effective way to improve the materials mechanical properties. The porous β-Si_3N_4 ceramics made from CPFAM also has a lower dielectric constant at >50% porosity, which is advantageous in many applications.

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