

Investigation of flexural strength and porosity of porous Si₃N₄ ceramics through orthogonal experimental design

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Porous Si₃N₄ ceramics by a gel casting preparation route have received considerable attention because of their excellent performance. In this paper, orthogonal experimental design L₁₆(4⁵) was used to investigate the preparation of porous Si₃N₄ ceramics by a gelcasting technique. Three variables including solid loading, monomer content and the ratio of monomers were studied. Through range analysis and variance analysis, the results suggest that the ratio of monomers has a significant influence on both the flexural strength and porosity of Si₃N₄ sintered bodies. For the flexural strength of a Si₃N₄ sintered body, the order of significance levels was as follows: the ratio of monomers, solid loading and monomer content. For the porosity of a Si₃N₄ sintered body, the order of significance levels was as follows: the ratio of monomers, monomer content and solid loading. The experimental results suggest also that solid loading has an optimum value where the flexural strength can achieve a maximum value.

Key words: Si₃N₄ ceramics, Orthogonal experimental design, Flexural strength, Porosity, Gel casting.

Introduction

Silicon nitride (Si₃N₄) ceramics have excellent mechanical properties (such as high strength, high fracture toughness, high thermal shock resistance and high chemical resistance), and then it have great promise for engineering applications [1, 2]. Porous Si₃N₄ ceramics with certain levels of porosity offer an interesting combination of strength and stiffness, and they are lighter and can also be machined more easily than dense Si₃N₄ ceramics [3].

Porous ceramics can be prepared by many approaches including polymeric sponge impregnation, foaming, extrusion molding, solid state sintering, additive pore forming agents, sol-gel, gel casting, etc [1-5]. Among these preparation approaches, gel casting is an innovative approach to the preparation of porous ceramics. During gel casting based on in situ polymerization of organic monomers, the monomers are polymerized to form a cross-linked polymer network which is rather strong. Therefore, gel casting shows an ability to fabricate uniform and complex-shaped green bodies with high green strength [6]. The process of the gel casting technique consists of the dispersion of a ceramic powder in an aqueous monomer solution to form a fluid and castable slurry that is subsequently gelled in a mould. The wet cast body has a uniform chemistry and density that contains a certain percent of organic binder. After drying, binder removal and

sintering take place as in other ceramic processes. Pores in the ceramic are formed during drying and organic binder removal from green body. Recently, this process has been extensively used in producing the porous ceramic parts of drug delivery systems, bio-ceramics and sensors, ceramic foams, and porous support systems for membranes [7-10].

So far, during the preparation of porous ceramics by gel casting, a number of routes for the porous ceramics (such as foaming, stacking of presintered granules or fibers, aerogel or sol-gel and pyrolysis of various organic additives) have been developed [4, 5]. However, little work has focused on the investigation of the porous ceramics preparation by merely increasing monomer content in the slurry without other organic additives during gel casting. Monomer and crosslinking agent herein not only can form a macromolecular network to hold the ceramic particles together, but also play a leading role in the formation of pores during the preparation of porous Si₃N₄ ceramics. In the meantime, the incorporation of a crosslinking agent into a polymer may also improve its physical properties, such as solvent resistance, toughness and the shrinkage of green body [11].

In this paper, we investigate the influence of solid loading, monomer content and the ratio of monomers on the flexural strength and porosity of porous Si₃N₄ ceramics. Orthogonal experimental design is one way to qualitatively analyze the correlations among the relevant variables at different levels through designing an orthogonal table and statistic analysis [12]. An orthogonal table L₁₆(4⁵) was used in the experiment, and the flexural strength and porosity of Si₃N₄ ceramics were set as the investigation targets. Three

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influencing factors including the solid loading, the monomer content and the ratio of monomers were chosen, and four levels were set for each factor.

Experimental

Materials

Si₃N₄ powders (mean particle size: 0.37 μm, α phase > 94 wt%) employed in this study were commercially available materials. Al₂O₃ (mean particle size: 1.07 μm, 99% purity) and Y₂O₃ (mean particle size: 4.74 μm, 99.9% purity) were used as the sintering additives. For gel casting purposes, acrylamide (AM, C₂H₃CONH₂) and *N*, *N*'-methylenebisacrylamide (Merck, MBAM, (C₂H₃CONH)₂(CH₂)) were applied in the process of gel casting as monomers for polymerization. A dispersant (1 wt%, ammonium salt of poly(acrylic acid)) was added to minimize agglomeration, and potassium persulphate (Merck, K₂S₂O₈) was used as an initiator. A proper amount of polyacrylamide (PAM) with an average molecular weight of approximately 3000,000 may eliminate the surface exfoliation phenomenon of green bodies cast in air, and it can also decrease the fluidity of the suspension to prevent Si₃N₄ powders from depositing [13]. Aqueous ammonia was used as a pH adjuster. All of these reagents were chemically pure.

Gel-casting procedure

In the first step, the PAM (2 wt%, based on silicon nitride) and dispersant (1 wt%, based on silicon nitride) were first completely dissolved in deionized water using mechanical stirring for 10 minutes, then monomers (AM and MBAM) were dissolved. The premixed solution served as a dispersing media for the ceramic powder.

The next step was to add silicon nitride powders and a suitable sintering additive (1 wt% Al₂O₃ and 2 wt% Y₂O₃, based on silicon nitride) to the premixed solution. The slurry was milled using agate balls in a polyethylene bottle for 12 h, and then it was degassed for 30 minutes. After adding the initiator, the slurry was degassed for another 10 minutes. All the above operations were conducted at room temperature. Afterward, the slurry was cast into a cylindrical glass mold having a length by diameter 40 × 7 mm, which was then kept at 65 °C for 40 minutes. After the monomers had polymerized, the green body was demolded and dried at room temperature and at 96% relative humidity to avoid the cracking and non-uniform shrinking caused by rapid drying. The temperature of the binder removal was determined from the result of thermal gravimetric analysis (TGA). Thermogravimetric analysis shows that the temperature range of the binder removal was from 220 to 550 °C. Therefore, the green body containing binder was placed in a furnace and heated from 220 to 550 °C in air using a heating rate of 10 K·h⁻¹ to control the gas release during pyrolysis of organic substances, and then the temperature was kept 550 °C for 8 h to burn out the residual organic substances thoroughly. After binder removal, sintering was performed

at a heating rate of 10 K·minute⁻¹ with 1 h holding time at 1,730 °C.

Methods for testing the performance of porous Si₃N₄ ceramics

The porosity of the sintered samples was measured by the Archimedes displacement technique. The bulk density (ρ_b) and the true density (ρ₀) of the sintered bodies were determined by the Archimedes' method in water and by the water displacement method, respectively. Then the porosity (P) was calculated as follows:

$$P = \left(1 - \frac{\rho_b}{\rho_0}\right) \times 100\% \quad (1)$$

The room temperature mechanical strength of the sintered bodies was determined by three-point flexural tests of specimens. The specimens were machined into test bars, and all the surfaces of the bars were ground with a 600-grit diamond wheel and the edges were beveled. The direction of both the diamond grinding and the beveling was parallel to the bar length. Three-point bending strength was measured on bars using a span of 16 mm and a crosshead speed of 0.5 mm·minute⁻¹ (Instron 1195; Instron, UK). By repeating the tests for silicon nitride three times for each specimen, the results are given as the mean values of three measurements. Fracture surfaces of the sintered bodies were observed using scanning electron microscopy (SEM; S-570; Hitachi) to estimate the microstructural uniformity of the specimens.

Orthogonal experiment design

The quantitative evaluation and statistical analysis of the effects of the influencing factors on the flexural strength and porosity were investigated through an orthogonal experimental design. The study highlights the importance of compositions (i.e., polymer, monomer, crosslinking agent, and solid loading).

Three influencing factors were investigated: solid loading, monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM). Four levels were set for each influencing factor, as shown in Table 1. The value ranges of influencing factors were determined in experiments to achieve good rheological properties and viscoelastic properties of silicon nitride aqueous suspensions. Solid loadings of 30%, 40%, 50% and 60% were used in the experiments, four levels of 10%, 15%, 20% and 25% were set for monomer contents (AM and MBAM), and four levels of 2 : 1, 3 : 1, 4 : 1 and 5 : 1 were set for the ratios of

Table 1. Influencing factors and levels of orthogonal experimental design

Level	Solid loading(%)	Monomer content(%)	Ratio of monomers
1	30	10	2 : 1
2	40	15	3 : 1
3	50	20	4 : 1
4	60	25	5 : 1

Table 2. The design of orthogonal table $L_{16}(4^5)$ and experimental results

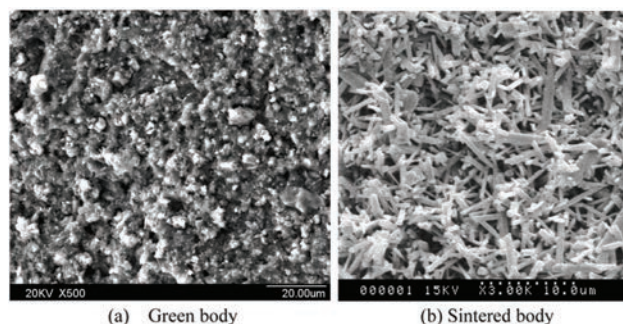
Experiment No.	Solid loading (%)	Monomer content (%)	Ratio of monomers	Flexural strength (MPa)	Porosity (%)
1	30	10	2 : 1	88.12	58.58
2	30	15	3 : 1	87.8	59.72
3	30	20	4 : 1	115.6	55.75
4	30	25	5 : 1	158.1	57.65
5	40	10	3 : 1	116.74	50.82
6	40	15	4 : 1	160.92	53.54
7	40	20	5 : 1	169.5	56.00
8	40	25	2 : 1	134.88	61.59
9	50	10	4 : 1	234.17	51.19
10	50	15	5 : 1	156.74	52.42
11	50	20	2 : 1	62.06	61.92
12	50	25	3 : 1	98.67	58.2
13	60	10	5 : 1	134.3	49.5
14	60	15	2 : 1	54.54	57.6
15	60	20	3 : 1	55.54	54.66
16	60	25	4 : 1	59.17	54.62

monomers (AM/MBAM). The orthogonal table $L_{16}(4^5)$ was designed, in which two blank columns were designated for the error evaluation. Based on the investigation factors and the corresponding levels, the orthogonal experimental table is shown in Table 2.

Experimental Results and Discussions

SEM micrographs of the fracture surfaces of the green body and the sintered body of porous Si_3N_4 ceramics are shown in Fig. 1. In the green body shown in Fig. 1 (a), Si_3N_4 powders were homogeneously bound by the organic binder. Pores in ceramic were formed during drying and organic binder removal from the green body. At the same time, in the sintering process, $\alpha\text{-Si}_3\text{N}_4$ grains were converted into elongated $\beta\text{-Si}_3\text{N}_4$ grains, and then these fine elongated $\beta\text{-Si}_3\text{N}_4$ grains were jointed to form a porous Si_3N_4 ceramic, as shown in Fig.1 (b).

The experimental results of flexural strength and porosity of porous Si_3N_4 ceramics are shown in table 2. Range analysis and variance analysis are adopted to investigate

**Fig. 1.** SEM fracture surface of samples.**Table 3.** Range analysis for the flexural strength and porosity of Si_3N_4 ceramics

Flexural strength			
Factors	Solid loading	Monomer content	Ratio of monomers
K ₁	112.41	143.33	84.90
K ₂	145.51	115.00	89.69
K ₃	137.91	100.68	142.47
K ₄	75.89	99.71	154.66
R	69.62	43.62	69.76
Porosity			
Factors	Solid loading	Monomer content	Ratio of monomers
K ₁	57.93	52.52	59.92
K ₂	55.49	55.82	55.85
K ₃	55.33	57.08	53.77
K ₄	54.10	58.02	53.89
R	3.83	5.50	6.15

the influences of each influencing factor on the performances of porous Si_3N_4 ceramics.

Range analysis

The range analysis is aimed to clarify the significance levels of different influencing factors on the flexural strength and porosity of porous Si_3N_4 ceramics. Based on the results of range analysis, the most significant factors can be revealed [12]. Table 3 summarizes the statistical analysis of the effects of different factors on the flexural strength and porosity of Si_3N_4 ceramics. The K value for each level of a parameter is the average of four values of experimental results shown in Table 2, and the range value (R) for each factor is the difference between the maximum value and minimum value of the four levels. According to the principle of range analysis [12], a larger range value (R) means that the corresponding factor has a more significant influence on the flexural strength or porosity of porous Si_3N_4 ceramics in the experiment. Based on the results of the range analysis, the significance sequence of all the influencing factors investigated was lined. From Table 3, we can easily determine that the superiority and the degree of the influence (sensitivity) of each design factor. For the flexural strength of porous Si_3N_4 ceramics, the order of significance levels was as follows: the ratio of monomers, solid loading and monomer content. For the porosity of porous Si_3N_4 ceramics, the order of significance levels was as follows: the ratio of monomers, monomer content and solid loading.

According to Table 3, the relations between the levels of each influencing factor and the properties of porous Si_3N_4 ceramics (flexural strength and porosity) can be obtained intuitively, as shown in Fig. 2, Fig. 3 and Fig. 4. The results indicate as follows: ① the flexural strength monotonically decreases with an increase of monomer content and the ratio of monomers; ② the flexural strength is low when the solid loading is too low or too high, and it can achieve a peak value when the solid

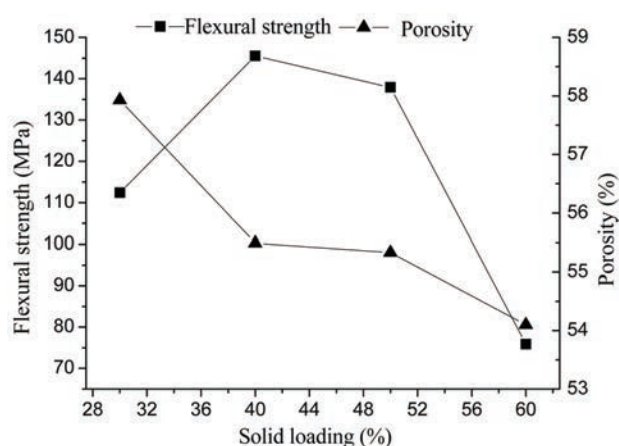


Fig. 2. The relations between experimental levels of the solid loading and flexural strength and porosity of Si_3N_4 ceramics.

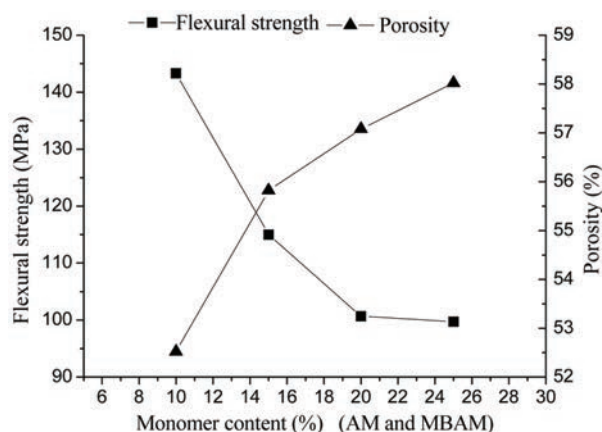


Fig. 3. The relations between experimental levels of the monomer content and flexural strength and porosity of Si_3N_4 ceramics.

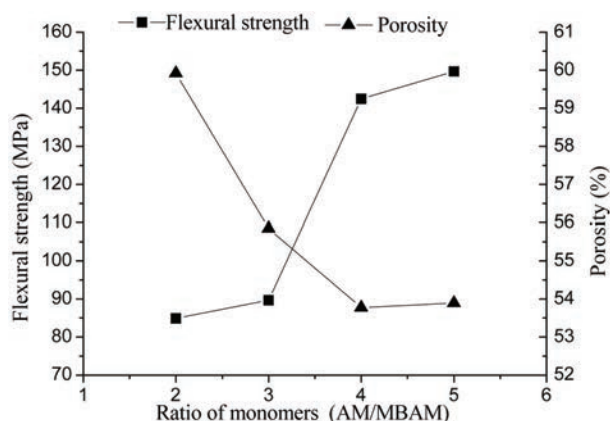


Fig. 4. The relations between experimental levels of the ratio of monomers and flexural strength and porosity of Si_3N_4 ceramics.

loading is a certain proper value; ③ the porosity increases with an increase of monomer content and the ratio of monomers, but it monotonically decreases with an increase of solid loading.

Variance analysis

In our experiments, two blank columns were set in the

Table 4. Analysis of variance for the flexural strength and porosity of Si_3N_4 ceramics

Factors	SS	DF	MS	F
Flexural strength of Si_3N_4 ceramics				
Solid loading	11831.89	3	3943.867	4.59105
Monomer content	3915.705	3	1305.217	1.51940
Ratio of monomers	15358.66	3	5119.553	5.9599
Error	5154.205	6	859.0	
Porosity of Si_3N_4 ceramics				
Solid loading	30.09	3	10.03	1.3654
Monomer content	69.13	3	23.04333	3.136926
Ratio of monomers	98.87	3	32.95667	4.486444
Error	44.075	6	7.345833	

$F_{0.01}(3,6)=9.15$, $F_{0.05}(3,6)=4.76$, $F_{0.1}(3,6)=3.29$

orthogonal table for error estimates. Thus it was unnecessary to repeat the experiments for each protocol [12]. In the experiment, the sum of squares of the deviation (SS), the degree of freedom (DF) and the mean squared deviation (MS) of the flexural strength and porosity of Si_3N_4 ceramics were determined and summarized in Table 4. The F value of a factor is the ratio of the MS value of the factor to that of the error line. By comparing the F value obtained with the theoretical one of a specific level and DF, the significance level can be determined for each factor [12].

As shown in Table 4, the ratio of monomers has a significant influence on the flexural strength of Si_3N_4 ceramics ($F = 5.9599$, $F > F_{0.05}(3,6)$). For the flexural strength of Si_3N_4 ceramics, since the F value of the solid loading is very approximately equal to 4.76, it can be considered that the solid loading also has a significant influence on the flexural strength of Si_3N_4 ceramics. The variance analysis also shows that the ratio of monomers has a significant influence on the porosity of Si_3N_4 ceramics (the F value is approximately equal to 4.76), and that the monomer content has a somewhat influence on the porosity of Si_3N_4 ceramics (the F value is approximately equal to 3.29).

Discussions of results

Based on the above range analysis and variance analysis, it can be concluded that the ratio of monomers has significant influences on both the flexural strength and porosity of porous Si_3N_4 ceramics, and the solid loading has some influence on the flexural strength of Si_3N_4 ceramics.

During the preparation of porous Si_3N_4 ceramics by the gel casting technique, the pores in ceramics mainly originate from the residual micropores during the removal of organic binders in the debinder process and from the joints of the $\beta\text{-Si}_3\text{N}_4$ phase in the sintering process. The kernel of the gel-casting process is the use of a monomer solution, which can be polymerized to form a strong, cross-linked polymer solvent gel. The macromolecular network resulting

from in-situ polymerization holds the ceramic particles together. The intensity of the macromolecular network gel increases with a decrease in the ratio of monomers (AM/MBAM)), and this makes Si_3N_4 particles distribute uniformly which can effectively prevent the drying shrinkage. In the meantime, a uniform distribution of Si_3N_4 particles is conducive to increase pore formation by the joints of the $\beta\text{-Si}_3\text{N}_4$ phase in the sintering process. However, when the ratio of monomers (AM/MBAM) increases, more monomers easily polymerize to form a linear macromolecular network, the macromolecular network becomes sparse and loose, and then Si_3N_4 particles are nonuniformly distributed and easily stack, which weakens pores formation by the joints of the $\beta\text{-Si}_3\text{N}_4$ phase in the sintering process. In the meantime, the sparse and loose three-dimension macromolecular network easily causes a drying shrinkage, and thus the porosity decreases. In conclusion, the ratio of monomers (AM/MBAM) has a great influence on the formation of a three-dimension macromolecular network which significantly influences the porosity of porous Si_3N_4 ceramics, and the porosity of porous Si_3N_4 ceramics decreases with an increase of the ratio of monomers (AM/MBAM), as shown in Fig. 4. The decrease of the porosity of porous Si_3N_4 ceramics accompanys an increase of flexural strength [2, 3]. Thus, the flexural strength of porous Si_3N_4 ceramics increases with an increase of the ratio of monomers (AM/MBAM), as shown in Fig. 4.

Solid loading has some influence on the flexural strength of porous Si_3N_4 ceramics, and the reasons are as follows: ① Solid loading has a great influence on the rheological properties of a Si_3N_4 slurry, the shrinkage of a green body, and the sintering at interfaces of Si_3N_4 particles. The spaces between Si_3N_4 particles in a slurry are affected by the solid loading. According to the Woodcock equation: [14]

$$\frac{h}{d} = \left(\frac{1}{3\pi\phi} + \frac{5}{6} \right)^{\frac{1}{2}} - 1 \quad (2)$$

where, h is the space between Si_3N_4 particles in a slurry; d is the diameter of Si_3N_4 particles; ϕ is the solid loading. It is known from equation (2) that increasing the solid loading makes the space between Si_3N_4 particles in a slurry decrease, and this leads to an increase of the viscosity of the slurry. The viscosity of a slurry affects moulding properties (uniformity of slurry, inner stresses distribution and the probability of occurrence of micro-cracks a green body), and finally it effects the flexural strength of the Si_3N_4 sintered body. ② An increase of solid loading creates a decrease in the uniformity of slurry, an increase of the inner stresses in the green body, and an increase in the probability of occurrence of micro-cracks in the green body, which makes the flexural strength of porous Si_3N_4 ceramics decrease. ③ Solid loading has a great influence on the drying shrinkage and the sintering shrinkage. Increasing the solid loading makes the space between Si_3N_4 particles in a green body decrease, which makes drying and sintering shrinkages decrease, which in

turn makes inner stresses and micro-cracks of a porous Si_3N_4 sintered body decrease and makes the flexural strength of Si_3N_4 sintered body increase. Solid loading also affects the density of a sintered body. Increasing solid loading makes the density of a Si_3N_4 sintered body increase, and then the sintering at interfaces of Si_3N_4 particles increase. In conclusion, solid loading has complex influences on the flexural strength of porous Si_3N_4 ceramics, and there is an optimum solid loading where the flexural strength can achieve a maximum value, as shown in Fig. 2.

Conclusions

In this paper, the gel casting preparation of porous Si_3N_4 ceramics without other organic additives except monomers was investigated. Three variables including solid loading, monomer content and the ratio of monomers were studied. Orthogonal experimental design was adopted. Through range analysis and variance analysis, the results suggest that the ratio of monomers has a significant influence on both the flexural strength and porosity of porous Si_3N_4 ceramics. For the flexural strength of porous Si_3N_4 ceramics, the order of significance levels was as follows: the ratio of monomers, solid loading and monomer content. For the porosity of porous Si_3N_4 ceramics, the order of significance levels was as follows: the ratio of monomers, monomer content and solid loading. The results also indicate as follows: ① the flexural strength monotonically decreases with an increase of monomer content and the ratio of monomers; ② the flexural strength is low when the solid loading is too low or too high, and it can achieve a peak value when the solid loading is a certain proper value; ③ the porosity increases with an increase of the monomer content and the ratio of monomers, but it monotonically decreases with an increase of solid loading.

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