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Research Article

Preparation of porous Si_3N_4 ceramics via tailoring solid loading of Si_3N_4 slurry and Si_3N_4 poly-hollow microsphere content

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Abstract: Porous Si_3N_4 ceramics were prepared by aqueous gelcasting using Si_3N_4 poly-hollow microspheres (PHMs) as pore-forming agent. The effects of solid loading of Si_3N_4 slurry and Si_3N_4 PHM content on the properties of porous Si_3N_4 ceramics were investigated. Only β-Si_3N_4 phase is observed in porous Si_3N_4 ceramics, and Si_3N_4 PHMs distribute uniformly both in Si_3N_4 green samples and porous Si_3N_4 ceramics. Results show that solid loading of Si_3N_4 slurry and Si_3N_4 PHM content could considerably influence the properties of porous Si_3N_4 ceramics. With the increase of solid loading of Si_3N_4 slurry (decrease of Si_3N_4 PHM content), the distributing state of Si_3N_4 PHMs changes from contacting with each other to just embedding in the matrix, thus their porosity decreases, while their shrinkage, flexural strength, and fracture toughness increase.

Keywords: porous Si_3N_4 ceramics; Si_3N_4 poly-hollow microspheres (PHMs); solid loading; aqueous gelcasting; mechanical properties

1 Introduction

Porous Si_3N_4 ceramics are one of the most promising structural and functional materials in the engineering applications (such as high-temperature gas/liquid filters, thermal insulators, catalyst carriers, antenna windows, and separation membranes, etc.), which is attributed to their unique properties such as low density, high porosity, acceptable dielectric properties, high specific surface area, high hardness, high fracture toughness, and so on [1–4]. Up to now, many researches have focused on the preparation of porous Si_3N_4 ceramics using various methods [5–16]. Compared with other preparation methods, adding pore-forming agent is more feasible due to its simple preparation process and low cost. At present, various pore-forming agents have been used to prepare the porous materials, such as benzoic acid [8], H_3PO_4 [9], starch [16], and so on. In addition, researchers have successfully used hollow spheres as pore-forming agent to prepare the porous materials [17–19]. However, in these researches, the pores usually could not distribute uniformly and the preparation processes are usually time-consuming and not environmentally friendly. Therefore, choosing proper pore-forming agent is considerably significant.

In recent years, researchers in Hebei Yonglong

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Bangda New Materials Co., Ltd., China, have proposed a kind of novel inorganic non-metallic spherical materials, namely ceramic poly-hollow microspheres (PHMs), which are the promising pore-forming agent to prepare porous ceramics. There are lots of micro-pores in ceramic PHMs, whose inner structures are completely different from those of the conventional hollow spheres. Furthermore, these ceramic PHMs are fabricated through a special route without any sacrificial cores, which combines the particle-stabilized foams and centrifugal atomizing technology together [20,21]. According to our previous researches, it is found that using ceramic PHMs as pore-forming agent to prepare porous ceramics has lots of advantages: (1) ceramic PHMs with porous microstructures could directly form pores and impurities could not be introduced into the porous ceramics, which could considerably shorten the time for removing the conventional organic pore-forming agent and effectively avoid the defects introduced by the residual organic pore-forming agent; (2) pore size of the porous ceramics could be effectively tailored due to the facile tailoring of the size of ceramic PHMs via adjusting the preparation parameters; (3) properties of the prepared porous ceramics could be tailored through several routes, such as changing the composition of ceramic PHMs in the preparation process, coating ceramic PHMs with some other materials (such as sintering additives), and using different kinds of ceramic PHMs as pore-forming agents, etc.; (4) warpage and shrinkage of the prepared porous ceramics could be effectively restricted through adding the calcined ceramic PHMs, which would have potential application in fabricating large-sized and complex-shaped ceramic components in the future.

In this paper, the Si_3N_4 PHMs were used as pore-forming agent to prepare porous Si_3N_4 ceramics via aqueous gelcasting. In order to increase porosity of porous Si_3N_4 ceramics, different contents of Si_3N_4 PHMs were added into Si_3N_4 slurry with different solid loadings, and the effects of solid loading of Si_3N_4 slurry and Si_3N_4 PHM content on the properties of porous Si_3N_4 ceramics were investigated.

2 Experimental procedure

2. 1 Materials

Si_3N_4 ceramic powders (α-phase > 91 wt%, average particle diameter: 5.2 μm, specific surface area: 4.3 m^2/g, Shanghai Junyu Ceramic-molded Product Co., Ltd., China) and some sintering additives (Al_2O_3 (99.9%, average particle diameter: 1.1 μm, specific surface area: 37.7 m^2/g, Shanghai Junyu Ceramic-molded Product Co., Ltd., China) and Y_2O_3 (99.95%, average particle diameter: 31.8 μm, specific surface area: 0.3 m^2/g, Shanghai Junyu Ceramic-molded Product Co., Ltd., China)) were used in this study. The Si_3N_4 PHMs were commercially available materials (Hebei Yonglong Bangda New Materials Co., Ltd., China). In this paper, the Si_3N_4 PHMs were calcined at 1600 ℃ for 0.5 h under the pressure of 0.1 MPa in nitrogen atmosphere, and the average diameter of the calcined Si_3N_4 PHMs was 69.79 μm. The compositions of Si_3N_4 PHMs were the same as those of the Si_3N_4–Al_2O_3–Y_2O_3 composite (1 wt% Al_2O_3, 2 wt% Y_2O_3, based on Si_3N_4 ceramic powders) used to prepare Si_3N_4 slurry.

In the gelcasting process, acrylamide (AM, Sinopharm Chemical Reagent Co., Ltd., China), N,N'-methylenebisacrylamide (MBAM, Sinopharm Chemical Reagent Co., Ltd., China), deionized water, 30 wt% ammonium polyacrylate (PAA-NH_4, Zibo Jinghe Chemical Dyestuff Co., Ltd., China) aqueous solution, 3 wt% ammonium persulfate (APS, Sinopharm Chemical Reagent Co., Ltd., China) aqueous solution, and N,N,N',N'-tetramethyl ethylenediamine (TEMED, Sinopharm Chemical Reagent Co., Ltd., China) were used as monomer, cross-linker, solvent, dispersant, initiator, and catalyst, respectively.

2. 2 Sample preparation

Figure 1 shows the flow chart of the preparation for porous Si_3N_4 ceramics by aqueous gelcasting using Si_3N_4 PHMs as pore-forming agent. The concentration of the premix solution was about 13 wt% and the ratio of AM and MBAM was 20:1. Adding contents of sintering additives and dispersant were 1 wt% Al_2O_3, 2 wt% Y_2O_3, and 1 wt% PAA-NH_4 (based on Si_3N_4 ceramic powders), respectively. Solid loadings of Si_3N_4 slurry were 15–25 vol%. Strong aqua ammonia was used to adjust the pH value of the slurry at about 10 [7]. After ball milling for 12 h, the slurry was degassed for 10 min under vacuum gauge pressure of –0.1 MPa. The calcined Si_3N_4 PHMs (27–22 vol%, calculated based on the whole volume of Si_3N_4 slurry with Si_3N_4 PHMs) were added into Si_3N_4 slurry with different solid

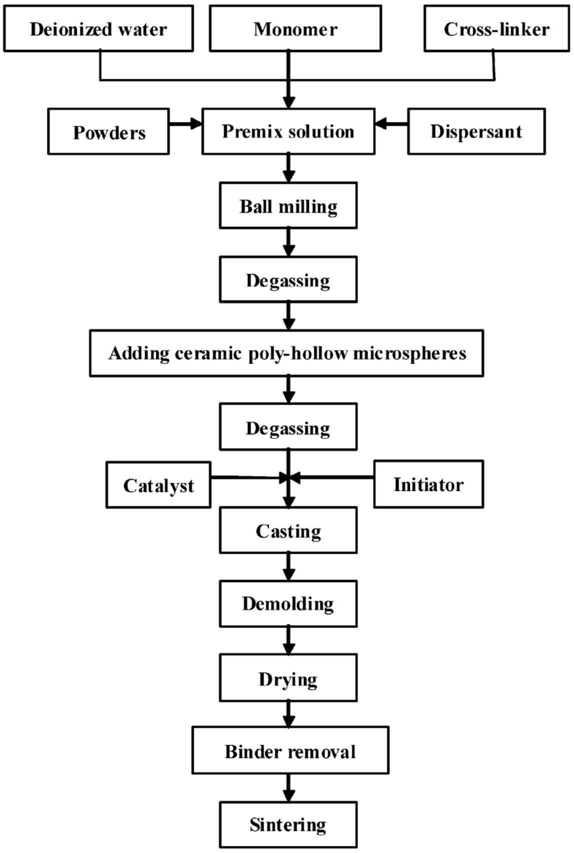

Fig. 1 Flow chart of the preparation for porous Si_3N_4 ceramics by aqueous gelcasting using Si_3N_4 PHMs as pore-forming agent.

loadings (15–25 vol%). The Si_3N_4 PHM content is the maximum content determined by the requirement of casting process in the aqueous gelcasting. The different samples were denoted as Si_3N_4-*m*-*n* (*m* stands for solid loading of Si_3N_4 slurry (vol%), *n* stands for Si_3N_4 PHM content (vol%)) (see Table 1), and then the slurry was degassed again. The catalyst (TEMED, 0.16 mL per 1 g AM) and initiator (APS, 0.16 mL per 1 g AM) were added into the slurry. The molds with slurry were put into an oven at 70 ℃ for 5 min to accelerate the gelation process. The binder was burned out from the dried green samples at 600 ℃ for 1 h. Finally, all the samples were sintered at 1750 ℃ for 1 h under the pressure of 0.1 MPa in nitrogen atmosphere.

2. 3 Characterization

The phases of the samples were analyzed by X-ray diffraction (XRD) method using Cu Kα radiation (D8 ADVANCE, Bruker, Karlsruhe, Germany). The microstructure observation of the samples was performed using environment scanning electron microscope (ESEM) (SSX-550, Shimadzu, Kyoto, Japan). The shrinkage of porous Si_3N_4 ceramics was calculated with the following formula:

$$S = \frac{D_0 - D}{D_0} \times 100\% \tag{1}$$

where D_0 and D represent the diameters of the green sample before drying and sintered ceramics, respectively. The porosity of porous Si_3N_4 ceramics was measured by the Archimedes method. Using the mechanical testing machine (AG-2000A, Shimadzu, Kyoto, Japan), the flexural strength of the specimens with dimension of $3\,mm \times 4\,mm \times 40\,mm$ was measured via the three-point bending test at a loading rate of 0.5 mm/min, and the fracture toughness of the specimens with dimension of 2.5 mm × 5 mm × 30 mm (notch length = 2.5 mm, notch width = 0.18 mm) was measured via single edge notched beam (SENB) method at a loading rate of 0.05 mm/min. The spans for flexural strength and fracture toughness testing are 30 mm and 20 mm, respectively.

3 Results and discussion

3. 1 Phase compositions and microstructures of the samples

Because the mechanical strength of the non-calcined Si_3N_4 PHMs is so low that they could be readily damaged during the mixing process and disperse in the solvent (such as deionized water), they should be calcined at proper temperature to acquire enough mechanical strength. Figure 2 shows the XRD patterns of the calcined Si_3N_4 PHMs and non-calcined PHMs. It is found that the main phase in the non-calcined Si_3N_4 PHMs is α-Si_3N_4, while there are α-Si_3N_4, β-Si_3N_4, and Si_2N_2O in Si_3N_4 PHMs calcined at 1600 ℃. The generated rod-like β-Si_3N_4 grains in the calcined Si_3N_4 PHMs could greatly improve the mechanical strength of the calcined Si_3N_4 PHMs.

Table 1 Samples with different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents

Sample	Solid loading of Si_3N_4 slurry (vol%)	Si_3N_4 PHM content (vol%, calculated based on the whole volume of Si_3N_4 slurry with Si_3N_4 PHMs)
Si_3N_4-15-27	15	27
Si_3N_4-20-24	20	24
Si_3N_4-25-22	25	22

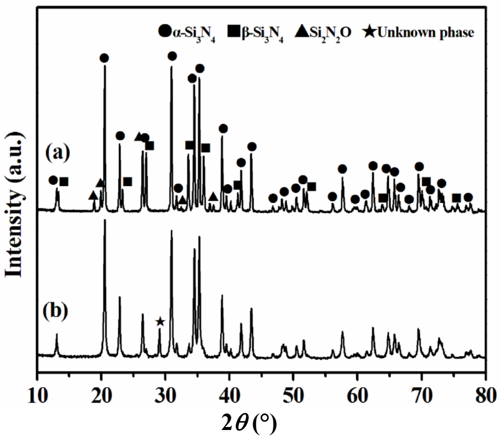

Fig. 2 XRD patterns of the (a) calcined Si_3N_4 PHMs and (b) non-calcined PHMs.

Figure 3 shows the SEM micrographs of the calcined Si_3N_4 PHMs and their inner structures. The surfaces of the calcined Si_3N_4 PHMs are smooth, which is attributed to fewer rod-like β-Si_3N_4 grains generated in the calcining process. As shown in Fig. 3(b), lots of micro-pores exist in the calcined Si_3N_4 PHMs, which would form the final pores in porous Si_3N_4 ceramics. Figure 4 shows the XRD patterns of porous Si_3N_4 ceramics with different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents. There is only β-Si_3N_4 phase in porous Si_3N_4 ceramics, which indicates that the α→β-Si_3N_4 phase transformation is complete in the sintering process.

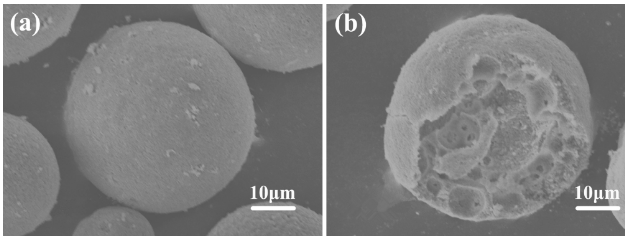

Fig. 3 SEM micrographs of the (a) calcined Si_3N_4 PHMs and (b) their inner structures.

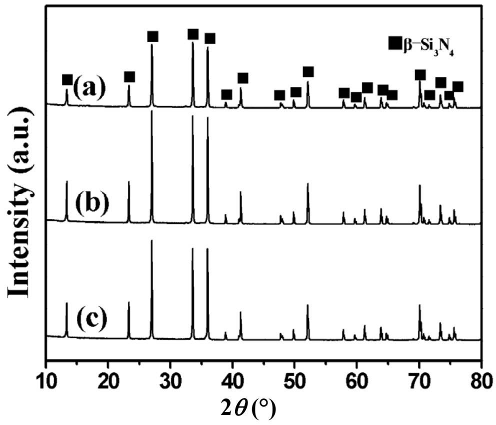

Fig. 4 XRD patterns of porous Si_3N_4 ceramics with different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents: (a) Si_3N_4-15-27, (b) Si_3N_4-20-24, (c) Si_3N_4-25-22.

Figure 5 shows the SEM micrographs of Si_3N_4 green samples and porous Si_3N_4 ceramics with different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents. It can be observed that Si_3N_4 PHMs distribute uniformly in both Si_3N_4 green samples and porous Si_3N_4 ceramics regardless of solid loading of Si_3N_4 slurry and Si_3N_4 PHM content. When solid loading of Si_3N_4 slurry is lower (15 vol%), more Si_3N_4 PHMs (27 vol%) could be added into the slurry, thus the added Si_3N_4 PHMs contact with each other in sample Si_3N_4-15-27 (see Fig. 5(b)). Under this condition, the matrix cannot completely fill the gaps among different Si_3N_4 PHMs, thus the bonding strength between ceramic PHMs and matrix is relatively low. In addition, it is found that there are two kinds of pores in sample Si_3N_4-15-27, one is the

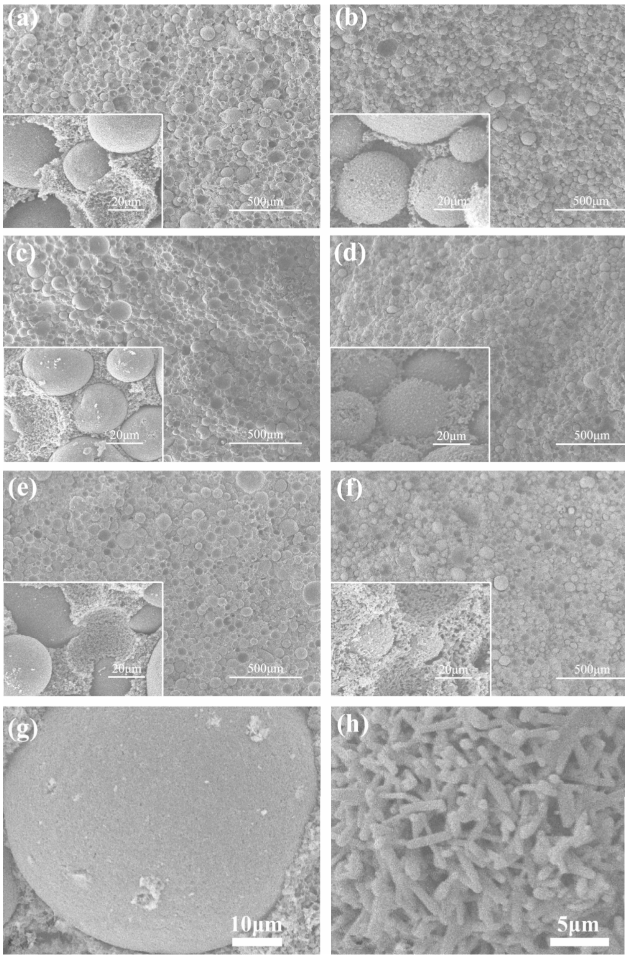

Fig. 5 SEM micrographs of (a, c, e, g) Si_3N_4 green samples and (b, d, f, h) porous Si_3N_4 ceramics with different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents: (a) and (b) Si_3N_4-15-27, (c, d, g, h) Si_3N_4-20-24, (e) and (f) Si_3N_4-25-22.

pores in Si_3N_4 PHMs (namely α-pores), and the other one is the pores among different Si_3N_4 PHMs (namely β-pores). However, when solid loading of Si_3N_4 slurry is higher (20 and 25 vol%), fewer Si_3N_4 PHMs (24 and 22 vol%) could be added into Si_3N_4 slurry, thus Si_3N_4 PHMs just embed in the matrix, and they cannot contact with each other in samples Si_3N_4-20-24 and Si_3N_4-25-22 (see Figs. 5(d) and 5(f)). Under this condition, the matrix could completely fill the gaps among different Si_3N_4 PHMs, thus the bonding strength between ceramic PHMs and matrix is relatively high. Moreover, regarding samples Si_3N_4-20-24 and Si_3N_4-25-22, the β-pores gradually disappear, the main pores in samples Si_3N_4-20-24 and Si_3N_4-25-22 are α-pores. In addition, it is found that the surfaces of Si_3N_4 PHMs in porous Si_3N_4 ceramics are coarser due to more rod-like β-Si_3N_4 grains generated in the sintering process (see Fig. 5(h)).

3. 2 Properties of the samples

Table 2 shows the properties of porous Si_3N_4 ceramics. With the increase of solid loading of Si_3N_4 slurry and decrease of Si_3N_4 PHM content, the shrinkage, flexural strength, and fracture toughness of porous Si_3N_4 ceramics increase, while the porosity decreases. Meanwhile, there are great differences between the properties of samples Si_3N_4-15-27 and Si_3N_4-20-24, while the properties of samples Si_3N_4-20-24 and Si_3N_4-25-22 vary slightly, which could be attributed to their completely different microstructures.

When solid loading of Si_3N_4 slurry is lower (15 vol%) and Si_3N_4 PHM content is higher (27 vol%), Si_3N_4 PHMs could contact with each other. In the processes of drying, binder removal, and sintering, the shrinking of the sample is restricted by the added Si_3N_4 PHMs. Accordingly, the shrinkage of porous Si_3N_4 ceramics is lower. Besides the added Si_3N_4 PHMs, gaps among different Si_3N_4 PHMs could also make certain contribution to the increase of porosity, so the porosity of porous Si_3N_4 ceramics is higher. In addition, due to the unsatisfactory bonding strength between ceramic PHMs and matrix, the flexural strength and fracture toughness are lower.

When solid loading of Si_3N_4 slurry is higher (20 and 25 vol%) and Si_3N_4 PHM content is lower (24 and 22 vol%), Si_3N_4 PHMs just embed in the matrix and they cannot contact with each other, so the restriction function of Si_3N_4 PHMs on the shrinkage is considerably affected. Therefore, the shrinkage of porous Si_3N_4 ceramics is higher. Because matrix fills all the gaps among different Si_3N_4 PHMs and fewer Si_3N_4 PHMs are added into the matrix, the porosity of porous Si_3N_4 ceramics is lower. Moreover, due to the satisfactory bonding strength between ceramic PHMs and matrix, the flexural strength and fracture toughness are higher.

Concerning samples Si_3N_4-20-24 and Si_3N_4-25-22, because their microstructures are similar, there are no great differences about their properties, which vary just depending on the different solid loadings of Si_3N_4 slurry and Si_3N_4 PHM contents. The overall solid loading of Si_3N_4 slurry with lots of Si_3N_4 PHMs is so high that it is difficult to further influence the shrinkage of porous Si_3N_4 ceramics. Therefore, the shrinkage of samples Si_3N_4-20-24 and Si_3N_4-25-22 is nearly the same. Furthermore, with the continual increase of solid loading of Si_3N_4 slurry and decrease of Si_3N_4 PHM content, the content of α-pores decreases, and fewer defects are introduced into the samples, thus the porosity of the samples decreases gradually, while the flexural strength and fracture toughness increase.

Overall, regarding all the samples, the bonding strength between Si_3N_4 PHMs and matrix is relatively low, thus the mechanical properties of the samples are affected. The low bonding strength between Si_3N_4 PHMs and matrix could be attributed to the calcining of Si_3N_4 PHMs, which could result in low diffusion in the sintering process and somewhat different shrinkages of the calcined Si_3N_4 PHMs and matrix. As mentioned above, Si_3N_4 PHMs must be calcined at proper calcining temperature to insure the mechanical strength of Si_3N_4 PHMs. In our recent work, the $CaSiO_3$ sintering additive has been successfully coated on the calcined Al_2O_3 PHMs, thus the bonding strength among different Al_2O_3 PHMs has been greatly improved, and the porous Al_2O_3 ceramics with enhanced mechanical properties have been obtained [22]. In addition, our recent work also shows that adding some Al_2O_3 PHMs

Table 2 Properties of porous Si_3N_4 ceramics

Sample	Shrinkage (%)	Porosity (%)	Flexural strength (MPa)	Fracture toughness (MPa·m$^{1/2}$)
Si_3N_4-15-27	11.16±0.28	50.97±0.63	4.99±0.13	0.13±0.01
Si_3N_4-20-24	16.07±0.38	40.19±1.59	30.87±2.30	0.59±0.02
Si_3N_4-25-22	16.06±0.24	38.62±1.88	48.60±5.27	1.07±0.06

in Si_3N_4 slurry with lots of Si_3N_4 PHMs could also effectively improve the bonding strength between ceramic PHMs and matrix. Accordingly, in order to improve the bonding strength between Si_3N_4 PHMs and matrix, some effective measures would be taken to prepare porous Si_3N_4 ceramics with high performance in the future, such as coating the calcined Si_3N_4 PHMs with sintering additive and using both Si_3N_4 and Al_2O_3 PHMs as pore-forming agents (in this case, small amount of Al_2O_3 PHMs plays the role as both sintering additive and pore-forming agent).

4 Conclusions

In this paper, porous Si_3N_4 ceramics were successfully prepared by aqueous gelcasting using Si_3N_4 PHMs as pore-forming agent. Solid loading of Si_3N_4 slurry and Si_3N_4 PHM content could greatly influence the properties of porous Si_3N_4 ceramics. When solid loading of Si_3N_4 slurry increases from 15 to 20 vol% (Si_3N_4 PHM content decreases from 27 to 24 vol%), the distributing state of Si_3N_4 PHMs changes from contacting with each other to just embedding in the matrix, which could effectively affect the properties of porous Si_3N_4 ceramics. Therefore, their porosity decreases greatly, while their shrinkage, flexural strength, and fracture toughness increase dramatically. When solid loading of Si_3N_4 slurry increases to 25 vol% (Si_3N_4 PHM content decreases to 22 vol%), the shrinkage of samples Si_3N_4-20-24 and Si_3N_4-25-22 is nearly the same, their porosity decreases slightly, while their flexural strength and fracture toughness increase slightly.

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