Novel porous Si_3N_4 ceramics prepared by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent

Jia-Min Wu, Xiao-Yan Zhang, Jin-Long Yang [*]

State Key Lab of New Ceramics and Fine Processing, School of Materials Science and Engineering, Tsinghua University, Beijing 100084, China

Abstract

In this paper, novel porous Si_3N_4 ceramics were prepared by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent. The effect of Si_3N_4 poly-hollow microsphere content on the phase composition, microstructure, shrinkage, porosity and mechanical properties of the prepared porous Si_3N_4 ceramics were investigated. It is found that there is only β-Si_3N_4 phase in all the prepared porous Si_3N_4 ceramics. Meanwhile, the SEM results show that the pores in the porous Si_3N_4 ceramics distribute uniformly, the added Si_3N_4 poly-hollow microspheres and the basal body contact closely. With the increase of Si_3N_4 poly-hollow microsphere content, the shrinkage of the porous Si_3N_4 ceramics decreases gradually, and the porosity of the porous Si_3N_4 ceramics decreases firstly and then increases. Furthermore, the flexural strength and fracture toughness of the porous Si_3N_4 ceramics decrease with the increase of the Si_3N_4 poly-hollow microsphere content.
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Keywords: Porous Si_3N_4 ceramics; Aqueous gelcasting; Si_3N_4 poly-hollow microspheres; Flexural strength; Fracture toughness

1. Introduction

Porous Si_3N_4 ceramics have lots of excellent properties, such as low density, high porosity, high hardness and fracture toughness, excellent thermal–chemical corrosion resistance, low thermal expansion, acceptable dielectric properties and so on,[1,2] thus they are promising materials in the area of industrial applications.[3–6] So far, porous Si_3N_4 ceramics have been prepared by many methods including combustion synthesis,[7] carbonthermal reaction,[8] oxidation bonding,[9] gelcasting,[10–12] direct foaming method,[13,14] freeze-drying,[15] tape casting,[16] adding pore-forming agent[2,3,17–19] and so on. Compared with other preparation methods, adding pore-forming agent is easier to realize, which is attributed to its simple preparation process and low cost.

As a novel colloidal forming method, gelcasting is a near-net-shape forming method, which was invented by the researchers of the Oak Ridge National Laboratory.[20] This forming method could prepare high-performance ceramics with uniform microstructure, excellent properties and complex shape. Up to now, this method has been successfully used to prepare many kinds of structural ceramics[21–23] and functional ceramics.[24–26] In view of the favorable advantages of gelcasting process, the combination of gelcasting and adding pore-forming agent could be a promising route to prepare high-performance porous ceramics.

In the preparation process of high-performance porous ceramics by adding pore-forming agent method, it is found that choosing proper pore-forming agent is highly important. Recently, polymethylmethacrylate (PMMA) microspheres have been used as pore-forming agent to prepare porous ceramics. In 2013, Zhou et al.[27] and Liu et al.[28] have successfully fabricated porous yttria-stabilized zirconia (YSZ) ceramics by gelcasting and dry pressing using mono-dispersed polymethylmethacrylate (PMMA) microspheres as pore-forming agent, respectively. In their researches, the PMMA microspheres must be completely removed through combustion to fabricate porous ceramics. In order to avoid cracking and other

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* Corresponding author. Tel.: +86 10 62792332; fax: +86 10 62773817.
E-mail address: jlyang@tsinghua.edu.cn (J.-L. Yang).

defects, the removal process of the PMMA microspheres is relatively time-consuming, and this process is not environmentally friendly.

As a kind of special materials, hollow spheres have potential applications in various areas due to their unique properties, such as low density, high specific surface area, good mechanical and thermal stability and high surface permeability.[29,30] In recent years, template-assisted synthesis is extensively adopted to prepare hollow spheres,[31] and different kinds of sacrificial templates have been used, such as polystyrene beads,[32] silica spheres,[33] liposomes,[34] etc. With the rapid development of porous materials, hollow spheres have been successfully used to prepare porous materials. Augustin et al.[35] produced hollow sphere structures using metallic hollow spheres, which were prepared using polystyrene spheres as sacrificial cores. In 2003, Thijs et al.[36] fabricated ceramic foams with ceramic hollow spheres, which were prepared through the pyrolysis of the sacrificial cores (such as peas). In these researches, the preparation process of porous materials is time-consuming and not environmentally friendly.

Recently, researchers in Yonglong Bangda New Materials Co., Ltd. have successfully produced a kind of novel ceramic hollow spheres, which were called ceramic poly-hollow microspheres. They were prepared through a special route without sacrificial cores and were commercially available. Compared with conventional hollow spheres, there are lots of micro-pores in the ceramic poly-hollow microspheres, whose inner structure is completely different from that of the conventional hollow spheres. The ceramic poly-hollow microspheres are novel inorganic non-metallic spherical materials, which are the promising materials to be used as pore-forming agent to prepare porous ceramics.

At present, there are few researches using Si_3N_4 poly-hollow microspheres as pore-forming agent to prepare porous Si_3N_4 ceramics. Because the compositions of the Si_3N_4 poly-hollow microspheres are completely the same as those of the starting raw materials (Si_3N_4 ceramic powders and other sintering additives), there are no impurities introduced into the basal body. Meanwhile, there is no air pollution occurring in the preparation process due to the inherent porous inner structure in the Si_3N_4 poly-hollow microspheres. Unlike the conventional adding pore-forming agent method, using ceramic poly-hollow microspheres as pore-forming agent to prepare porous ceramics could not only introduce size-controllable micro-pores, which are based on the size of the prepared ceramic poly-hollow microspheres, but also eliminate the complex and time-consuming processes for drying and removal of organic materials. Meanwhile, the ceramic poly-hollow microspheres with different compositions could also be added into the basal body to further improve the overall properties of the final ceramics. In addition, according to our previous researches, it is found that adding calcined ceramic poly-hollow microspheres into the basal body could restrict the warpage and shrinkage of the final ceramics, especially for the preparation of large-dimensional and complex-shaped ceramic components.

In this paper, Si_3N_4 poly-hollow microspheres were used as pore-forming agent, and the porous Si_3N_4 ceramics were prepared by aqueous gelcasting. The effect of Si_3N_4 poly-hollow microsphere content on the phase composition, microstructure, shrinkage, porosity and mechanical properties of the 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) were used in this study. Al_2O_3 ceramic powders (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 ceramic powders (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 as sintering additives. The Si_3N_4 poly-hollow microspheres were commercially available materials (Yonglong Bangda New Materials Co., Ltd., China). The compositions of the Si_3N_4 poly-hollow microspheres 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. Under nitrogen atmosphere (0.1 MPa), these Si_3N_4 poly-hollow microspheres were calcined at 1600 °C for 0.5 h.

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

2.2. Sample preparation

Fig. 1 shows the flow chart of the preparation for the porous Si_3N_4 ceramics by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent. The premix solution was prepared by mixing the monomer, cross-linker and deionized water. The concentration of the premix solution was about 13 wt.% and the ratio of AM and MBAM was 20:1. The Si_3N_4 ceramic powders, sintering additives (1 wt.% Al_2O_3, 2 wt.% Y_2O_3, based on Si_3N_4 ceramic powders) and dispersant (1 wt.% PAA–NH_4, based on Si_3N_4 ceramic powders) were added into the premix solution to make slurry with solid loading of about 33 vol.%. Strong aqua ammonia was used to adjust the pH value of the slurry at about 10.[1] After ball milling for 12 h, the slurry with low viscosity was obtained, then degassing was performed for 10 min under vacuum gauge pressure of −0.1 MPa. Afterwards, the calcaied Si_3N_4 poly-hollow microspheres (10-35 wt.%) were added into the prepared slurry, and then the slurry was degassed again. The adding content of the Si_3N_4 poly-hollow microspheres is based on the Si_3N_4 ceramic powders.
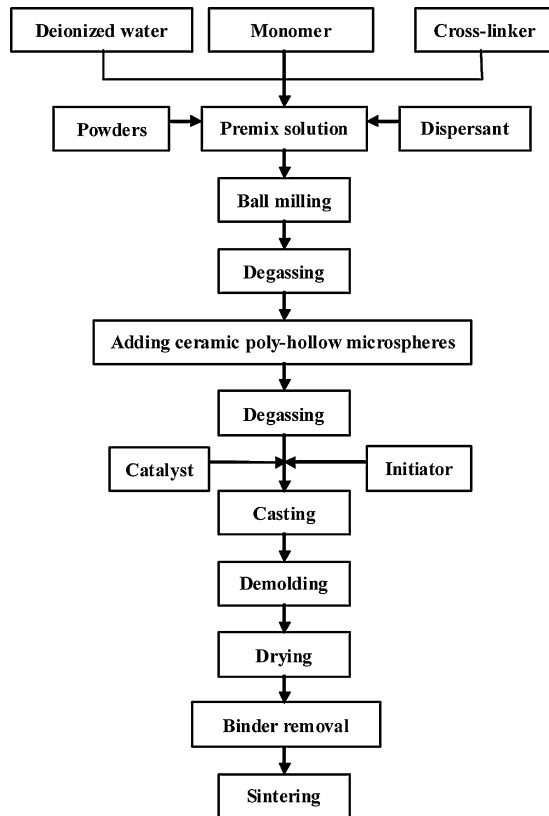
Fig. 1. The flow chart of the preparation for the porous Si_3N_4 ceramics by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent.

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

Subsequently, 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, then the slurry was cast into molds. In order to avoid the Si_3N_4 poly-hollow microspheres floating or depositing, the molds with slurry were put into an oven at 70 °C for 5 min to accelerate the gelation process. After demolding and drying, the binder was burned out from the dried green samples at 600 °C for 1 h. Finally, under nitrogen atmosphere (0.1 MPa), all the samples were sintered at 1750 °C for 1 h to form ceramics.

2.3. Characterization

The diameter of the Si_3N_4 poly-hollow microsphere was measured by laser particle size analyzer (Mastersizer 2000, Malven, Worcestershire, UK). The phases were analyzed using X-ray diffraction (XRD) method using Cu Kα radiation (D8 ADVANCE, Bruker, Karlsruhe, Germany). The microstructure observation was performed using environment scanning electron microscope (ESEM) (SSX-550, Shimadzu, Kyoto, Japan). The shrinkage of the 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 the Si_3N_4 ceramics was measured by the Archimedes method. Using the mechanical testing machine (AG-2000 A,
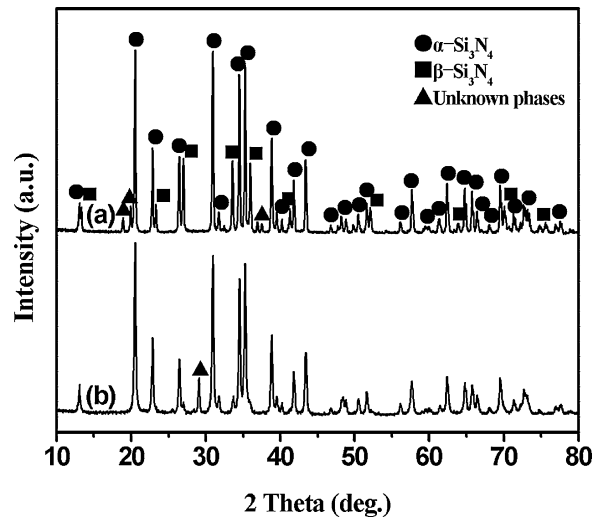
Shimadzu, Kyoto, Japan), the flexural strength of the specimens with dimension of 3 mm × 4 mm × 40 mm was measured via the three-point bending test, and the fracture toughness of the specimens with dimension of 2.5 mm × 5 mm × 30 mm and notch length of 2.5 mm was measured via single edge notched beam (SENB) method.

3. Results and discussion

3.1. Phase compositions and microstructures of the Si_3N_4 poly-hollow microspheres

According to our previous researches, the mechanical strength of the non-calcined Si_3N_4 poly-hollow microspheres is relatively low, so they would be damaged during the mixing process due to their mutual collision, and they are also easy to dissolve in the solvent (such as deionized water) gradually. Therefore, in the preparation process of the porous Si_3N_4 ceramics by aqueous gelcasting, in order to ensure the integrity of the Si_3N_4 poly-hollow microspheres, the Si_3N_4 poly-hollow microspheres should be calcined at a certain temperature to acquire enough mechanical strength.

Fig. 2 shows the XRD patterns of the Si_3N_4 poly-hollow microspheres. It is found that there is mainly α-Si_3N_4 phase in the non-calcined Si_3N_4 poly-hollow microspheres, while the calcined Si_3N_4 poly-hollow microspheres possess more β-Si_3N_4. In addition, there are some unknown phases in both the non-calined and calcined Si_3N_4 poly-hollow microspheres, which could be the mesophases and would disappear in the sintered samples. When the Si_3N_4 poly-hollow microspheres were calcined at 1600 °C for 0.5 h, the α → β-Si_3N_4 phase transformation occurs. However, because 1600 °C is relatively low, the α → β-Si_3N_4 phase transformation is incomplete, and a large amount of α-Si_3N_4 phase still exists in the calcined Si_3N_4 poly-hollow microspheres, which indicates that the calcined Si_3N_4 poly-hollow microspheres still possess certain sintering activity.
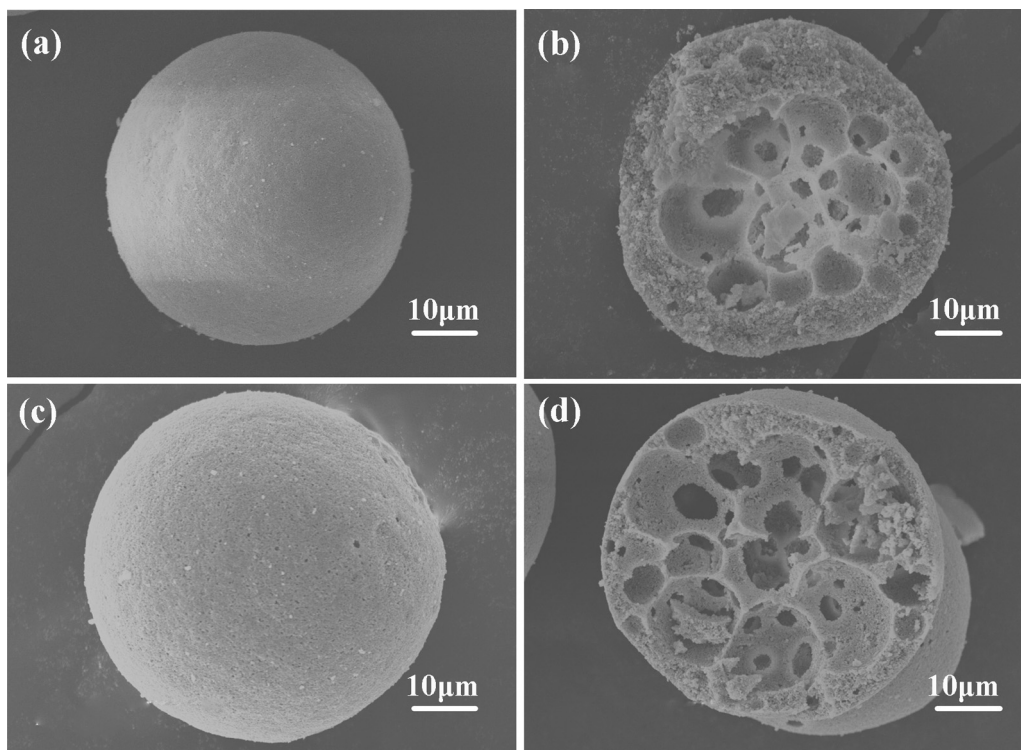
Fig. 3. The SEM micrographs of the (a) non-calcined Si_3N_4 poly-hollow microspheres and (b) their inner structures; (c) calcined Si_3N_4 poly-hollow microspheres and (d) their inner structures.

Fig. 3 shows the SEM micrographs of the Si_3N_4 poly-hollow microspheres and their inner structures. It is found that the surfaces of the non-calcined and calcined Si_3N_4 poly-hollow microspheres are all smooth, and the rod-like β-Si_3N_4 grains do not appear obviously in the calcined Si_3N_4 poly-hollow microspheres, which indicates that the calcining temperature (1600 °C) is not high enough to result in the complete α → β-Si_3N_4 phase transformation. Fig. 3(b) and (d) shows the SEM micrographs of the inner structures of the Si_3N_4 poly-hollow microspheres. It is found that lots of micro-pores exist both in the non-calcined and calcined Si_3N_4 poly-hollow microspheres. These micro-pores would form the final pores in the prepared porous Si_3N_4 ceramics.

Fig. 4 shows the particle diameter distribution diagram of the calcined Si_3N_4 poly-hollow microspheres. It is found that the particle diameters of the calcined Si_3N_4 poly-hollow microspheres range from 20 μm to 180 μm, and the average particle diameter of the calcined Si_3N_4 poly-hollow microspheres is 69.79 μm. Meanwhile, the particle diameter distribution of the calcined Si_3N_4 poly-hollow microspheres takes on normal distribution. By the way, because the non-calcined Si_3N_4 poly-hollow microspheres could be destroyed easily in the measuring process, there is no particle diameter measurement result of these Si_3N_4 poly-hollow microspheres.

3.2. Phase compositions and microstructures of the prepared green samples and ceramics

Fig. 5 shows the SEM micrographs of the Si_3N_4 green samples with different Si_3N_4 poly-hollow microsphere contents. It

is found that the surfaces of the Si_3N_4 green samples without Si_3N_4 poly-hollow microspheres are smooth and the Si_3N_4 particles distribute compactly. However, concerning the Si_3N_4 green samples with Si_3N_4 poly-hollow microspheres, there are lots of Si_3N_4 poly-hollow microspheres distributing uniformly.

Fig. 6 shows the XRD patterns of the porous Si_3N_4 ceramics with different Si_3N_4 poly-hollow microsphere contents. It is found that there is only β-Si_3N_4 phase in the prepared porous Si_3N_4 ceramics regardless of Si_3N_4 poly-hollow microsphere content adopted, which indicates that the α → β-Si_3N_4 phase transformation completes substantially at the sintering temperature of 1750 °C.
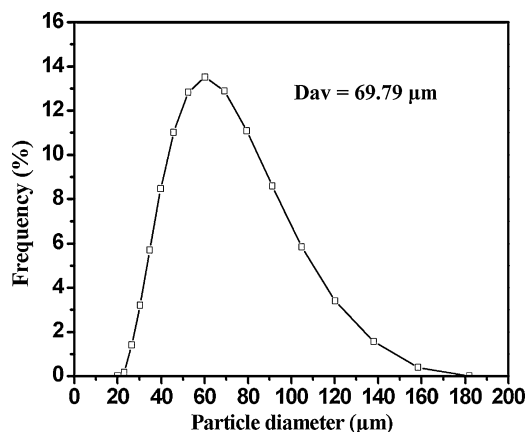

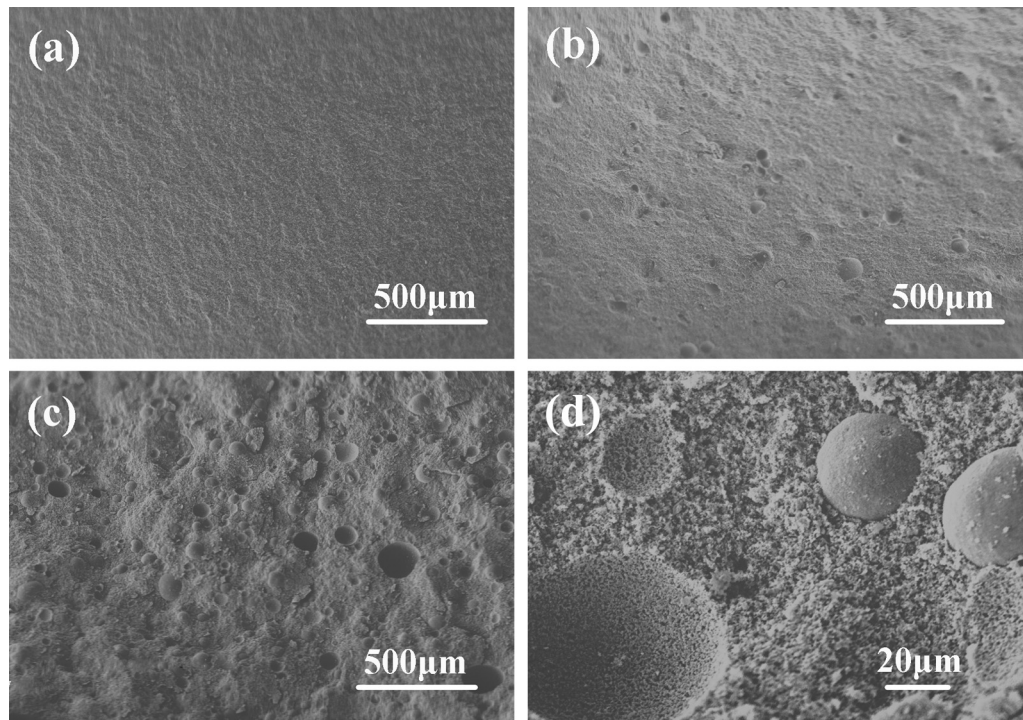Fig. 4. Particle diameter distribution diagram of the calcined Si_3N_4 poly-hollow microspheres.

Fig. 5. The SEM micrographs of the Si_3N_4 green samples with different Si_3N_4 poly-hollow microsphere contents: (a) 0 wt.%, (b) 10 wt.%, (c) 35 wt.%, and (d) 35 wt.% (local region).

Fig. 7 shows the SEM micrographs of the porous Si_3N_4 ceramics with different Si_3N_4 poly-hollow microsphere contents. It is found that there are no obvious pores in the Si_3N_4 ceramics without Si_3N_4 poly-hollow microspheres. Nevertheless, when the Si_3N_4 poly-hollow microspheres are added into the Si_3N_4 basal body, the Si_3N_4 poly-hollow microspheres distribute uniformly, the Si_3N_4 poly-hollow microspheres and the Si_3N_4 basal body contact closely. Moreover, as shown in Fig. 7(d), the rod-like β-Si_3N_4 grains overlap with each other in the porous Si_3N_4 ceramics, which could result in the improvement of the mechanical properties of the prepared porous Si_3N_4 ceramics.
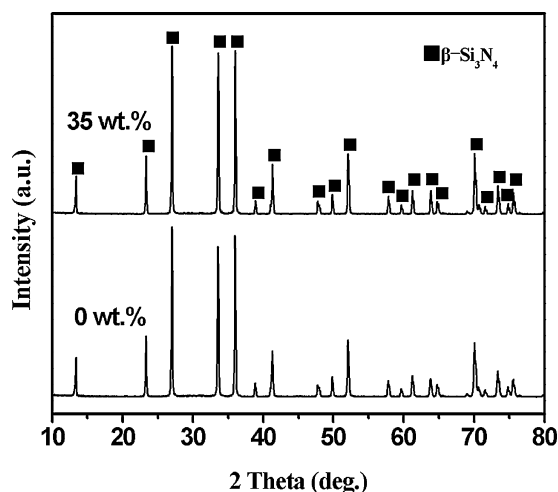

Fig. 6. XRD patterns of the porous Si_3N_4 ceramics with different Si_3N_4 poly-hollow microsphere contents.

3.3. Shrinkage and porosity of the porous Si_3N_4 ceramics

Fig. 8 shows the shrinkage of the porous Si_3N_4 ceramics as a function of Si_3N_4 poly-hollow microsphere content. With the increase of the Si_3N_4 poly-hollow microsphere content, the shrinkage of the porous Si_3N_4 ceramics decreases dramatically. When the Si_3N_4 poly-hollow microsphere content reaches 30 wt.%, with the continual increase of the Si_3N_4 poly-hollow microsphere content, the shrinkage of the porous Si_3N_4 ceramics hardly decreases. With the increase of the Si_3N_4 poly-hollow microsphere content, the overall solid loading of the Si_3N_4 slurry increases gradually. Meanwhile, the calcined Si_3N_4 poly-hollow microspheres possess relatively high mechanical strength, they could also restrict the shrinkage of the porous Si_3N_4 ceramics. Therefore, the more the calcined Si_3N_4 poly-hollow microspheres are added, the lower the shrinkage is. When the Si_3N_4 poly-hollow microsphere contents are 30 wt.% and 35 wt.%, the overall solid loadings of the Si_3N_4 slurry with plenty of Si_3N_4 poly-hollow microspheres would be so high that it is difficult to decrease the shrinkage of the porous Si_3N_4 ceramics, thus the shrinkages are nearly the same.

Fig. 9 shows the porosity of the porous Si_3N_4 ceramics as a function of Si_3N_4 poly-hollow microsphere content. It is found that the porosity of the porous Si_3N_4 ceramics decreases firstly and then increases with the increase of the Si_3N_4 poly-hollow microsphere content. On the one hand, the solid loading of the Si_3N_4 slurry is relatively low (33 vol.%), which could result in the relatively high porosity of the prepared Si_3N_4 ceramics without Si_3N_4 poly-hollow microspheres. On the other hand, as sintering additives, the adding contents of Al_2O_3 and Y_2O_3
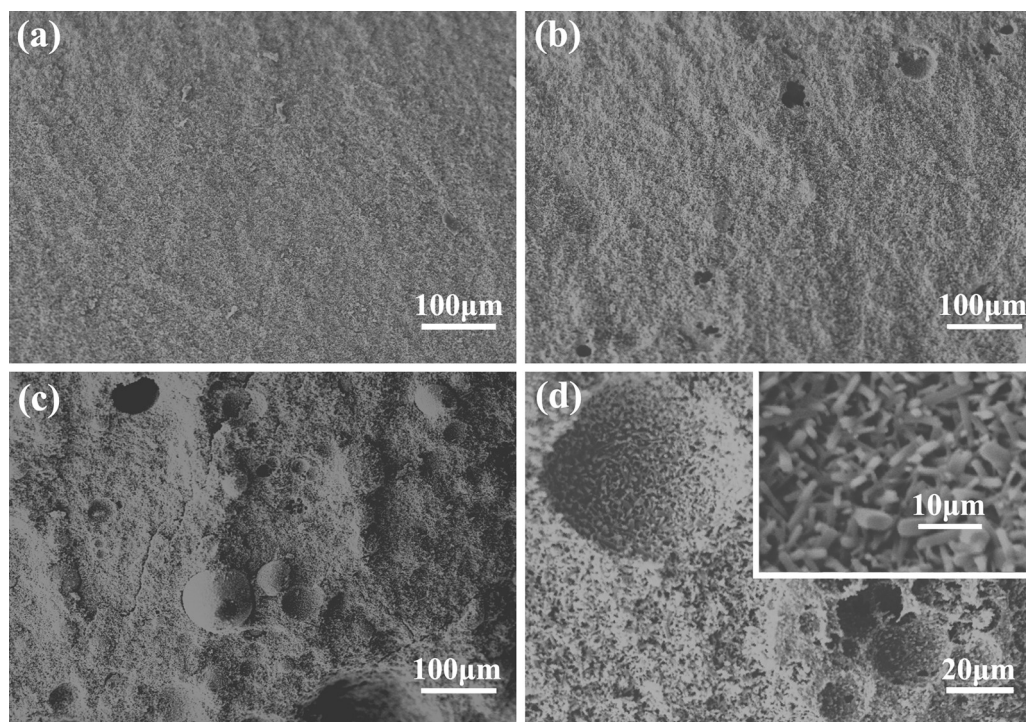
Fig. 7. The SEM micrographs of the porous Si_3N_4 ceramics with different Si_3N_4 poly-hollow microsphere contents: (a) 0 wt.%, (b) 10 wt.%, (c) 35 wt.%, and (d) 35 wt.% (local region).

ceramic powders are considerably low (1 wt.% Al_2O_3, 2 wt.% Y_2O_3, based on Si_3N_4 ceramic powders), which could also result in the non-compactness of the sintered Si_3N_4 ceramics. Therefore, the prepared Si_3N_4 ceramics without Si_3N_4 poly-hollow microspheres still possess porosity as high as 36.04%. When a small amount of Si_3N_4 poly-hollow microspheres (10 wt.%) is added into the slurry, the porosity of the porous Si_3N_4 ceramics is about 34.61%, which is lower than that of the prepared Si_3N_4 ceramics without Si_3N_4 poly-hollow microspheres. The concrete reason for this phenomenon should be investigated in the future. Subsequently, with the continual increase of the Si_3N_4 poly-hollow microsphere content, the Si_3N_4 poly-hollow microsphere content plays a main role in affecting the porosity. As a whole, adding Si_3N_4 poly-hollow microspheres could increase the porosity of the Si_3N_4 ceramics. However, with the increase of Si_3N_4 poly-hollow microsphere content, it is found that the viscosity of the slurry would increase fundamentally. When the Si_3N_4 poly-hollow microsphere content is higher than the upper limit (35 wt.%), the viscosity of the prepared slurry would be so high that it can not meet the requirements for casting. If the initial solid loading of the Si_3N_4 slurry is lower (<33 vol.%), thus more Si_3N_4 poly-hollow microspheres could be added into the Si_3N_4 slurry, so the porous Si_3N_4 ceramics with higher porosity could be obtained.

3.4. Mechanical properties of the porous Si_3N_4 ceramics

Fig. 10 shows the mechanical properties of the porous Si_3N_4 ceramics as functions of Si_3N_4 poly-hollow microsphere content. With the increase of the Si_3N_4 poly-hollow microsphere

content, the flexural strength and fracture toughness of the prepared porous Si_3N_4 ceramics decrease greatly. When lots of Si_3N_4 poly-hollow microspheres are added into the Si_3N_4 slurry, lots of defects would be introduced into the Si_3N_4 ceramics. The Si_3N_4 poly-hollow microspheres with lots of micro-pores could be considered as the circumferential starting cracks in the porous Si_3N_4 ceramics, thus adding the Si_3N_4 poly-hollow microspheres could deteriorate the mechanical properties of the prepared porous Si_3N_4 ceramics dramatically.
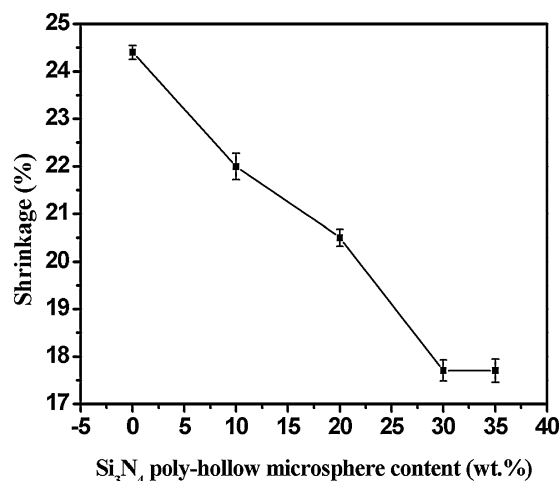

Fig. 8. Shrinkage of the porous Si_3N_4 ceramics as a function of Si_3N_4 poly-hollow microsphere content.
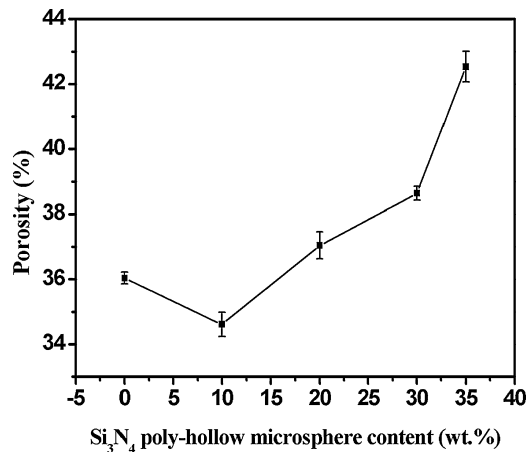
Fig. 9. Porosity of the porous Si_3N_4 ceramics as a function of Si_3N_4 poly-hollow microsphere content.
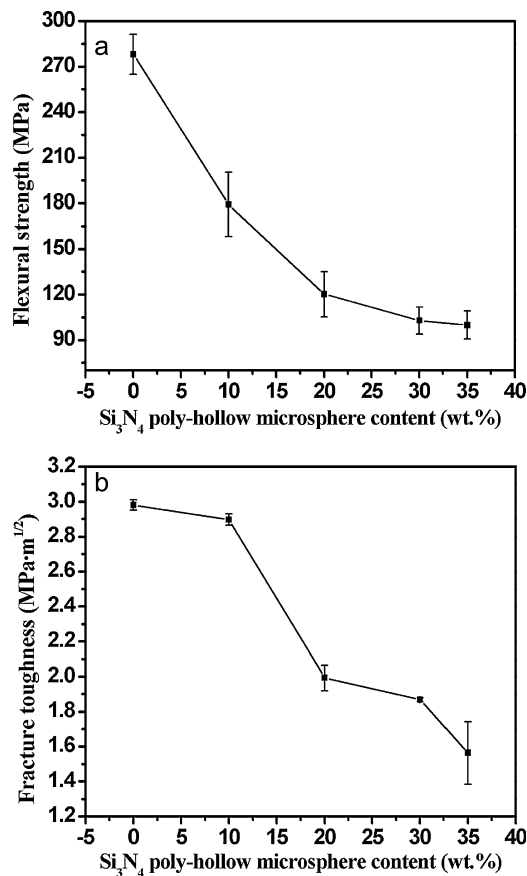

Fig. 10. Mechanical properties of the porous Si_3N_4 ceramics as functions of Si_3N_4 poly-hollow microsphere content.

4. Conclusions

In this paper, the porous Si_3N_4 ceramics were successfully prepared by aqueous gelcasting using Si_3N_4 poly-hollow microspheres as pore-forming agent. The Si_3N_4 poly-hollow microspheres content could significantly influence the microstructure, shrinkage and porosity of the porous Si_3N_4 ceramics, thus they would further influence the mechanical

properties of the porous Si_3N_4 ceramics. The XRD results show that there is only β-Si_3N_4 phase in all the prepared porous Si_3N_4 ceramics. Meanwhile, it is found that the Si_3N_4 poly-hollow microspheres distribute uniformly in the Si_3N_4 basal body, the Si_3N_4 poly-hollow microspheres and the Si_3N_4 basal body contact closely. With the increase of the Si_3N_4 poly-hollow microsphere content, the shrinkage of the Si_3N_4 ceramics decreases gradually, and the porosity decreases firstly and then increases. Furthermore, the flexural strength and fracture toughness of the Si_3N_4 ceramics decrease greatly with the increase of the Si_3N_4 poly-hollow microsphere content. It is a novel promising method to prepare porous Si_3N_4 ceramics using Si_3N_4 poly-hollow microspheres as pore-forming agent in the future.

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