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Effect of monomer content on physical properties of silicon nitride ceramic green body prepared by gelcasting

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Abstract

The gelcasting technique was employed to prepare Si_3N_4 green body. The monomers used in the research were acrylamide (AM) and *N*,*N*′-methylenebisacrylamide (MBAM). The influences of the monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM) on the warpage rate, shrinkage rate, and the flexural strength of Si_3N_4 ceramics green body were investigated. Both warpage rate and shrinkage rate of green body were found to decrease with the increase of monomer content, and monotonically increase with the ratio of monomers after drying. The variation of warpage rate with the ratio of monomers is evident when monomer content is 20 wt.%, but the variations are not evident when monomer contents are 40 and 55 wt.%. The flexural strength of the green body is highest at an optimum value of the monomers ratio, and increases with increasing monomer content, reaching 50–90 MPa when monomer contents are 40 and 55 wt.%.

Keywords: Gelcasting; Si_3N_4 green body; Warpage rate; Shrinkage rate; Flexural strength

1. Introduction

Gelcasting is an attractive new ceramic forming process that is used in manufacturing high-quality, complex-shaped ceramic parts for various industries [1–6]. The heart of the gelcasting technology is the use of an organic monomer solution that can be polymerized to form a strong, cross-linked polymer-solvent gel. The gelcasting process involves the preparation of an aqueous slurry of ceramic powder, which contains small quantities of monomer, cross-linker, gel initiators, catalysts, sintering aids, and other additives [7–10]. The aqueous slurry of the ceramic powder is poured into a mold, polymerized *in situ* to immobilize the particles in a gel, removed from the mold while still wet, then dried. After drying, binder removal and sintering are carried out.

So far, a number of routes to porous ceramics by use of gelcasting have been developed, such as foaming, stacking of presintered granules, and pyrolysis of various organic additives [11,12]. However, little work was focused on the preparation of porous ceramics by merely increasing monomer content in the slurry without other organic additives during gelcasting. Monomer and cross-linker herein not only form macromolecular network to hold the ceramic particles together, but also play a leading role in pore formation. This method can produce high-grade porous ceramics having more uniform pore distribution and mainly containing micropores rather than macropores. However, increasing monomer content can influence the properties of the ceramic green body (e.g., warpage, shrinkage, and strength of green body). Erik Adolfsson has investigated the influences of solid loading, drying conditions and the geometry of green body on the shrinkage and warpage of ceramic green body. The results showed that high solid loading, uniform drying, and symmetrical geometry of green body could reduce the shrinkage and warpage [13]. In essence, the warpage of green body during drying results from the shrinkage and collapse of the three-dimensional network structures of cross-linked polymer gels. The contents of monomer and cross-linker in slurry influence the three-dimensional network structures of cross-linked polymer gels. Although many researchers have investigated the preparation of Si_3N_4 ceramics by gelcasting [14–24], not much work has been done on the investigation of

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the influences of monomer and cross-linker on the properties of the green body.

In this paper, the preparation of porous Si_3N_4 ceramic green body by merely increasing monomer content during gelcasting is performed, and the influences of monomer and cross-linker on warpage, shrinkage and strength of green body is investigated.

2. Experimental

2.1. Materials

Aqueous gelcasting of Si_3N_4 was carried out using acrylamide (AM, $C_2H_3CONH_2$) and N,N'-methylenebisacrylamide (MBAM, $(C_2H_3CONH)_2(CH_2)$) monomers. Si_3N_4 powders (mean particle size: 0.37 μm, α phase >94 wt.%,) employed in the study were commercially available materials. Al_2O_3 (mean particle size: 1.07 μm, 99% purity) and Y_2O_3 (mean particle size: 4.74 μm, 99.9% purity) were used as the sintering additives. A dispersant (1 wt.%, ammonium salt of poly(acrylic acid)) was added to minimize agglomeration, and potassium persulphate (Merck, $K_2S_2O_8$) was used as initiator. A proper amount of polyacrylamide (PAM) with an average molecular weight approximately 3,000,000 was used, which can eliminate the surface exfoliation phenomenon of green bodies cast in air, and can also decrease the fluidity of the suspension to prevent Si_3N_4 powders from depositing. Ammonia aqueous was used as pH adjuster. All reagents were chemically pure.

2.2. Gelcasting procedure

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

The next step is to add silicon nitride powders and a suitable sintering additive (1 wt.%, Al_2O_3; 2 wt.%, Y_2O_3, based on silicon nitride powders) to the premix solution. The slurry with 40 wt.% of solid loading was degassed for 30 min after rolling for 12 h in polyethylene bottles, using agate balls. The slurry was degassed for another 10 min when the initiator (ammonium persulfate) was added. All the above operations were conducted at room temperature.

Finally, the slurry was cast into a cylindrical glass mold having the diameter of 40 mm and the height of 7 mm, and then the samples were kept at 65 °C for 40 min. After the monomers had polymerized, the green bodies were demolded. After gelcasting, the samples were dried in a commercial dryer, at 20 °C with relative humidity of 98% for 140 h.

3. Results and discussion

In order to investigate the influences of monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM) on the warpage, shrinkage and strength of green body during the preparation of Si_3N_4 ceramics by gelcasting, solid loading were kept constant (40 wt.%), and the drying conditions were invariable (temperature, 20 °C; relative humidity, 98%; drying time, 140 h). In order to achieve high porosity without any other organic additives, the concentration of monomers in the premix solution was varied from 20 to 55 wt.% (based on silicon nitride), and the ratio of monomers (AM/MBAM) was varied from 5 to 20.

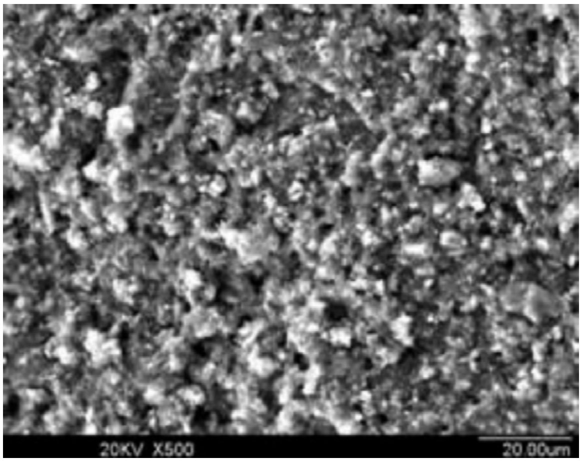


Fig. 1. Microstructures of Si_3N_4 green body acquired from slurries with solid loading 40 wt.%.

The microstructure of the green body as observed by SEM (Fig. 1) indicates that the powders in green body distribute compactly and homogeneously, and also the grains are connected by polymeric networks, which improve the strength of green body even to allow machining.

3.1. Warpage and shrinkage of Si_3N_4 green body

Here, the monomer content (AM and MBAM) and the ratio of monomers (AM/MBAM) are abbreviated as MC and RM, respectively.

Fig. 2 shows the shape comparisons of green bodies with different monomer content and the ratio of monomers after drying. Owing to addition of polyacrylamide, the surface exfoliation phenomenon of green bodies did not occur, and the surfaces of green bodies were smooth, as shown in Fig. 2. Due to different monomer content and the ratio of monomers in green bodies, there are significant differences in warpages of Si_3N_4 green bodies. For quantitative study of the warpage of green body, the warpage rate (WR) is defined by

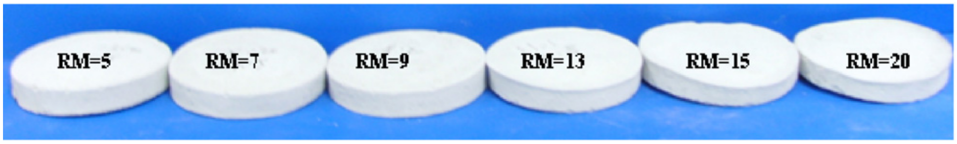
$$\mathrm{WR} = \frac{h}{D} \times 100\% \tag{1}$$

where h is the maximum height of warpage; D is the diameter of green body after drying.

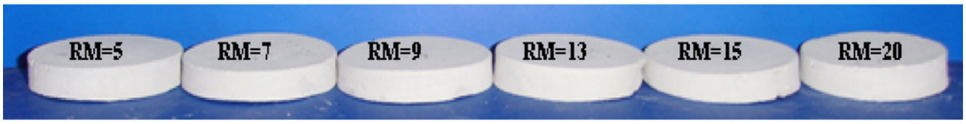
In order to investigate the shrinkage of Si_3N_4 green body after drying, the shrinkage rate (SR) is expressed as follows:

$$\mathrm{SR} = \frac{D_0 - D}{D} \times 100\% \tag{2}$$

(a) MC = 20 wt. %



(b) MC = 40 wt. %



(c) MC = 55 wt. %

Fig. 2. Shape comparison of Si_3N_4 green bodies with different the monomer contents (AM and MBAM) and the ratio of monomers (AM/MBAM).

where D_0 is the diameter of green body before drying; D is the diameter of green body after drying.

Figs. 3 and 4 show the influences of monomer content and the ratio of monomers on warpage rate and shrinkage rate, respectively. Increasing monomer content makes both warpage rate and shrinkage rate of Si_3N_4 green body decrease. In the meantime, both warpage rate and shrinkage rate increase monotonically with the ratio of monomers. The variations of the warpage rate and shrinkage rate of green bodies with monomer content and the ratio of monomers mean that the warpage and shrinkage concur during drying, and large shrinkage of green body always accompanies an apparent warpage. The variation of warpage rate with the ratio of monomers is notable when monomer content is 20 wt.%, but the variation is slight when monomer content is 40 or 55 wt.%.

The kernel of the gelcasting process is the use of a monomer solution, which can be polymerized to form a strong and cross-linked polymer-solvent gel [3]. The macromolecular network resulting from the *in situ* polymerization holds the ceramic particles together. The advantage of the gelcasting is the possibility of obtaining wet green body with an extremely high homogeneity. However, during the drying process of green body, warpage can be caused by inner stresses due to nonsymmetrical shrinkage, and can arise even in a wet cast material with a high homogeneity [25]. In the drying process of green body, the moisture, in the form of liquid water, is transported primarily by capillary forces to the part surface where it evaporates to the atmosphere at a constant rate [26], and the gel matrix yields to the large compressive stresses set up by the capillary forces. The Si_3N_4 particles, firmly attached to the polymer network, move towards each other when the network collapses, which in turn causes a bulk shrinkage of the green body. As the green body continues to dry, the gel which coats the individual Si_3N_4 particles begins to shrink while remaining attached to the particles. In the process of this shrinkage towards particle surfaces, the gel-matrix ruptures. Once all the particles touch each other, further movement among them ceases.

The kernel of the gelcasting process is a monomer solution that polymerizes upon the addition of free radicals to form a gel.

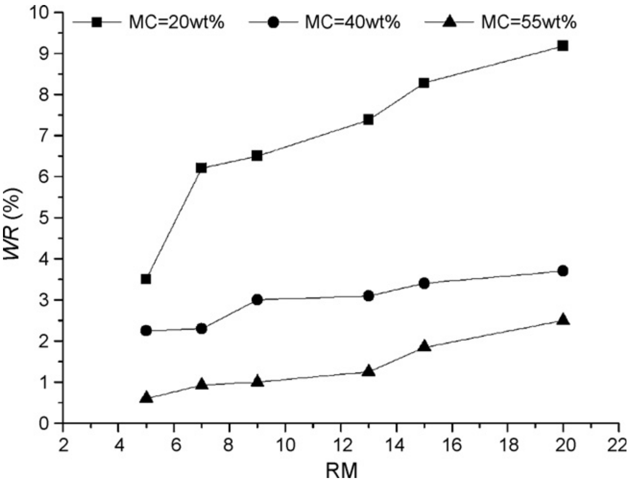


Fig. 3. The influences of monomer content and the ratio of monomers on warpage rate of Si_3N_4 green body.

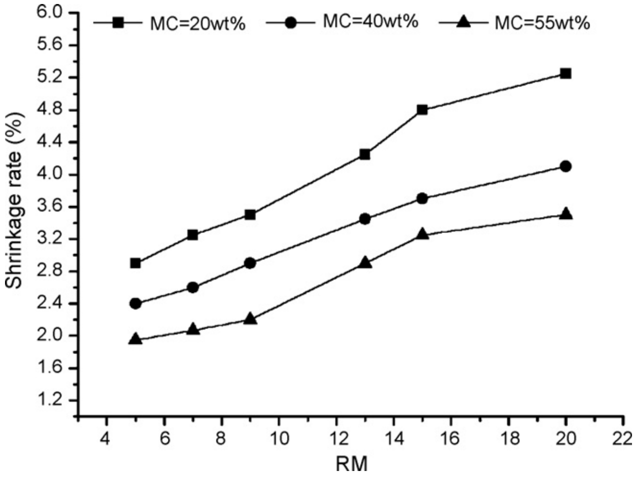


Fig. 4. The influences of monomer content and the ratio of monomers on shrinkage rate of Si_3N_4 green body.

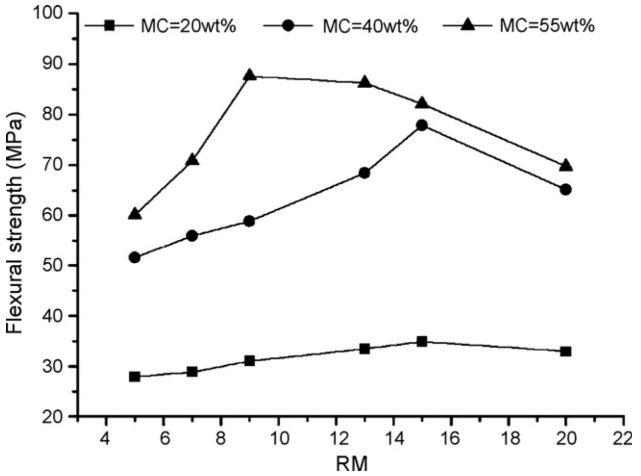


Fig. 5. The influences of monomer content and the ratio of monomers on the flexural strength of green body.

The monomer solution consists of the solvent (water), a chain forming monomer, a chain branching (cross-linking) monomer, and a free radical initiator. Increasing the monomer content can make cross-linking point of gel become more, and this makes the macromolecular network of gel more compact. The ceramic particle distribution in the gel network is more uniform with increasing the monomer content. During the drying of ceramic green body, the compact gel network and the uniform distribution of ceramic particles make the shrinking movement of ceramic particles more homogeneous, which is conducive to abate the warpage of green body. In the meantime, the intensity of macromolecular network gel increases with the increase of cross-linker content (i.e., the decrease of the ratio of monomers (AM/MBAM)). Therefore, both warpage and shrinkage of green body decrease with the increase of monomer content (AM and MBAM) and the decrease of ratio of monomers (AM/MBAM), as shown in Figs. 3 and 4.

3.2. Flexural strength of Si_3N_4 green body

Fig. 5 shows the influences of monomer content and the ratio of monomers on the flexural strength of green body. The variation of the flexural strength of green bodies with the ratio of monomers shows similar trends at different monomer contents. The flexural strength of green body first increases with the increase of the ratio of monomers, reaches maximum value and then decreases. Therefore, the results indicate that the ratio of monomers has an optimum value where the flexural strength of green body is highest.

When the cross-linker is excessive (i.e., the ratio of monomers is too small), the three-dimensional network structures of cross-linked polymer gels are coarse so as to make the toughness of network structures decrease when the green body is dried, and then the flexural strength of green body decreases [27]. In the meantime, when the cross-linker content is too small (i.e., the ratio of monomers is too high), the three-

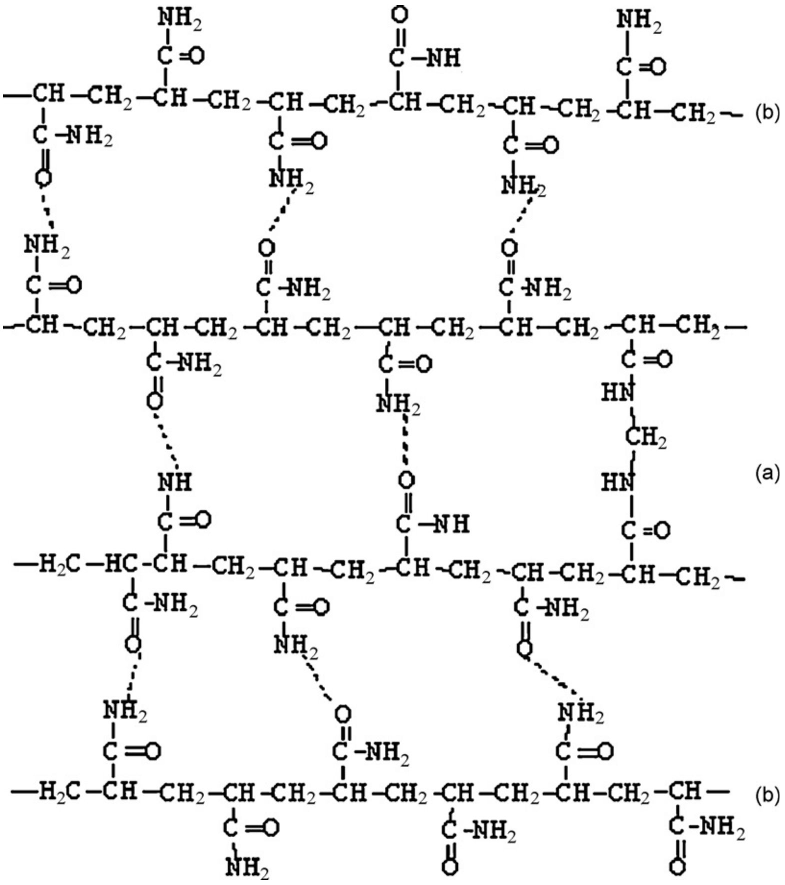


Fig. 6. The proposed structure of cross-linked PAM (a) gel after an addition of native PAM (b).

dimensional network structures are loose, and this results in the nonuniform distribution of Si_3N_4 particles in green body, which results in the decrease of the flexural strength of green body. Therefore, at a given monomer content, there is an optimum ratio of monomers, and the flexural strength of green body reach a maximum value. At the optimum ratio of monomers, the three-dimensional network of cross-linked polymer gels in slurry is compact, and the distribution of Si_3N_4 powders in green body is uniform.

At a given ratio of monomers, the flexural strength of green body increases with the increase of monomer content, as shown in Fig. 5. During gelcasting, the increase of monomer content makes the three-dimensional network structures compact. Since the strength of green body formed by gelcasting is mainly provided by the polymer gel, compact three-dimensional network of cross-linked polymer gels can enhance the flexural strength of green body.

Many earlier studies indicated that the flexural strength of Si_3N_4 green body formed by gelcasting was less than 40 MPa [28]. In this study the flexural strength of Si_3N_4 green body reached as high as 50–90 MPa when monomer contents are 40 and 55 wt.%.

Earlier studies did not add PAM during preparation of Si_3N_4 green body formed by gelcasting. In this study, in order to resolve the surface spallation problem, PAM is added in water-soluble polymer. During the polymerization process, PAM with free amino and keto groups can form a more complicated network structure through hydrogen bonding with the keto groups of the PAM polymerized by monomers [29], which results in an intimate mix of polymeric chains, as shown in Fig. 6. The high strength of green body is attributed to the enhanced polymer network due to the cross-linking through hydrogen bonding. Hence, the flexural strength of Si_3N_4 green body prepared by the suspension with addition of PAM increases notably compared to those without PAM. In the meantime, owing to addition of PAM, increasing monomer content can enhance polymer network through hydrogen bonding, as shown in Fig. 6. Therefore, Si_3N_4 green body formed by gelcasting can obtain high flexural strength when the monomer contents are 40 and 55 wt.% in the experiment.

Therefore, the Si_3N_4 green body can obtain relatively higher flexural strength when monomer contents are 40 and 55 wt.% in this study. Though PAM is added when monomer content is 20 wt.%, monomer content is too small, and then the influence of polymer network through hydrogen bonding on the flexural strength of green body is slight.

4. Conclusions

The gelcasting technique was employed to prepare Si_3N_4 green body, and the influences of monomer content and the ratio of monomers on warpage rate, shrinkage rate and the flexural strength of Si_3N_4 green body were investigated. The following conclusions can be drawn from this study:

(1) Increasing monomer content makes both warpage rate and shrinkage rate of Si_3N_4 green body to decrease. Both warpage rate and shrinkage rate monotonically increase with the ratio of monomers. The variations of warpage rate with the ratio of monomers are evident when monomer content is 20 wt.%, but the variations are not evident when monomer contents are 40 and 55 wt.%.
(2) The flexural strength of green body first increases with the increase of ratio of monomers reaching the maximum and then decreased. The ratio of monomers has an optimum value where the flexural strength of green body is highest.
(3) The addition of PAM can notably enhance the flexural strength of Si_3N_4 green body. The flexural strength of Si_3N_4 green body can reach 50–90 MPa when monomer contents are 40 and 55 wt.%.

Acknowledgments

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