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Effect of solid loading on gelcasting of silica ceramics using DMAA ☆

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Abstract

Silica ceramics with low porosity, high strength, low dielectric constant and loss were fabricated by gelcasting using a low-toxicity N′N-dimethyl acrylamide (DMAA) gel system. Effect of solid loading on rheological properties of slurries, properties of green bodies and sintered ceramics were investigated. The solid loading of suspension that can meet requirements for casting is as high as 68 vol%. However, it is found that the highest flexural strength of 15.4 MPa for green bodies and 67.4 MPa for sintered ceramics is obtained at the solid loading of 64 vol% and 66 vol%, respectively. Ceramics with dielectric constant of 3.27 and the lowest dielectric loss (1 MHz) of 7.82×10^{-4} are obtained at the solid loading of 64 vol%. Solid loading has a critical effect on properties of green and sintered silica bodies.

Keywords: Silica ceramics; Gelcasting; Solid loading; Low-toxicity

1. Introduction

Silica ceramics possess prominent corrosion and thermal shock resistance (no breakage after thermal shock between 25 and 1100 °C for more than 30 times), low thermal expansion coefficient (0.54×10^{-6} °C^{-1}, 0–800 °C) and dielectric constant (3.1–3.8), low thermal conductivity (2.09 W/m. K), and good insulating property (resistivity: 10^{15} Ω. m at room temperature). These properties make silica ceramics an excellent candidate as structural and functional materials in many fields, such as glass, metal, aerospace and polysilicon industry [1–4]. Gelcasting is a near net shape method for fabricating complex shape products and has rapidly developed in the past few decades. Acrylamide (AM) is the first gel monomer that has been used in gelcasting process and is used frequently [5]. AM has been used in gelcasting of silica ceramics by Hu [6] et al. In their study, the maximum flexural strength of sintered silica ceramics is about 40 MPa and bulk density of ceramics with the maximum strength is about 2.05 g/cm^3 (nano silica was added as sintering aids). However, industry has been reluctant to use this technique because AM is a neurotoxin. In recent years, many non-toxicity natural materials have been used in gelcasting systems like chitosan [7], agarose [8], starch [9], cellulose ethers [10], etc., but low strength of green bodies seems inevitable in these systems. Therefore, developing new low-toxic gel systems which have similar or superior properties to the AM system, has become an area of intense interest in the field for years. Low-toxic gel, 2-hydroxyethyl methacrylate (HEMA), has been used in gelcasting of fused silica ceramics by Yu [11] et al. In their study, the maximum four-point flexural strength of silica ceramics is about 28 MPa and bulk density of ceramics with the maximum strength is about 1.79 g/cm^3. But monomer content in their study reaches 30% in the premix solution and flexural strength of green bodies is just about 4 MPa. N′N-dimethyl acrylamide (DMAA) is a water soluble low-toxicity monomer which has shown excellent properties similar to AM in gelcasting of SiC [12], AlN [13] and ZTA [14].

So far, most of the researches on gelcasting have focused on the preparation of high solid loading and low viscosity suspensions and the process control of gelation. It is no doubt that preparation of slurries with solid loading as high as possible is very important in gelcasting. However, little

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attention has been placed on the effect of solid loading on sintered ceramics. Jiao et al. [15] investigated the effect of solid loading of slurries on properties of ZTA ceramics by gelcasting. They found that pore size distribution of green bodies prepared by high solid loading slurries exhibits double peaks. But they did not explain the reasons why double peaks appeared and did not study their effect on sintered ceramics. Zhang et al. [14] investigated the effect of solid loading on gelcasting of ZTA. They found that agglomeration which can degrade flexural strength of ceramics appeared in the highest solid loading. But they did not explain the reasons why decrease of mechanical properties occurred in ceramics with other higher solid loading. What′s more, there are almost no reports about the influence of solid loading on dielectric properties of ceramics.

In the present work, silica green bodies were prepared by gelcasting using the DMAA system which was followed by pressureless sintering. Silica ceramics obtained by the present gelcasting method show excellent properties as well as that obtained in AM system. Effect of solid loading on rheological behaviors of silica slurries, mechanical and dielectric properties of silica green bodies and sintered ceramics were investigated. It was found that solid loading has a critical effect on gelcasting of silica ceramics.

2. Experimental

2.1. Raw materials

Commercial amorphous silica powders (d_{50}: 3.98 μm, purity: 99.9%) were used as raw materials in this investigation. DMAA (Kowa Co. Ltd., Japan), N,N′-methylenebisacrylamide (MBAM, Tianjing Chemical Reagent Research Institute, China), acrylic acid-2-acrylamido-2-methypropane sulfonic acid copolymer (AA-AMPS, Taihe Water Treatment Co., Ltd., Shandong, China) and ammonium persulfate (APS, Lingfeng Chemical Reagent Co., Ltd., Shanghai, China) were used as gel monomer, crosslinker, dispersant and initiator, respectively.

2.2. Experimental procedure

Firstly, premix solution was prepared by dissolving DMAA (10 wt%) and MBAM (1 wt%) in distilled water. Then, silica powder, dispersant and mill ball were added to the premix solution. After ball milling for 5 h, the gelcasting slurry was obtained. Secondly, the slurry was degassed in a vacuum deaeration mix after adding APS (2 wt% of DMAA) as initiator. Then, the slurry was casted into a stainless steel mold and soaked in a specific temperature for an hour. After being dried in a specific condition, green bodies were obtained. Sintering was carried out in an ordinary electric furnace at 1250 °C for 4 h, which ensures that silica ceramics will not have a large number of crystallization and makes silica ceramics as densified as possible and thus brings about the expected excellent properties of silica ceramics [16].

2.3. Characterization

R/S Rheometer (R/S CC25, Brookfield Corporation, USA) was used to characterize rheological behaviors of slurries. Scanning electron microscope (SEM, Model JSM-5900, Japan) was used to observe microstructure of green and sintered bodies. Dielectric properties were measured by impedance analyzer (Agilent 4294A) and the test frequency is 1 MHz. Flexural strength was examined using an universal testing machine (CMT-6203, MTS System Corporation, China) by the three-point flexural method with a sample dimension of 3 mm × 4 mm × 40 mm. The Archimedes method was employed to determine bulk density and apparent porosity of green and sintered bodies. Four samples were used to determine the average value in mechanical and dielectric tests.

3. Results and discussion

3.1. Rheological properties of slurries

Fig. 1 shows the effect of solid loading on viscosity and shear stress of silica slurries. It can be seen that viscosity and shear stress increase with solid loading as a result of the reduction of the free water between particles. In addition, the space between particles reduces also when solid loading increases, which will enhance the interaction of particles and thus lead to the increase in viscosity and shear stress of the slurries.

When solid loading exceeds 66 vol%, viscosity and shear stress show a sharp increase, which suggests that solid loading is close to the critical value. However, the viscosity of 68 vol% slurry is 0.39 Pa. s at shear rate of 97.96 s^{-1}, which indicates that the slurry is still suitable for casting.

3.2. Properties of green bodies

Properties of silica green bodies and sintered ceramics at different solid loading are listed in Table 1. It can be seen that flexural strength of green bodies increases and then decreases with solid loading. At low solid loading, particles show a looser packing, which results in low strength of green bodies.

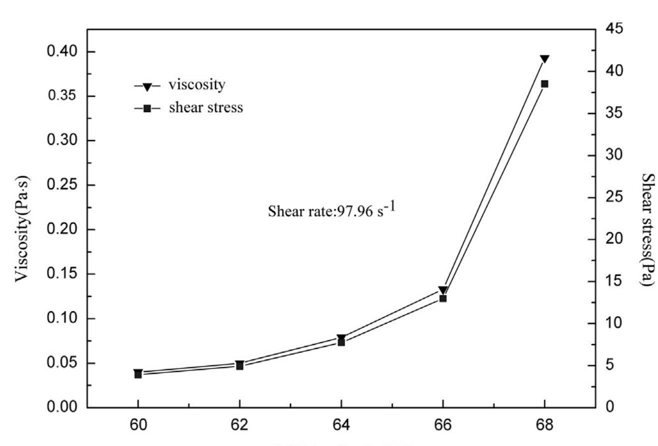

Fig. 1. Effect of solid loading on rheological properties of slurries.

However, when solid loading exceeds a critical value, the obvious decrease of polymer contents in green bodies will also lead to the reduction of strength. As it can be expected, density of green bodies shows a linear increase with solid loading.

Microstructure of green bodies is shown in Fig. 2. It can be seen that green bodies exhibit homogeneous microstructure when solid loading is under 64 vol%. However, obvious agglomeration phenomenon is observed in the 66 vol% and 68 vol% green bodies. When solid loading is too high, not only gases in the slurry cannot be easily removed, but also agglomeration of silica particles becomes serious, which will cause inhomogeneous structure of green bodies. In addition, it can be seen in Fig. 3 that the idle time increases with solid loading, which is alien to other researcher′s reports [13,17]. The main reason may be that both the initiator APS and silica is an acidoid. The dissociation equations of APS and silica powders in lower temperature aqueous solution are as below:

$$(NH_4)_2SO_8 \leftrightarrow 2NH_4^{+} + S_2O8_2^{-} \quad (1)$$

$$S_2O8^{2-} + 2H_2O \leftrightarrow 2HSO_4^{-} + H_2O_2 \quad (2)$$

$$2HSO_4^{-} \leftrightarrow H^{+} + SO_4^{2-} \quad (3)$$

$$Si\text{–}OH + H_2O \leftrightarrow SiO^{-} + H_3O^{+} \quad (4)$$

From the Eqs. (3) and (4), it can be seen that the dissociation of silica powders can restrain the dissociation of APS. This is why the idle time increases in Fig. 3. The prolongation of idle time will intensify the sedimentation and agglomeration of silica powders. The inhomogeneity in structure will also contribute to the decrease in flexural strength of green bodies.

3.3. Properties of sintered ceramics

3.3.1. Density and flexural strength of ceramics

As can be seen in Table 1, sintering linear shrinkage and bulk density of the sintered ceramics decreases and increases with solid loading respectively, which is identical to the variation of bulk density and apparent porosity of green bodies. However, the ceramics with 66 vol% solid loading show the maximum flexural strength. With the increase of solid loading, the increase in density of silica ceramics is beneficial for the increase of flexural strength. However, inhomogeneity structure caused by high solid loading will also show harmful effect on the mechanical properties. As can be seen in Fig. 4, the ceramics with 66 vol% and 68 vol% solid loading show poor homogeneity compared with the ceramics with solid loading of 60 vol%, 62 vol% and 64 vol%. The inhomogeneity in microstructure will cause stress concentration, and microcracks was indeed observed in 68 vol% ceramics. Therefore, although the 68 vol% ceramics have the highest density, the flexural strength shows an observable decrease.

3.3.2. Dielectric constant and loss

The dielectric properties and material density are closely related. Walton gives the relationship between dielectric constant and porosity [18]

$$\log \varepsilon_p = (1-p) \log \varepsilon_o$$

Table 1
Effects of solid loading on properties of green and sintered bodies.

Solid loading (%)	Flexural strength of green bodies (MPa)	Bulk density of green bodies (g/cm^3)	Apparent porosity of green bodies (g/cm^3)	Sintering linear shrinkage (%)	Bulk density of ceramics (g/cm^3)	Apparent porosity of ceramics (%)	Flexural strength of ceramics (MPa)	ε_r	$\tan\alpha$ ($\times 10^{-4}$)
60	14.4 ± 0.7	1.46 ± 0.01	31.6 ± 0.3	6.38 ± 0.17	1.81 ± 0.01	16.3 ± 0.1	57.3 ± 4.1	3.02 ± 0.09	10.53 ± 0.88
62	15.1 ± 0.5	1.50 ± 0.01	29.8 ± 0.3	6.07 ± 0.15	1.89 ± 0.01	13.0 ± 0.2	62.8 ± 0.8	3.13 ± 0.04	9.23 ± 0.58
64	15.4 ± 0.3	1.54 ± 0.01	28.7 ± 0.2	5.79 ± 0.15	1.94 ± 0.02	11.7 ± 0.5	64.5 ± 1.8	3.27 ± 0.06	7.82 ± 0.59
66	14.5 ± 1.0	1.58 ± 0.01	25.9 ± 0.3	5.21 ± 0.18	1.95 ± 0.01	11.5 ± 0.3	67.4 ± 2.7	3.35 ± 0.03	11.95 ± 4.08
68	14.3 ± 0.8	1.60 ± 0.01	25.2 ± 0.3	4.62 ± 0.16	1.95 ± 0.02	10.7 ± 0.4	62.6 ± 3.8	3.38 ± 0.03	16.59 ± 4.12

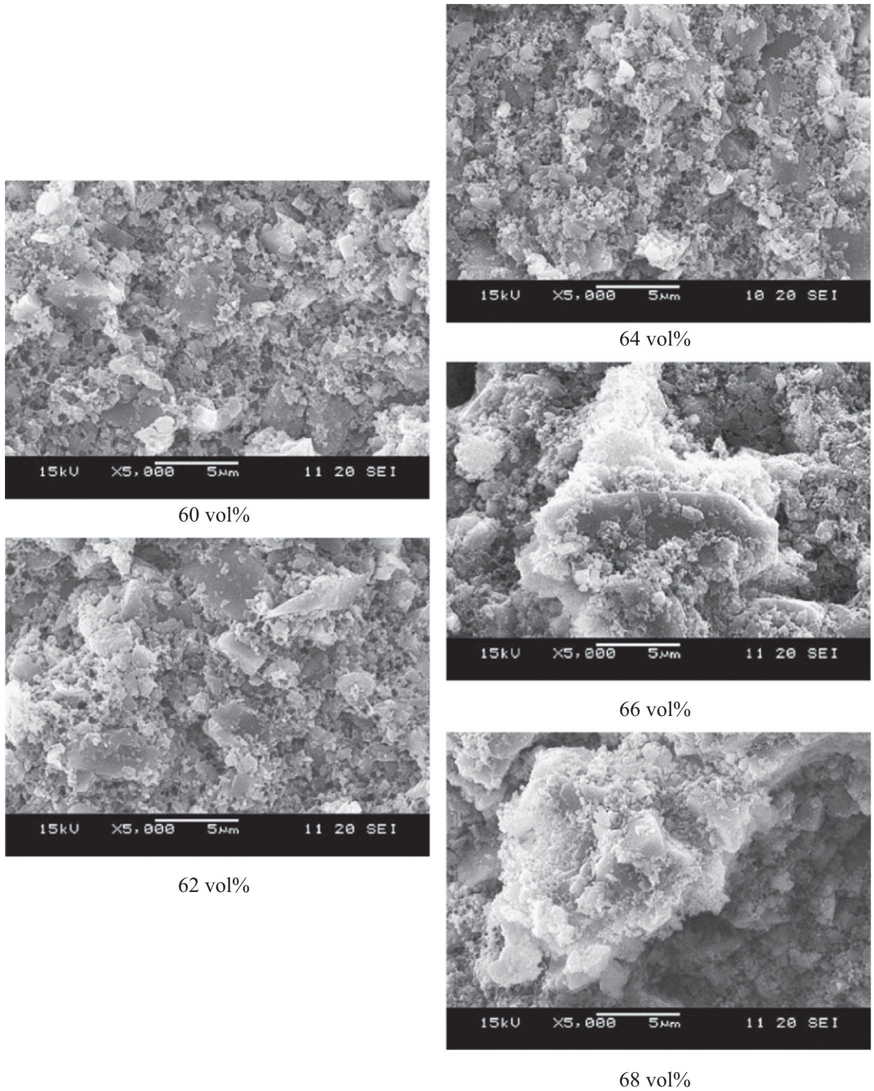

Fig. 2. SEM micrographs of silica green bodies with different solid loading.

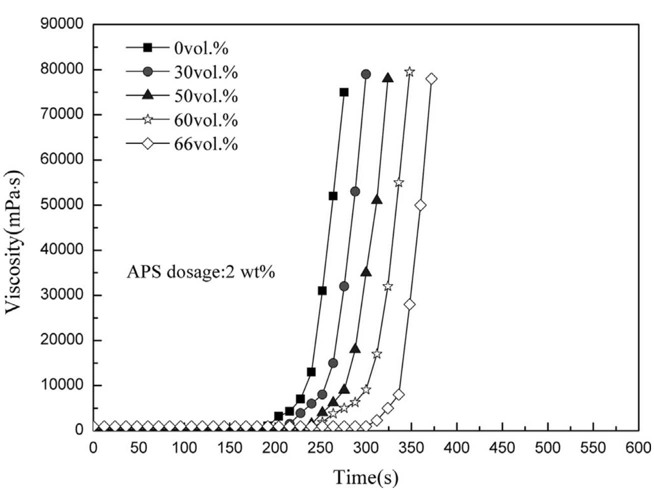

Fig. 3. Idle time of slurries with different solid loading.

where p is the porosity and $1-p$ can be regarded as the relative density; ε_p and ε_o are the dielectric constants of the porous and fully dense materials, respectively. The dielectric constant results in Table 1 basically follow this relationship, that is, the greater the density of silica ceramics is, the greater the dielectric constant is. However, the dielectric loss doesn't show monotone variation with solid loading. With the increase of solid loading, the increase in density of silica ceramics will lead to the decrease of dielectric loss. When the solid loading is above 64 vol%, the inhomogeneity in structure will deteriorate significantly the dielectric properties and result in the obvious increase of dielectric loss.

4. Conclusions

A low-toxicity monomer DMAA was used in gelcasting of silica ceramics. A discussion of experimental data leads to the following conclusion:

1. High solid loading slurries with low viscosity were prepared.
2. When solid loading varies from 60 vol% to 68 vol%, the flexural strength of green bodies increases and decreases. Green bodies with 64 vol% solid loading have the maximum strength of 15.4 MPa.

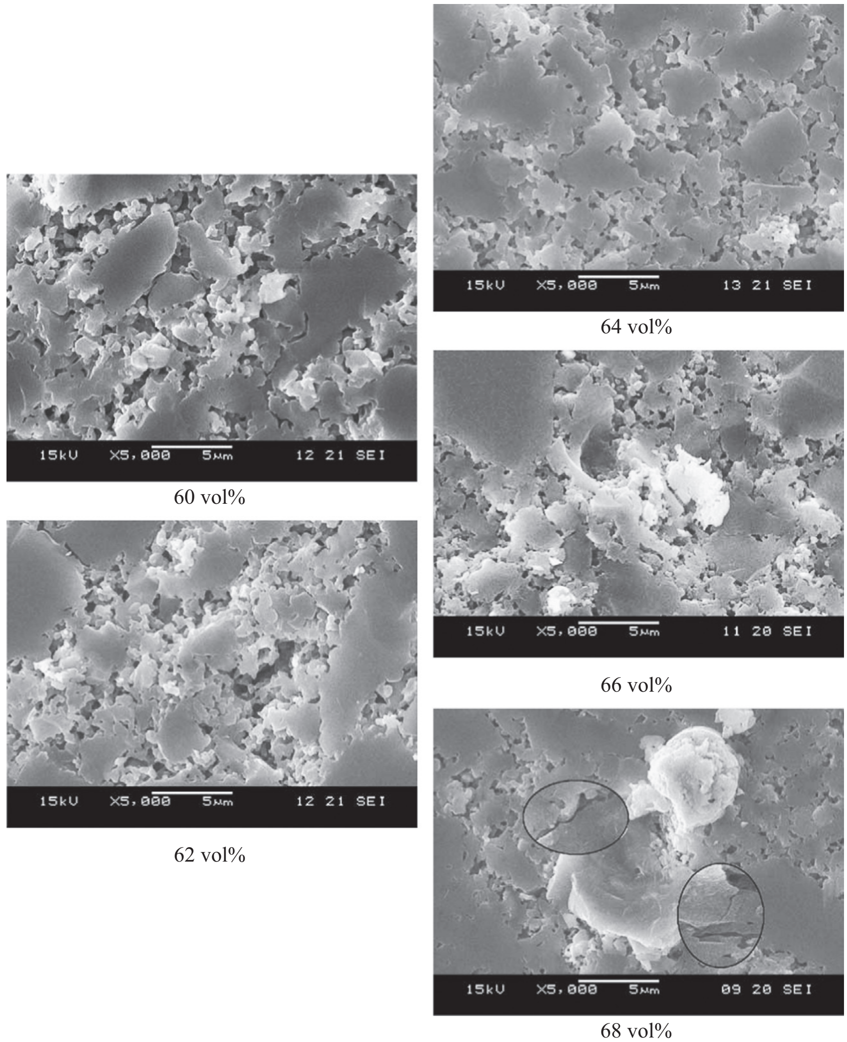

Fig. 4. SEM micrographs of silica ceramics with different solid loading.

3. Sintering linear shrinkage and bulk density of the sintered ceramics decreases and increases with solid loading respectively, which is identical to the variation of bulk density and apparent porosity of green bodies.
4. With the increase of solid loading, the increase in density of silica ceramics is beneficial for the increase of flexural strength and dielectric constant and the decrease of dielectric loss. However, inhomogeneity structure caused by high solid loading will also show harmful effect on the mechanical properties and dielectric loss. Ceramics with the 66 vol% solid loading have the maximum strength of 67.4 MPa and the lowest dielectric loss 7.82×10^{-4} is obtained in ceramics with the 64 vol% solid loading.

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