Ceramics International 33 (2007) 133–139

CERAMICS
INTERNATIONAL

www.elsevier.com/locate/ceramint

Gel-casting without de-airing process using silica sol as a binder

Deyu Kong[a,*], Hui Yang[b], Su Wei[a], Dongyun Li[b], Jiabang Wang[b]

[a] *College of Architecture & Civil Engineering, Zhejiang University of Technology, Hangzhou 310014, PR China*
[b] *College of Materials & Chemistry Engineering, Zhejiang University, Hangzhou 310027, PR China*

Received 27 June 2005; received in revised form 7 July 2005; accepted 16 August 2005

Abstract

This work reports a gel-casting technology without de-airing process developed to prepare mullite-based ceramics green body using silica sol as a binder. Concentrated alumina slurry dispersed in silica sol with high solid volume loading but low viscosity was successfully prepared at about pH 9.5. In-situ consolidation of the slurry was realized through adjustment of NH_4Cl concentration to control the gelation time of the slurry. High compaction and uniform green body without air entrapped was obtained by gel-casting technology without de-airing process, and dense complex-shaped mullite-based ceramics were produced through the new gel-casting system.

Keywords: D. Mullite; Alumina; Gel-casting; De-airing

---

1. Introduction

In order to obtain optimal performance and high reliability, advanced ceramic materials should have a microstructure characterized by a small defect size, and well-distributed homogeneous grain boundary composition. With the rapid development of technology, traditional forming processing (such as dry pressing, isostatic pressing and so on) is unable to meet the more and more strict service requirement in engineering [1,2]. Therefore, many novel forming technologies, such as gel-casting [3], direct coagulation casting [4] and so on, have been developed in recent decades [2]. Especially, gel-casting technology rapidly became a focus in ceramic forming field due to its high strength, high density, and low cost and machinable property of the formed green bodies since it was developed by Janney and Ometete in 1991 [3]. The basic principle of the gel-casting forming process is that a suspension from ceramic powder and mixed water solution of monomer and cross-linker is poured into a mold, polymerized in-situ to immobilize particles in a gelled part, removed from the mold, and then dried. However, its inevitable shortcoming, the commonly used monomer acrylamide that exhibits neural toxicity [5], limits its application. More and more researchers studied non-toxic or low toxicity polymers [5,6], or natural gel formers, such as chitosan gels [7], gelatine [8], polymer-sodium alginate [9], and protein [10], etc. in the process.

The challenge in gel-casting process lies in achieving a homogeneous suspension with high solids loading (>50 vol.%) and low viscosity (less than 1 Pa s) in the slip [3]. For oxide powders, such as Al_2O_3, the solids loading of a practical slurry has exceeded 60 vol.% by using polyelectrolyte as dispersants, which can create electrostatic stabilization via a polyelectrolyte and a significant electrical double-layer repulsion [5–10]. However, it has been reported that the presence of dispersants [11] or other organic materials, such as gelatin [8], egg-white [12], and even the aqueous monomer [13], etc., will result in air entrapped in the slurry during the dispersing, milling, and casting operation. In fact, the water-soluble monomer methacrylamide (MAM) and cross-linker methylene bisacrylamide (MBAM) used in aqueous gel-casting of slurries appear to encourage formation of bubbles too [13]. The observation of the monomer and cross-linker that encourage bubble formation is supported by the literature, which classifies amides and *n*-substituted amides as foaming agents [11]. The pores that result from the presence of bubbles in the slurries are usually significantly larger than the pores that result from incomplete densification and, thus, are more detrimental to material properties. Therefore, prevention of bubble formation in aqueous slurries or their complete elimination prior to casting is an important factor for the overall success of gel-casting as a

---

* Corresponding author.
E-mail address: kongdeyu@mail.hz.zj.cn (D. Kong).

0272-8842/$32.00 © 2005 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
doi:10.1016/j.ceramint.2005.08.006

commercial manufacturing process. However, complete elimination of bubbles from aqueous gel-casting slurries, especially those with particle loadings as high as 55 vol.%, appears to be a difficult task. The task becomes more difficult because the effects of various additives in the slurries and their cross-interactions on the formation and elimination of air bubbles is not well understood [13]. Therefore, Waesche and Steinborn [14] showed the increasing need for thorough de-airing with increasing viscosity of the slurry. An optimum has to be found between too extensive de-airing, which might lead to a liquid loss by evaporation and a drastic change in the slurry rheology, and too short de-airing, which leaves entrapped bubbles.

In this paper, a novel gel-casting technology without de-airing process was developed to prepare mullite-based ceramics green body using non-toxic silica sol as a binder. Concentrated alumina slurry dispersed in silica sol with high solid loading but low viscosity was successfully prepared. In situ consolidation of the slurry was realized through adjustment of the NH_4Cl concentration as electrolyte to promote gelation of the silica sol in the slurry. High compaction and uniform green body without entrapped pores was obtained by gel-casting technology without de-airing process, because there existed no surfactants and any other organic materials in the slurry, only a small amount of very unstable bubble were entrapped, which can be automatically eliminated without de-airing process. It is believed that the knowledge gained through this investigation will be helpful to fabricate mullite-based ceramic parts with high reliability and low cost.

2. Experimental procedure

In this study, commercially available α-Al_2O_3 (Henan Zhengzhou Zhongtian Alumina Company) and silica sol (NS-30, Zhejiang Shangyu Yuda Chemical Engineering Co. Ltd.) were used as the raw materials. The particle size distribution of the alumina powder was analyzed by a laser analyzer (Winner 2000, China), as given in Fig. 1. The sedigraph median particle diameter $d_{50} = 1.68$ μm and the specific surface area is 1.08 m^2/g. Chemical compositions and properties of silica sol are shown in Table 1. The electrolyte used was 3.6 mol/L NH_4Cl solutions. The reactive organic monomers used in the control experiments were monofunctional acrylamide, $C_2H_3CONH_2$ (AM), and difunctional N,N'-methylene-bisacrylamide $(C_2H_3CONH_2)_2CH_2$ (MBAM). The initiator was ammonium persulfate $(NH_4)_2S_2O_8$ and the reaction was accelerated by using the catalyst N,N,N',N', tetra-methyllethylenediamine (TEMED). The pH values of suspensions were adjusted using 1 mol/L HCl. All reagents used were chemically pure.

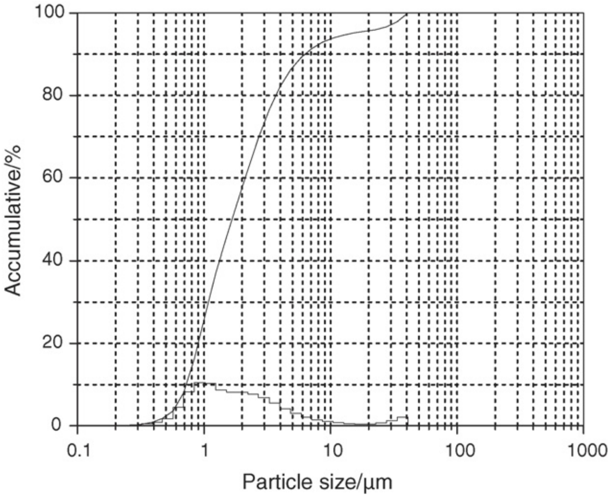

Fig. 1. Particle size distribution of the alumina powder.

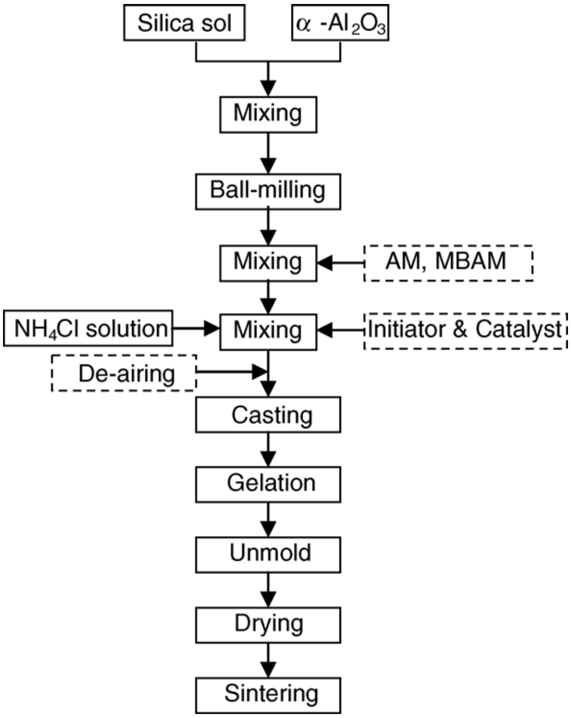

Fig. 2. Procedure for gel-casting of the alumina slurry dispersed in silica sol.

The flow chart of the present gel-casting process was shown in Fig. 2. The slurries were prepared through directly dispersing the alumina powders in the silica sol with various pH values, which were adjusted in advance using 1 mol/L HCl solution in one-way direction, by mechanically stirring for 30 min. For gel-casting process, the slurry was further ball-milling for 2 h to promote dispersion and admixing process with an experimental planetary mill.

As revealed, at pH above 7 but lower than 11, it was found that ammonium ions (structure-breaker) were more efficient in destabilizing silica colloidal particles than the sodium ions (structure-maker) [15–17]. And the addition of salt with

Table 1
Compositions and properties of silica sol

SiO_2 (wt.%)	30.3
Na_2O (wt.%)	0.1
pH	9.5
Density (g cm^{-3})	1.23
Viscosity (mPa s)	5.8
Particle size (nm)	8–20

various concentrations can cause a time-dependent gelation of the silica sol [17]. Thus, the gelation time of the slurry was controlled through adjustment of the NH_4Cl concentration in the slurry by adding NH_4Cl solution while continuously stirring in this program.

The suspension was degassed under vacuum for a certain time. During the de-airing process, the vacuum level is controlled by introducing water into the bottom of the bell jar during de-airing. This assures that the vacuum level will not exceed the vapor pressure of water, which can avoid drying of the slurry resulting in the formation of flakes of dried material, which can act as flaws in the cast part.

After the slurry was degassed, the slurry was cast into a 100 mm × 100 mm × 8 mm plastic mold. After the slurry gelled, the green body was de-molded and dried at 45 °C under controlled humidity to avoid cracking and non-uniform shrinkage due to rapid drying. The dried green bodies were cut and ground into specimens of about 4 mm × 8 mm × 70 mm for the bending strength measurement. Before their measurement, each of the specimens was ground by using SiC abrasive of 14.0, 7.0 and 3.5 μm, respectively. The obtained green bodies were then sintered at 1650 °C for 2 h.

In the control experiments, the organic monomers were added with free water:AM:MBAM = 12:1:0.05 in the prepared concentrated suspension. The suspension was degassed under vacuum for a certain time. Both the initiator, a 5 wt.% aqueous solution of ammonium persulfate, and catalyst, TEMED, were then added and stirred slowly to avoid sucking in as little air as possible. The suspension was degassed for another 5 min and then was cast into a 100 mm × 100 mm × 8 mm plastic mold. After the monomers polymerized, the green body was de-molded and dried under the same condition as the green body without containing monomer.

The pH values of the silica sol and the slurry were measured with a kind of pH meter (Inolab pH/ORP, German). Viscosity measurements were done with a kind of rotational viscometers (Model NXS-11A, Chengdu Instrument Factory, China). The gelation time was determined by visual observation. The prepared suspensions (8 ml) were placed into the glass tube. The gelation time was determined while the test tube was gently inverted. The time when the sample stopped flowing was classically taken as the gel point.

The bulk density (ρ_0) and the true density (ρ) of the green and the sintered bodies were determined by Archimedes' method in water and by water displacement method, respectively. Then the porosity (P) was calculated as follows:

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

Three-point bending strengths of green body specimens were determined from as-ground specimens with 63 mm span using 15 test pieces of 4 mm × 8 mm × 70 mm for each group of samples. Fracture surfaces of the green and sintered bodies were observed using SEM (SIRION, Holland) to estimate the microstructure uniformity of the specimens.

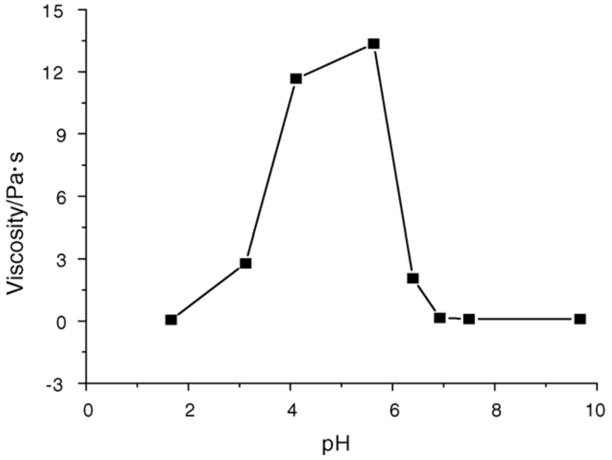

Fig. 3. Viscosity as a function of pH for 35 vol.% alumina slurry dispersed in 30.3 wt.% silica sol.

3. Results and discussions

3.1. Preparation of concentrated suspension

The viscosity (at about 36 s^{-1}) of the slurries with alumina volume loading of 35 vol.% dispersed in 30.3 wt.% silica sol is plotted as a function of pH values in Fig. 3. The measured pH value of the slurry was about 9.56 when the alumina powders were directly dispersed in the silica sol without any pH value adjustment. And the measured viscosity of the slurry was 125.0 mPa s. It has been proposed that the dispersion of alumina in silica sol at basic condition is dominated by a new colloid stabilization mechanism, nanoparticle halo, which has been reported in detail elsewhere [18]. With decreasing the pH value, the viscosity of the slurry increased slowly when the pH value was still over about pH 7.0. But the viscosity increased rapidly with further decreasing the pH value. The slurry showed the highest viscosity at around pH 5.63. Then the viscosity decreased rapidly with decreasing the pH value and the slurry showed very low viscosity below pH 2.0.

As indicated in Fig. 3, the pH value should be controlled either at very low pH value by adding HCl or at about pH 9.56 without adjustment of the pH value to prepare slurries with low viscosity but high solid volume loadings. However, it has been reported that silica sol is very stable at pH below 4–5 even when a high monovalent salt concentration is used [19]. In contrast to most colloids, silica sols can be destabilized for lower salt concentrations as the pH value is increased away from the isoelectric point (iep). This was ascribed to the presence of a thick hydration layer at pH close to the iep, resulting from hydrogen bonding of the water molecules with the protonated silanol sites, and to its destruction at pH above 7 [15,20]. But at pH above 7 but lower than 11, where many negative sites are present on the surface, it was found that ammonium ions (structure-breaker) was more efficient in destabilizing silica colloidal particles than the sodium ions (structure-maker) [15–17]. And the addition of salt with various concentrations can cause a time-dependent gelation of the silica sol. Thus, all the slurries were prepared without any

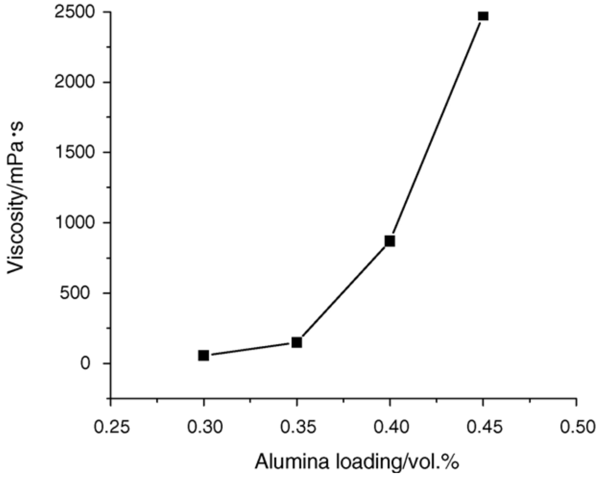

Fig. 4. Viscosity vs. alumina volume loading of the slurries near pH 9.5.

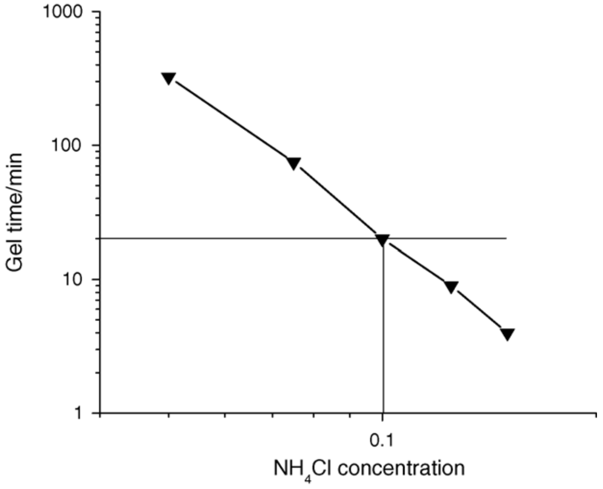

Fig. 5. Gel time vs. NH_4Cl concentration of the slurry.

adjustment of the pH value for gel-casting process, and the gelation time of the slurry was controlled through adjustment of the NH_4Cl concentration in the slurry by adding NH_4Cl solution in this program.

Fig. 4 gives viscosity versus alumina volume loading for the slurries near pH 9.5 at about $50\ s^{-1}$. The viscosity keeps increasing with increasing of the solid volume loading in the slurry. When the alumina volume loading is below 35 vol.%, the viscosity increases slowly with increasing the solids content, but increases rapidly when it is beyond 40 vol.%, and the viscosity reaches around 871 mPa s when the solids content is 40 vol.%. Gel-casting system generally requires well-dispersed concentrated ceramic slurries having viscosity less than 1 Pa s [3]. Thus, the maximum alumina volume loading for gel-casting in this program was about 40 vol.%. Taking the density of the silica as 2.2 g/cm^3, the calculated solid (alumina and silica) volume loading of the slurry is about 50 vol.%.

3.2. Control of the gelation time

As revealed by literature [17], the addition of salt with various concentrations can cause a time-dependent gelation of the silica sol. Thus, the gelation time of the slurry can be controlled through adjustment of the NH_4Cl concentration in the slurry by adding NH_4Cl solution. The gelation time of the concentrated slurry with alumina volume loading of 40 vol.% as a function of the NH_4Cl concentration of the slurry was plotted in Fig. 5. It can be seen that the gelation time increases with increasing the NH_4Cl concentration. And the mathematical relationship between gelation time and NH_4Cl concentration of the slurry is in the double logarithm form as Eq. (2),

$$\log t = -4.0176 \log C - 2.6917 \qquad (2)$$

with linear regression coefficient of over 0.99. In general, the gelation time of the slurry should be controlled about 20 min to avoid the sedimentation of particles in highly dispersed suspensions during the gelling process. Thus, the concentration of the NH_4Cl in the slurry should be controlled at about 0.10 M, the corresponding gelation time was about 20 min, for the gel-casting process without de-airing. And for the gel-casting process with de-airing step, the concentration of the NH_4Cl in the slurry should be adjusted to control the solidification time to be about 20 min after the slurry was de-aired and cast.

3.3. Effect of de-airing on porosity

Fig. 6 showed the effect of de-airing time on porosity of the green body utilizing gelation of the silica sol through adjustment of the NH_4Cl concentration or utilizing the polymerization of the monomer. For the gel-casting process with monomer, the de-airing time had a great influence on the porosity of the green body. The porosity reached as high as 48.3% for the green body without de-airing process. With increasing the de-airing time, it decreased obviously and was only 41.4% after a 40 min de-airing process. Further, de-airing did not result in a further obvious decrease of the porosity. However, for the gel-casting process with silica sol,

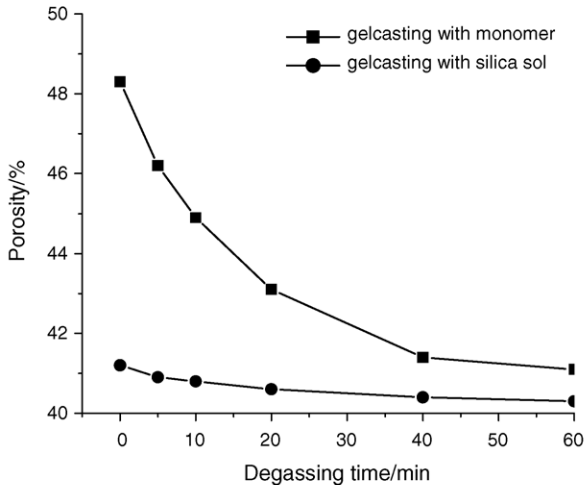

Fig. 6. Effect of de-airing time on porosity of the green body (a) with silica sol and (b) with monomer.

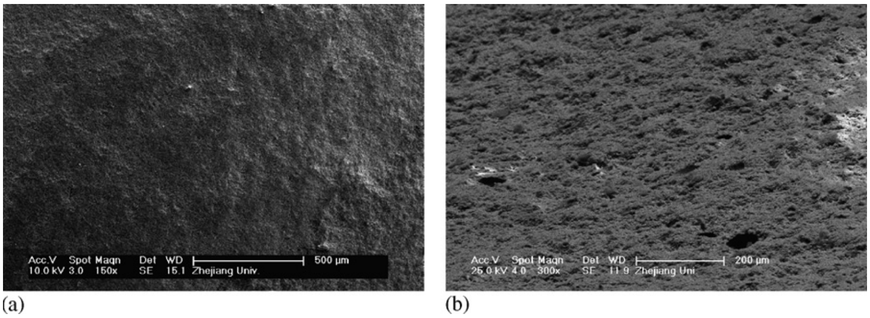

Fig. 7. Microstructure of the green bodies by gel-casting without de-airing process.

the de-airing process had little effect on the green body. With increasing the de-airing time, the green body did not show an obvious decrease of the porosity. The porosity was just 41.2% for the green body without de-airing process, and it was just 40.3% after a 60-min de-airing process. Fig. 7 gives microstructure of the green body without de-airing process. There existed entrapped pores on the fracture surface of the green body gel-casting with monomer. However, no entrapped pores can be seen on the surface of the green body gel-cast with silica sol.

It is well known that foams are inherently unstable systems [11]. Like almost all systems containing two or more immiscible phases, foams involve thermodynamic conditions in which the primary driving force is to reduce the total interfacial area between the phases—that is, they are thermodynamically unstable. In spite of their ultimate tendency to collapse, foams can be prepared that have a lifetime of minutes, days, or even months. For a practical foam, one or several of the following conditions will be beneficial for extending the persistence of foams [11]: (1) a high viscosity in the liquid phase, which retards hydrodynamic drainage as well as providing a cushion effect to absorb shocks resulting from random or induced motion; (2) a high surface viscosity, which also retards liquid loss from between interfaces and dampens film deformation prior to bubble collapse; (3) surface effects, such as Gibbs and Marangori effects which act to ‘‘heal’’ areas of film thinning due to liquid loss; (4) electrostatic and steric repulsion between adjacent interfaces due to the adsorption of ionic and non-ionic surfactants, polymers, etc., which can oppose drainage through the effects of the disjoining pressure; and (5) retardation of gas diffusion from smaller to larger bubbles. The addition of surfactants and/or polymers to a foaming system can alter any or all of the above system characteristics and therefore enhance the stability of the foam. They may also have the effect of lowering the surface tension of the system, thereby reducing the work required for the initial formation of the foam, as well as producing smaller, more uniform bubbles.

A notable characteristic of stable films is their resistance to mechanical disturbance. Gibbs [11] considered the important property to be the elasticity of the film E,

$$E = 2A\frac{\mathrm{d}\sigma}{\mathrm{d}A} \tag{3}$$

where A is the area of the film and σ is surface tension. For the case of a two-component system, Eq. (3) can be put in the form [11]

$$E = 4(\Gamma_2')^2\left(\frac{\mathrm{d}\mu_2}{\mathrm{d}m_2}\right) \tag{4}$$

Here Γ_2' is the surface excess of component 2, μ_2 is the chemical potential of that component, and m_2 is its amount per unit area of film. Qualitatively, E gives a measure of the ability of a film to adjust its surface tension in an instant of stress. If the surface should be extended, the surface concentration of the surfactant drops, and the local surface tension rises accordingly; the film is thus protected against rupture. For pure liquids, E as given would be zero, and this is in accord with the observation that the pure liquids do not give stable foam.

Therefore, for the gel-casting system containing dispersant or other organic materials, such as gelatin, egg-white, and even the aqueous monomer, etc., the foams formed in the slurry are relatively stable, due to the high E of the film of the foam. However, for the gel-casting system using silica sol as binders in this work, the foams formed are not stable, and can be automatically eliminated quickly during the gel-casting process. Thus, the slurry need not to de-air, and the gel-cast green body showed high compaction and uniform without entrapped pores.

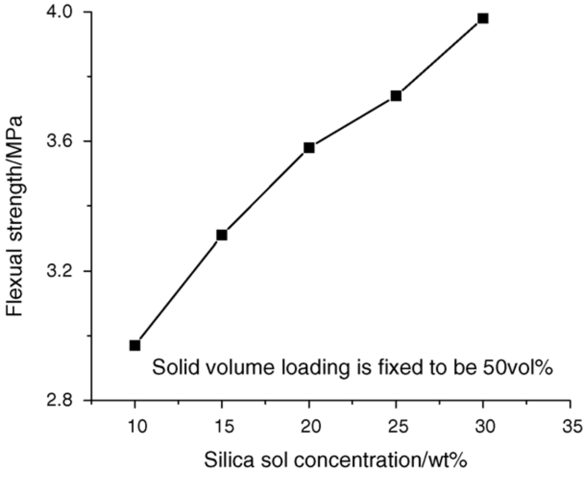

Fig. 8. Flexural strength of the green body vs. silica sol concentration in the slurry.

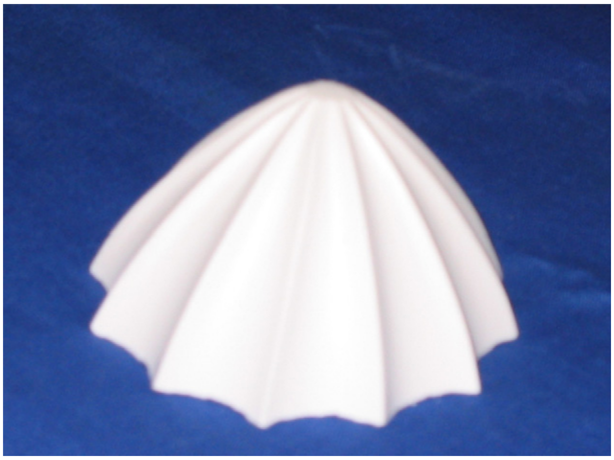

Fig. 9. Green body obtained by gel-casting technology without de-airing step.

3.4. Green strength

It indicates that the silica colloidal particles help to enhance the strength of the green body [19]. This is due to the combination of silica colloidal particles around the alumina particles by condensation of silanol groups into ≡SiOSi≡ after drying. Fig. 8 gives the flexural strength of the green body versus silica sol concentration in the slurry. The strength increases with increasing the silica sol concentration. When the silica sol concentration is 10 wt.% and 30 wt.%, the measured green strengths of the gel-cast bodies utilizing the gelation of the silica sol without de-airing process reached about 2.97 MPa and 3.98 MPa, which can meet the strength requirement for the machining of the green body [7]. Fig. 9 gives the green body obtained by gel-casting with silica sol but without de-airing step.

3.5. Microstructure of the sintered body

The obtained green body was sintered at 1650 °C for 2 h. The SEM micrograph of the sintered body was shown in Fig. 10. It should be noted that the ceramics by gel-casting with silica sol without de-airing process has a high density and uniform microstructure.

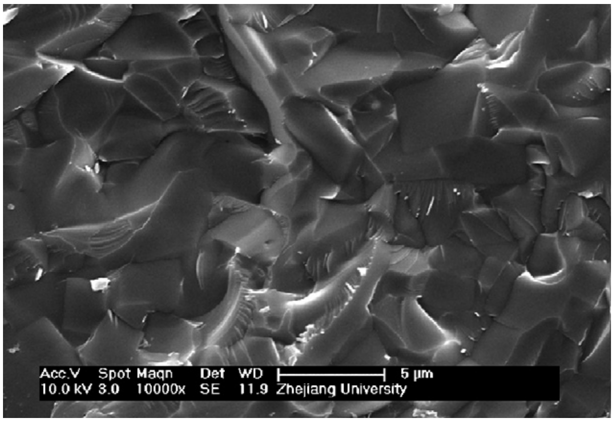

Fig. 10. Microstructure of the sintered body by gel-casting without de-airing step.

4. Conclusions

A novel gel-casting technology without de-airing process has been developed to prepare mullite-based ceramics green body. Through investigation of the effect of pH values on the viscosity of the alumina slurry dispersed in the silica sol, concentrated alumina slurry dispersed in silica sol with high solid loading but low viscosity was successfully prepared, utilizing the stabilization mechanism of silica nanoparticle halos around alumina particles at about pH 9.5. In situ consolidation of the slurry was realized through adjustment of the NH_4Cl concentration as electrolyte to promote gelation of the silica sol in the slurry. High compaction and uniform green body without entrapped pores has been obtained by gel-casting technology without de-airing process, because there existed no surfactants in the slurry, thus only a small amount of unstable bubble were entrapped, which can be automatically eliminated without de-airing process. And dense, homogeneous near-net-shape mullite-based ceramics has been successfully fabricated.

Reference

[1] F.F. Lange, Powder processing science and technology for increased reliability, J. Am. Ceram. Soc. 72 (1989) 3–15.
[2] W.M. Sigmund, N.S. Bell, L. Bergstrom, Novel powder-processing methods for advanced ceramics, J. Am. Ceram. Soc. 83 (2000) 1557–1574.
[3] O.O. Omatate, M.A. Janney, R.A. Strelow, Gelcasting, a new ceramic forming process, Am. Ceram. Soc. Bull. 70 (1991) 1641–1649.
[4] T.J. Graule, L.J. Gauckler, F.H. Baader, Direct coagulation casting-a new green shaping technique. Part I: Processing principles, Ind. Ceram. 16 (1996) 31–35.
[5] M.A. Janney, O.O. Omatete, C.A. Walls, S.D. Nunn, R.J. Ogle, G. Westmoreland, Development of low-toxicity gelcasting systems, J. Am. Ceram. Soc. 81 (1998) 581–672.
[6] M. Potoczek, E. Zawadzak, Initiator effect on the gelcasting properties of alumina in a system involving low-toxic monomers, Ceram. Int. 30 (2004) 793–799.
[7] M. Bengisu, E. Yilmaz, Gelcasting of alumina and zirconia using chitosan gels, Ceram. Int. 28 (2002) 431–438.
[8] L.J. Vandeperre, A.M. De Wilde, J. Luyten, Gelatin gelcasting of ceramic components, J. Mater. Proc. Technol. 135 (2003) 312–316.
[9] J. Yu, Y. Kanno, Z.-P. Xie, Fabrication of alumina green body through gelcasting process using alginate, Mater. Lett. 57 (16/17) (2003) 2530–2534.
[10] O. Lyckfeldt, J. Brandt, S. Lesca, Protein forming—a novel shaping technique for ceramics, J. Eur. Ceram. Soc. 20 (2000) 2551–2559.
[11] D. Myers (Ed.), Surfactant Science and Technology, VCH, Weinheim, Germany, 1988, pp. 145–175.
[12] S. Dhara, P. Bhargava, Egg white as an environmentally friendly low-cost binder for gelcasting of ceramics, J. Am. Ceram. Soc. 84 (2001) 3048–3050.
[13] S. Dhara, P. Bhargava, R.K. Sri, Deairing of aqueous gelcasting slurries, Am. Ceram. Soc. Bull. 83 (2004) 9201–9206.
[14] R. Waesche, G. Steinborn, Influence of slip viscosity on the mechanical properties of high purity alumina made by gelcasting, Key Eng. Mater. 132–136 (1997) 374–377.
[15] M. Colic, M.L. Fisher, Effect of the size and affinity for water of excluded ions on interparticle forces, Chem. Phys. Lett. 291 (1998) 24–30.

[16] J. Depasse, Coagulation of colloidal silica by alkaline cations: surface dehydration or interparticle bridging? J. Colloid Interface Sci. 194 (1997) 260–262.

[17] J.L. Trompette, M. Meireles, Ion-specific effect on the gelation kinetics of concentrated colloidal silica suspensions, J. Colloid Interface Sci. 263 (2003) 522–527.

[18] D.Y. Kong, H. Yang, Y. Yang, et al. Dispersion behavior and stabilization mechanism of alumina powders in silica sol, Mater. Lett. 58 (2004) 3503–3508.

[19] R.K. Iler, The Chemistry of Silica, Wiley, New York, 1979.

[20] H.A. Lawrence, M. Egon, Stability of colloidal silica: I Effect of simple electrolytes, J. Colloid Interface Sci. 31 (1969) 287–296.