ELSEVIER

Ceramics International 30 (2004) 2061–2066

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Preparation of alumina by aqueous gelcasting

Jianfeng Tong*, Daming Chen

The National Key Laboratory of Advanced Composite Materials, Beijing Institute of Aeronautical Materials, P.O. Box 81-3, Beijing 100095, China

Received 15 May 2003; received in revised form 28 May 2003; accepted 10 July 2003

Abstract

The alumina ceramic was prepared by aqueous gelcasting. The effects of zeta potentials, solid loading, dispersant content and milling time on the alumina suspension were studied systematically. The dispersant content has remarkable effects on the viscosity of the suspension. The appropriate dispersant concentration for alumina aqueous slurry with the solid loading of 55 vol.% is 0.6 wt.%. It can be seen that all suspensions (50–56 vol.% solid loading) exhibited a shear-thinning behavior and relatively low viscosity, which was suitable for casting. The degree of shear thinning and the viscosity at high shear rates increased with increasing volume fraction of solid. As the milling time prolongs, viscosity of the suspension decreases first, then the plateau appears and the average diameter keeps changeless. When the milling time was shorter than 20 h, the viscosity of slurries decreased gradually as the time of milling increased. After 20 h milling, the viscosity of the slurry tended to be consistent. Therefore, the ball milling time should be equal to or more than 20 h to obtain a stable suspension at equilibrium. The time available for casting the slurry (idle time) can be controlled by the amounts of initiator and catalyst added to the slurry as well as by the processing temperature. Micrograph of the gelcast green body was homogeneous.

Keywords: D. Alumina; Slurry; Gelcasting

1. Introduction

Gelcasting is an attractive new ceramic forming process for making high-quality, complex-shaped ceramic bodies [1–5]. In this process, a ceramic powder slurry is prepared with a water-based monomer solution and then polymerized in situ after casting into a mold, producing a macromolecular network to hold the ceramic particles together. It is not limited to use with any particular ceramic powder because the processing additives are all organic and leave no cation impurities behind in the fired part. Distinct advantages of the gelcasting over the conventional ceramic forming process such as dry pressing, slip casting, tape casting, and injection molding are near-net-shape forming, high green density, low levels of organic additives, and machinability in the green state due to a high strength [1,2].

Both non-aqueous and aqueous solvents can be used gelcasting. But aqueous system is preferred because the use of water as the solvent has many advantages, e.g. less departure from traditional ceramic processing and no environmental problems for disposal. In the aqueous gelcasting, acrylamide (AM) and methylenebisacrylamide (MBAM) are commonly used to make monomer solutions [1–3].

According to the previous studies [1,2], the composition of monmer solution, the amounts of initator and catalyst additions, and the temperature, humidity of drying atmosphere are important processing parameters to be controlled for optimum gelcasting. In this paper, the results of our investigation on preparation of aqueous alumina slurries with high loading were reported, and the effect factors of aqueous alumina slurries were studied.

2. Experimentmal procedure

2.1. Materials

The alumina powder used here was a commercial grade, which was producted by Zibo aopeng Co. Ltd. in China. Fig. 1 shows an SEM micropraph of alumina powders. It can be seen that the average size of the powder was 4.0 μm. The chemical composition of the powder is shown in Table 1. The average ratio of surface area of alumina powder is 15 m^2/g.

The essential components of the gelcasting process are the reactive organic monomers: monofunctional

* Corresponding author.
E-mail address: jftong@yahoo.com (J. Tong).

0272-8842/$30.00 © 2004 Published by Elsevier Ltd and Techna S.r.l.
doi:10.1016/j.ceramint.2003.07.009

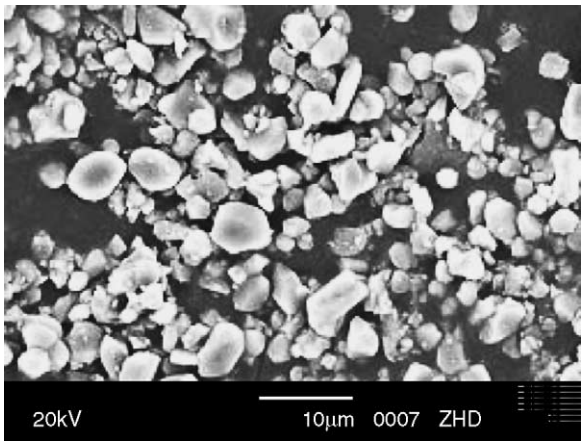


Fig. 1. SEM micrograph of alumina powders.

acrylamide, $C_2H_3CONH_2$ (AM), and difunctional, *N*,*N*-methylenebisacrylamide, $(C_2H_3CONH)_2CH_2$ (MBAM). These monomers were dissolved in deionized water to give premix solution. The premix solution undergoes free-radical-initiated vinyl polymerization in the presence of an initiator such as ammonium presulfate, $(NH_4)S_2O_8$. The reaction is acceleeeeerated by heat or by the catalyst *N*,*N*,*N*,*N*-tetramethylenediamine (TEMED). The resulting cross-linked polymer is an elastic hydrogel that serves as the binder.

2.2. Procedure

The gelcasting process flow chart is shown in Fig. 2. The monomers were dissolved in deionized water to make solution with a composition of 2.5 wt.% AM, 0.125 wt.% MBAM. Gelcasting slurries were prepared by ball-milling the alumina powder in the monomer solution. JA282 (Beijing Institute of Aeronautical Materials, Beijing, China), 0.5 wt.% were added as a dispersant for the alumina powders. In the slurries, the solid loading was about 55 vol.%, and the total amount of organic monomers was 3.2 wt.% for the powder. Both the initiator, 1 wt.% aqueous solution of ammonium persulfate, and the catalyst, TEMED, were added just before casting into a mold. After gelation, the disk-shaped samples were demolded and dried in lab atmosphere.

2.3. Properties measurement

Zeta potentials at different suspension pH were measured by zeta potential meter. The rheological properties of the gelatine solution and mixed ceramic slurry were measured

Table 1
Chemical composition of alumina powders

Al_2O_3	SiO_2	Fe_2O_3	Na_2O	K_2O
>99.8%	<0.01	<0.005	<0.005	<0.005

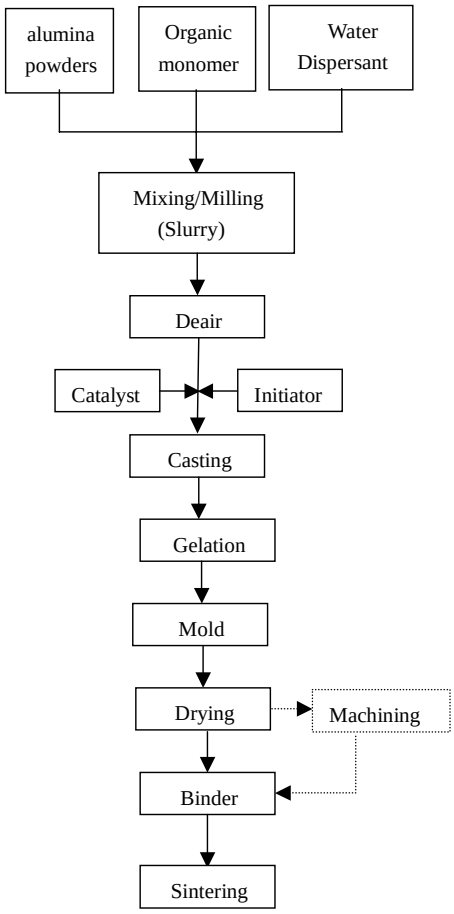


Fig. 2. Gelcasting process of alumina flow chart.

by a rotary rheometer (RV-30, US). The dried green body was cut into sample bars of 6 mm × 5 mm × 36 mm. The sintered plate was cut into samples of 3 mm × 4 mm × 36 mm and then polished. Their room temperature mechanical strength was examined by three-point flexure test with space of 30 mm (crosshead speed of 0.5 mm/min). The microscopic morphology was observed by SEM (Jonel-2000).

3. Results and discussion

3.1. Effects of pH on zeta potential of alumina suspension

The zeta potentials at different suspension pH were measured, as shown in Fig. 3. When dispersant is added, the isoelectric points (pH_{iep}-value) were decreased from 3.2 to 5.3. At low pH, far from pH_{iep}-value, the alumina particles have a high positive zeta potential and are colloidally stable. In the vicinity of the pH_{iep}, the particles have a low zeta potential which may either positive ($pH < pH_{iep}$) or negative ($pH > pH_{iep}$), suspensions prepared within this region are colloidally unstable and consist of large agglomerates that are likely to lead to porous gelcast ceramics. At high pH, far from pH_{iep}-value, the particles have a high negative zeta

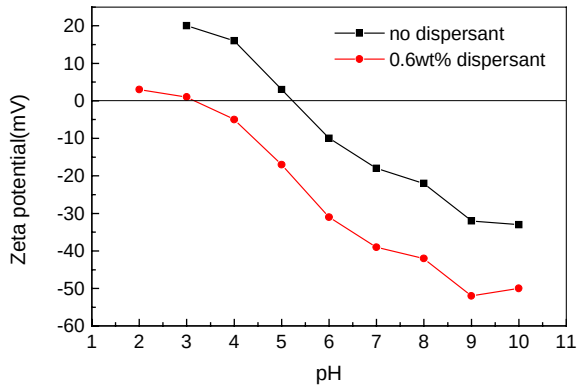


Fig. 3. Zeta potentials of alumina as a function of pH.

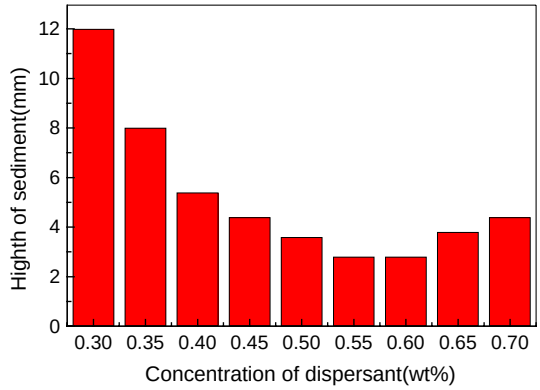


Fig. 4. Variation of slurry viscosity with dispersant concentration.

potential and are colloidally stable. The profiles in Fig. 3 show that the zeta potential is maximized at pH = 9, which can provide better colloidal stability.

3.2. Rheology

3.2.1. Effect of dispersant on the slurry rheology

We have selected JA281 as dispersant of the alumina aqueous slurry. The effects of dispersant content on the rheology of slurry are shown in Fig. 4. It is observed from the figure that the viscosity of the slurry shows a minimum at a particular dispersant concentration beyond which, the slurry viscosity increases again. Therefore, the appropriate dispersant concentration for alumina aqueous slurry is 0.6 wt.%.

It is well known that the dispersant capability, which is a polyunsaturated ester molecule, is not only due to steric stabilization, but also the state of dispersant in the surface of the particles. The three states of dispersant in the surface of the particles are shown in Fig. 5. When the state of dispersant in the surface of the particles is saturated adsorption, the dispersant capability can exert well, both unsaturated adsorption and over-saturated adsorption are bad to the dispersing of particles in the solvent.

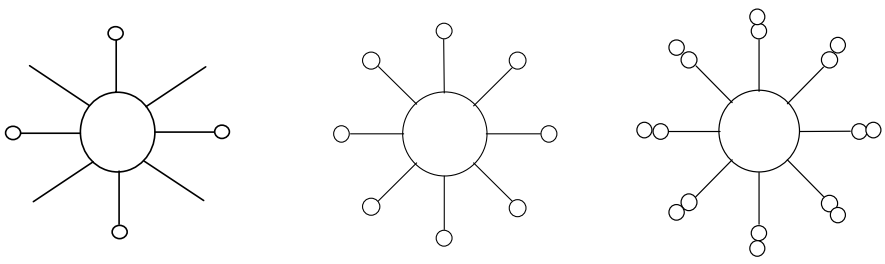
3.2.2. Effect of solid loading on the slurry rheology

Fig. 6(a) gives the plots of apparent viscosity versus applied shear rate of stable suspensions after milling for 24 h. It can be seen that all suspensions (50–56 vol.% solid loading) exhibited a shear-thinning behavior and relatively low viscosity, which was suitable for casting. Fig. 6(b) shows the plots of shear stress versus the applied shear rate of stable suspensions after milling for 24 h. It can be seen that 50–56 vol.% suspensions do not possess a thixotropy hysteresis.

Concentrated colloidally stable suspensions exhibited shear-thinning behavior in steady shear because of a pertubation of the suspension structure by shear [8–16]. At low shear rates, the suspension structure was close to equilibrium because thermal motion dominated over the viscous forces. At higher shear rates, the viscous forces affect the suspension structure and shear thinning occurred. At very high shear rates, the viscous forces dominated and the viscosity plateau measured the resistance to flow of a suspension with a completely hydrodynamically controlled structure. The degree of shear thinning and the viscosity at high shear rates increased with increasing volume fraction of solid.

3.2.3. Effect of milling time on the slurry rheology

Typical plots of apparent viscosity versus different times of ball milling for different volumes fraction of solid are given in Fig. 7. The appropriate milling times are different for the suspensions with different solid loading. For the suspension with 56 vol.% solid loading, when the milling time was shorter than 20 h, the viscosity of slurries decreased gradually as the time of milling increased. It showed that the absorption of the dispersant on particles



(a) (b) (c)

Fig. 5. The state of dispersant in the surface of the particles. (a) Unsaturated adsorption, (b) saturated adsorption, (c) over-saturated adsorption.

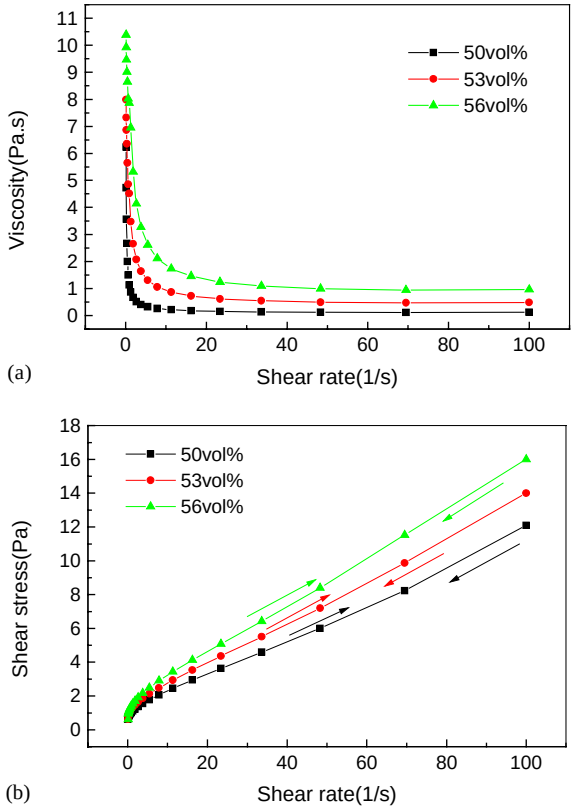


Fig. 6. Rheological behavior of the suspensions with different solid loading (ball milling at 24 h). (a) Apparent viscosity vs. shear rate, (b) shear stress vs. shear rate.

did not reach equilibrium and the suspension was unstable until the ball milling time is equal to or more than 20 h. After 20 h milling, the viscosity of the slurry tended to be consistent. Therefore, the ball milling time should be equal to or more than 20 h to obtain a stable suspension at equilibrium.

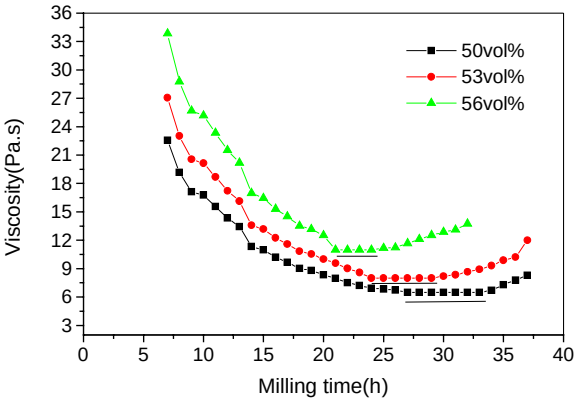


Fig. 7. Effect of milling time on the slurry viscosity.

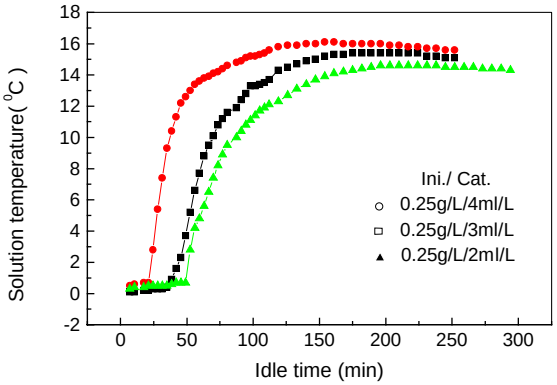


Fig. 8. Effect of content of the catalyst on the gelation rate.

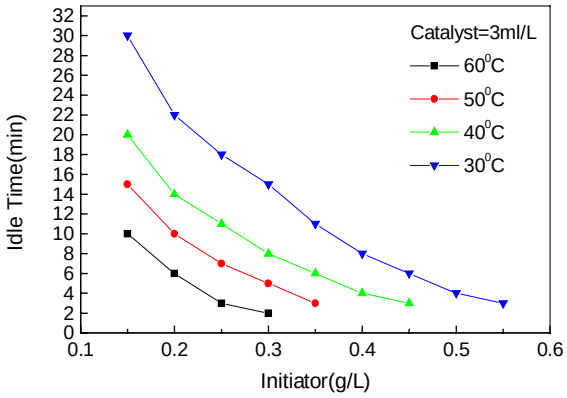


Fig. 9. Idle time as a function of initiator content and temperature.

3.3. Gelation

3.3.1. The effect of initiator, catalyst and temperature on gelation rate

In the present study, the initiation of polymerization in premixes was determined by changes in solution temperature, since the reaction is exothermic. The process was monitored in terms of idle time, t_{idle}, the time between the addition of the initiator, or the initiator/catalyst,

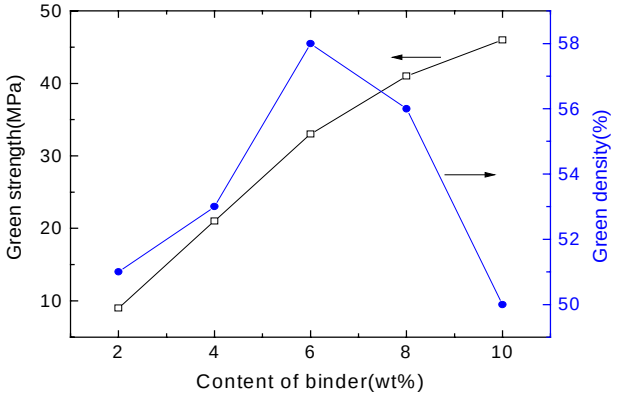


Fig. 10. Effect of binder content on the density and strength of green bodies.

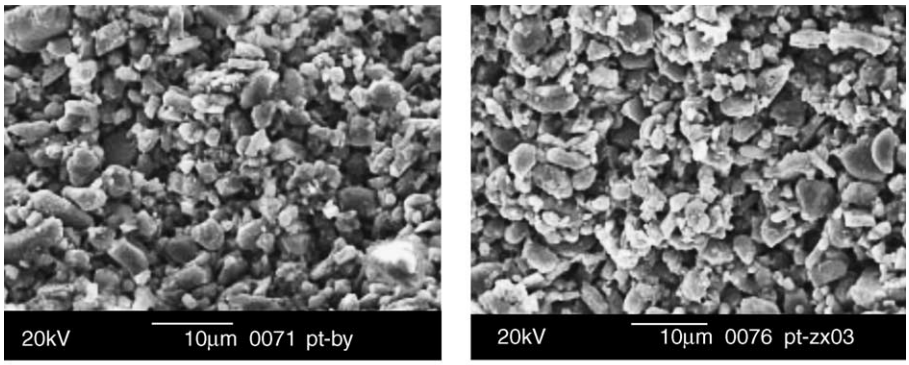


Fig. 11. Micrograph of gelcast green bodies. (a) Edge section, (b) center section.

and the commencement of polymerization. This is equivalent to the time available for casting the slurry during processing. Fig. 8 shows the change in temperature of a premix solution during gelation and indicates the idle time. The idle time can be controlled by the concentration of the reagents, and the temperature. Idle time generally ranged from 5 to 60 min. Fig. 8 shows the variation of idle time with the amount of initiator and catalyst, and Fig. 9 shows the variation of idle time with initiator and solution temperature. These data show clearly that polymerization is accelerated by an increase in initiator, catalyst, or temperature.

3.3.2. The density and strength of gelcast green bodies

The effect of polymer content on the green on the green density (corrected to organic content) and strength of the gelcast sample is shown in Fig. 10. The density maximum was obtained at a polymer content of ∼5 wt.%. The green strength, on the other hand, increased more or less linearly with the binder content. The density maximum obtained was 58% at which the strength measured was 25 MPa.

3.3.3. Micrograph of gelcast green bodies

Fig. 11 shows SEM photocopy of a dry body. It can be seen that powders are connected by slender polymer chains, which are responsible for the strength of the green body. On the other hand, it can be seen that the micrographs of the edge and center section were homogeneous.

4. Conclusion

(1) The aqueous gelcast alumina slurry has low viscosity at high solid loading.
(2) The characteristics of the slurry are connected with dispersant, solid loading and milling time.
(3) The density and strength of gelcast green bodies can be controlled by varying the monomer concentration.
(4) The time available for casting the slurry (idle time) can be controlled by the amounts of initiator and catalyst added to the slurry as well as by the processing temperature.
(5) Micrograph of gelcast green body were homogeneous.

References

[1] M.A. Janney, O.O. Ometete, U.S. Patent Number 5145908 (1992).
[2] O.O. Ometete, M.A. Janney, R.A. Strehlow, Gelcasting—a new ceramic forming process, Ceram. Bull. 10 (70) (1991) 1641.
[3] M.A. Janney, U.S. Patent Number 4894194 (1990).
[4] Lange, F.F. Valamakanni, V. Bhasker, U.S. Patent Number 5188780 (1991).
[5] T.N. Tiegs, D.E. Wittmer, U.S. Patent Number 5456877 (1994).
[6] J.A. Yanez, et al., Shear modulus and yield stress measurement of attactive alumina particle networks in aqueous slurries, J. Am. Ceram. Soc. 11 (79) (1996) 2917.
[7] P.C. Hidber, et al., Citric acid—a dispersant for aqueous alumina suspensions, J. Am. Ceram. Soc. 7 (79) (1996) 1857.
[8] J.S. Reed, Principles of Ceramics Processing, 2nd ed., Wiley, New York, 1995.
[9] A.C. Young, O.O. Ometete, M.A. Janney, et al., Gelcasting of alumina, J. Am. Ceram. Soc. 3 (74) (1991) 612.
[10] J.P. Maria, J.O. Kiggans, T.N. Tiegs, Gelcasting of sintered reaction bonded silicon nitride for improved mechanical properties, Ceram. Eng. Sci. Process. 16 (1995) 51071.
[11] T. Carisey, A.L. Werth, D.G. Brandon, Control of texture in Al_2O_3 by gelcasting, J. Eur. Ceram. Soc. 15 (1995) 1.
[12] D.M. Baskin, M.H. Zimmerman, K.T. Faber, Forming single-phase laminates via the gelcasting technique, J. Am. Ceram. Soc. 3 (74) (1991) 612.
[13] D.J.S, Introduction to Colloid and Surface Chemistry, Boston, MA, 1980.
[14] M. Mooney, The viscosity of concentrated suspension of spherical particles, J. Colloid Sci. 6 (1956) 162.

Further reading

L.J. Gauckler, T. Graule, U.S. Patent Number 5788891 (1996).
S.L. Morissette Chemorheology of aqueous-based alumina-poly(rinyl alcohol) gelcasting suspensions, J. Am. Ceram. Soc. 3 (82) (1999) 521.
J. Cesarano III I.A. Aksay Processing of highly concentrated aqueous α-Al_2O_3 suspensions with poly(methacrylacid)polyelectrolyte, J. Am. Ceram. Soc. 4 (71) (1990) 250.

H. Vrij, Overbeek, On the theory of the stablization of dispersions by adsorbed macromolecules. I. Statistics of the change of some configurational properties of adsorbed macromolecules on the apporch of an impenstrable interface, J. Phys. Chem. 75 (1971) 1–65.
H. Vrij, Overbeek, On the theory of the stablization of dispersions by adsorbed macromolecules. II. Interaction between two flat particles, J. Phys. Chem. 75 (1971) 2094.
L.J. Strble, C.F. Zukoski, G.C. Maitland (Eds.), Flow and Microstructure of Dense Suspension, Materials Research Society, Pennsylvania, 1992.
D.M. Baskin M.H. Zimmerman K.T. Faber forming single-phase laminates via the gelcasting technique, J. Am. Ceram. Soc. 3–74 (1991) 612.