Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2905–2911

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Process dependant setting behavior of aqueous gelcast AlN slurries

Guo Jian *, Qiu Tai, Yang Jian, Feng Yongbao, Zhang Chao, Zhang Wenpeng, Guo Tianhao

College of Materials Science and Engineering, Nanjing University of Technology, Nanjing 210009, PR China

Received 21 September 2011; received in revised form 22 November 2011; accepted 25 November 2011
Available online 7 December 2011

Abstract

In this study, AlN powder modified to improve anti-hydrolysis property with aluminum dihydrogen phosphate and phosphoric acid by mechanical milling was applied to prepare M-AlN gelcasting slurry. The effect of various parameters such as concentration of monomer and crosslinker, amount of initiator, solid content and temperature on the idle time was discussed for low-toxic N,N-dimethylacrylamide and N,N′-methylenbisacrylamide (DMAA and MBAM) system. The results suggested that the idle time of M-AlN gelcasting slurries decreased with increasing concentration of monomer and crosslinker, amount of initiator, temperature and the volume fraction of M-AlN. The calculated activation energy of 52.5 vol.% M-AlN was 29.46 kJ/mol. The M-AlN green body with optimum bulk density and maximum flexural strength was obtained when the amount of APS was 1.2 wt.% (on the monomers base), polymerization temperature was 65 °C, and polymerization time was 60 min for constant DMAA and MBAM (10 wt.%, 1 wt.% in the premix solution, respectively) in 52.5 vol.% M-AlN slurry. The bulk density of AlN sintered ceramic is greater than 3.27 g/cm^3, which presents relative density value of 99.3% of theoretical.

Keywords: Gelcasting AlN; Gelation; Idle time; Flexural strength

1. Introduction

Gelcasting [1–3] is a facile near net shape colloidal forming process for fabricating complex, three-dimensional ceramic materials. Firstly, ceramic powders are dispersed in premixed solution, which has been prepared by dissolving polymerizable organic monomers and crosslinker in deionized water. Secondly, the slurries are degassed in a vacuum deaeration mixer after adding initiator and catalyst, and then cast into stainless steel mould. Finally, the gelled wet green bodies are demoulded and dried at special temperature and humidity for several hours. Green bodies exhibit high strength, low organic content, good uniformity and easy machining. In addition, the superiority of gelcasting in low cost makes it suitable for industrialized production. Therefore, gelcasting is believed to have wide development prospects. So far, it has been used in different ceramics, for example, alumina [4,5], zirconia [6], silicon carbide [7], silicon nitride [8].

It is critical to control the gelation time of slurry in gelcasting. Gelation has an influence not only on strength of green bodies and sintering property, but also on work efficiency. When monomer begins to polymerize, apparent viscosity of slurry is increased sharply. Thus, idle time can be determined through viscosity measurement against time. To explore optimal induction period, deaerate and cast within permissible time, the idle time was investigated by researchers. Morissette and Lewis's [9] showed the chemorheological properties of aqueous based alumina-PVA suspensions cross-linked with an organotitanate coupling agent using stress viscometry and oscillatory measurement techniques. Based on Morissette and Lewis's theoretical effort, the chemorheology of gelation of aqueous based alumina-organic monomers suspensions was further studied by Babaluo et al. [10]. They found that the presence of alumina powder caused reduction of activation energy of suspensions, hence shorter idle times were observed. Potoczek [11] reported the effect of ceramic filler on polymerization rate of monomeric systems used in gelcasting, and pointed out the initiation time of gelcasting suspensions with constant MAM–MBAM volume fraction decreased with increasing initiator/accelerator concentration, temperature and the volume fraction of solids. In spite of abundant literature on various gel systems in gelcasting technology as well as various

* Corresponding author. Tel.: +86 25 83587262; fax: +86 25 83587268.
E-mail addresses: guojian686@126.com (G. Jian), qiutai@njut.edu.cn (Q. Tai).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.11.066

ceramic materials manufactured by this technique, few papers have been published about gelation process of slurry in aqueous gelcasting of AlN ceramics.

In this work, AlN powder modified (M-AlN) was used to prepare aqueous gelcasting slurries, and then the stress viscosimetry was used to investigate the effect of various parameters such as the concentration of monomer and crosslinker, amount of initiator, solid content and temperature on the idle time in N,N-dimethyl acrylamide and N,N′-methylenbisacrylamide (DMAA and MBAM) gelcasting system. Taking densities of AlN green bodies and ceramics, and flexural strength of green bodies as measurement index, the optimum gelation technology was drawn up.

2. Materials and experimental methods

2.1. Row materials

A commercial AlN powder (Advanced Technology & Materials Co., Ltd., Beijing, China) with an average particle size of 3 μm was used as the raw material. AlN powder was surface modified with aluminum dihydrogen phosphate and phosphoric acid by mechanical milling. The detailed process has been published elsewhere [12,13]. The modified AlN (M-AlN) powder can keep high stability in the subsequent process of high energy aqueous ball milling. N,N-dimethyl acrylamide (DMAA, Kowa Co. Ltd., Japan), N,N′-methylenbisacrylamide (MBAM, Chemical Reagent Research Institute, Tianjin, China) and ammonium persulfate (APS, Ling Feng Chemical Reagent Co., Ltd., Shanghai, China) were used as monomers, cross-linking agent and initiator, respectively. The dispersant used for stabilizing M-AlN slurries was ammonium polyacrylate (NH_4PAA, Transea Chemical Ltd., Shanghai, China) with an average molecular weight of 8000. The pH value of slurries was adjusted by HCl and tetramethyl ammonium hydroxide (25% water solution, AR, Shanghai Ke Feng Chemical Reagents Co., Ltd., China).

2.2. Preparation of aqueous M-AlN ceramic slurries

First of all, NH_4PAA and M-AlN powder were added into premixed solution (deionized water, DMAA and MBAM) in turn. Secondly, to improve dispersibility of the powder and fluidity of the slurries, the pH value of slurries was adjusted to designated value with HCl and TMAH after mechanical milling for 0.5 h. Then aqueous M-AlN slurries were obtained after further milling for 2 h.

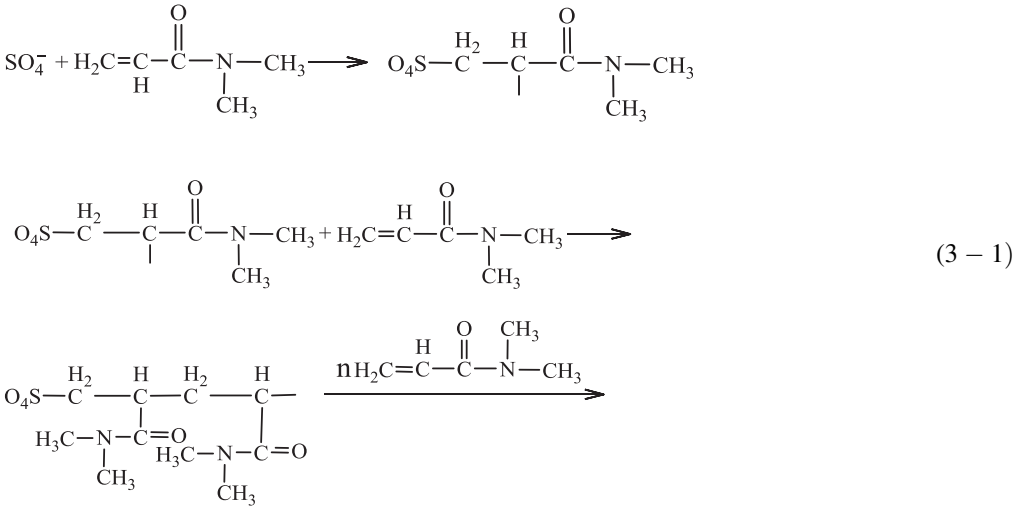
2.3. Characterization

R/S Rheometer (R/S CC 25, Brookfield Corporation, USA) was used to characterize the rheological behaviors of slurries during gelation. The slurries were subjected to a constant 6 s^{-1} shear rate and the viscosity value was registered every 6 s. All measurements were started immediately after adding initiator. Flexural strength was examined using a universal testing machine (CMT-6203, MTS System Corporation, Shanghai) at a loading rate of 0.5 mm/min. The sample dimension for flexural strength was 3 mm × 4 mm × 30 mm. Archimedes method was employed to determine the bulk density of green bodies and sintered ceramics. The Lnt_{idle} as abscissa and $1/T$ as ordinate, linear fitting was carried out according to Arrhenius equation by using Origin Software.

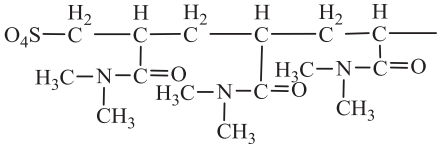
3. Results and discussion

3.1. Emulsion polymerization process

DMAA is converted to DMAA radicals in the initiation process, and then active macromolecules are produced from the DMAA radicals:

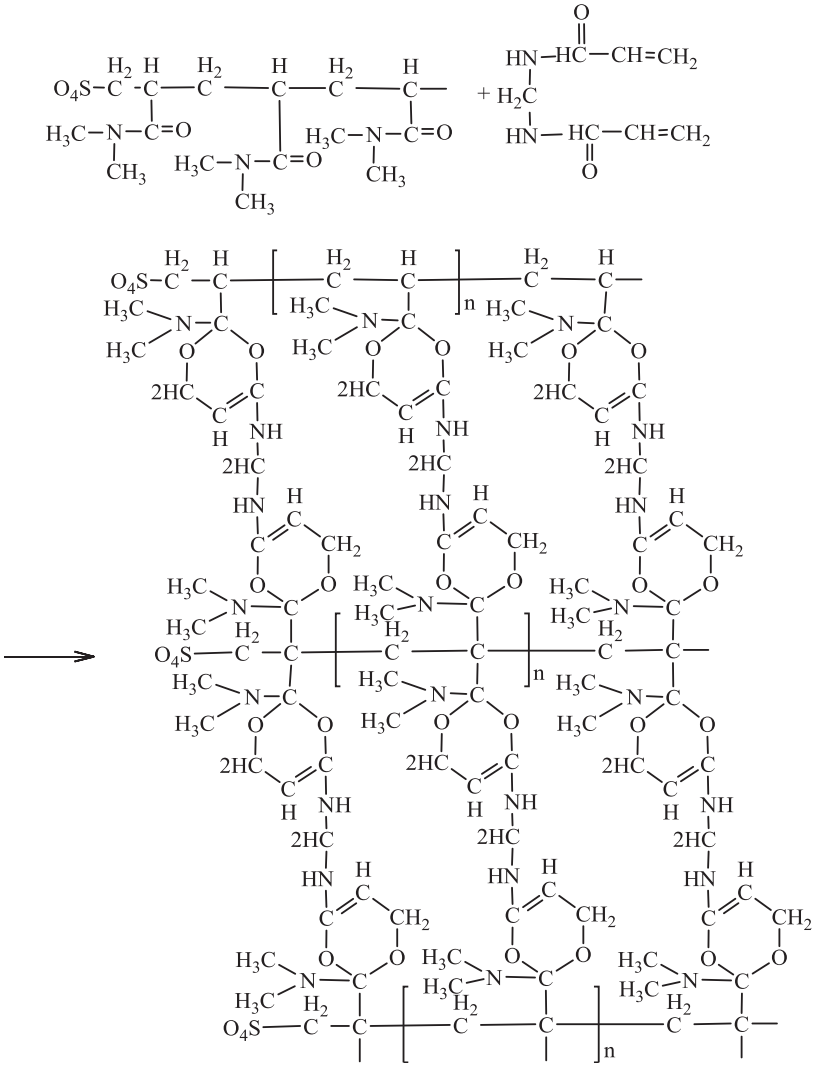


(3 – 1)



(3 − 2)

Three-dimensional net structures are formed through the action of MBAM and active macromolecules. AlN powders will fill into the holes of three-dimensional net structures.



(3 − 3)

The idle time and flexural strength is related to polymerization rate and molecular weight of polymer, respectively. To a certain extent, flexural strength increases with the increase of molecular weight of polymer.

The main reasons for idle phenomena are cage effect [14], induced decomposition and oxygen inhibition polymerization. The concept, such as cage effect, is explained as follow: primary radicals of APS decomposition surrounded by M-AlN powder and solvent is unable to initiate DMAA, and even is converted to stable material by elimination reaction, leading to low initiation efficiency of APS. Induced decomposition is, in essence, a reaction about radical transferring to initiator. Primary radicals terminate and convert to stable molecules during induced decomposition; meanwhile, new radicals form. But an APS molecule is consumed in the induced decomposition, reducing the initiation efficiency of APS.

3.2. Effect of amount of APS

The amount of APS is one of important influence factors for polymerization rate and molecular weight of polymer. In order to deaerate and cast the slurry into the mould more effectively, it is necessary to investigate the idle time of aqueous M-AlN slurries at room temperature (25 °C). The slurries are measured

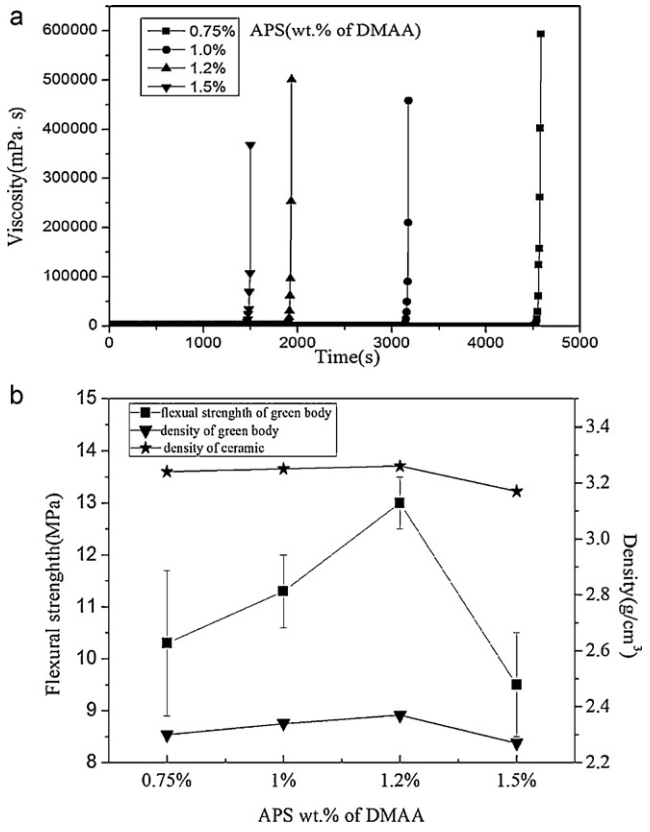


Fig. 1. (a) The viscosity variation versus time with respect to the amount of APS when the DMAA and MBAM are constant (10% and 1 wt.%, respectively) in 52.5 vol.% M-AlN slurry. (b) Effect of the amount of APS on bulk density and flexural strength of green bodies.

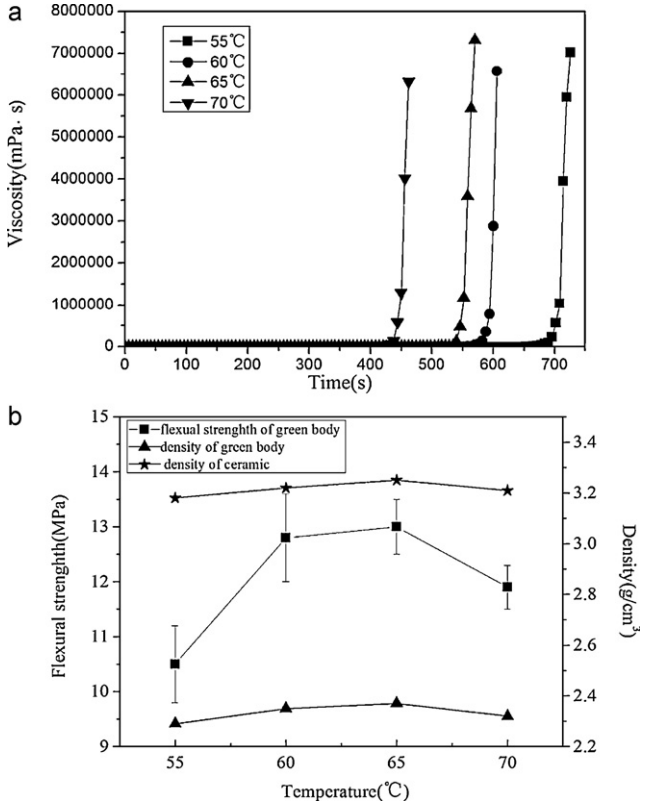


Fig. 2. (a) The variation of viscosity with temperature for constant DMAA, MBAM and APS concentration (10%, 1%, and 1.2 wt.%, respectively) in 52.5 vol.% M-AlN slurry. (b) Effect of the polymerization temperature on bulk density and flexural strength of green bodies.

at a constant 100 s^{-1} shear rate and the viscosity value is registered every 6 s. Fig. 1(a) presents the viscosity variation versus time with respect to the amount of APS when the DMAA and MBAM are constant (10% and 1 wt.%, respectively) in 52.5 vol.% M-AlN slurry. It is well known that the polymerization reaction will speed up with the increase of the amount of APS, and the idle time and molecular weight of polymer decreases. Fig. 1(b) shows the effect of the amount of APS on bulk density and flexural strength of green bodies. As seen in Fig. 1(b), the green body with optimum bulk density and flexural strength was obtained by adding 1.2 wt.% APS. The more amounts of APS, the more primary radicals decomposed from APS, resulting in the increase of active points of chains propagation, and the decrease of chain length of polymers [15]. On the contrary, at the lower amount of APS, the polymerization time is so long that the sedimentation of M-AlN particles in the slurry occurs, leading to distortion and less uniformity of green bodies.

3.3. Effect of temperature

Temperature is also an important factor on polymerization rate and molecular weight of polymer. In a certain range of temperature, the polymerization reaction speeds up with the increase of polymerization temperature, but molecular weight of polymer decreases.

The variation of viscosity with temperature for constant DMAA, MBAM and APS concentration (10%, 1%, and 1.2 wt.%, respectively) in 52.5 vol.% M-AlN slurry is shown in Fig. 2(a). As can be seen in Fig. 2(a), the idle time decreases dramatically with the increase in temperature. The idle time is inversely proportional to the production rate of free radicals, which is bound up with the slurry temperature. This relationship can be expressed by Arrhenius type Eq. (3-4):

$$t_{idle} = A \exp\left(\frac{E_a}{RT}\right) \tag{3-4}$$

where R is gas constant and E_a is the activation energy of gelation. The activation energy of gelcation of aqueous AlN slurries reflects the needed input energy in gelation reaction. The lower the activation energy is, the easier the gelation to react. To control idle time more effectively at different gelation temperature under certain conditions, and avoid gelation time too long or too short, it is significant to evaluate activation energy of gelcation of aqueous AlN slurries. Fig. 3 shows Arrhenius plot of measured idle time for AlN (52.5 vol.%) slurry with APS concentration of 1.2 wt.%, from which the activation energy was calculated to be 29.46 kJ/mol.

Fig. 2(b) shows the effect of the polymerization temperature on bulk density and flexural strength of green bodies. At low temperature, the polymerization rate proceeds slowly, and

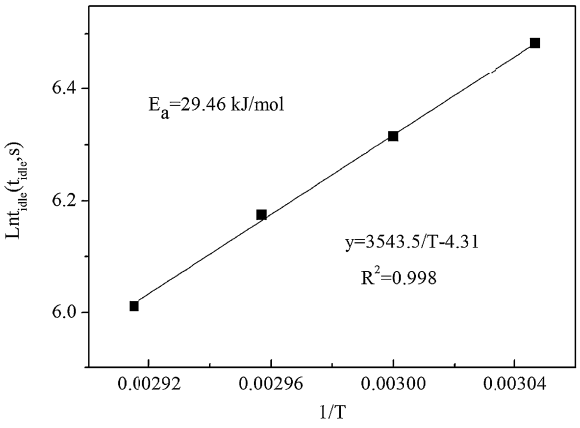
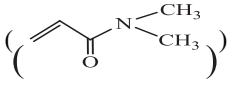


Fig. 3. Arrhenius plot of idle time (t_{idle}) for M-AlN slurry.

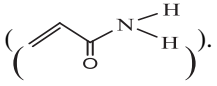
polymerization time is too long, which leads to the sedimentation of AlN particles in the slurry is great. At high temperature, the rate of polymerization is high and temperature gradient is great in the slurry, which leads to stress and defect in the green bodies [16]. It is seen that the bulk density and flexural strength of green body reach the maximum when polymerization temperature is 65 °C.

3.4. Effect of DMAA concentration

Fig. 4 illustrates the viscosity variation versus time with respect to DMAA concentration for constant APS and MBAM concentration (1.2% of DMAA for APS and 1 wt.%, respectively) in 52.5 vol.% M-AlN slurries at 65 °C. It can be seen that idle time decreases with the increase of the DMAA concentration, which is because of the increase of DMAA radical concentration and the decrease of cage effect. The polymerization rate, as well as the percentage of acrylamide conversion was found to increase with an increasing concentration of acrylamide [17]. Polymerization of DMAA is similar to that of acrylamide in that DMAA



has similar structure to acrylamide



).

3.5. Effect of MBAM concentration

Fig. 5 shows the influence of different MBAM concentration on the viscosity of 52.5 vol.% M-AlN slurries with 10% DMAA and 1.2 wt.% APS of DMAA at 65°C. It is evident from Eq. (3-3) that, MBAM plays a crosslinking role in the gelation reaction of slurries. DMAA concentration affects idle time more markedly than MBAM concentration by comparing Figs. 4 and 5.

3.6. Effect of solid content

The apparent viscosity variation versus time for slurries with various solid contents of AlN at constant temperature of 65 °C

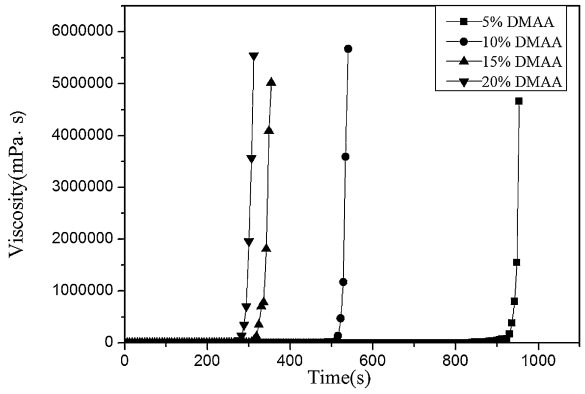


Fig. 4. The viscosity variation versus time with respect to DMAA concentration for constant APS and MBAM concentration (1.2% of DMAA for APS and 1 wt.%, respectively) in 52.5 vol.% M-AlN slurries at 65 °C.

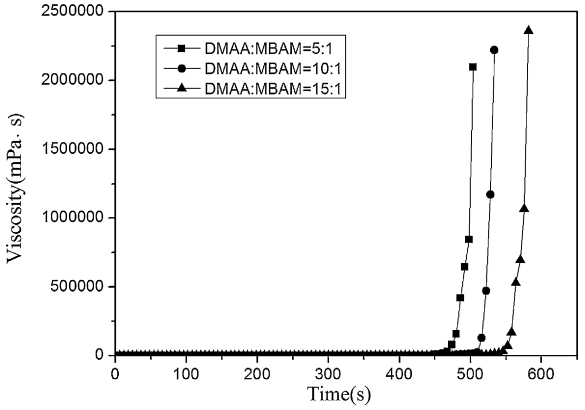


Fig. 5. The influence of MBAM concentration on the viscosity of 52.5 vol.% M-AlN slurries with 10% DMAA and 1.2 wt.% APS of DMAA at 65 °C.

is plotted in Fig. 6. It is found that idle time decreases significantly with a rise in solid content, suggesting that the gelation can be promoted by M-AlN particles. Fig. 1(a) indicates that the gelation of AlN slurry could take place at temperature (25 °C). As a contrast, at the same time, premix solution with 1.2% APS of DMAA was placed at temperature (25 °C), gelation of premix solution was not observed within several days, which demonstrates that AlN particles promote or

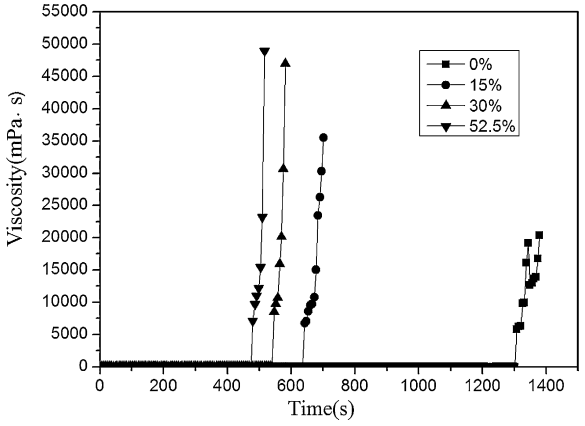


Fig. 6. The apparent viscosity variation versus time for slurry with various solid contents of AlN at constant temperature of 65 °C.

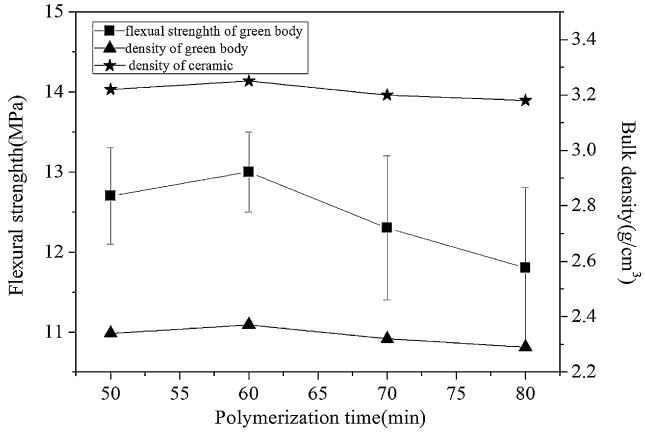


Fig. 7. The Effect of polymerization time on bulk density and flexural strength of green bodies.

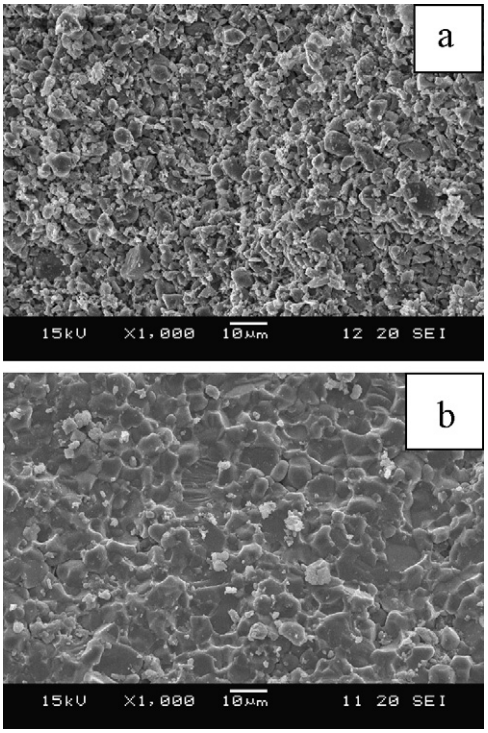


Fig. 8. The SEM of the fracture surface of the (a) green body and (b) sintered ceramic at 1850 for 3 h.

participate in the decomposition of APS into free radicals. Morterra and Magnacca [18] studied surface chemistry and surface structure of catalytic alumina by vibrational spectroscopy of adsorbed species, and deduced that the surface of alumina acted as Lewis acid or Lewis base sites. Potoczek [11] reported a catalytic effect of alumina grains onto polymerization rate of methacrylamide-based gelcasting system, and stated the interaction of alumina powders with inactive initiator molecules can be viewed as a Lewis acid-base reaction occurring at the surface of powders. Electrons from base-sites at alumina surface may participate in decomposition of initiator molecules $S_2O_8^{2-}$ into free radicals. Because M-AlN particle has similar micelle structure to alumina particle, the surface of M-AlN may act as Lewis acid or Lewis base sites, which is useful to polymerization of DMAA.

3.7. Effect of polymerization time

Fig. 7 shows the effect of polymerization time on bulk density and flexural strength of green bodies. It can be seen that bulk density and flexural strength of green body reach their maximum when polymerization time is 60 min at 65 °C. As the polymerization time decreases, the extent of gelation and flexural strength of green bodies decreases. On the contrary, long polymerization time causes fast volatile speed of water in the AlN slurry and high cost. The faster the volatile speed of water is, the more cracks and defects will form in the green body. Fig. 8 shows the SEM of the fracture surface of the green body and sintered ceramics. As can be seen, green body of aqueous gelcast AlN has high microstructural uniformity with small pores, AlN sintered ceramic has a homogeneous grain size and presents some small pores, formed during burn out of gelcast additives. The bulk density of AlN sintered ceramic is greater than 3.27 g/cm^3, which presents relative density value of 99.3% of theoretical.

4. Conclusions

The results suggest that the idle time of M-AlN gelcasting slurries decreased with increasing concentration monomer and crosslinker, amount of initiator, temperature and the volume fraction of solids. The calculated activation energy of 52.5 vol.% M-AlN slurry was 29.46 kJ/mol. The AlN green body with optimum density and the maximum flexural strength was obtained when the amount of APS was 1.2 wt.% (on the monomers base), polymerization temperature was 65 °C, and polymerization time was 60 min for constant DMAA and MBAM concentration(10 wt.%, 1 wt.% in the premix solution, respectively) in 52.5 vol.% M-AlN slurry. The bulk density of AlN sintered ceramic is greater than 3.27 g/cm^3, which presents relative density value of 99.3% of theoretical.

Acknowledgement

We acknowledged the financial support from the Scientific Innovation Research of College Graduate in Jiangsu province (project No. CXZZll-0325) and the Project Funded by the Priority Academic Program Development of Jiangsu Higher Education Institutions.

References

[1] O.O. Omatete, M.A. Janney, R.A. Strehlow, Gelcasting—a new ceramic forming process, J. Am. Ceram. Soc. Bull. 70 (10) (1991) 1641–1649.
[2] M.A. Janney, O.O. Omatete, Method for molding ceramic powders using a water-based gel casting processing, U.S. Patent No. 5,028,362, July 2 (1991).
[3] O.O. Omatete, M.A. Janney, S.D. Nunn, Gelcasting: from laboratory development towards industrial production, J. Eur. Ceram. Soc. 17 (23) (1997) 407–413.

[4] C. Tallon, R. Morenow, M. Isabel Nieto, Gelcasting performance of alumina aqueous suspensions with glycerol monoacrylate: a new low-toxicity acrylic monomer, J. Am. Ceram. Soc. 90 (5) (2007) 1386–1393.
[5] M. Potoczek, Gelcasting of alumina foams using agarose solutions, Ceram. Int. 34 (2008) 661–667.
[6] E. Adolfsson, Gelcasting of zirconia using agarose, J. Am. Ceram. Soc. 89 (61) (2006) 897–902.
[7] I. Ganeshw, D.C. Jana, S. Shaik, N. Thiyagarajan, An aqueous gelcasting process for sintered silicon carbide ceramics, J. Am. Ceram. Soc. 89 (10) (2006) 3056–3064.
[8] Y. Huang, Water-based gelcasting of surface-coated silicon nitride powder, J. Am. Ceram. Soc. 84 (4) (2001) 701–707.
[9] S. Morissette, L.J.A. Lewis, Chemorheology of aqueous based alumina poly(vinylalcohol) gelcasting suspensions, J. Am. Ceram. Soc. 82 (3) (1999) 521–528.
[10] A.A. Babaluo, M. Kokabi, A. Barati, Chemorheology of alumina aqueous acrylamide gelcasting systems, J. Eur. Ceram. Soc. 24 (2004) 635–644.
[11] M. Potoczek, A catalytic effect of alumina grains onto polymerization rate of methacrylamide based gelcasting system, Ceram. Int. 32 (2006) 739–744.
[12] G. Jian, Q. Tai, Surface modification of AlN powder by aluminum dihydrogen phosphate and phosphoric acid, Electron. Compon. Mater. 2 (2010) 37–40.
[13] G. Jian, Q. Tai, Research on ball milling modification technology of aluminum nitride powder by aluminum dihydrogen phosphate and phosphoric acid, Inorg. Chem. Ind. 3 (2010) 30–33.
[14] Z.R. Pan, Free Radical Polymerization, Chemical Industry Press, Beijing, China, 1983.
[15] J.J. Li, Technology of Domestic Ceramics, Wuhan University of Technology Press, Wuhan, China, 1991.
[16] L.G. Ma, Y. Huang, J.L. Yang, et al., Control of the inner stresses in ceramic green bodies formed by gelcasting, Ceram. Int. 32 (2006) 92–98.
[17] M. Patra, B.K. Sinha, Polymerization of acrylamide initiated by $KMnO_4$-cyclohexanone redox system in presence of surfactant, Pure Appl. Chem. 37 (7) (2000) 691–706.
[18] C. Morterra, G. Magnacca, A case study: surface chemistry and surface structure of catalytic aluminas, as studied by vibrational spectroscopy of adsorbed species, Catal. Today 27 (1996) 497–532.