

Gelcasting of alumina ceramics in the mixed acrylamide and polyacrylamide systems

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Abstract

Ceramic gelcasting without inhibition of gelation due to the presence of oxygen must be performed in a nitrogen atmosphere to avoid surface spallation of the green body, which is a complex and expensive process. This study shows that the surface spallation of ceramic green bodies gelcast in air could be suppressed by introducing a proper amount of water-soluble polymer, polyacrylamide (PAM), to the acrylamide monomer solution. The dispersion of Al₂O₃ powder in a water solution containing PAM was investigated. The rheological behavior and the gelling behavior of the alumina suspension were analyzed. Flexural strength and microstructure of the gelcast green and sintered bodies were studied.

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1. Introduction

Gelcasting is a new ceramic forming technique gaining increasing attention. The process involves the casting of a slurry that consists of ceramic powder, water and water-soluble organic monomers. After casting, the monomer in the slurry is polymerized to form a gelled network which holds the ceramic powders together in a mold. Compared to other casting methods, gelcasting results in much more homogeneous materials with little density difference over the parts and produces green body with higher flexural strength. However, the gelcasting technique is also confronted with two main problems: surface spallation^{1,2} and toxicity of the monomer used.^{3,4}

The Oak Ridge National Laboratory (USA)¹ first reported flaws and spallation on the surface of dried green bodies gelcast in air. Their study concluded that the inhibition of gelation caused the surface spallation phenomenon due to the presence of oxygen hindering polymerization of the monomer in the system.^{5,6} Surface spallation could result in green bodies with a powdery

surface that can be of a few millimeters thick. This will reduce the strength and make it difficult to control the dimension of the final products, and thus it must be avoided in production. It was found that gelcasting ceramics in a nitrogen atmosphere could suppress the effect of oxygen inhibition and hence prevent surface spallation from occurring.^{7,8} In industrial production, however, a technical operation under nitrogen introduces complexity with significant increase in the production cost.

The present study has attempted to resolve the surface spallation problem by introducing a water-soluble polymer, polyacrylamide (PAM), into the acrylamide-based system. The effects of the polymer on gelcasting of alumina and the surface spallation phenomenon of green bodies were investigated.

2. Experimental procedure

2.1. Materials

The starting ceramic powder used in this experiment with an average particle size of 3.47 μm was a commercial high-purity α-Al₂O₃ powder. Calcium carbonate,

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silicon dioxide, and kaolin were used as its sintering aids. For gelcasting, acrylamide [$C_2H_3CONH_2$] (AM) was used as the monomer, N,N' -methylenebisacrylamide [$(C_2H_3CONH)_2CH_2$] (MBAM) as a coupling agent, N,N,N',N' -tetramethylethylenediamine (TEMED) as a catalyst, ammonium persulphate as an initiator and ammonium citrate as a dispersant. Polyacrylamide (Aldrich Chemical Company, Inc. USA) used in the study has an average molecular weight of 10 000. All reagents are chemically pure.

2.2. Preparation of suspensions

2.2.1. Determination of PAM amount

A proper amount of PAM may eliminate the surface-spallation phenomenon of green bodies cast in air, but decreases the fluidity of the suspension. To determine the optimum amount of PAM, which is enough to eliminate the surface-spallation phenomenon of green bodies cast in air, the following experiments were performed. The suspensions with different amounts of PAM were gelcast. The amount of PAM and the degree of surface-spallation are shown in Table 1. The suspension with 2.8 wt.% PAM (based on alumina) has a better fluidity and has no surface-spallation phenomenon. Thus 2.8 wt.% PAM was chosen as additive for the suspensions in following experiments.

2.2.2. Process of gelcasting with PAM

The preparation of suspensions is similar to that of Ref. 9. The 2.8 wt.% PAM (based on alumina) and 0.25 wt.% dispersant (based on alumina) were first completely dissolved in a premix solution which was prepared by dissolving proper amounts of AM and MBAM in deionized water (mass ratio is 50:1:315), to produce a complex solution. Alumina powder and its sintering aids were then added into the solution. Suspensions with solids loading of 50 vol.% were mixed manually first and then milled for 24 h in a nylon resin jar using

alumina balls as ball-milling media to break down the agglomerates formed during solvent evaporation and to achieve a good homogeneity. The prepared suspensions were subjected to measurements for the rheological property. 100 μ l initiator and 50 μ l catalyst were added to the suspension (30 ml) to form a slurry which was used for measurement of gelation characteristics and to fabricate cast samples for microstructure and mechanical property study.

Binder burnout and subsequent sintering were carried out in stationary air and conducted separately. Binder burnout was operated at 700 °C for 2 h, with a heating rate of 2 °C/min and a naturally cooling. Sintering was carried out at 1550 °C for 2 h with a heating rate of 1 °C/min from room temperature to 1250 °C and a rate of 0.5 °C/min from 1250 °C to 1550 °C and a cooling rate of 1 °C/min to 1000 °C, followed by natural cooling.

2.3. Methods and measurements

The shear viscosity is measured using a Modular Compact Rheometer (MCR300, Paar Physica, Germany) with a concentric-cylinder having a diameter of 27 mm. Steady state shear flow curves are measured at a shear rate range between 0.1 and 250 s^{-1} , the duration between measuring points is 10 s and each measurement lasts 3 min. The temperature ramp rotation mode is used to measure the temperature dependence of the slurry viscosity.

A suspension was made at a loading of 5 vol.% solids. This suspension was allowed to age for 24 h with continuous stirring. The 0.4 ml of the above suspension was then diluted to 200 ml to give a final working solution with loading of 0.01 vol.% solids for analysis. Tests were performed on alumina, in two different solutions: 10^{-2} mol/l potassium nitrate (KNO_3) without PAM, and 2.8 wt.% PAM in 10^{-2} mol/l potassium nitrate (KNO_3). The pH was adjusted with HCl and NaOH solutions of appropriate concentration. Zeta potential was calculated from the measured electrophoretic mobility in the pH interval from 3 to 12 for alumina using the ELS (Electrophoretic Light Scattering) method (Brookhaven Instrument Corporation, USA).

Bulk densities of dried green and sintered bodies were determined by the Hg immersion method based on Archimedes' principle. The flexural strengths of bars of green and sintered body (in the present research, six samples have been tested), were examined by three-point flexure test with a span of 30 mm at a loading rate of 0.5 mm/min. The bars of green and sintered bodies were 0.5 cm \times 0.6 cm \times 4.2 cm and 0.3 cm \times 0.4 cm \times 3.6 cm, respectively. Fracture surfaces of the green and sintered specimens were examined with a scanning electron microscope (JSM-6460LV, JEOL, Japan).

Table 1
The relationship of sample surface and polymer amount

Amount of PAM (wt.%)	Surface of sample	Viscosity (Pa s)	
		Shear rate 1.18 s^{-1}	Shear rate 48.1 s^{-1}
0	Spallation	0.45	0.10
1.0	Spallation	0.65	0.26
2.0	Spallation	1.68	2.81
2.5	Spallation	4.78	4.24
2.8	Without spallation	5.91	5.43
3.0	Without spallation	7.30	9.42
4.0	Without spallation	33.5	37.8

PAM content is based on alumina.

3. Results and discussion

3.1. Dispersion of Al₂O₃ powder

Fig. 1 shows the zeta-potential of the Al₂O₃ powder in water with and without PAM as a function of pH. Error bars of ±2 mV indicate the reproducibility of the values. Adding PAM affected the surface charge of the particles in dispersion and their zeta potential. With 2.8 wt.% PAM added to the slurry, the zeta potential–pH curve shifted toward a lower pH region, and the isoelectric point of the slurry moved from pH 7.4 to pH 3.6. Increased zeta-potential values (higher than –30 mV) were observed at pH > 10.5, and the slurry with PAM could be well-dispersed in a much wider pH range compared to that without PAM. The shift of the isoelectric point of the oxide powders toward lower pH values is typical of the PAM function and similar behavior has been observed for Al₂O₃ slurries with an addition of NH₄-PMA.¹⁰

3.2. Rheological properties of Al₂O₃ suspensions with PAM

In further examining the colloidal behavior, we present in this section the curves of the rheological behavior. Fig. 2(a) shows the variation of steady-state viscosity as a function of shear rate for the suspensions with and without PAM. In Fig. 2(a) it can be seen that the suspension without addition of PAM displays relatively strong shear thinning behavior and the degree of shear thinning decreases significantly after the addition of PAM. Using PAM, highly concentrated suspensions can be prepared but their fluidity may be compromised. Concentrated stable suspensions usually exhibit the shear thinning behavior due to perturbation of the suspension structure by shearing.¹¹ Another obvious characteristic in Fig. 2(a) for the suspension with an

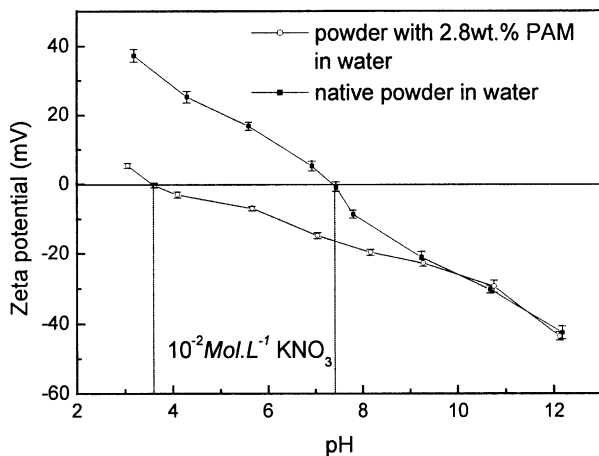


Fig. 1. Zeta potential of the Al₂O₃ powder in water with and without 2.8 wt.% PAM as a function of pH.

addition of PAM is the shear thickening (dilatancy). At high shear rates (> 4 s⁻¹, depending on solid loading), the viscosity increases as the shear rate increases. Hoffman¹² suggested that shear thickening is a consequence of an order-to-disorder transition of the particle micro-structure.

Fig. 2(b) shows the corresponding variation of shear stress as a function of shear rate for the suspensions with and without PAM of Fig. 2(a). The rheological behavior depicted in Fig. 2(b) has been analyzed using the Herschel–Bulkley model:¹³

$$\tau = \tau_y + k\gamma^n \tag{1}$$

where τ_y is the yield stress, τ is the shear stress, γ is the shear rate, n is the shear rate exponent and k is a constant. The yield stress values presented in Table 2 are calculated from this model. The suspension with addition of PAM exhibits obviously a higher yield stress compared to the suspension without PAM.

Shih et al.¹⁴ recently reported that the suspension yield stress (τ_y) scales with the solids concentration (Φ) in the following form:

$$\tau_y \sim (1-1.5\alpha\zeta^2) \left(A/24_{s_0}^{3/2} \right) (1/R^{d-3/2}) \Phi^m \tag{2}$$

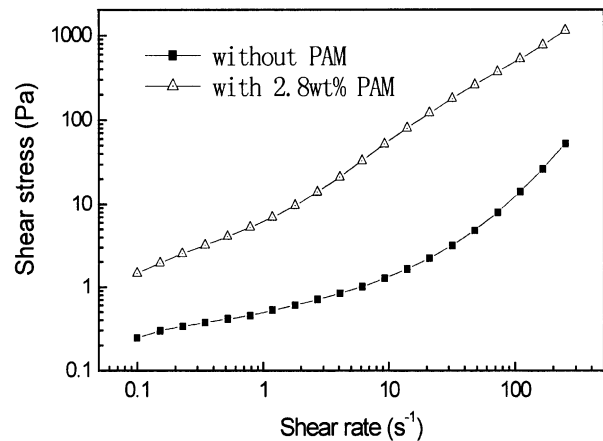
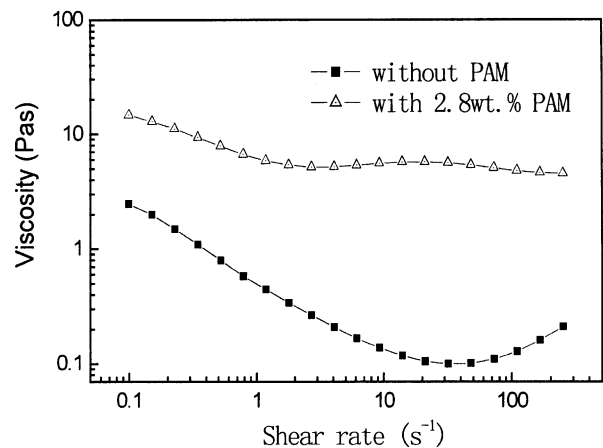


Fig. 2. The curves of the rheological properties for the suspensions with and without 2.8 wt.% PAM.

Table 2
Hershel–Bulkley parameters τ_y , and n of alumina suspensions (50 vol.%, 0.25 wt.% dispersant, 25 °C) for 2.8 wt.% PAM

Sample	Monomer content ^a (wt.%)	Polymer content (wt.%)	Yield stress τ_y (Pa)	Constant k	Shear rate exponent n	Correlation ratio R_{xy}
A	3.2	0	0.3238	0.0863	0.9698	0.9214
B	3.2	2.8	1.3252	4.7269	0.9973	0.9987

^a Contents of the monomer and polymer are based on alumina.

where α is a constant related to the Debye thickness (k^{-1}) and the surface separation (s_0) between particles; ζ the zeta potential; A the Hamaker constant; R the particles radius; d the Euclidean dimension; and $m = (d + X)/(d - D_f)$ with D_f and X the fractal dimension of the clusters and the backbone of the clusters, respectively. It can be concluded that shear stress (τ_y) increases with the decrease in the zeta potential at given the solids concentration from Eq. (2). The result of the present research is fit to this equation.

3.3. Gelling characteristics of Al_2O_3 slurries with PAM

As is well-known, the reaction of free radical polymerization is exothermic. When the polymerization starts, the temperature of the system is enhanced. Thus, the gelling characteristics of the suspension may be described by the relationship between temperature and time.

Fig. 3 shows how the temperature of alumina slurry with and without PAM varies with time. It can be seen that the increase in the temperature of slurry without PAM is more rapid and reaches a higher level at shorter time, compared to ones of slurry with PAM. The initial increase in temperature (i.e. the consolidation starting point) occurs at different time between the PAM-containing system (about 800 s) and the one without PAM (about 700 s). Above 700 s, the monomers start to polymerize, resulting in an increased temperature because of exothermic reaction. Besides, the

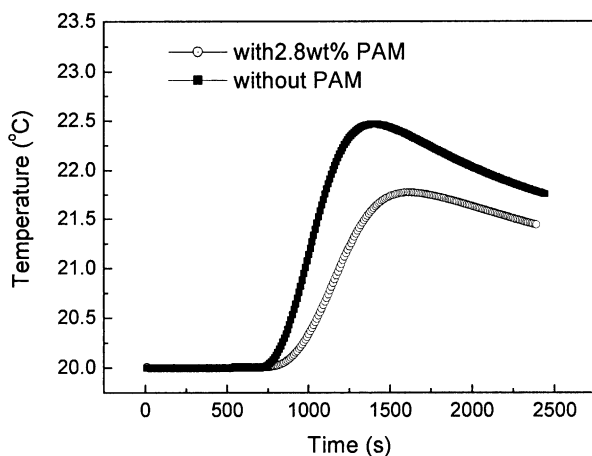


Fig. 3. The relationship of the temperature versus time.

increase in temperature terminates at about 1300 s (i.e. the consolidation completing point) for the PAM-free system, but for the PAM containing system the consolidation continues at least at 1650 s. A possible reason for the suspension with PAM to have a longer time for initial increase in the temperature compared to the PAM-free system is that the contact among monomers AM would be interfered and hindered by PAM in the solution. Hence longer time would be required for AM to become hydrogel in the presence of PAM. Further work would be required to confirm this.

3.4. Surface of gelcast alumina green bodies

Fig. 4 shows annular cylinders of alumina obtained by gelcasting. Fig. 4(a) and (b) are green bodies gelcast from slurry without addition of PAM and slurry with addition of 2.8 wt.% PAM, respectively. The surface of the green body gelcast in air from the slurry without addition of the polymer shows surface spallation phenomenon, but surface without spallation is observed in the green bodies gelcast in air from the slurry containing 2.8 wt.% PAM. The mechanism of eliminating surface spallation by PAM is similar to our previous Ref. 15.

3.5. Properties of alumina green and sintered bodies

Fig. 5(a) presents the SEM micrograph of alumina green body obtained from the system with PAM addition and Fig. 5(b) gives the SEM micrograph of green body without PAM. It can be seen that a satisfactory microstructure with very few pores has been achieved

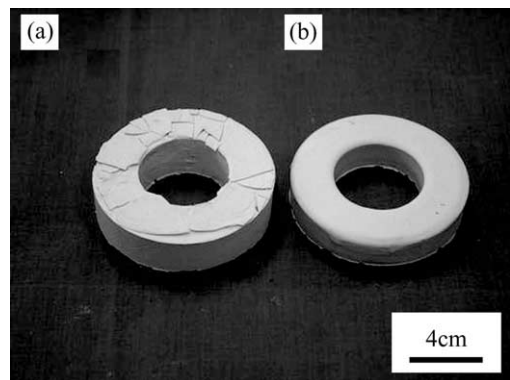


Fig. 4. Alumina green body surfaces gelcast in air from slurries without PAM (a) and with 2.8 wt.% PAM (b).

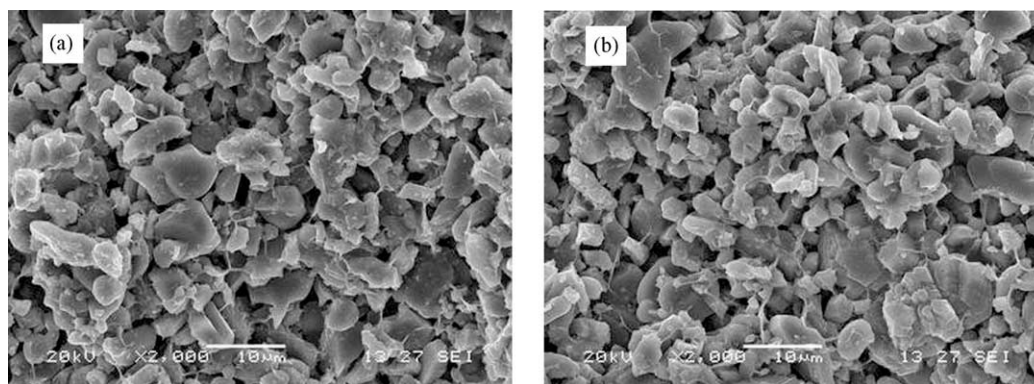


Fig. 5. The microstructures of green bodies prepared from suspension without PAM (a) and with 2.8 wt.% PAM (b).

for both systems and obvious polymer network can be observed in both green bodies. The variation in density and green strength of dried bodies with and without 2.8 wt.% PAM were shown in Table 3. Density of the green body prepared from the suspension with PAM increased obviously compared to that without PAM. Green strength, on the other hand, showed a significant increase after addition of PAM. After addition of 2.8 wt.% PAM the density and strength of the green body were approximately 58.6% of theoretical density (3.85 g cm^{-3} , the mixed density of alumina and sintering aids) and 43.38 MPa, respectively.

Previous studies indicated that the strength of green body formed by gelcasting was provided by the polymer gel.^{16,17} But for the monomer solution with 2.8 wt.% PAM, as the polymerization proceeds, the native PAM with free amino and keto groups are likely to form a more complicated network structure through hydrogen bonding with the keto groups of the PAM polymerized by monomers, resulting in an intimate mix of polymer chains (as shown in Fig. 6). The relatively high gel strength obtained for the monomer-polymer system with respect to a pure monomer system is attributed to the enhanced polymer network due to this cross-linking through hydrogen bonding. Hence, the flexural strength of the green body prepared from the suspension with addition of PAM increased significantly compared to those without PAM.

Fig. 7 illustrates the SEM micrograph of alumina ceramics. It should be noted that the ceramics have a

high density and uniform microstructure without developing a huge grain growth. The flexural strengths are about 350 MPa for both ceramics obtained from the sole AM system and ones from the mixed PAM and AM system (as shown in Table 3).

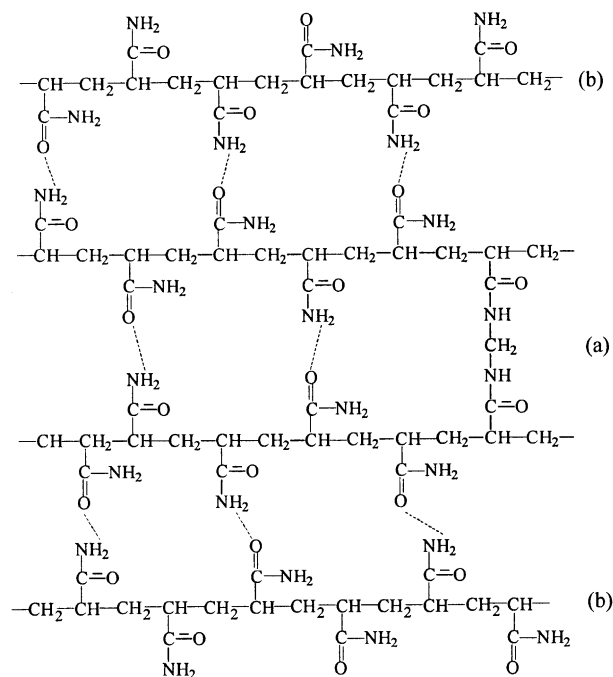


Fig. 6. The proposed structure of cross-linked PAM (a) gel after an addition of native PAM (b).

Table 3
The bulk density and flexural strength of dried green and sintered bodies with and without 2.8 wt.% PAM

PAM content	Flexural strength of green body (MPa)	Density of green body (g cm^{-3})	Flexural strength of sintered body (MPa)	Density of sintered body (g cm^{-3})
0	37.11 ± 1.67	2.176	351.85 ± 19.10	3.71
2.8 wt.%	43.38 ± 4.58	2.323	347.63 ± 24.72	3.68

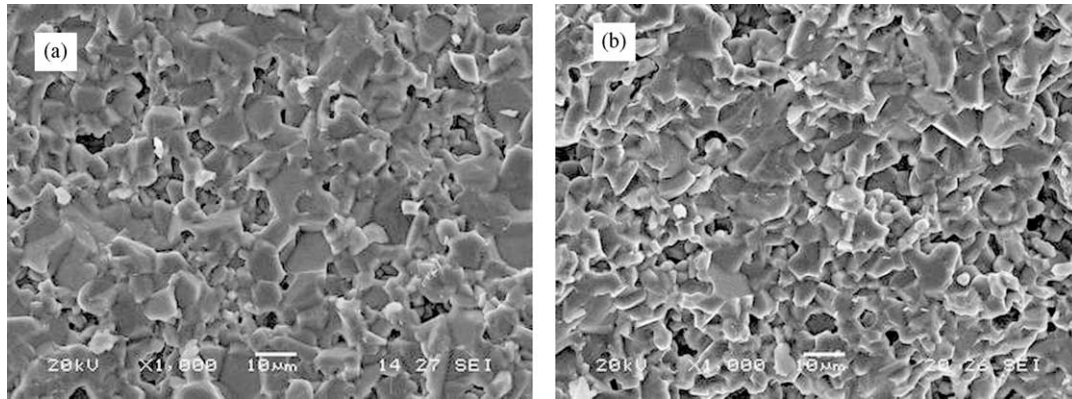


Fig. 7. The microstructures of sintered bodies prepared from suspension without PAM (a) and with 2.8 wt.% PAM (b).

4. Conclusions

- The results presented in this work show that surface spallation phenomenon of green bodies gelcast in air can be eliminated by adding a small amount of PAM to the monomer solution. It is found that using PAM, highly concentrated suspensions (~ 50 vol.% solids loading) can be prepared with a small reduction in fluidity of the slurries (0.1 Pa s, at shear rate of 48.1 s $^{-1}$).
- With 2.8 wt.% PAM added to the slurry, the zeta potential–pH curve shifts toward a lower pH region, and the isoelectric point of the slurry shifts to pH 3.5 as the added PAM results in a reduction of the positive shear-plane potential.
- After adding PAM in the AM-containing slurry, the suspension exhibits shear thinning behavior with yield stress. The increase of the temperature becomes more rapid and reaches a higher level at a lower period for the sole AM system compared to the PAM/AM mixed system.
- The flexural strength of green bodies prepared from the PAM/AM mixed slurry is higher than that from the AM only system. The relatively high green body strength 43 MPa obtained for the PAM/AM system is attributed to the cross-linking between the native PAM and polymerized PAM chains through hydrogen bonding and polymer gel. A dense and homogeneous microstructure is observed for the alumina samples prepared from the slurries containing mixed PAM and AM. The flexural strengths are about 350 MPa for both ceramics

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