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Ceramics International 28 (2002) 159–164

CERAMICS INTERNATIONAL

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Effect of rheological properties of the suspension on the mechanical strength of Al_2O_3–ZrO_2 composites prepared by gelcasting

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Received 24 January 2001; received in revised form 12 April 2001; accepted 16 June 2001

Abstract

The bending strength and Weibull modulus of sintered ZTA parts prepared from Al_2O_3–ZrO_2 (15 vol.%) suspension by the gelcasting process were investigated. The solid loading of the suspension that can meet the casting process requirements can reach 55%. However, it is found, surprisingly, that the highest bending strength and the largest Weibull modulus reached values as high as 791.58 ± 33.42 MPa and 24.38 only when the solid loading of the suspension was 50 vol.%. The reason for this phenomenon is that the microstructure of the sintered samples is to a large extent determined by the structure and the rheological behavior of the suspension because the gelcasting process is an in situ curing process. © 2002 Published by Elsevier Science Ltd and Techna S.r.l.

Keywords: A. Suspension; Al_2O_3–ZrO_2 composites; Rheology; Bending strength; Gelcasting

1. Introduction

Ceramic gelcasting has rapidly developed in the past decade due to its capability of near-net-shape processing of fine ceramic pieces. The advantages of the technique include dimensional accuracy and complex shaping capabilities, as well as reducing the cost of manufacturing. Fundamental research has been carried out by Young et al. [1] as well as Omatete et al. [2–4], showing the general feasibility of the process and its advantages in comparison with other liquid forming processes. Omatete et al. [5] discussed in detail the key aspects of gelcasting: premix solution; rheology of gelcasting slurries; drying process of gelcast parts; binder burnout; green strength of dried gelcasting parts, etc. Wasche et al. [6] investigated the influence of slip viscosity on the mechanical properties of high purity alumina by gelcasting. They suggested that the interaction of rheological behavior of the suspension and the generation of flaws in the green body are of crucial importance in view of an optimized microstructure for the gelcasting process. However, their efforts were mainly on the effect of different degassing time of suspension on the microstructure of sintered samples.

So far, most of the researches on gelcasting have focused on the preparation of suspensions, such as the effect of dispersants and pH on the viscosity and rheological behaviors of suspensions [7], and the process control on gelcasting, such as the concentration of monomer, usage of catalysts and initiators, and degassing time [1–6] etc. The main object of these researches on rheological behavior was to prepare suspensions with high solid loading, for it is believed that the advantages of gelcasting over traditional wet-forming can only be achieved with high solid loading suspensions [5]. A relationship between the rheological behavior of the suspension and the mechanical properties of the samples is little known. In the present work, the effects of rheological behaviors of suspensions on the mechanical properties of Al_2O_3–ZrO_2 composites are investigated. The results suggest that the rheological behavior of the suspensions may have a critical influence on the mechanical properties of the sintered samples prepared by the in situ gelcasting process from different suspensions.

2. Experimental procedures

2.1. Materials

Commercially available α-Al_2O_3 (0.44 μm, Ceralox APA-0.5w/MgO, USA) and t-ZrO_2 ($Ce_{0.03}Y_{0.016}Zr_{0.954}O_2$, 0.4 μm, Beijing Founder Ceramics Technology Co. Ltd., China) were used in this investigation. The polyelectrolytes

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0272-8842/02/$22.00 © 2002 Published by Elsevier Science Ltd and Techna S.r.l.
PII: S0272-8842(01)00072-4

(ammonium polyacrylate, PAA, Mw = 3000–5000, Tianjing Chemical Industry Research Institute, China) was used as a dispersant. The standardized analytical grade $(CH_3)_4NOH$ (TMAH) was used for adjusting pH value of the suspension.

The essential components of the gelcasting process are the reactive organic monomers: monofunctional 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 a premix solution. The premix solution undergoes free-radical-initiated vinyl polymerization in the presence of an initiator such as ammonium persulfate $(NH_4)_2S_2O_8$. The reaction can be accelerated by using heat or the catalyst N,N,N′,N′-tetramethylethylenediamine (TEMED) or both. The resulting cross-linked polymer is an elastic hydrogel [8,9] to be used as the binder.

2.2. Experimental Procedure

The gelcasting process was similar to that of previous studies [1–5]. The premix solution was prepared with AM/MBAM = 23.3:1 (AM: 14.0 wt.%, MBAM: 0.6 wt.%). After 1 dwb% (dry-weight basis) dispersant was added, the solution was mixed with alumina powder and zirconia powder, and resultant suspensions with 40, 45, 50, 53, and 55 vol.% solid loadings, respectively, were adjusted to pH = 10 by adding TMAH aqueous solution. The suspensions were then ball-milled for 48 h to promote dispersion and admixing process. The suspensions were degassed in a rotary evaporator under vacuum until no further release of air bubbles was observed. 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 suspensions were degassed for another 5 min. During the degassing process, the temperature was kept at 0–1 °C to prevent excess evaporation of water and polymerization of the monomers. Each suspension was then cast into a 80×60×8 mm stainless steel mold, which was kept at about 70 °C. After the monomers polymerized, the green body was demolded and dried at room temperature under controlled humidity to avoid cracking and non-uniform shrinkage due to rapid drying. The dried green bodies were sintered at 1580 °C for 2 h. Each sintered body was cut and ground into specimens of about 3×4×36 mm for the bending strength measurement and specimens of about 4×6×30 mm for the SENB toughness measurement. Before their measurement, each of the specimens for the bending strength was ground by using SiC abrasive of 28, 14, 7 and 3.5 μm, respectively, for 30 min and each of the specimens for the toughness was cut a notch with depth of about 0.4–0.5 times of the specimen height.

2.3. Physical and chemical property measurements

Zeta potentials were determined by a Zetaplus Analyzer (Brookhaven Instrument Corp., USA). 1 m mol/l NaCl was used as the solvent and the powder concentration was maintained at 0.05 vol.%. The pH adjustment was carried out by using HCl and NaOH solutions.

The rheological properties of the concentrated suspension prepared were measured by a rotation rheometer (MCR 300 Modular Compact Rheometer, Germany). In measurements of shear stress (τ), the thixotropic hysteresis loop (i.e. shear rate was first increased and then decreased between two fixed values) was performed for each sample. Three-point bending strengths of sintered specimens were determined from as-ground specimens with 30 mm span using 20 test pieces of 3×4×36 mm for each group of samples. Fracture toughness (K_{IC}) was measured using single edge notch beam (SENB) method with 24 mm span using at least 6 test pieces of 4×6×30 mm for each group of samples. All measurements were repeated to check for reproducibility and sample alignment. The two-parameter Weibull equation was used in the characterization of the reliability of composite materials [10]. Fracture surface of sintered bodies was observed by using SEM (JSM-6301F Scanning Microscope, Japan) to estimate the microstructure uniformity and porosity of the specimens.

The relative density of sintered bodies was determined by Archimedes' principle in water. The formula $(l_0–l)/l_0$ was adopted to calculate the linear sintering shrinkage, where l_0 and l were the length of the specimen before and after sintering, respectively.

3. Results and discussion

3.1. Effects of pH on ζ-potential of unary suspension

The zeta potentials of Al_2O_3 and ZrO_2 were measured individually, as shown in Fig. 1. The isoelectric points (pH_{iep}-value) were 5.8 and 4.9 for Al_2O_3 and ZrO_2, respectively. At low pH, far from the pH_{iep}-value of either powder, only 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 be 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. Lastly, at high pH, far from the pH_{iep}-values of both powders, the particles have a high negative zeta potential and are colloidally stable. The profiles in Fig. 1 show that the saturation zeta potential and the breadth of the pH range over which the potential is nearly maximized, provide better colloidal stability at high pH for both powders.

3.2. Rheological behavior of composite suspensions

Low viscosity and high solid loading are beneficial for both mixing and casting in slurry processing. It is, therefore, important to maintain slurry fluidity while optimizing solid loading. The study had been performed on suspensions containing 40–55 vol.% of composite powders. Typical plots of apparent viscosity (η) versus shear rate ($\dot{\gamma}$) after different times of ball milling for a 55 vol.% suspension are given in Fig. 2. When the milling time was shorter than 48 h, the viscosity of slurries decreased gradually as the time of milling increased. It showed that the absorption of the dispersant on particles did not reach equilibrium and the suspension was unstable until the ball milling time is equal to or more than 48 h. After 48 h milling, the viscosity of the suspension tended to be consistent. Therefore, the ball milling time should be equal to or more than 48 h to obtain a stable suspension at equilibrium.

Fig. 3(a) gives the plots of apparent viscosity versus applied shear rate of stable suspensions after milling for 48 h. It can be seen that all suspensions (40–55 vol.% solid loading) exhibited a shear-thinning behavior and relatively low viscosity (of less than 1 Pa·s at the shear rate of 10 s^{-1}), which was suitable for casting. Fig. 3(b) shows the plots of shear stress versus the applied shear rate of stable suspensions after milling for 48 h. It can be seen that 53 and 55 vol.% suspensions possess a thixotropy hysteresis and their yield stresses were 1 and 3.5 Pa, respectively. This phenomenon was associated with the shear-thinning behavior of the suspensions and indicated a flocculated state of particles within the liquid. The decrease in thixotropy, viscosity and degree of shear-thinning with the decrease of the solid loading of a suspension implied that the degree of powder agglomerate decreased. The thixotropy disappeared, as the solid loading of the suspension was less than 50 vol.%.

Concentrated colloidally stable suspensions exhibited shear-thinning behavior in steady shear because of a pertubation of the suspension structure by shear [11]. 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

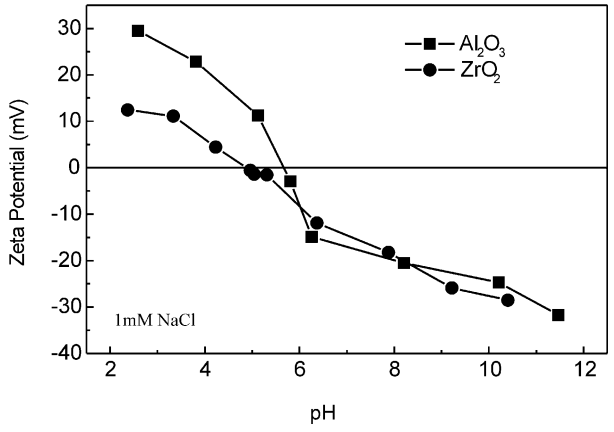

Fig. 1. Zeta potentials of Al_2O_3 and ZrO_2 as a function of pH.

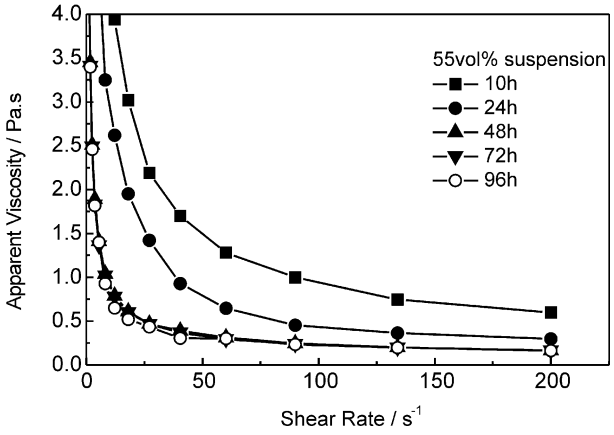

Fig. 2. Effect of ball-milling time on rheological behavior of 55 vol.% suspension.

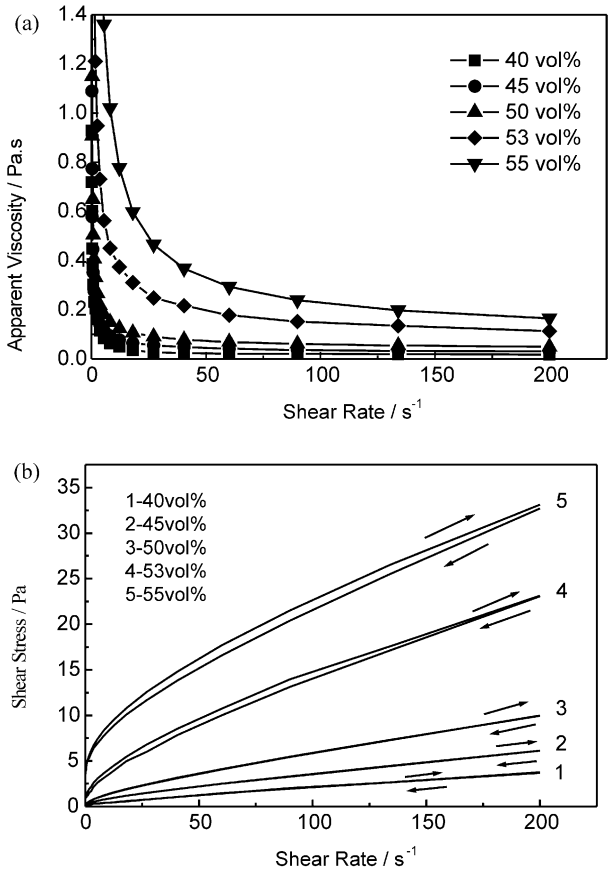

Fig. 3. Rheological behavior of the suspensions with different solid loadings (ball-milling at 48 h): (a) apparent viscosity versus shear rate; (b) shear stress versus shear rate.

controlled structure. The degree of shear thinning and the viscosity at high shear rates increased with increasing volume fraction of solid.

For most systems, the properties of the suspension change drastically at a certain critical particle concentration, ϕ_g, which corresponds to the formation of a space-filling particle network [12]. At $\phi < \phi_g$, the suspensions have no yield stress. Above ϕ_g, the suspensions can sustain a stress before yielding and the elasticity may be significant.

Based on the description above, it can be believed that the first three suspensions with solid loadings of 40, 45 and 50 vol.%, respectively, each had a particle concentration less than ϕ_g, so no yield stress can be observed for them. However, for 53 and 55 vol.% suspensions with particle concentration higher than ϕ_g, its high solid content resulted in the average separation distance between particles in suspension becoming shorter and formed a space-filling particle network, making flow more difficult. When a stress larger than the yield stress was applied, the gelled structure was broken into smaller units (flocs), which then moved past each other. If the floc attrition was affected by the strength of the hydrodynamic and attractive forces, pseudoplastic behavior was observed and viscosity decreased with shear rates. The strong shear forces at high shear caused flow units to be smaller and flow was facilitated. The destruction of flocs released constrained solvent, which resulted in a decrease of the effective volume fraction of the flocs. This phenomenon created thixotropic behavior in the system.

Gelcasting is a kind of forming process during which suspensions cure in situ. The structure of a suspension is almost completely kept in the forming bodies after the gelcasting process. This means that the microstructure of the forming body is identical with or similar to that of the suspension. In the case of flocs existing in the suspension, the flocs are "frozen" as aggregates in the forming bodies after gelcasting process. It is well know that dense ceramic materials with good mechanical properties cannot be obtained by sintering green bodies with aggregates. Therefore, the suspensions with 53 and 55 vol.% solid loading are not suitable for gelcasting, although they have higher solid loading and their fluidity and low viscosity can meet the requirements of gelcasting process. On the other hand, the suspensions with solid loadings less than 50 vol.% in which no or a few flocs existed are more suitable to be used in the gelcasting process. Green bodies of high uniformity can be prepared by gelcasting from these suspensions and ZTA materials with high mechanical properties can be obtained after sintering.

3.3. Mechanical properties and Weibull modulus

Fig. 4 shows the relationship between mechanical properties of sintered samples and the solid loading of the suspension from which the samples were formed by

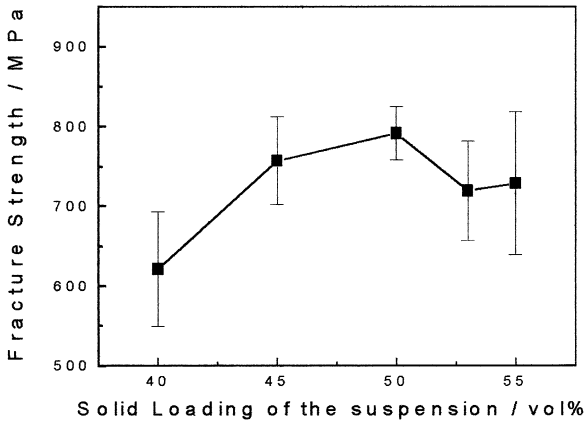

Fig. 4. Bending strength and fracture toughness of sintering bodies prepared from different suspensions.

gelcasting. The bending strength of sintered bodies, all of which were sintered at 1580 °C for 2 h, increased gradually from 621.35±71.91 MPa to 791.58±33.42 MPa as the solid loadings of the suspensions changed from 40 to 50 vol.%. Their Weibull moduli had the same tendency and reached the highest value of 24.38, as shown Fig. 5. However, as the solid loading exceeded 50 vol.%, both bending strength and Weibull modulus of sintered bodies began to decrease. On the other hand, the fracture toughness of sintered bodies increases monotonously as the solid loading of the suspension increase from 40 to 55 vol.%.

It is well known that the mechanical properties of ZTA ceramics are greatly influenced by microstructure including relative density (porosity), grain size, ZrO_2 content and its distribution, microstructural flaw etc. [13]. From Fig. 6, it can be seen that the sintered sample prepared from the suspension with the lowest solid loading, 40 vol.%, had the lowest relative density and highest sintering shrinkage. As the solid loading of suspensions increased, the relative densities of sintered

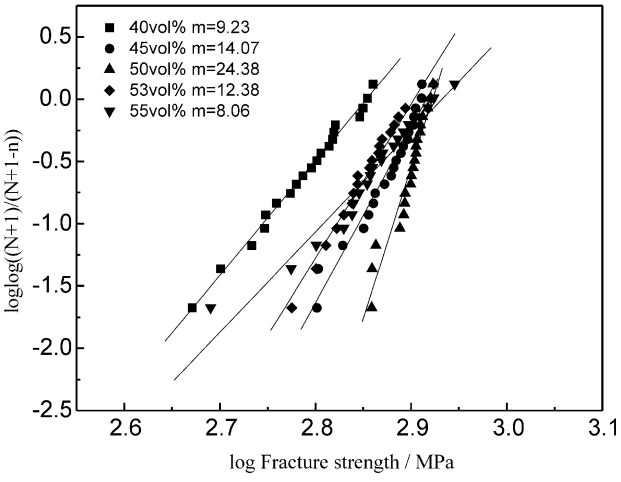

Fig. 5. Weibull distribution of sintering bodies prepared from different suspensions.

samples increased while the sintering shrinkage decreased. The occurrence of the phenomenon is mainly due to the packing behavior in the suspensions and the gelcasting procedure, as previously discussed. Fig. 7 also showed that the porosity of the sintered bodies decreased with increasing the solid loading of the suspension.

In general, sintered samples with higher relative density exhibit better mechanical properties. However, there is also an influence of microstructure uniformity on mechanical properties. In the system investigated, the suspensions with solid loading below 50 vol.% had uniform microstructure, from which the microstructures of sintering samples developed. When the solid loading exceeded 50 vol.%, some kind of flocs developed in the suspension, as discussed above. The flocs were maintained in the green bodies after gelcasting process. Flocs in green bodies often act as sources for flaws occurring during sintering.

The critical flaw size c which initiates failure can be estimated from the relation [14],

$$c = \frac{K_{IC}^2}{\pi \sigma_f^2},$$

where K_{IC} is the fracture toughness of the material and σ_f is the bending strength.

The data in Table 1 show the calculated critical flaw size for each composition. The critical flaw size decreased gradually from 30 to 22 μm as the solid loadings of the suspensions changed from 40 to 50 vol.%. However, as the solid loading exceeded 50 vol.%, the critical size began to increase. This emphasizes the fact that a suspension with uniform microstructure will bring to

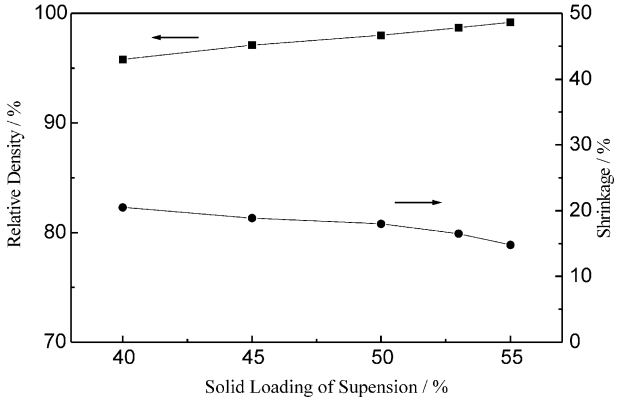

Fig. 6. Relative density and shrinkage of sintering specimen as a function of solid loading.

Table 1
Mechanical properties and calculated flaw sizes of ZTA (Al_2O_3/15 vol.% ZrO_2)

Solid loading of the suspension (vol.%)	Bending strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	Calculated flaw sizes (μm)
40	621.35±71.91	5.96±0.19	30.0
45	757.05±55.03	6.4±0.28	22.7
50	791.58±33.42	6.58±0.37	22.0
53	719.44±62.12	6.66±0.33	27.3
55	728.56±89.46	6.87±0.27	28.3

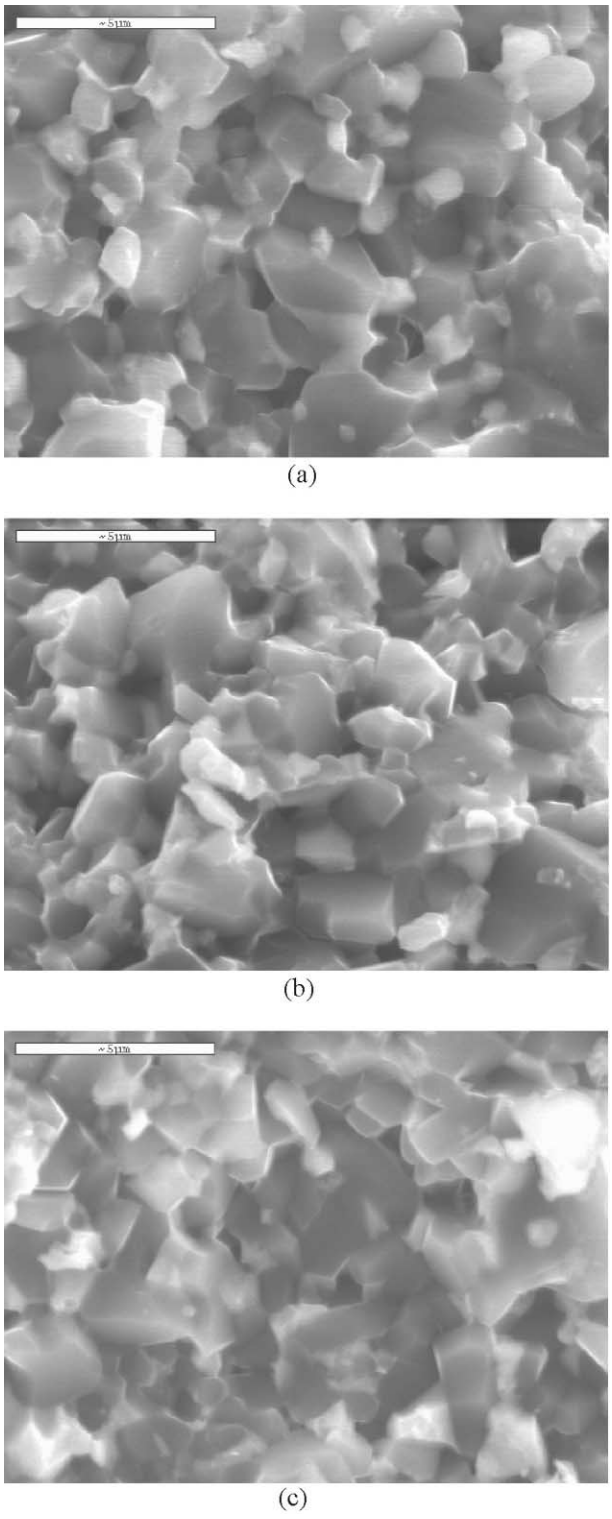

Fig. 7. SEM photographs of fracture surfaces of the sintered samples prepared from suspensions with (a) 40 vol.%; (b) 50 vol.%; (c) 55 vol.%.

sintered compacts with relatively small flaws, thus improving mechanical strength and reliability of the ZTA.

4. Conclusions

Al_2O_3–ZrO_2 composites with high bending strength and high Weibull modulus have been successfully fabricated by the gelcasting process. The rheological behavior of composite suspensions was determined; results indicate that there were remarkable differences among the different suspensions. The mechanical properties were found to depend on the solid loading of the suspensions. A discussion of experimental data leads to the following conclusions:

1. fracture toughness increases uniformly with increasing the solid loading of suspensions;
2. bending strength and Weibull modulus increase with increasing solid loading up to a maximum of 791.58 ± 33.42 MPa and, respectively 24.38 at 50% solid loading;
3. all suspensions exhibit a shear-thinning behavior and relatively low viscosity, but more than 50 vol.% suspensions possess thixotropy hysteresis and yield stresses; and
4. although suspensions with good casting behavior could be prepared also for higher solid concentrations, a decrease of strength, as well as of Weibull modulus were observed beyond a 50% solid fraction. This result was explained as being due to flocculation occurring in the suspension: the flocs may act as sources of flaws in the sintered compact.

Acknowledgements

The authors thank the National Science Foundation of China (Grant No. 59872018) and The High Technology Research and Development Program (Grant No. 863-715-06-0100) of the People's Republic of China who supported this research.

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