JOURNALOF

Ceramic Processing Research

Suspension characteristics and rheological properties of TBA-based freeze casting alumina/zirconia slurries

Joo-Hyeok Lee, Tae-Young Yang, Seog-Young Yoon and Hong-Chae Park*

School of Materials Science and Engineering, Pusan National University, Pusan 609-735, South Korea

The sedimentation bulk density and rheology of TBA-based alumina and alumina/zirconia mixed suspensions have been studied in terms of oxide loading (20, 30 vol.%), and types of additives (dispersant, dispersant/binder, dispersant/surfactant, dispersant/surfactant/binder). Citric acid, ethoxylated acetylenic diol (Dynol 604), poly(vinyl butyral) (PVB), and tertiary-butyl alcohol (TBA) have been used as the dispersant, surfactant, binder, and liquid medium, respectively. The sedimentation density significantly increased upon adding the dispersant; the effect was more pronounced with an alumina/zirconia suspension most likely due to the high specific surface area of zirconia. With a further addition of the binder, the sedimentation density decreased. The suspension viscosity generally behaved in an opposite manner to the sedimentation density, i.e. a low sedimentation density gave a high low-shear viscosity, indicative of the formation of a highly ordered structure in the suspended particles. The low shear rate rheology showed a shear thinning; in a such case, the degree of shear thinning was greatly increased with a high solid loading (30 to 20 vol.%). TBA-based alumina/zirconia suspension mixed with 5 vol.% zirconia gave an intermediate sedimentation density and the rheological behavior of pure alumina and 15 vol.% zirconia-containing alumina suspensions, implying the alumina and zirconia particles are non-interacting with each other.

Key words: Alumina/zirconia, Freeze casting, Tertiary-butyl alcohol, Sedimentation density, Rheology, Shear thinning.

Introduction

Porous ceramics are widely used for industrial and environmental applications; such applications include the filtration of molten metals, and particulate removal from the exhaust gases of diesel engines, supports for catalytic agents, and electrodes in fuel cells [1-3]. Freezing casting (freeze drying) has attracted much interest as a new forming method which can be used to fabricate porous ceramic components [4-7]. This method involves the preparation of a ceramic slurry that is poured into a mold, it is then frozen and the suspension liquid sublimated away. The removal of the frozen liquid by sublimation can lead to porous ceramics with uniquely shaped pore channels, e.g. long-range ordered and/or gradient pore structures [8].

The colloidal processing of freeze casting slurries is essential, since it enables ceramic particles to give a desirable fluidity when they are cast into a mold and to form a uniformly packed green body; developing into a more dense and homogeneous microstructure of the walls surrounding pore channels during sintering. Usually, freeze casting slurries need the addition of various processing additives, such as a dispersant for particle deflocculation, and a binder and surfactant for improved green strength and wettability. In spite of their environmental and health problems, organic solvents have often been used as the

E-mail: hcpark1@pusan.ac.kr

temporary vehicles for freeze casting, which can allow a flexible freezing process [8-10].

Generally, the rheological behavior of a suspension is sensitive to the state of the particle dispersion, and this is actually affected by selected solvents and processing additives. Methodical studies on the stability of freeze casting slurries are difficult owing to the chemical multiplicity of a dispersion system. In dispersion processing, ceramic particle surfaces may be combined with solvents [11] and also organic additives (dispersant, binder, plasticizer, and sometimes surfactant), which are often interactive [12]. It has been reported that the dispersion stability may be affected by a wide variety of solvents and processing additives, but different results can be obtained in any given dispersion system [13, 14]. In the dispersion system consisting of several different processing additives, such as freeze casting slurries, a competitive adsorption of these components takes place onto the particle surfaces, which affects the suspension stability and rheological behavior. In this study, we report the effects of incorporating multiple processing additives on the suspension stability and rheological behavior of alumina/zirconia powders in tertiary-butyl alcohol (TBA). Relatively few papers describing such relationships in TBA-based ceramic systems have been reported. TBA selected as the freezing vehicle in this processing, has its high freeze temperature (25.3 °C) and particularly its inherent solidification characteristics to grow preferentially into a straight direction [8, 15]; consequently, the control of the freezing process is easy and unidirectional pore channels are possibly formed over a long range after sublimation. Alumina (Al₂O₃)/zirconia

^{*}Corresponding author: Tel:+82-51-5102392

Fax: +82-51-5120528

 (ZrO_2) composites are undoubtedly considered as potential engineering ceramics, due to their excellent mechanical and thermal properties [16, 17].

Experimental Procedure

Commercial-grade Al₂O₃ (AES-11, Sumitomo Chemical Co., Japan) and 3 mol.% Y₂O₃-doped ZrO₂ (TZ3YS-E, Tosho Co., Japan) powders were used as starting materials (Fig. 1). The alumina consists of agglomerated particles with a mean particle size of 0.56 µm (measured by laser scattering in distilled water) and a BET surface area of 9.1 m²/g. Zirconia shows a relatively strong tendency to agglomeration, with a mean particle size of 0.49 µm and a BET surface area of 14.2 m²/g. A reagent-grade tertiarybutyl alcohol (TBA, Junsei Chemical Co., Japan), as received, was used as a solvent to prepare the suspensions. Citric acid (Aldrich Chemical Co., USA) and ethoxylated acetylenic diol (Dynol 604, Air Products and Chemicals, USA) served as the dispersant and surfactant, respectively. Poly(vinyl butyral) (PVB, Aldrich Chemical Co., USA) was used as a binder.

Three types of alumina (100A) and, 5 (95A5Z) and 15 vol.% (85A15Z)) zirconia-containing alumina slurries were prepared by adding 20 and/or 30 vol.% powders into TBA, with only the dispersant ('d') present, with the dispersant/surfactant ('d/s'), the dispersant/binder ('d/b') and with the dispersant/surfactant/binder ('d/s/b'), respectively; then, 0-2.5 wt.% dispersant and 0.5 wt.% binder, based on oxide powder and 0.25 wt.% surfactant, based on the TBA solvent were added. Formulated slurries were ball-milled at 40 °C for 24 h using a high alumina lining and ball media.

To investigate the effect of processing additives on the dispersibility of oxide particles in TBA, sedimentation tests were carried out with 10 vol.% suspensions. Each warm suspension of known weight was poured into a 20 ml graduated cylindrical glass tube. The tubes were shaken several times, and treated ultrasonically in a water bath controlled at 40 °C to break down any soft agglomerated particles. The suspension particles were then allowed to settle until the sediment height no longer changed with time. The sedimentation bulk density was determined by dividing the weight of the oxide powder by the sedimentation bulk volume, measured directly from the height of the sediment. The rheological properties of slurries were measured using a controlled stress rheometer (Rheolab



Fig. 1. SEM images of as-received (a) Al₂O₃ and (b) ZrO₂ powder.

MC1, Anton Paar, Germany). Measurements were performed at ~30 °C with a cone and plate fixture, with a cone diameter of 5 cm and angle of 1°. Additionally, the effect of temperature on the apparent viscosity in a given slurry system was examined in the range 25-60 °C at a constant shear rate (100 s^{-1}). The morphology of freeze casting slurries was observed using a scanning electron microscope (SEM, JSA-840A, Jeol, Japan).

Results and Discussion

Sedimentation bulk densities of alumina and alumina/ zirconia suspensions with 10 vol.% solid loading are shown in Figs. 2 and 3. The processing additives affected the sedimentation bulk density, but the degree of this effect was somewhat different with individual suspension constituents. When added alone, the dispersant greatly improved suspension; in this case, the sedimentation bulk density exhibited a maximum value with 0.5 wt.% dispersant, compared with further additions. Alumina/zirconia suspensions containing zirconia with relatively high specific surface area showed a high packing density compared with pure



Fig. 2. Sedimentation bulk density of alumina and alumina/zirconia suspensions with different amounts of dispersant; solid loading 10 vol.%.



Fig. 3. Sedimentation bulk density of alumina and alumina/zirconia suspensions with processing additives; solid loading 10 vol.%.

12

10

alumina. A minor increase in sedimentation bulk density with the introduction of additional surfactant (ethoxylated acetylenic diol), compared with only the dispersant was shown. Generally, the dispersant stabilizes the suspension state by adsorption of polymer electrolysis on solid particles. When the dispersant is properly adsorbed on the particles, the suspension maintains a stable dispersion state with a slow sedimentation rate; consequently, a final packing density may be improved. In reverse, the introduction of excessive dispersant can increase the ionic strength of particles and then the dispersion effect is rather reduced. Therefore, it is necessary to adsorb a monolayer of particles with a minimum amount required of dispersant. When the multiple processing additives are simultaneously added, the dispersibility of suspensions appears to depend on the competitive adsorption of additives onto the particle surfaces [18, 19].

The sedimentation bulk density clearly decreased with addition of the binder. This could be due to the polar unshared -OH side groups of a binder (PVB) supplying particle surfaces with adsorption force and dipole attraction of these side groups also causing polymer-polymer network formation among the particles, resulting in an agglomerated structure. Another possible reason could well be that such dipole attraction of a binder considerably offsets the repulsive energy between particles, created by the electrical double layer and steric hindrance. Also, the large molecular weight of the binder and its mechanically soft nature ties up particles, directly contributing to the agglomeration and sedimentation.

The effect of processing additives on the dispersion rheology has been investigated for alumina/zirconia suspensions with a solid loading of 20 and 30 vol.%; the viscosity-shear rate relationships are shown in Fig. 4. Regardless of zirconia content and solid loading, viscosity functions exhibited a shear thinning showing a rapid decrease of viscosity with increasing rate of shear, followed by a Newtonian plateau at a high rate of shear (> 100 s⁻¹). Generally, the flow resistance (i.e. viscosity) increases when the degree of agglomeration and strength of suspended particles increase. With increasing shear rate, the relatively weak agglomerate structure begins to break down by the applied viscous force applied and the viscosity is finally independent of the shear rate. The shear thinning viscosity is described by a power law model [20]:

$$\eta = m\gamma^{n-1} \tag{1}$$

in which *m* (with units of N·S^{*n*}/m²) and the dimensionless quantity *n* are constant characteristics of the fluid. Clearly when n = 1 and $m = \mu$, one obtains a Newtonian fluid. If n < 1, the fluid is said to be pseudo-plastic, and if n > 1 the fluid is described as dilatants. The majority of engineering fluids are shear thinning with the value of *n* ranging from 0.15 to 0.6.

The initial viscosity (at 3 s⁻¹, expressed as η_3 here) for the 95A5Z suspension with only the dispersant was

Fig. 4. Apparent viscosity of (a) 95A5Z and (b) 85A15Z suspensions with processing additives as a function of shear rate.

approximately 6 at 30 vol.% solid loading and 1.8 ($Pa \cdot s^{-1}$) at 20 vol.%. η_3 decreased slightly with the surfactant but greatly increased with the addition of the binder. The large increase in viscosity with the addition of the binder is consistent with the large decrease of the sedimentation density with the binder (Fig. 3). The PVB used as a binder in our experiments is a high molecular weight flexible polymer, tying up many particles in a bundle; in this case, tying up many particles in suspension directly contributes to the particle interactions and hence increases the low shear viscosity. With an increase in the shear rate, the degree of particle interaction was gradually reduced, finally resulting in a Newtonian flow, i.e. particles seemed to be in equilibrium with the surroundings. Therefore, if it could be possible to make further stable suspensions under this circumstance, the experimental time allowed should be longer than the relaxation time of the dispersion. In such a situation, the resistance to flow i.e. the viscosity is governed by the particle-particle interactions in addition to the volume occupied by the solid particles described below [21]:



30vol%

- d

20vol%

----- d

$$\eta = \eta_{\rm s} \left(1 + 2.5\phi + 6.2\phi^2 \right) \tag{2}$$

In this equation η is the viscosity of the suspension, η_s the viscosity of the suspending medium and ϕ the volume fraction of particles. At low ϕ (< 0.02), the higher order terms are neglected and Equation (2) becomes the Einstein equation, showing a linear increase of viscosity with ϕ . In our experiments, the solid content is over 20 vol.% and hence interactions between the particles should play an important role in determining the suspension viscosity.

When the suspensions contain additives other than the solid particles, the effective volume of the particle should increase due to the presence of an adsorbed layer, and an effective volume fraction, ϕ_{eff} can be approximately expressed as follow [22]:

$$\phi_{\rm eff} = \phi (1 + 2\delta/D_{\rm p})^3 \tag{3}$$

in which D_p is the particle diameter, δ the thickness of the absorbed layer, and ϕ the volume fraction of solid.

As shown in Fig. 4, with 30 vol.% alumina/zirconia (95A5Z, 85A15Z) loading, η_3 increased in the order of d/s < d < d/s/b < d/b, an order nearly consistent with the reverse of values for the sedimentation density. When the suspensions form higher ordered structures, the viscosity increases and the sedimentation density decreases. In comparison with 95A5Z suspensions with 30 vol.% solid loading, suspensions without the binder (d, d/s) showed lower η_3 for 85A15Z. However with the binder present (d/b, d/s/b), similar η_3 values were obtained in two types of suspensions. This implies that PVB can effectively tie up more of the alumina particles than zirconia particles, possibly due to the relatively large average particle size of alumina. However, with dispersant and dispersant/surfactant additions, the η_3 for 85A15Z suspensions decreased, compared with 95A5Z. This indicates that zirconia provides more adsorption sites (higher S_{BET}) for the dispersion, compared with alumina. Consequently, the suspension viscosity decreases since almost all the dispersant or dispersant/surfactant additives are adsorbed onto the particle surfaces, this leading to improved dispersibility of suspensions in spite of a minor increase in the effective particle volume, described in Equation (3). As the solid content increases from 20 to 30 vol.%, η_3 increased by over five times of magnitude; then, by comparison with 30 vol.% suspensions the effect of processing additives on suspension viscosity might be ignored.

The effect of temperature on suspension rheology has been investigated at a shear rate of 100 (s⁻¹) for 30 vol.% of TBA-based freeze casting alumina and alumina/ zirconia slurries, and viscosity-temperature relationships are given in Fig. 5. With an increase in the temperature applied, the viscosity functions generally showed a shear thinning; then, the viscosity value was in the increasing order of 85A15Z < 95A5Z < 100A. The onset of the viscosity drop, viz. the start of power law behavior, is a sign of a break up of the equilibrium structure of orien-



Fig. 5. Apparent viscosity of TBA-based 100A, 95A5Z and 85A15Z suspensions as a function of temperature.

tation along the flow direction. Suspensions with a certain level of 3-dimensional structure could become oriented along the flow direction, and this would give a lower viscosity, possibly by interlayer slip. An increased temperature in a suspension system induces the viscosity reduction of TBA solvent (η_s in Equation (2)); as a result, interlayer slip could be improved. Regardless of the oxide type, the onset of the viscosity drop started at about 28 °C, somewhat higher than the freezing temperature of TBA (25.3 °C). In particular, the second plateau region in the 100A suspension was observed at 30-40 °C; different from alumina/zieconia mixtures.

SEM micrographs of TBA-based freeze casting slurries are shown in Fig. 6. In spite of the change in the particle size distribution and morphology of the powder after ball milling for 24 h in the TBA solvent, a substantial amount of the large agglomerated particles remained; however, their particle size was relatively uniform. This implies that the suspension structure built up by the primary binding of the particles by polymer chains is fairly uniform.

Conclusions

The effects of additive types and oxide loading on the sedimentation bulk density and suspension rhology have been carried out for alumina and alumina/zirconia suspended in a TBA liquid medium. The addition of a dispersant improved the sedimentation density, with the effect somewhat pronounced for a surfactant addition; however, additional introduction of a binder lowered the sedimentation density. In reverse, a decrease in the lowshear viscosity when a dispersant and a dispersant/surfactant were added was generally observed. However, the introduction of additional binder greatly increased the lowshear viscosity, possibly due to the primary binding of the particles by soft polymer chains. Alumina and zirconia particles appear to be non-interactive based on the sedimentation and rheology behaviors. This may imply both types of particles are effectively surrounded by the



Fig. 6. SEM micrographs of TBA-based (a) 100A, (b) 95A5Z and (c) 85A15Z suspensions with 30 vol.% solid loading.

various additives; then, zirconia particles with a relatively high specific surface area appeared more effective.

Acknowledgement

This work was supported by National Research Foundation of Korea Grant funded by the Korea Government (2009-0064292).

References

- 1. R.W. Rice, "Porosity of Ceramics" (Marcel Dekker, 1998) p. 539.
- M. Scheffler and P. Colombo, "Cellular Ceramics: Structure, Manufacturing, Properties and Applications" (Weinheim: Wiley-VCH, 2005) p. 645.
- L.J. Gauckler, M.M. Waeber, C. Conti and M. Jacobduliere, J. Metals 37 (1985) 47-50.
- K.H. Zuo, Y.P. Zeng and D. Jiang, Int. J. Appl. Ceram. Technol. 5 (2008) 198-203.
- T. Fukasawa, M. Ando, T. Ohji and S. Kanzaki, J. Am. Ceram. Soc. 84 (2001) 230-232.
- T. Montz and H.J. Richter. J. Am. Ceram. Soc. 89 (2006) 2392-2398.
- U.G.K. Wegst, M. Schecter, A.E. Donius and P.M. Hunger, Phil. Trans. R. Soc. A 868 (2010) 2099-2121.

- R. Chen, C.A. Wang, Y. Huang, L. Ma and W. Lin, J. Am. Ceram. Soc. 90 (2007) 3478-3484.
- 9. Y.H. Koh, J.H. Song, E.J. Lee and H.E. Kim, J. Am. Ceram. Soc. 89 (2006) 3089-3093.
- A. Macchetta, I.G. Turner and C.R. Bowen, Acta. Biomater. 5 (2009) 1319-1327.
- M.D. Sack and C.S. Khadilkar, J. Am. Ceram. Soc. 66 (1883) 488-494.
- 12. U. Paik, V.A. Hackley and H.W. Lee, ibid. 82 (1999) 833-840.
- 13. R. Moreno, Am. Ceram. Soc. Bull. 71 (1992) 1521-1531.
- 14. U. Paik, Kor. J. Ceram. 4 (1998) 292-296.
- R. Chen, Y. Huang, C.A. Wang and J. Qi, J. Am. Ceram. Soc. 90 (2007) 3424-3429.
- 16. N. Claussen, ibid. 59 (1976) 49-51.
- 17. S.M. Olhero, I. Ganesh and P.M.C. Torres, *ibid.* 92 (2009) 9-16.
- K. Mikeska and W.R. Cannon, in Advances in Ceramics, Vol. 9, edited by J.A. Mangel and G.L. Messing (American Ceramic Society, 1983) p. 143.
- W.R. Cannon, R. Becker and K.R. Mikeska, in Advances in Ceramics, Vol. 26, edited by M.F. Yan, K. Niwa, H.M. O'Bryan and W.S. Young (American Ceramic Society, 1989) p. 525.
- 20. H.A. Barnes, J.F. Hutton and K. Walters, "An Introduction to Rheology" (Elsevier, 1989) p. 19.
- 21. G.K. Batchelor, J. Fluid. Mech. 83 (1977) 97-117.
- D.A.R. Jones, B. Leary and D.V. Boger, J. Coll. Interface Sci. 150 (1992) 84-96.