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Dispersion stability of Y-TZP/Ce-TZP powder system and slip casting

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The zeta potential and apparent viscosity measurements of 3Y-TZP, 12Ce-TZP and 3Y-TZP/12Ce-TZP suspensions, has allowed the slip casting conditions for the preparation of multilayer composites have been examined. The influence of heat treatment on the sintered density, microstructure and crystalline phase of multilayer composites was also studied. The isoelectric point of both 3Y-TZP and 12Ce-TZP suspensions was near pH 8 and that of 3Y-TZP/12Ce-TZP was at pH 8.6. The suspensions exhibited pseudoplastic flow, showing a decrease in viscosity with increasing shear stress. A small (0.3 wt%) addition of an organic deflocculant gave 3Y-TZP and 3Y-TZP/12Ce-TZP suspensions with 15 and 20 vol% solid contents an appropriate fluidity for slip casting, but an additional electrolyte was required to reduce viscosity in 12Ce-TZP. Dense (>98% of theoretical) multilayer composites with grain size of 0.3–2.2 μm were obtained after sintering at 1500°C.

1. Introduction

Yttria-stabilized tetragonal zirconia (Y-TZP) exhibits high strength and toughness [1–3]. However, its fracture toughness is drastically reduced by low temperature aging in air or humid atmosphere [4–8]. On the other hand, ceria-stabilized tetragonal zirconia (Ce-TZP) has superior thermal and chemical stability, high fracture toughness but relatively low strength, compared with Y-TZP. Consequently, an improvement in toughness is expected by adequately designing multilayers consisting of the two component materials.

The most used technique for the fabrication of multilayer composites is the doctor-blade process [9, 10], which enables preparation of thin and wide sheet, however, processing using slip casting allows formation of complex-shaped pieces by pouring well dispersed suspensions into plaster molds. One important control in slip casting technology is to control the rheological properties of slip systems consisting of ceramic powder and dispersant. The rheological properties in solid/liquid system depend especially on the dispersion state of the particles.

Pierre (1952) [11] has studied pH/viscosity relationships in the system zirconia-water-PVA-HCl and later, Masson *et al.* [12] reported the slip casting of CaO-stabilized zirconia in ethanol based suspensions. Also, Taguchi *et al.* [13] reported on the slip casting of Y-PSZ, focussing on the affect of solids content on relative density and firing shrinkage. Moreno *et al.* [14] studied the rheological and casting parameters of 3Y-PSZ powder obtained by a coprecipitation route and the effect of thermal treatments on the stability of the tetragonal phase and grain size development. Delsio *et al.* [15] investigated the mass mobility, rheology and sedimentation bulk density in more concentrated but inhomogeneous 2Y-PSZ/alumina suspensions (15 vol% solids) and then compared the results with low concentration particles systems (0.1 vol% solids).

The present study investigates some of the important processing parameters, which influence the dispersion stability of solid particles/aqueous suspension systems. It also focuses on the effect of heat treatment on tetragonal phase stability and grain growth behaviour.

2. Experimental procedure

Commercial-grade 3 mol% Y_2O_3-ZrO_2 (3Y-TZP) and 12 mol% CeO_2-ZrO_2 (12Ce-TZP) powders produced by Tosho Co. (Japan), were used as starting materials. Average particle size and specific surface area of 3Y-TZP and 12Ce-TZP were 0.5 μm, 7.2 m^2/g and 0.4 μm, 7.7 m^2/g, respectively. Both TZP powders consisted mainly of tetragonal with minor amounts of monoclinic phase.

The colloidal stability of 3Y-TZP, 12Ce-TZP and 3Y-TZP/12Ce-TZP (1 : 1, molar ratio) aqueous suspensions (0.04 g/cc) was studied by zeta potential measurements (Zetasizer, Model ZET 5004, Malvern). The pH adjustments were carried out by adding HCl (4N) and NaOH (4N) for the acid and basic conditions, respectively. After ball milling for 9 h, viscosity measurements in 3Y-TZP, 12Ce-TZP and 3Y-TZP/12Ce-TZP aqueous suspensions with a solid loading of 15 and 20 vol% were conducted using a viscometer (Model DV-II$^+$, Brookfield). After ball milling, the 15 vol% suspensions of 3Y-TZP, 12Ce-TZP and 3Y-TZP/12Ce-TZP exhibited pH values of 8.4, 7.4, 7.7, respectively, similar to the 20 vol% suspensions.

Multilayer composites were obtained by sequential solid casting of 12Ce-TZP (layer ‘A’), 3Y-TZP/12Ce-TZP (layer ‘B’) and 3Y-TZP (layer ‘C’) suspensions containing 0.3 wt% dispersant, into plaster of Paris molds (50 mm × 25 mm × 15 mm) and then by drying in air and oven. Firing was accomplished at 1400–1600°C for 2 h. In the case of the 12Ce-TZP suspension, its viscosity was so high that additional electrolyte (20% ammonia water) was used to lower the viscosity. The laminated structure was examined using a stereoscopic microscope (WILD M10, Leica). The sintered bulk density was measured by the water immersion method. Crystalline phases were identified by XRD (D-MAX 1400, Rigaku). The sintered polished and thermally etched surfaces were examined using SEM, (JSM-840A, Jeol).

3. Results and discussion

Fig. 1 shows the zeta potential versus pH curves for three TZP aqueous suspensions. The isoelectric point (*iep*) of 3Y-TZP/12Ce-TZP corresponds to ~ pH 8.6; this value was somewhat high compared with 3Y-TZP (pH_{iep} 7.9) and 12Ce-TZP (pH_{iep} 8). The isoelectric point of TZP was at a higher pH than that of pure zirconia (pH_{iep} 5–6.5) [14,16], due to the relatively high pH_{iep} of the stabilizer [17]. However, it is unreasonable to consider the high pH_{iep} of TZP with only soluble stabilizer; the *iep* of 3Y-TZP and 12Ce-TZP was nearly same, in spite of the relatively high pH_{iep} of Y_2O_3 (8.95) compared to CeO_2 (6.75) [17]. Also the *iep* of the mixture 3Y-TZP/Ce-TZP did not follow the common of mixture. It is known that the *iep* of solid oxides in aqueous suspensions is influenced by several factors such as positive charge, hydration, impurity, structure, chemical defect, cation charge and size, etc. Also, the zeta potential is mainly governed by the surface properties of solid particles in suspension. Therefore, it is thought to be difficult to predict with confidence the *iep* of solid solutions containing them, by simply comparing the *iep* of the pure oxide components. In the case of a solid solution, it does not appear that a solid solution containing soluble material of high *iep* always has a higher pH_{iep} than one containing that of low *iep*.

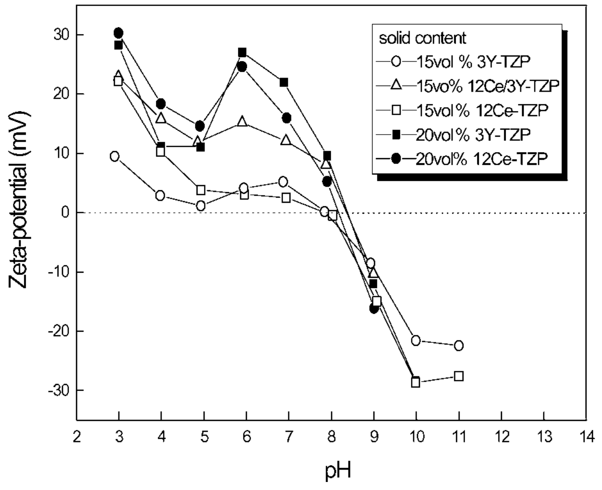


Figure 1 Zeta-potential of 3Y-TZP, 3Y-TZP/12Ce-TZP and 12Ce-TZP aqueous suspensions as a function of pH.

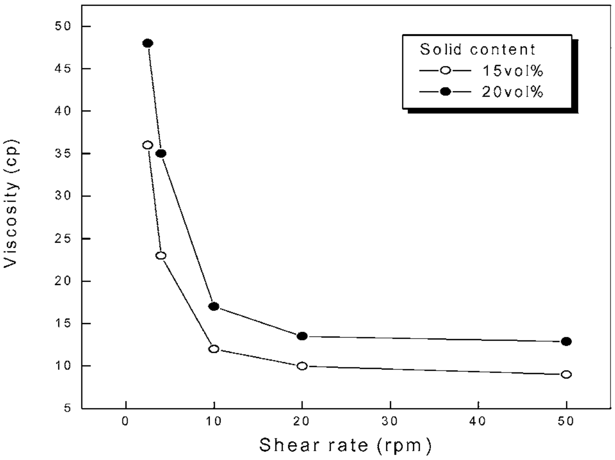


Figure 2 Apparent viscosity of 3Y-TZP aqueous suspensions as a function of shear rate.

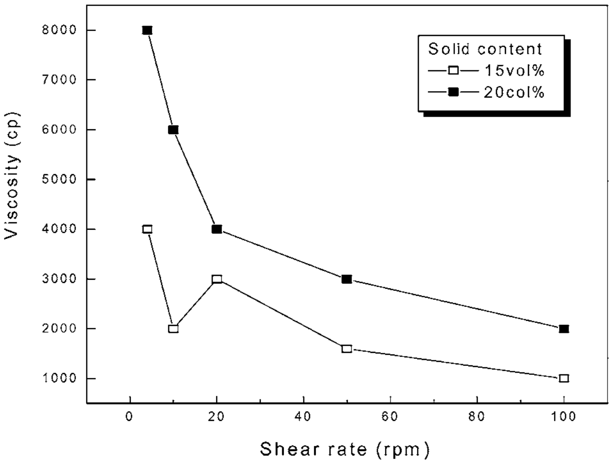


Figure 3 Apparent viscosity of 12Ce-TZP aqueous suspensions as a function of shear rate.

The electrical double-layer theory is valid in a dilute suspension. Thus, it is desirable to contain as high solids loading as possible in the slip casting suspension. Therefore, the zeta potential alone is insufficient to explain the behavior of such concentrated suspension, because interparticle forces are long range and their effect changes with distance [18]. Figs 2–4 show the change of apparent viscosity versus shear rate in 3Y-TZP, 12Ce-TZP and 3Y-TZP/12Ce-TZP slips with 15 and 20 vol% solids loading. The viscosity depends on the solids loading of the slips. The slips exhibited pseuduo-plastic flow, in which the viscosity decreases with increasing shear rate. It is considered that the effective volume fraction of dispersed solid particles, including interagglomerate voids decreases, due to the fracture of agglomerate structure formed by interparticle attraction with increasing shear rate.

The viscosity of 12Ce-TZP suspensions was so high (Fig. 3) that NH_4OH solution was added to suspensions to control pH (~8.7). Fig. 5 shows the effect of pH change on viscosity of suspensions for a fixed

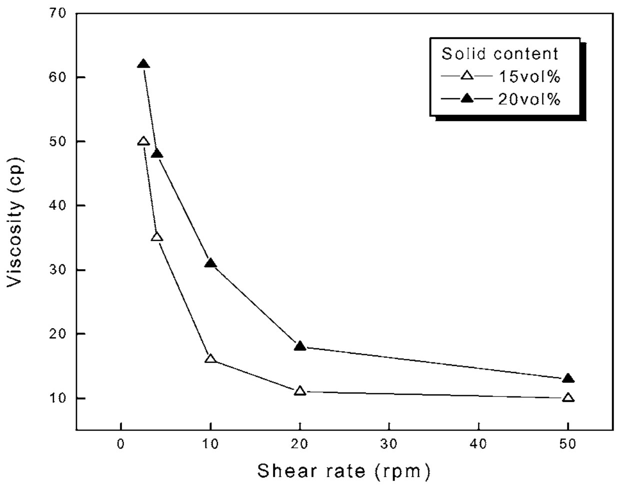


Figure 4 Apparent viscosity of 3Y-TZP/12Ce-TZP aqueous suspensions as a function of shear rate.

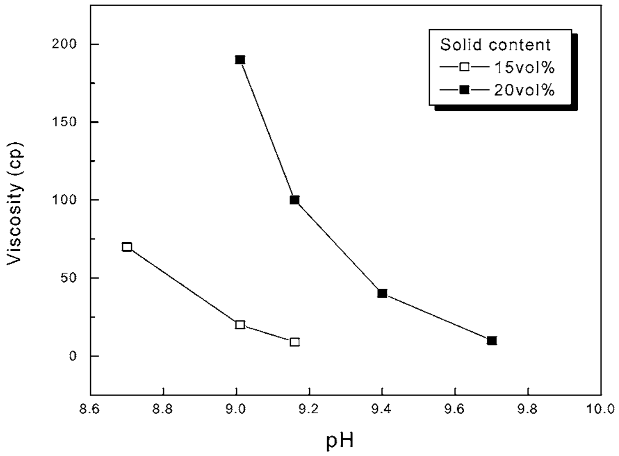


Figure 5 Apparent viscosity of 12Ce-TZP aqueous suspensions as a function of pH (shear rate = 50 rpm).

shear rate of 50 rpm. The viscosity of suspensions is sensitively dependent on the pH and decreased remarkably, together with an increase in the pH above *iep* (pH 7.4). The change of viscosity of suspensions having a maximum and minimum viscosity within a given pH range (∼8.7) was examined as a function of shear rate (Figs 6, 7). In the case of suspensions with the same solids loading, the effect of shear rate on dispersion stability was large in high pH systems compared with low pH. The reasons are considered as follows:

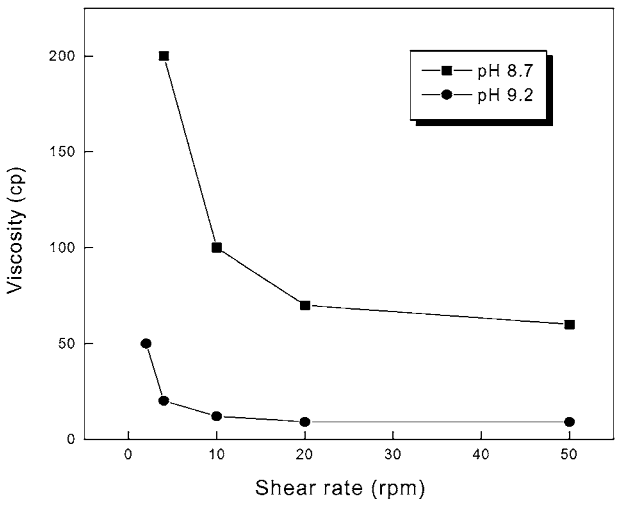


Figure 6 Apparent viscosity of 15 vol% 12Ce-TZP aqueous suspensions as a function of shear rate.

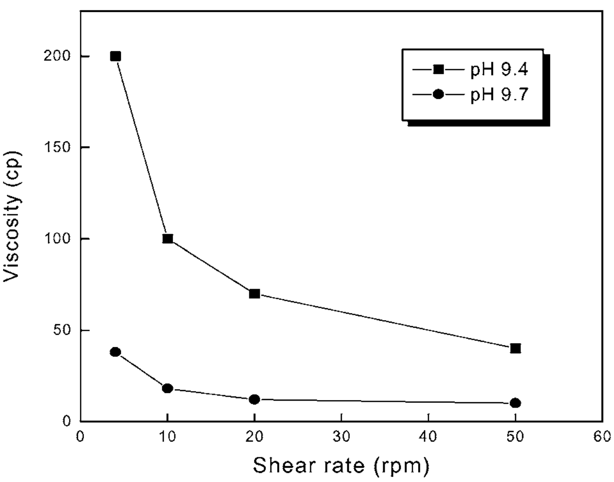


Figure 7 Apparent viscosity of 20 vol% 12Ce-TZP aqueous suspensions as a function of shear rate.

(i) with lowering pH in suspensions containing the same amount (0.3 wt%) of deflocculant, zeta potential and repulsive potentional energy between double-layer particles are relatively small

(ii) in this case, therefore, larger amounts of agglomerate particles which were broken down by the shear flow forces together with increasing shear rate, was contained.

The conclusion can be drawn that the degree of dispersion in containing agglomerate particles depends on the amount of deflocculant added and the shear rate.

Fig. 8 shows the three-layer structure with layer thickness of 1.0–1.4 mm. By means of XRD analysis, tetragonal and minor amounts of monoclinic

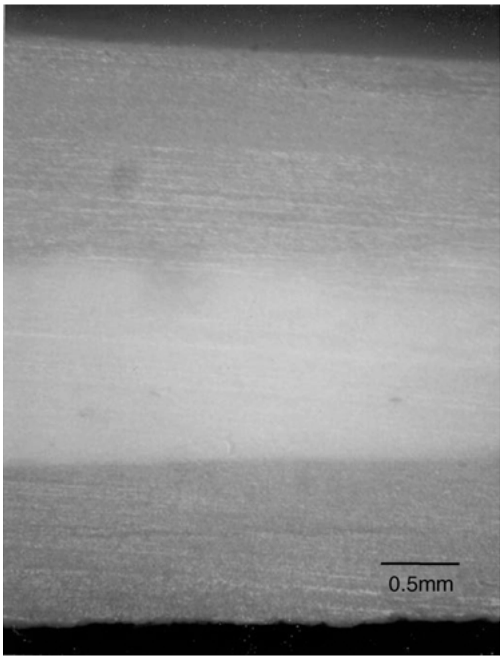


Figure 8 Optical micrograph showing three-layered structure sintered at 1500°C.

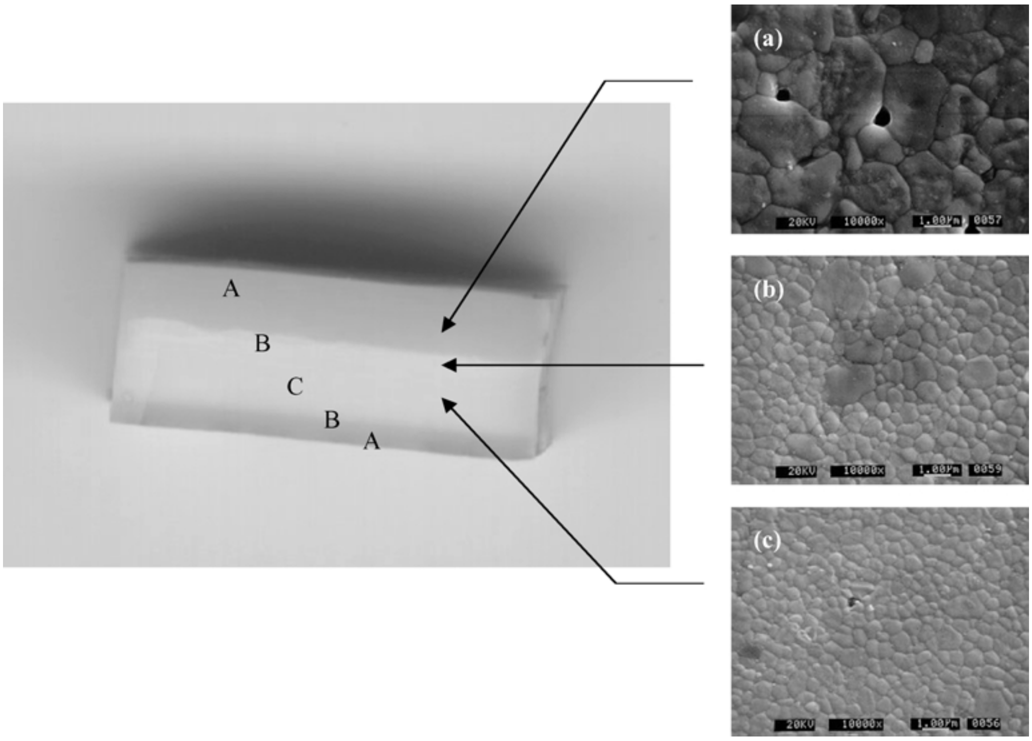
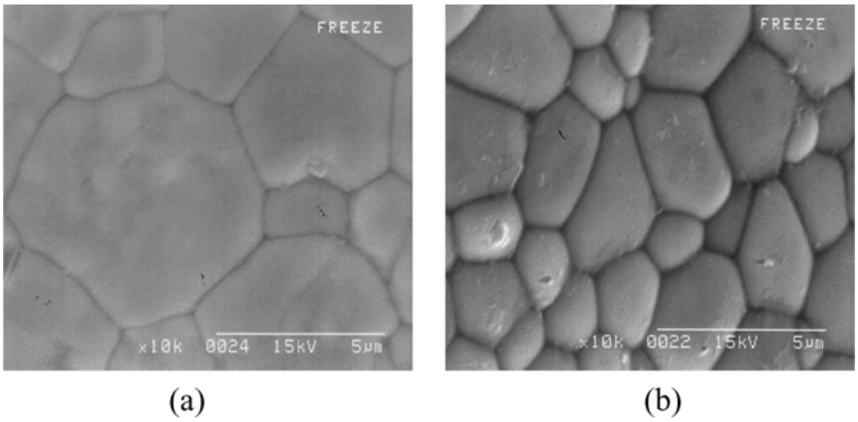


Figure 9 Scanning electron micrographs of the layer (a) 'A' (12Ce-TZP), (b) 'B' (3Y-YZP/12Ce-TZP) and (c) 'C' (3Y-TZP) of the 1500°C-sintered material.



(a) (b)

Figure 10 Scanning electron micrographs of the layer (a) 'A' (12Ce-TZP) and (b) 'C' (3Y-TZP) of the 1600°C-sintered material.

phases were confirmed in the 1500°C-sintered materials. The relative densities of mutilayer sintered materials were 94.7 (1400°C), 98.7 (1500°C) and 98.1% (1600°C). The microstructures of each layer in the 1500°C-sintered material are shown in Fig. 9. Generally, the layer 'C' (3Y-TZP) (<0.3 μm) consisted of small grains, compared with the layer 'A' (12Ce-TZP) (<2.2 μm). With increasing sintering temperature to 1600°C, the grain growth was considerably larger in the 3Y-TZP (layer 'C') than in the 12Ce-TZP (layer 'A') (Fig. 10).

4. Conclusions

(1) The isoelectric point of zirconia differs somewhat according to the kind of stabilizer added: the pH_{iep} of 3Y-TZP, 3Y-TZP/12Ce-TZP and 12Ce-TZP aqueous suspensions are 7.9, 8.6 and 8, respectively.

(2) The viscosity of 15 vol% 12Ce-TZP aqueous suspensions with only 0.3 wt% deflocculant (Darvan-C) is sufficiently high to prevent casting of the slips. The viscosity is lowered considerably by adjusting pH to ∼9.2 using additional NH_4OH.

(3) High density mutilayer composites each consisting of two phases (major phase tetragonal), can be prepared by sintering at 1500°C, for 2 h.

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