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Sintering behaviour of slip-cast Al_2O_3 – Y-TZP composites

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The sintering behaviour of alumina–Y-TZP composites prepared by slip-casting technique were studied. Slip-cast samples containing varying amounts of Y-TZP ranging up to 90 vol% were prepared and evaluated. Sintering studies were carried out at 1450°C to 1600°C. Sintered samples were characterised where appropriate to determine phases present, grain sizes, bulk density and mechanical properties. Good correlation was obtained between the calculated prepared powder density and experimental results. The sintered bulk density of the composites was observed to increase with increasing Y-TZP content and sintering temperature up to 1550°C. Maximum hardness values ($>$14 GPa) were obtained for all samples containing $<$60 vol% Y-TZP and when sintered at 1550°C. It has been found that the additions of up to 50 vol% Y-TZP was effective in suppressing Al_2O_3 grain growth.

1. Introduction

Yttria-tetragonal zirconia polycrystals ceramics (Y-TZP) have been extensively studied for high-performance applications due to its relatively high fracture toughnesses (6–15 $MPam^{1/2}$), high bending strength (1000–1500 MPa) and good wear resistance [1–4]. In contrast, alumina ceramics (Al_2O_3) exhibit low fracture toughness ($<$5 $MPam^{1/2}$) and low bending strength ($<$600 MPa) [5].

In order to improve the properties of alumina ceramics, the incorporation of zirconia (ZrO_2) particles in the matrix of alumina ceramics have been investigated [6, 7]. It has been shown that the toughness and strength of aluminazirconia composites can be increased when compared to the monolithic ceramics [8–11]. For instance, bending strength up to 2400 MPa and fracture toughness of 17 $MPam^{1/2}$ have been reported for composite containing 20 wt% Al_2O_3 [9]. This phenomenon is attributed mainly to stress-induced tetragonal (t) to monoclinic (m) phase transformation of the (t) particles in the matrix (transformation toughening) and to certain extent, a crack deflection mechanism i.e. the interaction between crack and dispersed particles [10, 12].

The improvement in properties is also greatly dependent on the elimination of heterogeneity in the green body that could create flaws, isolated pores, voids and residual stresses [13]. For example, Lange [14] reported that defects introduced during the fabrication process were responsible for the decrease in fracture strength in both the sintered and isostatically hot-pressed composites. Therefore, variables such as history of the starting powders, the mixing process (e.g. ball milling, attrition milling, etc.) which in turn determine the homogeneity of the mixture and the fabrication technique (e.g. hot pressing, slip-casting, etc.) are critical factors controlling the final properties of the composite system.

For processing of composite ceramics, hot pressing technique and hot isostatic pressing have been found to be very effective for the preparation of fine-grain microstructure and high density body [9, 15]. However, this method has its limitation such as the final shape of the component is limited to simple circular or square geometry. Similarly, the conventional dry or isostatic pressing are more suited for the fabrication of simple and uniform shaped items. Although complex-shaped articles may be manufactured using such forming techniques, the process can be uneconomical due to the costly and labour intensive machining that would be required to meet the final dimensions of the component.

Wet forming techniques, in particular injection moulding and slip casting are alternative solution for the manufacturing of complex-shaped items. However, unless the production numbers are large, injection moulding may prove to be an expensive process. This is mainly due to the initial high capital investment required to purchase the specialised equipment and the ongoing tooling cost [16]. In contrast, slip casting represents a simple, reliable, flexible and economical method of producing ceramics and ceramic composites of any shapes and sizes [17–20]. Despite these benefits, slip casting can be complicated due to the unknown casting parameters such as solid loadings and deflocculant/binder system. In addition, the casting parameters also vary from one ceramic system to another and therefore requires optimisation study to be carried out and this can be time consuming [18, 21, 22].

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The aims of this work were to study the effects of employing slip-casting technique to fabricate well dispersed alumina–Y-TZP composites and to identify the optimum sintering conditions for these composites. Evaluation of the materials involved sintering studies conducted at a range of temperatures, with compositions assessed in terms of phase retention, densification, microstructural evolution, grain sizes and hardness.

2. Experimental procedure

2.1. Starting materials

The as-received commercially available materials : Y-TZP powder containing 3 mol% yttria and Al_2O_3 (Kyoritsu Co. Ltd., Japan) were used in this study. The chemical analysis and properties of these powders are given in Table I. Both the starting materials have similar mean particle size ~0.3 μm. However, the specific gravity of Y-TZP is 5.73 i.e. about 1.5 times heavier than Al_2O_3.

2.2. Preparation of slurry

The optimum conditions for preparing slurry were carried out by examining the viscosity of the individual materials. Polyacrylate (Rohm & Haas D-3019, Germany) and deionised water were used as the dispersant and solvent respectively. Rheological characteristics of the slurry were examined by using a viscometer (Brookfield, UK). Viscosity measurements were taken at three time intervals i.e. 15 s, 30 s and 60 s.

2.3. Fabrication of green body

A simple flow chart, which shows the steps involved in preparing the Al_2O_3–Y-TZP composites using slip-casting technique is presented in Fig. 1. In the present work, the amount of starting powders, dispersant and deionised water required to make the slip were calculated by keeping the volume fraction of the alumina constant whilst varying the fraction of zirconia as dispersion phase. The slurry solids content was kept at 45 vol%. The prepared slip were ball-milled for 4 h using Y-TZP milling media. After filtration, the slip was kept in a vacuum dessicator under magnetic stirring for 2 h to remove trapped air bubbles before casting into a gypsum mould. After 24 h of soaking time, the green rectangular compacts (~5 × 15 × 50 mm) were removed from the mould and dried in air for 24 h prior to oven drying at 110°C. Sintering studies were carried out over the temperature range 1450°C–1600°C, at a furnace ramp rate of 5°C/min and holding time of 2 hours. All sintered samples were polished to a 1 μm finish prior to testing.

TABLE I Characteristics of the starting powders

	Al_2O_3	Y-TZP	
Chemical composition			
Al_2O_3	99.80	<0.01	wt%
ZrO_2	—	94.70	wt%
SiO_2	0.02	<0.01	wt%
Fe_2O_3	0.01	<0.01	wt%
Na_2O	0.06	—	wt%
MgO	0.05	—	wt%
TiO_2	—	<0.01	wt%
Y_2O_3	—	5.20	wt%
Mean particle diameter	0.3	0.3–0.4	μm
Specific surface area	—	9–12	m^2/g
Specific gravity	3.96	5.73	

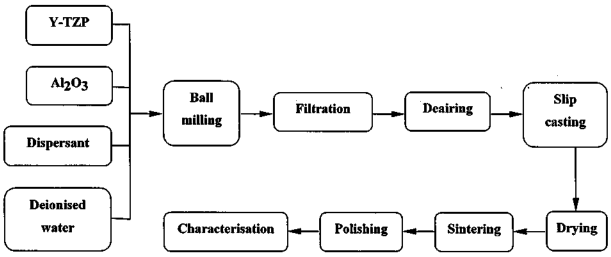

Figure 1 Schematic diagram showing the steps involved in the slip-casting process.

2.4. Characterisation and properties evaluation

Prepared powder densities were measured by using a AccuPyc 1330 Pycnometer. The bulk densities of the sintered samples were measured by water immersion method. Phase analysis by X-ray diffraction (XRD) of polished samples was carried out at room temperature using Cu-Kα as the radiation source. The fraction of surface monoclinic (m) and tetragonal zirconia (t) content were obtained using the method of Toraya *et al.* [23]. Microhardness measurements were made on polished samples using the Vicker's indentation method. The indentation load was kept constant at 10 N and a loading time of 15 seconds was employed. Average microhardness values were taken from ten measurements. In addition, microstructural evolution was examined by scanning electron microscopy (SEM). The grain size was determined on thermally etched specimens from SEM micrographs using the line intercept analysis [24].

3. Results and discussion

3.1. Rheological characteristics of slurry

Rheological characteristics of the monolithic ceramics were studied in order to determine the optimum conditions for preparing the slurry of the composites. Typical results showing the effects of dispersant addition on the viscosity of the two monolithic ceramic slurries taken after 30 s are presented in Fig. 2. The amount of dispersant is expressed as weight percentage to solids in the slip. Viscosity measurement made for both ceramics after 15 s and 60 s also exhibited similar trends as depicted in Fig. 2.

The high viscosity that was observed in both the slips for low level additions (<0.10 wt%) of dispersant were due to the low concentration of dispersant being insufficient to deflocculate the slip. Optimal deflocculation in both ceramics occurred between 0.10 wt% and 0.20 wt% polyacrylate dispersant level, where the resistance to flow was minimised. Higher levels of dispersant (>0.20 wt%) resulted in an increase in the viscosity of both ceramics but at a slower rate.

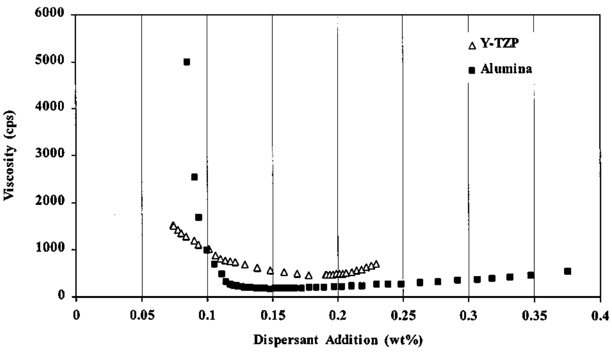

Figure 2 The effect of dispersant on the viscosity of the alumina and Y-TZP slurries containing 55 vol% water content.

In the present study, the optimum amount of dispersant required for the preparation of composites was assumed to be the least amount that required for the individual monolithic ceramics to disperse simultaneously. As shown in Fig. 2, this minimum amount was taken as 0.10 wt%.

3.2. Powder density

In order to obtain the powder densities of the prepared green composites, remnants of the cast samples from each batches were ground, sieved and ovendried at 110°C for 48 h prior to cooling in a dessicator to room temperature. Density of the powder was measured by a pycnometer using 99.99% helium gas in order to obtained an accurate result. The obtained pycno-density of these powders were also compared with the expected theoretical densities calculated from a simple mixture rule (see Equation 1) and are presented in Fig. 3.

$$\left(\frac{\text{vol\% Al}_2\text{O}_3}{100}\times 3.96\right)+\left(\frac{\text{vol\% (Y-TZP)}}{100}\times 5.73\right) \tag{1}$$

As can be noted from Fig. 3, a good correlation was obtained between the measured pycno-density and calculated powder density. Therefore, it can be inferred that the formulation and steps employed to prepare the composites in the present work is consistent. Also, from Fig. 3 it can be noted that the density of the powder composite increase with increasing Y-TZP content in the system. This was expected due to the higher density of the starting Y-TZP powder (i.e. 5.73) if compared to alumina (i.e. 3.96).

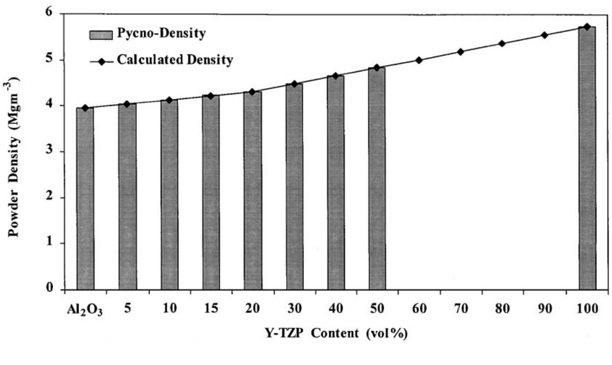

Figure 3 Comparison between the measured powder density (Pycnodensity) and the calculated density with respect to vol% Y-TZP in formulation.

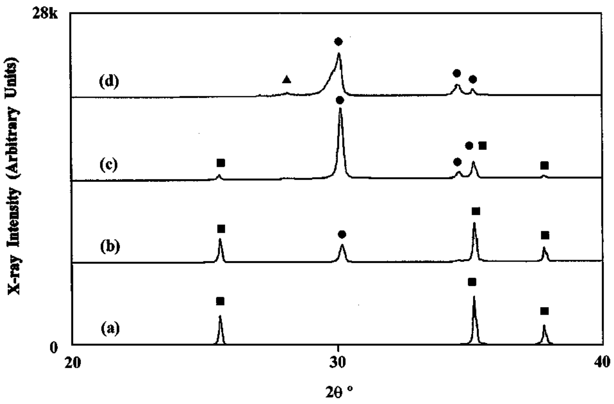

Figure 4 Typical room temperature XRD profile of slip-cast samples sintered at 1450°C: (a) 0 vol% Y-TZP (100 vol% Al_2O_3); (b) 5 vol% Y-TZP; (c) 50 vol% Y-TZP and (d) 100 vol% Y-TZP (0 vol% Al_2O_3). The peaks have been identified as (■) α-Al_2O_3, (▲) m-ZrO_2 and (●) t-ZrO_2.

3.3. Phase analysis

Typical room-temperature XRD patterns of the slip-cast Al_2O_3–Y-TZP composites sintered at 1450°C are presented in Fig. 4. Similar XRD profiles were obtained for composites sintered at 1500°C, 1550°C and 1600°C. Only X-ray spectra corresponding to tetragonal zirconia and Al_2O_3 were detected in the composite system. Secondary phases resulting from possible reaction between Al_2O_3 and ZrO_2 or between Al_2O_3 and Y_2O_3 were not observed.

The general observation is that the relevant peaks of Al_2O_3 decreased with a concomitant increased in the intensity of the tetragonal peaks as the Y-TZP content in the matrix increased. The XRD spectrum corresponding to the monoclinic phase was only observed in all the monolithic slip-cast Y-TZPs.

The retention of tetragonal phase as a secondary phase in the zirconia matrix at room temperature has been well documented by Lange *et al.* [25, 26]. According to Lange *et al.*, the phase transformation from tetragonal to monoclinic symmetry is controlled by a critical grain size (d_c) phenomenon, i.e. above which spontaneously phase transformation would occur. Lange *et al.* also further explained that d_c is related to the matrix constraint i.e. the stiffness of the system. In general, the higher the total stiffness of the matrix, the larger would be the d_c. Since stiffness is a measure of elastic modulus and the elastic modulus of alumina (~400 GPa) is approximately twice that of zirconia (~200 GPa), it can be inferred that the amount of tetragonal phase retention at room temperature would decrease with increasing zirconia addition in the matrix due to the reduction in the total stiffness of the matrix.

In the present work, although the amount of monoclinic phase detected in all the monolithic slip-cast Y-TZP samples were small (~5 to 7%), the existence of d_c is not ruled out. It has been reported elsewhere [4] that for other commercial Y-TZP ceramics, a critical

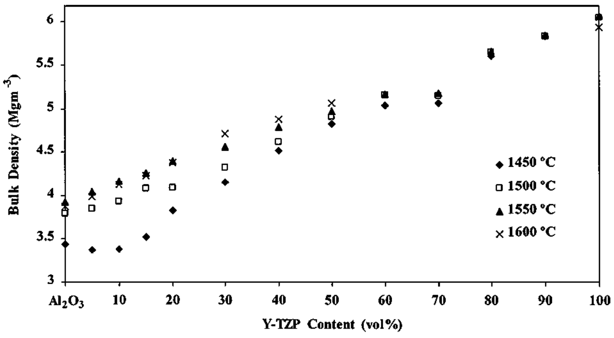

Figure 5 The effects of sintering temperature and zirconia content on the bulk density of the composite system.

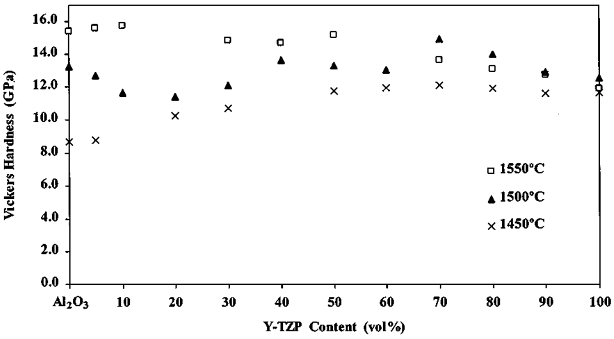

Figure 6 Room temperature Vickers hardness variations of Al_2O_3–Y-TZP ceramics composite. (Indentation load = 10 N).

grain size does exist and varied according to the history of the starting material [27].

3.4. Sintered bulk density

The sintered bulk density of the Al_2O_3–Y-TZP composites are shown in Fig. 5. The general trend, which can be observed from Fig. 5, is that the bulk density increases with sintering temperature and Y-TZP content. Also, it is surprising to note that regardless of sintering temperature the bulk densities remained constant ∼5–5.1 Mg m^{-3} for all samples containing 60–70 vol% Y-TZP content. As for the composites containing up to 10 vol% Y-TZP and sintered at 1450°C, no improvement in bulk density was observed. However, the bulk density of these samples started to increase with further addition of Y-TZP above 15 vol% as shown in Fig. 5.

The bulk densities of the monolithic slip-cast ceramics are given in Table II. In general, the bulk density of the Y-TZP ceramics was relatively high (>6 Mg m^{-3}) and did not change significantly when sintered between 1450°C–1550°C. However, a lower bulk density value was obtained for Y-TZP samples sintered at 1600°C (see Table II). On the other hand, the bulk density of the alumina ceramics increased to a maximum value of 3.93 Mg m^{-3} when sintered at 1550°C. In both the slip-cast materials, maximum density was attained for samples sintered at 1550°C, see Table II. The decreased in bulk density in both ceramics when sintered at 1600°C could be related to grain growth and the formation of porosity, which will be discuss later.

3.5. Vickers hardness

The room-temperature Vickers microhardness of the materials sintered at 1450°C, 1500°C and 1550°C, as a function of zirconia content are shown in Fig. 6. The hardness of the composites sintered at 1600°C could not be measured due to the high amount of porosity (see Fig. 7), thus making it difficult to measure the indent diagonals. The presence of porosity in Al_2O_3 samples sintered at 1600°C is also the reason for the decrease in bulk density as given in Table II. This intergranular porosity (Fig. 7) were also observed in other slip-cast Al_2O_3 ceramics fired at lower temperatures. In contrast, the additions of Y-TZP to Al_2O_3 in the composite system was beneficial in suppressing porosity and promoting densification when sintered at 1600°C, see Fig. 5 and Fig. 8.

TABLE II Bulk density (Mg m^{-3}) of the monolithic slip-cast ceramics

Sintered temperature (°C)	1450	1500	1550	1600
Y-TZP	6.06	6.05	6.08	5.95
Alumina	3.44	3.79	3.93	3.87

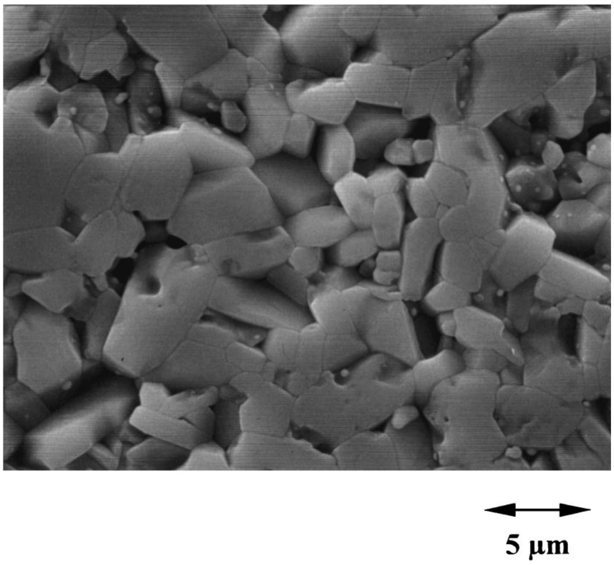

Figure 7 SEM micrograph of sintered (1600°C) slip-cast alumina ceramics showing the presence of intergranular porosity.

However from Fig. 6, it can be noted that the hardness of the composites increased with increasing Y-TZP content for samples sintered at 1450°C. In contrast, an opposite trend was observed for composites sintered at 1550°C. It can also be noted from Fig. 6, that for the 1550°C sintered composites, the addition of up to 10 vol% Y-TZP content were beneficial in improving the hardness when compared to the monolithic alumina ceramics i.e. the measured hardnesses were 16 GPa for composite containing 10 vol% Y-TZP content and 15.2 GPa for the monolithic slip-cast alumina.

For composites sintered at 1500°C and containing up to 60 vol% Y-TZP, the hardness were observed to fluctuate between 11 to 13 GPa before reaching a maximum

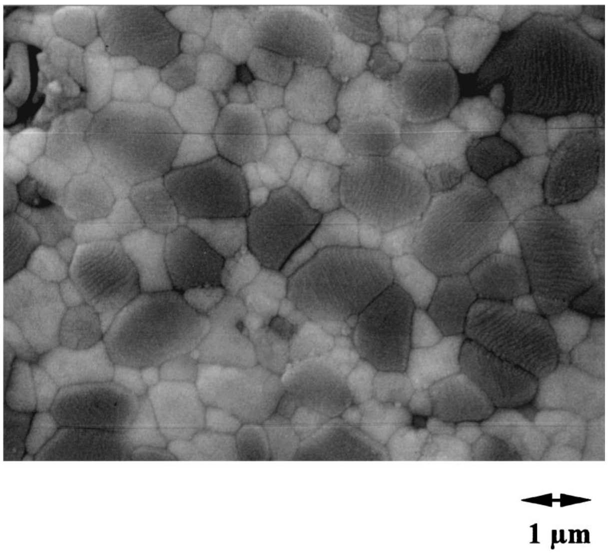

Figure 8 SEM micrograph of sintered (1600°C) composite containing 50 vol% Y-TZP showing low levels of residue porosity. Dark phase is the Al_2O_3 and the light phase is (t)-ZrO_2.

value of 15 GPa for composite containing 70 vol% Y-TZP. However, >70 vol% Y-TZP and regardless of sintering temperature, the hardness of all samples exhibited a similar trend i.e. the hardness decreased with further additions of Y-TZP, see Fig. 6.

As for the monolithic alumina ceramics, the hardness value increased by almost two fold when sintered at 1550°C if compared to the hardness of samples sintered at 1450°C (see Fig. 6). In the case of the monolithic Y-TZP ceramics, the sintering temperature had negligible effect on the hardness as shown in Fig. 6. However, the measured hardness of the Y-TZP ceramics ($\sim$12 GPa) is lower than the alumina ceramics sintered at 1550°C ($\sim$16 GPa).

3.6. Microstructural evolution

Typical sintered (1450°C and 1550°C) microstructures of the monolithic alumina ceramics, the composites containing 5 and 50 vol% Y-TZP content and the monolithic Y-TZP ceramics are presented in Figs 9–11 respectively.

A distinct observation which can be made from Figs 8 and 10, is that the addition of Y-TZP resulted in an equiaxed grain structure comprising mainly of tetragonal zirconia and alumina grains. Also, it should be noted from Figs 9 and 10 that the presence of Y-TZP significantly affects the growth of Al_2O_3 grains in the composite system, i.e. increasing Y-TZP content reduces the size of the Al_2O_3 grains throughout the sintering regime employed, see Table III. In addition, increasing the firing temperature from 1450°C to 1600°C also have a pronounced effect on the rate of grain growth. The Al_2O_3 grain sizes were observed to increase with decreasing Y-TZP content and increasing sintering temperature. The presence of some abnormal large Al_2O_3 grains (>3 μm) was noted mainly in the monolithic slip-cast alumina samples when sintered at 1600°C.

In general, the addition of 50 vol% Y-TZP was found to be effective in suppressing Al_2O_3 grain growth regardless of sintering temperature, see Table III. It is also evident from Figs 8 and 10, that the distribution of secondary phase is uniform and the (t)-ZrO_2 grain sizes in the composite system are approximately the same as the tetragonal grain sizes measured in the monolithic Y-TZP ceramics sintered at the respective temperature (see Figs 10 and 11).

TABLE III The effect of Y-TZP content and sintering temperature on the average grain sizes

Y-TZP (vol%)	Average Al_2O_3 grain size (μm)			
	1450°C	1500°C	1550°C	1600°C
0	0.82	1.48	1.62	2.60
5	0.72	1.16	1.40	2.36
50	0.56	1.00	1.15	1.20
	Average (t)-ZrO_2 grain size (μm)			
100	0.43	0.46	0.48	0.64

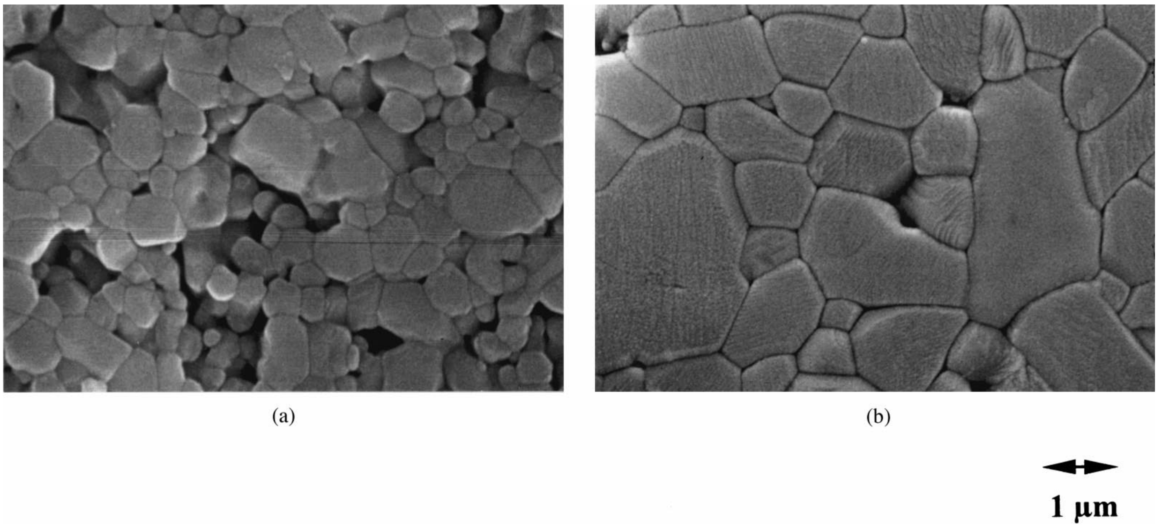
(a)
(b)

Figure 9 SEM micrograph of typical sintered microstructures of slip-cast monolithic Al_2O_3 ceramics. (a) Sintered at 1450°C—showing high degree of porosity and (b) Sintered at 1550°C—exhibiting a dense microstructure with less pronounced residue porosity.

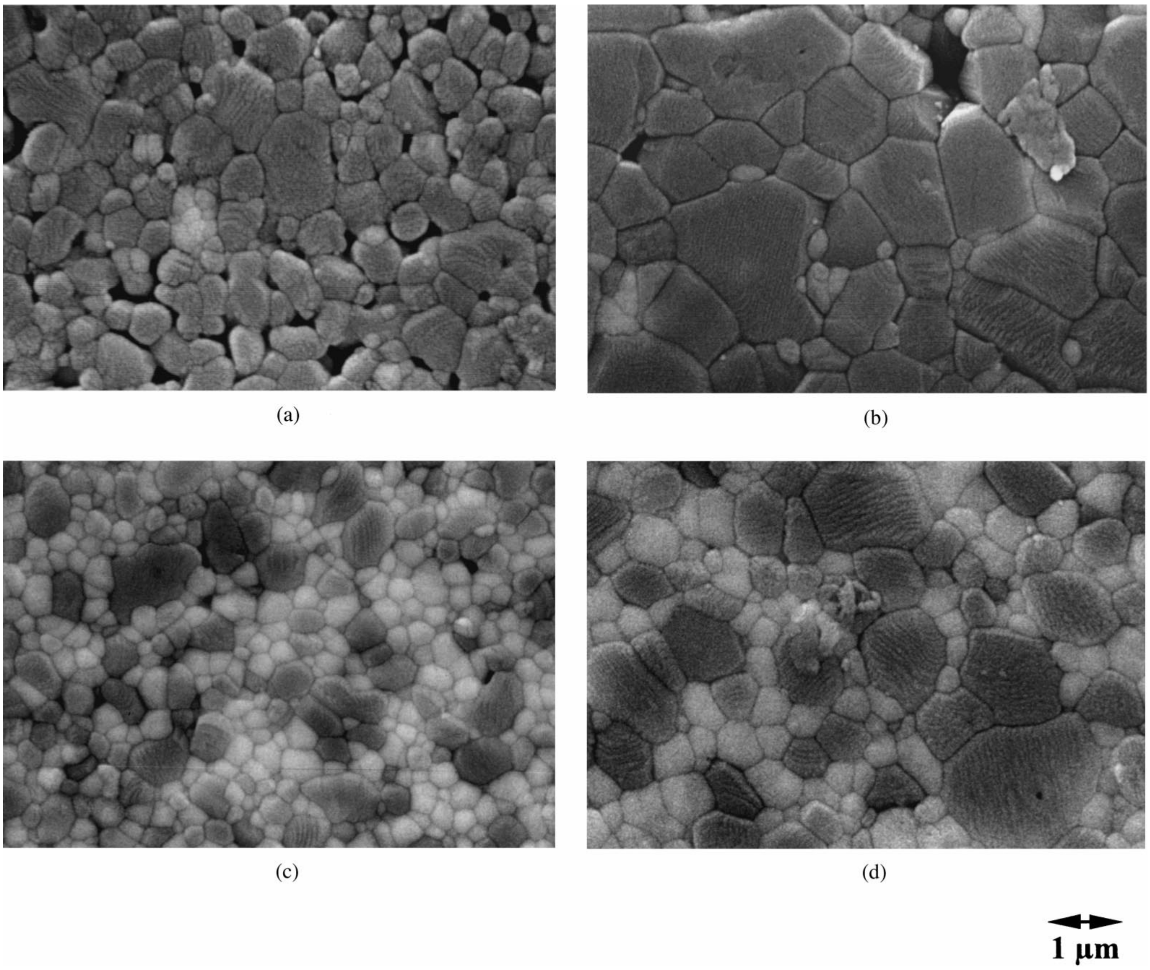
(a) (b) (c) (d)

Figure 10 SEM micrograph of composites sintered at 1450°C (a & c) and 1550°C (b & d). Samples (a) & (b) contained 5 vol% Y-TZP while (c) & (d) composed of 50 vol% Y-TZP, as the dispersion phase. Note that the additions of Y-TZP was beneficial in suppressing Al_2O_3 grain growth.

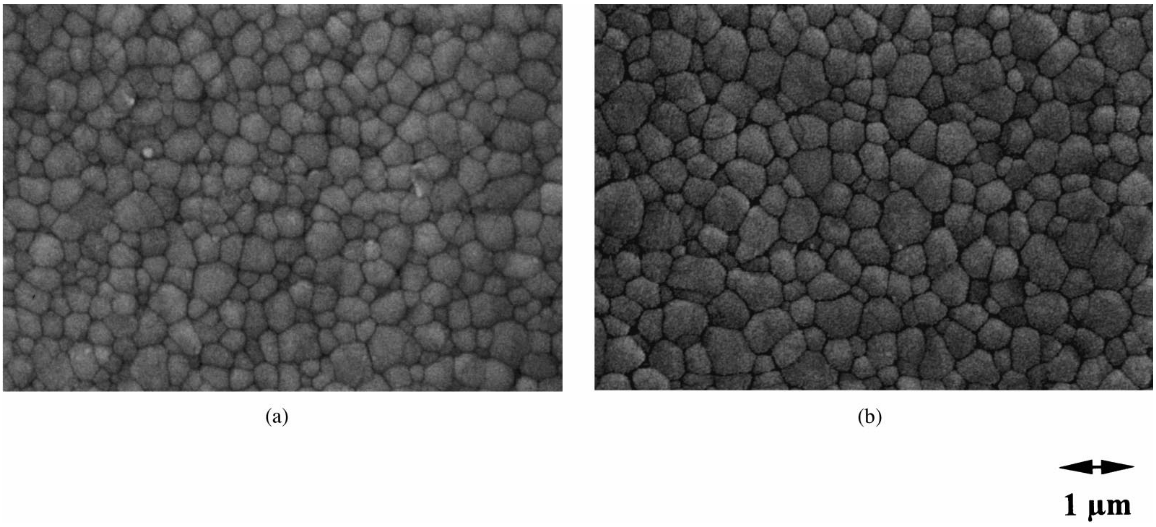
(a) (b)

Figure 11 Microstructural evolution of slip-cast monolithic Y-TZP ceramics sintered at (a) 1450°C and (b) 1550°C. Note the homogeneous distribution of fine equiaxed (t) grains.

4. Conclusions

1. In the present work, it has been found that slip-casting can be employed to fabricate a well dispersed and homogeneous composite consisting of Y-TZP additions in varying amounts to alumina.

2. A consistent and homogeneous slip can be achieved by using a solid to water ratio of 45 : 55 with 0.10 wt% polyacrylate as dispersant.

3. The characteristics and properties of slip-cast composites were dependent on the firing temperature and the amount of Y-TZP additions. One of the consequences of increasing the zirconia content was the reduction in the alumina grain size.

4. Regardless of sintering temperature, the bulk density of the composites were found to increased with increasing Y-TZP content. In general, the measured bulk

density in the composite system is directly proportional to the amount of tetragonal phase retained in the system.

5. The decreased in bulk density with increasing sintering temperature $>1550^\circ$C in both the slip-cast monolithic ceramics was attributed to grain growth phenomenon and residue porosity found mainly in the Al_2O_3 ceramics.

6. The hardness of the composites containing <60 vol% Y-TZP content was generally higher (>15 GPa) when sintered at 1550°C if compared to other ceramics tested in the present work.

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