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Net-shape forming of ZrO_2-based ceramics and the effect of shaping process on superplastic deformation

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In this study, a slip casting method was used for the production of tensile specimens for superplastic deformation from zirconia powders containing 3 and 8 mol% yttria. It was seen that the slip casting process allowed the production of complex, net-shape and economical production of a relatively small number of individual shapes. The factors affecting the casting characteristic of the slip system, namely, solid content, slip viscosity, dispersing agent concentration and moulding conditions were investigated and optimum values for the above were determined. The effect of shaping process on superplastic deformation was also investigated for slip-cast and die-pressed specimens. It was seen that superplastic ductility obtained from slip-cast specimen was higher than that of die-pressed one. The reason for ductility enhancement was due to the homogeneous dispersion of the powder and elimination of agglomerates in slip-cast specimen, compared to die-pressed specimen in which agglomeration caused non-homogeneous sintering leaving crack-like voids responsible for early fracture.

1. Introduction

Ceramic components are hard to cut and machine, because of their high hardness, requiring extensive use of high-priced diamond cutting tools, and the processes are also time consuming. It is evident that machining of parts accounts for 40 to 60 percent of the total cost and this ratio may go even higher under some conditions of product shape and dimensional accuracy [1]. The key to reducing production cost, which is a large factor in making ceramics viable for practical use, lies in reducing the amount of machining. Therefore the forming process is required to give products a shape as close as possible to that of the final product (net-shape).

Slip casting offers many possibilities and even some advantages over some other methods. First, a wide variety of particle size distribution can be slip cast into test samples. second, tooling is relatively inexpensive, often costing much less than equivalent injection moulding tooling. Third, the process is more readily adaptable to larger shapes. Finally, it is possible to produce near-net shape parts [2].

In the literature, most of specimens for superplastic deformation were produced by uniaxial and isostatic pressing followed by sintering and machinig [3, 4]. However, the high cost of these processes are a disadvantage for industrial application and the subsequent machining of specimens from blanks usually represents a considerable fraction of the total cost of specimen preparation.

In the present study, a slip casting method has been used as a net shape forming technique to produce sound and defect-free bodies. The casting behaviour and rheological properties of slips have been studied in order to determine the optimum conditions under which the ceramic powders can be easily cast for preparation of superplastic tensile specimens. The effect of shaping process on superplastic deformation was also investigated for slip-cast and die-pressed specimens.

2. Experimental procedures

The materials used were fine-grained 3 mol% yttria-stabilized tetragonal zirconia (3Y-TZP) and fine-grained 8 mol% yttria-stabilized cubic zirconia (8Y-CSZ); both powders were supplied by Mandoval Ltd. Zirconia Sales (U.K.) Ltd. The average particle sizes were 0.2 μm for 3Y-TZP and 0.3 μm for 8Y-CSZ. The chemical compositions are listed in Table I.

Distilled water and surfactant (Dispex A40, supplied by Allied Colloids U.K) were used for enhancing

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TABLE I Chemical composition of the powders

	Composition in wt%							
Materials	$ZrO_2(+HfO_2)$	Y_2O_3	Al_2O_3	SiO_2	TiO_2	Fe_2O_3	Na_2O	CaO
3Y-TZP	93.8	5.4	0.25	0.11	0.12	0.003	0.02	0.06
8Y-CSZ	85.9	13.6	0.25	0.1	0.10	0.003	0.01	0.02

dispersion of the powders in slip. The ball milling procedures were carried out using plastic containers and zirconia balls. A Synchro-Lectric viscometer was used for viscosity measurements. A batch of specimens were also prepared by die-pressing at 40 MPa. The green density of the slip-cast and the die-pressed specimens was measured from the volume and weight. The density of sintered specimens was determined by the Archimedes method.

High temperature uniaxial tensile tests were carried out in air using an Instron 4505 testing machine. A single zone vertical split furnace (supplied by Carbolite Furnaces Ltd.) with molybdenum disilicide elements was mounted on the crosshead of the test frame; tensile load was applied using high density sintered alumina rods in a pin loading mechanism. Careful specimen alignment was essential to avoid fracture on loading. After achieving the desired (uniform) test temperature, usually at a heating rate of 423 K/h, the assembly was held at that temperature for ~10 minutes. A small tensile load was then applied on the specimen as a preload and the aligment checked before testing. Deformation was continuously monitored using a computerized system equipped with a data acquisition facility that allowed tests to be controlled under a constant strain rate.

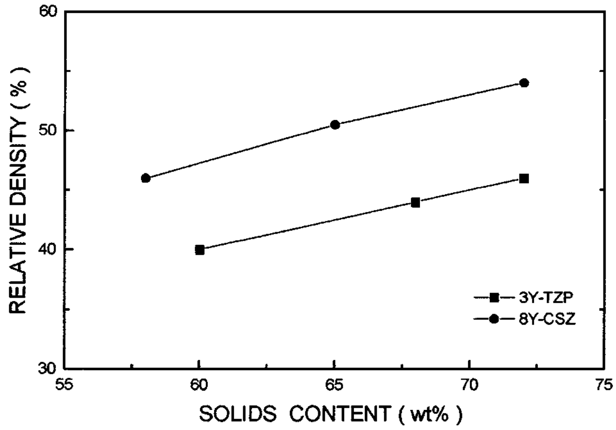

Figure 1 Relative density of slip-cast specimens versus solid content in the experimental mixtures.

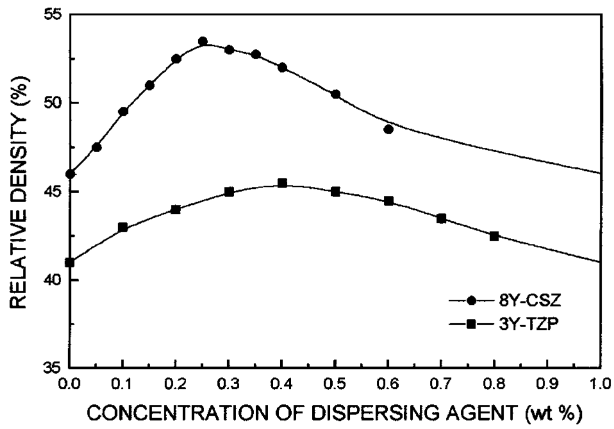

Figure 2 Relative density of slip-cast specimens versus dispersing agent concentration in the experimental mixtures.

3. Experimental results

3.1. Specimen preparation by slip casting

3.1.1. Determination of solid content and dispersing agent concentration

To determine the optimal solid content for the powders, a suspension containing various amounts of powder in aqueous solution was prepared. A few drops of ammonium salt was used as a dispersing agent. The suspension was placed in a plastic container with zirconia balls and milled for 4 hours to achieve good dispersion. The suspension was then cast in a plaster mould and kept until sufficient set was achieved. For the determination of optimal concentration of the dispersing agent (varying from 0.0 to 1 wt%), a fixed solid content was used with 72 wt% for 3Y-TZP and 8Y-CSZ. Similarly, the suspension was cast as described above.

After slip-casting, the specimens had sufficient set and were removed from the moulds and dried overnight at room temperature. The green density of the cast specimens was determined from volume and weight measurements. Figs 1 and 2 show the relative density change with solid content and dispersing agent concentration, respectively.

3.1.2. The main steps in slip casting

3.1.2.1. Slurry preparation. A typical slurry was prepared by dispersing the appropriate powder (3Y-TZP, 8Y-CSZ) in distilled water with a dispersing agent. Table II shows the optimum solid contents and dispersing agent concentrations. The slurry was ball milled for 4 hours for 3Y-TZP and 8Y-CSZ to obtain a good dispersion. The milled slurry was filtered into a beaker to separate the zirconia balls and the slurry was then allowed to settle for 1 day for 3Y-TZP and 2 days for 8Y-CSZ. After that, the sediment was discarded and the slurry was used for casting.

3.1.2.2. Slurry casting. The slurries prepared as described in Section (i) were injected by a syringe into a plaster moulds, that allowed the liquid fraction of the slurry to be absorbed by the mould. The mould assembly used for the slip-casting has been given elsewhere [5]. The time of the mould release was an important experimental variable that depended on rheological conditions such as viscosity, milling time

TABLE II Optimum parameters for slip casting

Powders	Solid cont. (wt%)	Dispersing agent con. (wt%)	Mould release time (min.)	Grain size (μm)
3Y-TZP	72	0.4	24	0.2
8Y-CSZ	72	0.25	7	0.3

(Table II). Also, the mould conditions such as surface smoothness and mould temperature had an important effect on obtaining sound green specimens. To obtain green specimens with a good surface finish, the mould surfaces were ground to achieve smooth surface using 240 grinding paper. After casting, the specimens were carefully removed from the mould and dried at room temperature overnight.

3.2. Specimen preparation by die-pressing

To see the effect of shaping process on superplastic deformation, a small number of specimens were also produced by die-pressing from 3Y-TZP powder. The powders were compacted in a steel die into tensile specimen shape at a pressure of 40 MPa, followed by sintering at temperature of 1650 K for 1 hour.

3.3. Densification

Prior to densification, green specimens were presintered at 1123 K to make them handlable and obtain smooth surfaces by grinding off the casting protrusions and rough surfaces. All specimens were pressureless sintered in air at a heating rate of 473 K/h. It was found that densities greater than 95% of the theoretical value could easily be achieved by pressureless sintering. After sintering, it was seen that the dimensions of the sintered specimens varied with composition due mainly to differences in green densities. A plot of percentage of theoretical density versus sintering temperature is shown in Fig. 3. It is seen from Fig. 3 that for 8Y-CSZ a maximum density of 99% was obtained at 1773 K whereas the same density for 3Y-TZP was achieved at 1650 K.

3.4. The effect of shaping process on superplastic deformation

To determine the effect of shaping process on superplastic deformation in 3Y-TZP, tensile specimens, prepared by the production processes of die-pressing and slip casting, superplasticaly tested to failure at temperature of 1773 K and at strain rate of 1.10^{-4} s^{-1}. Fig. 4 shows the profiles of specimens, produced by two shaping processes. The higher ductility is clearly visible in specimen c and there was no evidence of necking within the gauge length of any of the deformed specimens. An elongation to failure of 390% was achieved from the slip-cast specimen, compared to the elongation to failure of 300% obtained from the die-pressed specimen. The true stress, true strain curves of 3Y-TZP specimens prepared by two shaping processes are shown in Fig. 5. The general characteristic of these curves are that after an initial strain hardening region, the flow stress reached a peak, then the stress decreased slowly until final fracture.

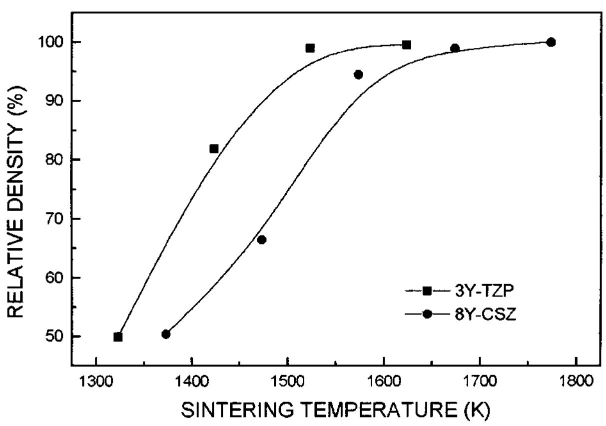

Figure 3 Relative density versus sintering temperature.

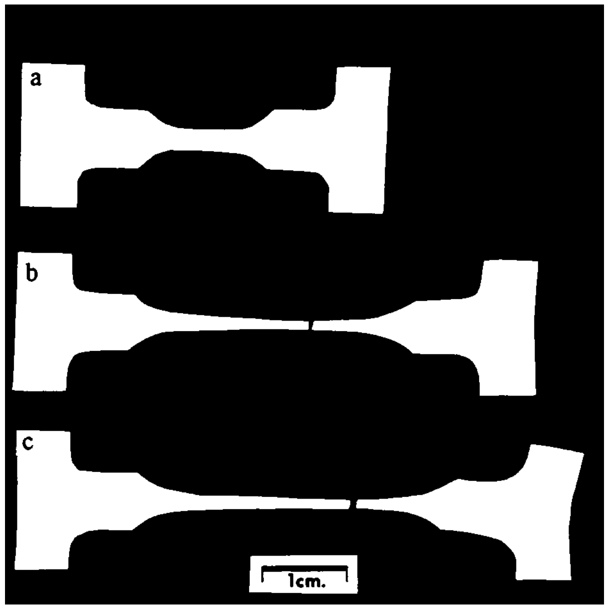

Figure 4 Specimen profiles of 3Y-TZP deformed at 1773 K and 1.10^{-4} s^{-1} a) undeformed specimen, b) specimen prepared by die-pressing $e_f = 300\%$, c) specimen prepared by slip-casting, $e_f = 390\%$.

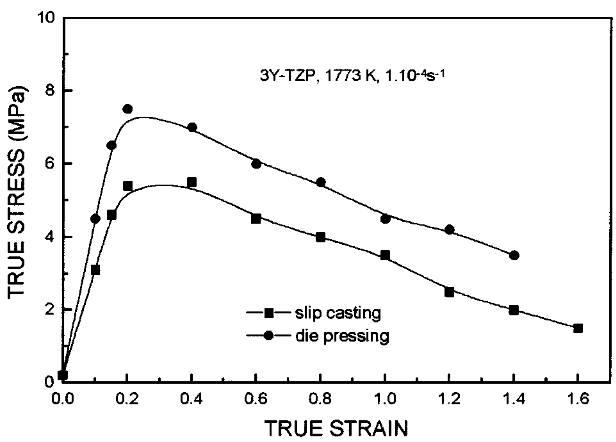

Figure 5 True stress-true strain relationships of 3Y-TZP prepared by two shaping processes and tested at 1773 K and 1.10^{-4} s^{-1}.

4. Discussion

In the present study, a slip casting method has been used as a net shape forming technique to produce sound and defect-free bodies. The casting behaviour and rheological properties of slips have been studied in order to determine the optimum conditions under which the ceramic powders can be easily cast for preparation of superplastic tensile specimens. The ceramic powders used were castable under limited conditions. Relationship between the relative density of the cast specimens and the solid content was shown in Fig. 1. The relative density increased linearly in all powder mixtures with increasing solid content. Aqueous suspensions with solid contents of 72 wt% for 3Y-TZP and 8Y-CSZ could easily be cast, but suspensions exceeding these solid contents were very difficult to cast. This is because the state of a particular dispersion is affected mainly by the suspension solid loading. The viscosity of the suspensions increases rapidly when the weight percent of solid in the suspension is increased beyond these critical values and the suspension shows pseudoplastic behaviour. Aqueous suspensions below these critical values have low viscosity and Newtonian flow behaviour. The Newtonian flow behaviour observed is characteristic of suspensions in which particle-particle electrostatic repulsive forces are large [6].

In addition to the solid content, dispersing agent concentration is also important in determining the green density and viscosity of the slip. This can be seen in Figs 2 and 6. Generally, the lowest viscosity is required in order to achieve a high green density [7]. As seen in Fig. 6, the optimum dispersing agent concentrations are 0.4 wt% for 3Y-TZP and 0.25 wt% for 8Y-CSZ, corresponding to the minimum viscosity. For the lower amounts of dispersing agent, electrical charges are present at the surface of the particles and the repulsive forces are ineffective. On the other hand, when the dispersing agent concentrations become too high, the ionic strength increases, the electrostatic repulsion energy decreases, and as a result flocculation takes places [6].

In order to achieve full densification during sintering, grain growth has to be suppressed. Experience with zirconia systems has provided ample evidence that the grain size of the cubic phase is much larger than that of the tetragonal phase, suggesting the possibility of a lower sintered density in the cubic phase regime [8]. This fact is in accord with the density data for the alloys; greater than 99% of theoretical density in 3Y-TZP and about 97% in 8Y-CSZ at 1623 K.

Besides the advantages of the slip casting method, a further important effect seen in the present work was the elimination of agglomerates; the agglomerates often shrink away from the surrounding powder matrix during sintering causing crack-like voids responsible for early fracture and leaving big pores in the microstructure after sintering. To demonstrate this, two sets of specimen were prepared by the production processes of die-pressing and slip casting from 3Y-TZP. For the die-pressing tests, the powder was die-pressed into pellets under a compaction pressure of 20 MPa. The same size pellets were slip cast for comparison. Samples obtained by these processes were then sintered at a heating rate of 473 K/hr. Fig. 7 shows the sintering curves of 3Y-TZP, prepared by two shaping processes. Samples processed by slip casting had a faster sintering rate and lower temperatures and the optimum sintering temperature was lower than that of the die-pressed one. In particular, the former achieved a density of 99% of its theoretical value at 1623 K, while the latter reached the same value at 1650 K. The reason is probably due to the fact that die-pressing yields less efficient packing of the powder, and larger pores than slip casting; these features are known to retard effective sintering. Similar observations have been recorded by Xue and Chen [9] showing the superiority of slip casting, compared to die-pressing for Al_2O_3 and also by Wang [10] on 3Y-TZP and CuO doped Al_2O_3.

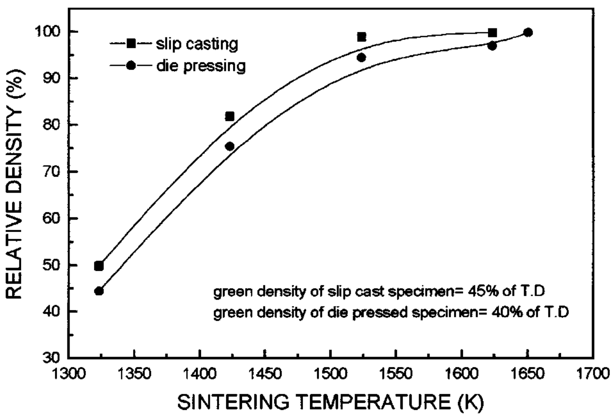

Figure 7 Sintering curves of 3Y-TZP specimens prepared by slip-casting and die-pressing.

Enhancement of superplastic ductility in zirconia ceramics has been considered to be due to a number of contributing factors, including the presence of a low viscosity grain boundary (glassy) phase or doping with transition metal oxides. These additives possibly act in a multiple role as sintering aids, grain growth inhibitors and modifiers of grain boundary strength and grain boundary chemistry. Conventionally, reducing the strain rate or increasing the test temperature (but necessarily avoiding grain growth) also promotes larger elongations at lower stress levels [11–17]. All these methods contribute to higher elongations at relatively lower stress levels. High deformation rates, high ductility and low forming temperatures are primary requirements for industrial applications of superplastic ceramics. In the present study, it was seen that the shaping process is also important to enhance the superplastic ductility. Superplastic ductility obtained from slip-cast specimen was higher than that of die-pressed one. The reason for ductility enhancement was due to the homogeneous dispersion of powder and elimination of agglomerates

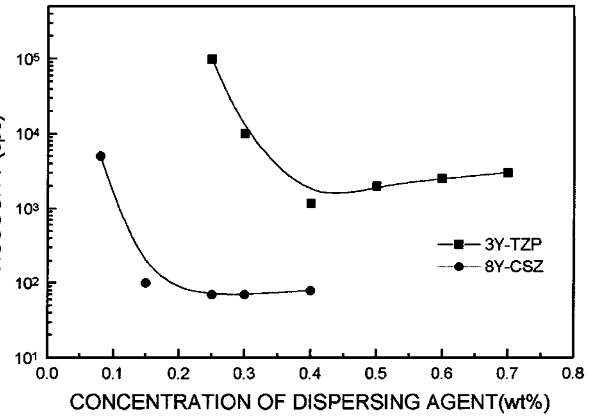

Figure 6 Variation of viscosity of slip as a function of concentration of dispersing agent.

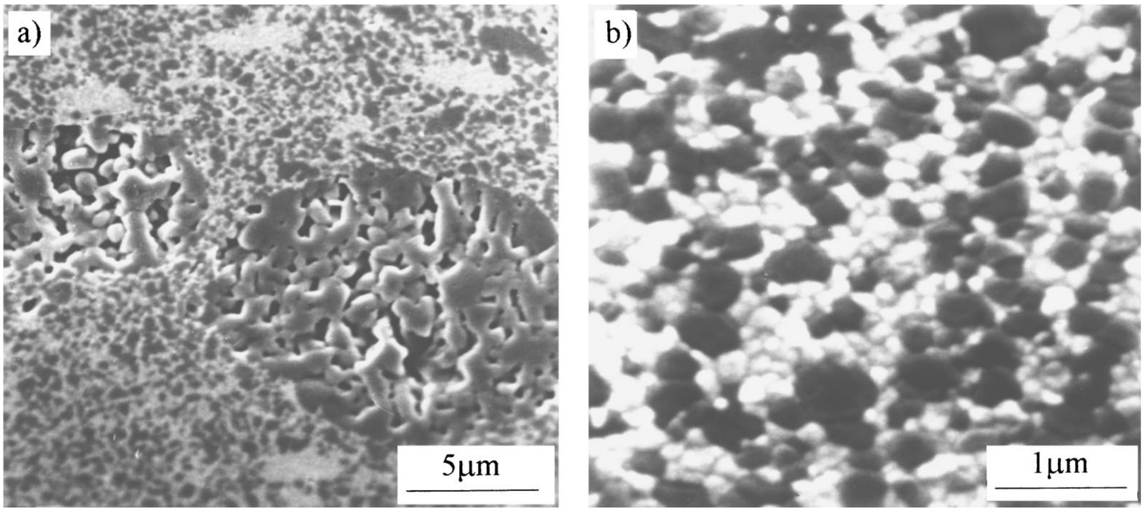

Figure 8 Micrographs showing the effect of processing route on the agglomeration of 3Y-TZP containing 60 wt% Al_2O_3, a) specimen prepared by die-pressing and b) specimen prepared by slip-casting [18].

in slip-cast specimen, compared to die-pressed specimen in which agglomeration caused non-homogeneous sintering leaving crack-like voids responsible for early fracture (Fig. 8).

5. Conclusions

1) A slip casting method was used as a net shape forming technique to produce sound and defect-free superplastic tensile specimens. From the results achieved it is apparent that slip casting is feasible provided that the casting behaviour and rheological properties of the slip are chosen to obtain optimum casting conditions. The most important processing parameters are the concentrations of solid particles and dispersing agent.

Aqueous suspensions with solid contents of 72 wt% for 3Y-TZP and 8Y-CSZ gave good castable behaviour and low viscosities. To achieve low viscosities with this solid concentration in aqueous suspension, the dispersing agent concentrations were also carefully chosen. These were 0.4 wt% for 3Y-TZP and 0.25 wt% for 8Y-CSZ. The subsequent densifying process involved pressureless sintering which gave specimens with a good surface finish without visible cracks and with densities in the range of 95 to < 99.99% theoretical density.

2) It was seen that for 8Y-CSZ a maximum density of 99% was obtained at 1773 K whereas the same density for 3Y-TZP was achieved at 1650 K. This different sinterebility behaviour for 8Y-CSZ and 3Y-TZP arise from severe grain growth in cubic phase regime (in 8Y-CSZ), whereas at high sintering temperatures, tetragonal phase (in 3Y-TZP) was stable and grain growth was very sluggish.

3) It has been demonstrated that shaping process is also important to enhance the superplastic ductility. The elongation to failure of 390% was achieved from the slip-cast specimen, whereas, at the same test conditions, the elongation to failure of 300% obtained from the die-pressed specimen. Lower superplastic ductility in die-pressed specimen resulted by the presence of agglomeration which caused non-homogenous sintering leaving crack-like voids responsible for early fracture.

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