Sintering and characterisation of nano-sized yttria-stabilised zirconia

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Abstract: Two types of commercially available nano-sized, ZrO_2 – 3mol%Y_2O_3 (Y-Tetragonal Zirconia Polycrystals (TZP)) powders were investigated. BET surface area analysis showed the powders to be nano-sized as determined using Equivalent Spherical Diameter (ESD_{BET}) theory. Dilatometry analysis showed that one of the powders underwent complete shrinkage during isothermal sintering; the other did not. The point of maximum densification rate for the powders differed by approximately 100°C. A dramatic expansion associated with the tetragonal to monoclinic transformation was observed by dilatometry for unstabilised zirconia, but not for TZP samples. X-ray diffraction showed that the starting TZP powders contained some monoclinic zirconia, but confirmed that discs sintered from this powder were wholly tetragonal. For one powder type, the fracture toughness of discs decreased almost linearly with increasing sintering temperature, whereas for the other the fracture toughness was relatively stable across the temperature range. Two-step sintering enabled a maximum fracture toughness of 6.12 MPa $m^{1/2}$ to be achieved.

Keywords: yttria-stabilised zirconia; sintering; density.

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1 Introduction

Yttria-stabilised, zirconia-based ceramics can yield sintered parts with excellent mechanical properties. Refractory and chemical durability properties have broadened their potential to include high temperature chemistry and ceramic biomaterial applications (Basu et al., 2004a; Esquivias et al., 1998; Lu and Chen, 1987; Piconi and Macauro, 1991). As tetragonal zirconia possesses high strength, high toughness and good wear resistance over a wide temperature range, a key aim in zirconia research is to exploit the transformability of tetragonal ZrO_2 phase at room temperature (Kimel and Adair, 2002). The fraction of *T*-phase retained at room temperature is dependent on the size of the grains, on stabiliser content, on environmental conditions and on the degree of constraint exerted on the grains by the matrix (Bartolomé et al., 2004; Hirvonen et al., 2006; Lange, 1986; Tsubakino and Matsuura, 2002). In the zirconia-yttria system, tetragonal-only phase ceramics known as Tetragonal Zirconia Polycrystals (TZP) can be obtained. Y-TZP materials, containing approximately 2–3% mol Y_2O_3, are completely constituted by tetragonal grains with sizes of the order of hundreds of nanometres (Piconi and Macauro, 1991). The metastability of the tetragonal phase means that high toughness can be achieved via stress-induced transformation toughening.

Rieth et al. was the first to obtain ceramics at room temperature with a tetragonal only phase, using the ZrO_2-Y_2O_3 system (Rieth et al., 1976). This research was subsequently followed up by Gupta et al. (1978). Polycrystalline TZP materials are generally fabricated from coprecipated powders, that is, ZrO_2 plus the alloying addition. These powders are in the size range of 10–200 nm. Depending on the reactive nature of powders as well as the form of the phase equilibria, firing is conducted in the range 1300–1500°C for Y-TZP. The final grain size after fabrication is ~0.5–2 μm, depending on sintering temperature, hold time and stabiliser content (Hannink et al., 2000). Fracture toughness of 2.5–14 MPa $m^{1/2}$ with hardness of 11–13.5 GPa have been reported for TZP's when sintering took place in the temperature range 1400–1500°C (Basu et al., 2004a,b; Chung et al., 1997; Cutler et al., 1992; Pedzich and Wajler, 2006; Zhao et al., 1998).

In early stages of development of TZP ceramics, high densities were difficult to achieve within a reasonable sintering time because of using low sintering temperature. To overcome the low-density problems, Hot Isostatic Pressing (HIP) has become a popular technique to increase density without excessive grain growth (Basu et al., 2004a,b; Cutler et al., 1992). More recently, high-quality nano-powders have become available which enable densities >98% of theoretical to be achieved at 1400°C, with a resulting grain size <0.5 μm (Bartolomé et al., 2004; Chung et al., 1997; Xu et al., 2004a,b). Basu reported fully dense sintered ceramics, by hot pressing for 1 hr at 1450°C (Basu et al., 2004a).

Esquivias et al. reported a sintering schedule that gave the smallest grain size (average grain size <300 nm) in their characterisation of 5 mol% yttria doped zirconia powder (Esquivias et al., 1998). This involved heating at 5°C/min upto 1100°C and then at 1°C/min upto 1400°C and holding at this temperature for 2 hr. Duran et al. prepared Y-TZP (3 mol% Y_2O_3) having crystalline size of 6 nm by a chemical coprecipitation method (Duran et al., 1997). Using this powder it was possible to achieve fully dense bodies with 80 nm grain size by pressureless sintering at a temperature as low as 1000°C for 2 hr. Ran et al. used both 0.8 mol%-CuO doped 3Y-TZP and undoped 3Y-TZP and studied their sintering behaviour in air where they heated the sample at a rate of 2°C/m, held for 2 hr at 1400°C and finally cooled at 4°C/min (Ran et al., 2006). They recorded grain sizes of less than 1 μm which indicated the grain growth of Y-TZP was not significantly large during sintering and was about the same as for the pure 3Y-TZP system.

Other authors have investigated the possibility of using two-step sintering to achieve high densities and fine grain sizes. In two step sintering the sample is first heated at a higher temperature, where the pores between the aggregate and agglomerates are eliminated and a fast grain growth is observed, then cooled at a lower temperature with longer dwelling time until it is fully dense without further grain growth (Kim, 1993; Polotai et al., 2005; Wang et al., 2006a). Zhou-Berbon et al. used a double sintering method, where they presintered the samples with a heating rate of 2°C/m upto a temperature of 1008°C based on dilatometric findings and sintered again to two different temperatures (1650°C for 2 hr and 1550°C for 1 hr) (Zhou-Berbon et al., 1996). They reported high density (>99% Dth) with average grain size 1.5 μm for 1650°C for 2 hr, and fully dense with average grain size ≈0.67 μm for 1550°C for 1 hr.

Robert et al. synthesised nanocrystalline YSZ powders. They found that a high density (>98% Dth) and fine average grain size could be achieved by using two-step sintering (Robert et al., 2003). Polotai et al. proposed a combination of controlled atmosphere and flexible sintering, which yielded a fine and uniform pore microstructure before isothermal treatment and relatively fast densification without significant grain growth (an average grain size of ~100 nm) during the final stage of two-step sintering in pure $BaTiO_3$ (Polotai et al., 2005). Chen and Wang proposed a cost-effective two-step sintering process to prepare dense, nanostructured Y_2O_3 ceramics of grain size 25–50 nm by exploiting the kinetic 'window' that separates grain-boundary diffusion from grain growth (Chen and Wang, 2000). Chen explained the feasibility of densification without grain growth where grain-boundary migration may involve an activation process that has higher activation energy than grain-boundary diffusion, thus, it is active at higher temperature but is suppressed at lower temperature.

2 Experimental procedure

2.1 Particle size analysis

Two types of nano-size 3Y-TZP powders were procured; Tosoh 3Y-TZ-E grade (Tosoh Ltd., Japan) and Technox 2000 grade (Dynamic-Ceramic Ltd., UK). Pure, unstabilised zirconia (American Premalox Ceramics Ltd.) was also procured. Particle size analysis was carried out using a Malvern Mastersizer S (Malvern Ltd., UK). Powder was dispersed in water mixed with dispersants, and agitated in an ultrasonic bath for 5 min. Dispersants used included Calgon and Daxad 11 (Geo Specialty Chemicals Ltd., USA). High resolution transmission electron microscopy (JEOL 100 CX Transmission electron microscope, JEOL UK Ltd.) was also used to examine the particle size and shape of the powders.

2.2 Surface area measurement

BET surface area analysis (Gemini, Micromeritics, USA) was carried out. Powder was out-gassed under helium at 200°C for 2 hr prior to analysis.

2.3 Thermal analysis

Differential Thermal Analysis/Thermo Gravimetric Analysis (DTA/TGA) (Stanton Redcroft, UK) was carried out with platinum crucibles at heating and cooling rates of 10°C/min, using 20 mg of sample, and alumina as a reference.

2.4 Powder compaction and sintering

A uniaxial press (Moore and Son, Birmingham, UK) was used to form discs. Approximately 3 g of powder was added to a 26 mm diameter steel die to make individual discs. A load of 20 kg.cm^2 was applied for 20 sec. Discs were sintered in a horizontal tube furnace (Carbolite, Sheffield, UK) in air using a ramp rate of 2°C/min and holding for 2 hr in the temperature range 1350–1500°C. The cooling rate was 3°C/min to room temperature. For two-step sintering, discs were heated to 1000°C at 30°C/min and then to 1500°C at 20°C/min. The samples were then cooled to 1380°C using a cooling rate of 40°C/min. Discs were held for 4–12 hr and then cooled to room temperature with a cooling rate of 3°C/min.

2.5 Dilatometry analysis

Bar shaped samples were made by uniaxially pressing powder in a custom made steel die under a load of 20 kg.cm^2 for 20 sec. Bars measured 5 × 5 × 2 mm. Dilatometry (Model 402 E, Netzsch Ltd., Germany) measurements were carried out in air from room temperature to 1540°C, using heating and cooling rates of 10°C/min.

2.6 Density measurement

A small volume helium pycnometer (Accupyc 1330, Micromeritics, UK) was used to measure the density of as-received powder. Mean values and standard deviations were determined from five successive measurements.

Density of sintered discs was measured according to the Archimedes method (Sartorius AG, Weighing Technology Ltd.), using a water medium. Mean values were determined from three successive measurements.

2.7 Hardness and fracture toughness measurement

Vickers hardness was measured using a Zwick hardness tester (Type 5030 SKV, Indentec Ltd., UK) with a standard diamond indenter. Ten measurements were used to obtain an average value for a load of 20 kg. The same instrument was used to measure fracture toughness, according to the well known Lawn and Wilshaw method (Lawn, 1993).

2.8 XRD analysis

X-ray diffraction (Bruker AXS D8 Advance, USA) analysis with Cu-Kα radiation was carried out to determine the phase structure of powders and sintered disc samples.

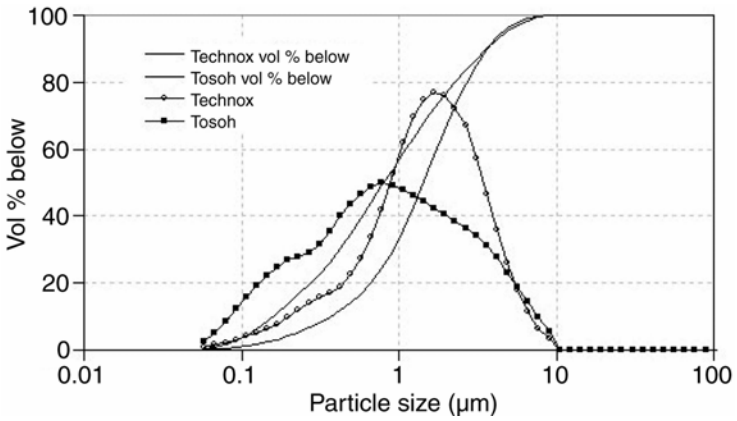
2.9 Young's Modulus measurement

Disc samples were uniaxially pressed and conventionally sintered. The Tosoh discs were heated to 1450°C and held for 2 hr, the Technox heated to 1500°C and held for 2 hr. After sintering the discs measured approximately 40 mm in diameter and 3 mm in thicknes. An impulse excitation frequency tester (Lemmens Electronika Grindosonic, Belgium) was used to measure the resonant frequency of these discs, and from this Young's Modulus, *E* was calculated according to ASTM standard C 1259-01 (ASTM, 2001).

3 Results and discussion

As-received nano-powders were dispersed in water and sonicated. Particle size analysis D (4, 3) values of 1.29 μm (Tosoh) and 1.78 μm (Technox) were measured. The particle size distribution of the powders is shown in Figure 1.

Figure 1 Particle size distributions for Tosoh and Technox powders



From Figure 1 it can be seen that only 13% of Tosoh powder and 4% of Technox powder had a particle size <200 nm. Attrition milling of the powder failed to effect a measured reduction in particle size. It was therefore believed that, water caused these powders to agglomerate. Another possibility was that the powder particle size was close to the lower limit of the instruments specified size range measurement capability, which ranged form 0.05–880 μm.

An alternative particle size analyser (Malvern, HPP5001 HPPS) with a measurement range 0.6–6000 nm was also employed. Powder dispersed in de-ionised water again yielded particle sizes in the micrometer range. A sample of powder was then filtered through a 0.45 μm filter (Acrodisc, Sigma Aldrich), resulting in an average particle size of 147 nm. Repeated analyses consistently yielded 147 nm, which showed that this powder was finely dispersed and not agglomerating over time. However, without filtering – this result could not be achieved. It was believed that this value represented the quantity of powder <200 nm observed when the less-sensitive particle size equipment was employed.

A valid particle size measurement of the non-filtered sample was impossible due to the likelihood of water-induced agglomeration. Many authors use dry powders and an Equivalent Spherical Diameter (ESD_{BET}) approach to avoid agglomeration effects when analysing nano-powders (Duran et al., 2003; Kimel and Adair, 2005; Seidensticker et al., 1993). Seidensticker et al. used this approach for 3Y-TZ grade Tosoh powder and calculated a BET equivalent diameter of 61.2 nm, based on a BET surface area of 16.1 m^2/g and a powder density of 6.08 g/cm^3. Seidensticker et al. also used sedimentation size analysis to measure a mean particle diameter of 170 nm. They also quote a crystallite diameter of 26.9 nm, pointing to aggregation of the nano-powder as the reason for the discrepancy between particle diameter and crystallite diameter (Seidensticker et al., 1993). Tuan et al. claimed a mean particle size D_{50} of 230 nm for the same powder (Tuan et al., 2006).

Liu et al. used 3Y-TZ-E grade Tosoh powder for hollow fibre membrane applications but only refer to the powder as having submicrometer particle diameters (Liu et al., 2006). Kunes et al. investigated 3Y-TZ-E powder for slip-casting applications. They used the alkali-free polyelectrolyte Dolapix CE64 as a deflocculant and measured a mean D_{50} particle size of 280 nm by Low-Angle Laser Light Scattering (LALLS) (Kunes et al., 2000).

In order to measure primary particle size, the specific surface area of the powders was measured, yielding values of 14.52 m^2/g for Tosoh and 6.42 m^2/g for Technox. The ESD_{BET} was calculated from the following equation (Kimel and Adair, 2005):

$$\mathrm{ESD} = \frac{6}{\rho_{\mathrm{part}} \mathrm{SSA}} \tag{1}$$

ρ_{part} is the density of the powder particle and SSA is the specific surface area of the powder. The density of the powder was 5.98 g/cm^3 for Tosoh and 6.03 g/cm^3 for Technox as determined from pycnometry analysis. This translated to particle sizes of 69 and 155 nm, respectively using Equation (1). Figure 2 shows the transmission electron micrographs for Tosoh and Technox powders. Tosoh powder particles are spherical with uniform size distribution of around 40–70 nm. This result agrees with the particle size obtained using ESD_{BET}. Technox powder particles are also spherical and uniformly distributed. The average particle size for Technox powder appears to be

<100 nm which is smaller than the value obtained using ESD_{BET}. Considering the values obtained from laser diffraction-based particle size analysis, it is clear that both powders are heavily prone to agglomeration in water.

Figure 2 High-resolution transmission electron microscopy of (a) Tosoh powder and (b) Technox powder

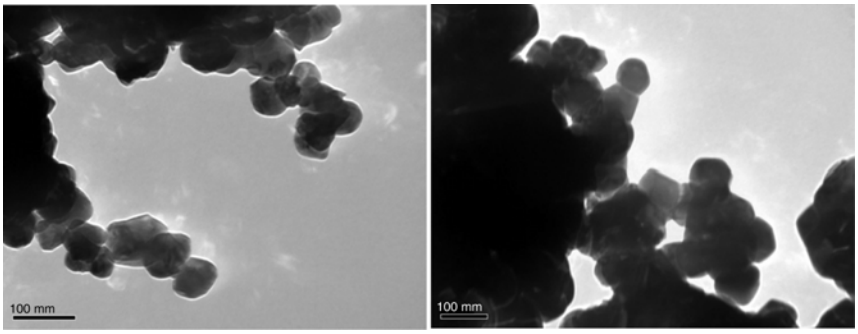
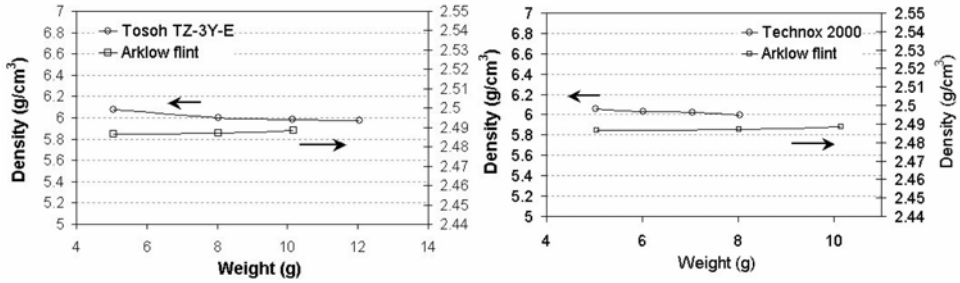


Figure 3 shows helium pycnometry data for the Tosoh and Technox powders, and also for a standard of known density (Arklow flint, $\rho = 2.48$ g/cm^3).

Quantities of powder >5 g resulted in stable density values, that is, 2.48 g/cm^3 correct to two decimal places for the standard of known density (Arklow Flint). In a paper describing the optimum design of the constant-volume gas pycnometer for determining the volume of solid particles, Tamari highlights the importance of sample chamber filling (Tamari, 2004). According to Consolmango and Britt, the volume of small meteorites could not be determined accurately and the relative uncertainty in the measurement of sample volume decreased when the meteorite size and thus the filling factor, increased (Consolmagno and Britt, 1998).

Figure 3 Pycnometry density measurements for different quantities of powder for (a) Tosoh (b) Technox (arrows indicate relevant axes)



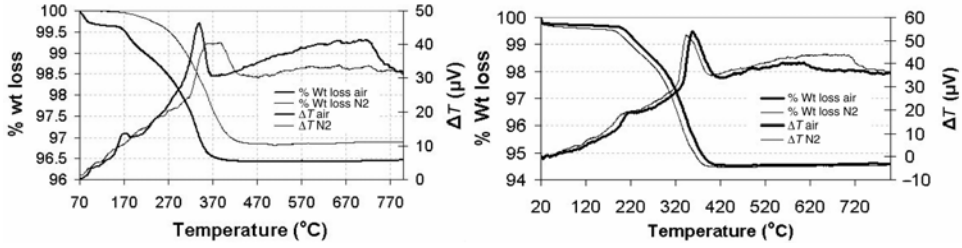
For the Tosoh powder, stabilisation of density results occurred for quantities >8 g and between 6 and 7 g for Technox. An average was taken yielding a density value of 5.98 g/cm^3 for the as-received, Tosoh nano-zirconia powder, and 6.03 g/cm^3 for Technox. The reason for the difficulty in achieving a stable result for the zirconia powders is debatable. The light nature of nano-powders could potentially mean that some powder is displaced at high gas pressures, leading to result inaccuracy. Tamari recommends submitting the powder to an initial low gas pressure, an approach which was employed as a precaution in this study (Tamari, 2004).

Thermal analysis was carried out on the as-received, binder-containing Tosoh powder (see Figure 4(a)). For the sample run under nitrogen, binder burnout commenced at approximately 150°C and was completed by 475°C, corresponding to 3.1% weight loss. A broad exothermic peak began at 320°C and ended at around 440°C, corresponding to combustion of the binder. No other peaks were observed above 450°C.

The sample run under air behaved differently. A small exothermic peak was observed at 175°C and a large sharp exothermic peak at 343°C. The peak at 175°C is believed due to combustion of organics, a reaction which is hindered under nitrogen. The position of the second peak occurs at a lower temperature in air than in nitrogen. This suggests that the binder burn-off is aided by the air. A percentage weight loss of 3.6% was recorded in air compared with 3.1% in nitrogen. Residual unreacted carbon was found to remain when a nitrogen atmosphere was used. According to Knapp et al. basic thermal mechanisms of binder removal are thermal degradation, oxidative degradation and evaporation. Thermal degradation occurs by free radical reactions when no oxygen is present in the atmosphere. Degradation in combustive atmospheres often occurs at lower temperatures of decomposition, as oxygen acts as a reactant with autocatalytic processes (Knapp and Halloran, 2006). According to Lewis, the mechanisms which can affect polymer degradation include polymer chemistry and structure, polymer loading, chemical interactions at polymer-ceramic interfaces, heat/mass transport, component geometry, firing atmosphere and heating cycle (Lewis, 1997).

The Technox powder sample run under air behaved similarly to the Tosoh powder. Binder began to burn out with a sharp gradient near 200°C and finished at around 430°C. The weight loss was 5.5%. The DTA pattern showed two peaks, one small exothermic peak at 223°C and a second exothermic peak at 363°C. The Technox powder behaved almost identically when run under nitrogen or air. The exothermic peak at 363°C shifted slightly to 351°C but the overall weight loss was the same. Many ceramic applications require reductive atmospheres. For these situations it is more suitable to have binder additives which volatilise efficiently in inert atmospheres (Ghosh et al., 2006). Furthermore, oxidative atmospheres can sometimes inhibit polymer degradation reactions; their effects depending on the specific polymer as well as the temperature range of decomposition.

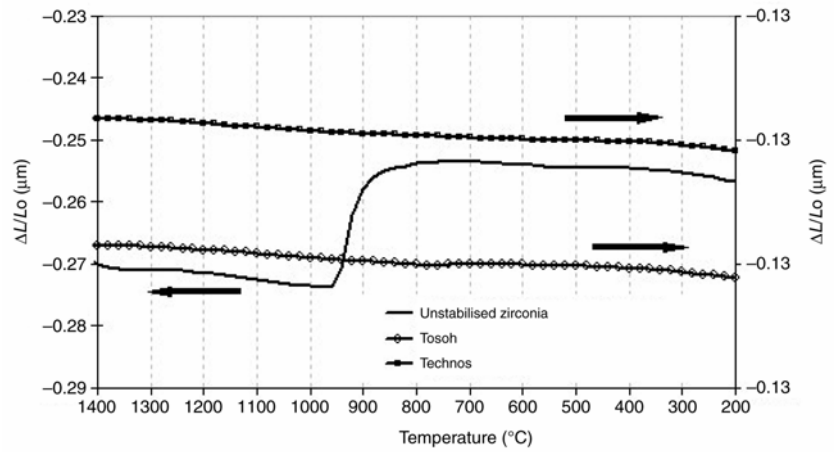
Figure 4 DTA/TGA curves for (a) Tosoh grade powder and (b) Technox grade powder under static air and flowing nitrogen atmospheres



Of interest in this work was the retention of a tetragonal-only phase after sintering. According to Piconi (1), for un-stabilised zirconia, a $T \rightarrow M$ transformation takes place in the temperature range of about 100°C below 1070°C during cooling from sintering. This transformation is associated with a volume expansion of approximately 3–4%.

Dilatometry was employed to detect the $T \rightarrow M$ transition for the TZP nano-powders. Unstabilised monoclinic zirconia powder was also analysed for comparison purposes. Figure 5 plots the shrinkage/expansion behaviour on cooling from 1400°C.

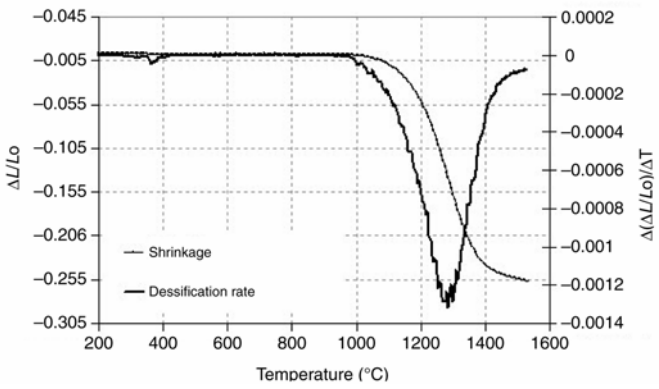
Figure 5 Dilatometric analysis of unstabilised zirconia, Tosoh and Technox samples cooled from 1400°C (arrows indicate axes of relevance)



A sharp expansion was observed for the unstabilised sample in the region 880–960°C, as compared with the Tosoh and Technox samples, which both shrunk slightly over the cooling range. This sharp exotherm was attributed to the $T \rightarrow M$ transition.

Dilatometry was also employed to investigate the densification behaviour of the Tosoh and Technox powders during sintering. In Figures 6 and 7 shrinkage and densification rate are plotted against temperature.

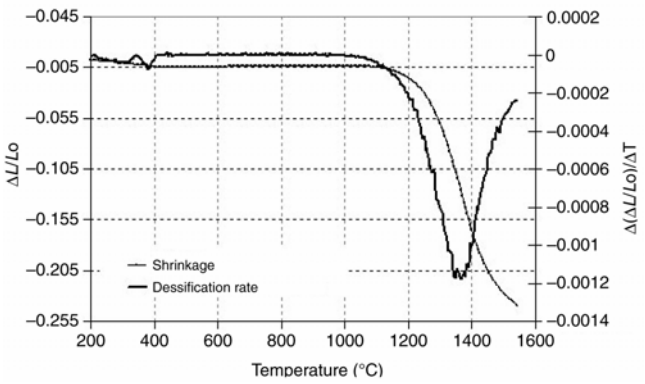
Figure 6 Shrinkage and densification rate of 3Y-TZP Tosoh as measured using dilatometry in static air with an isothermal heating rate of 10°C/min



For the Tosoh sample, an event occurred at 370°C corresponding to the elimination of binder. Shrinkage initiated at about 990°C. The shrinkage gradient was sharp with a final linear shrinkage of approximately 25.6%. The densification rate reached a maximum at 1284°C. Shrinkage reached completion by 1530°C. For the Technox sample, shrinkage

initiated at about 1020°C. Densification had not reached completion by 1540°C; the shrinkage curve had not levelled out, as compared with the Tosoh sample. The maximum densification rate occurred at 1380°C; approximately 100ºC higher than for the Tosoh sample. Sintering occurred quickly over a smaller temperature range. Duran et al. used dilatometry-generated densification rate maximas in their sintering behaviour study of high purity $BaTiO_3$. They observed a major densification rate peak at 1250ºC which corresponded to a maximum in densification of about 99.3% Dth (Duran et al., 1997). Above 1250ºC a small de-densification occurred and densification decreased to about 97% Dth at 1300ºC, which they attributed to gas release from the decomposition of barium carbonate in the barium titanate environment and the high mobility of the grain boundaries.

Figure 7 Shrinkage and densification rate of 3Y-TZP Technox, as measured using dilatometry in static air with an isothermal heating rate of 10°C/min.



In order to further investigate the densification and mechanical properties of sintered parts, discs were sintered in the temperature range 1350–1550ºC. Values for % Dth were calculated based on taking a density value of 6.08 g/cm^3 for Tosoh. This value was chosen based on work carried out by Basu et al. who reported a density of 6.08 g/cm^3 for TZ-3Y (Tosoh) which was hot-pressed at 1450ºC for 1 hr in a vacuum (Basu et al., 2004a). This is the highest value reported in the literature for sintered TZ-3Y zirconia. Often, the percentage theoretical density of sintered parts would be calculated based on the density of starting powder. However, in this work a value of 5.98 g/cm^3 was measured for Tosoh powder density and it was therefore, felt that the powder was not 100% tetragonal. This was confirmed by XRD analysis (see Figure 8 (c)).

Figure 8 XRD patterns of (a) unstabilised zirconia powder; (b) sintered Tosoh disc; (c) Tosoh powder and (d) sintered Technox disc

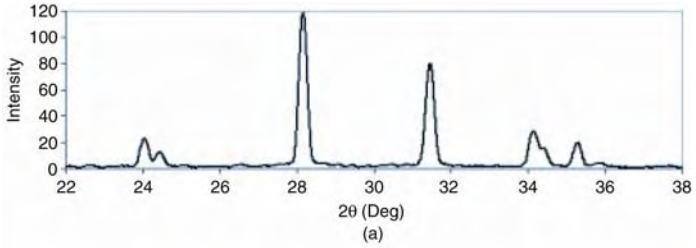
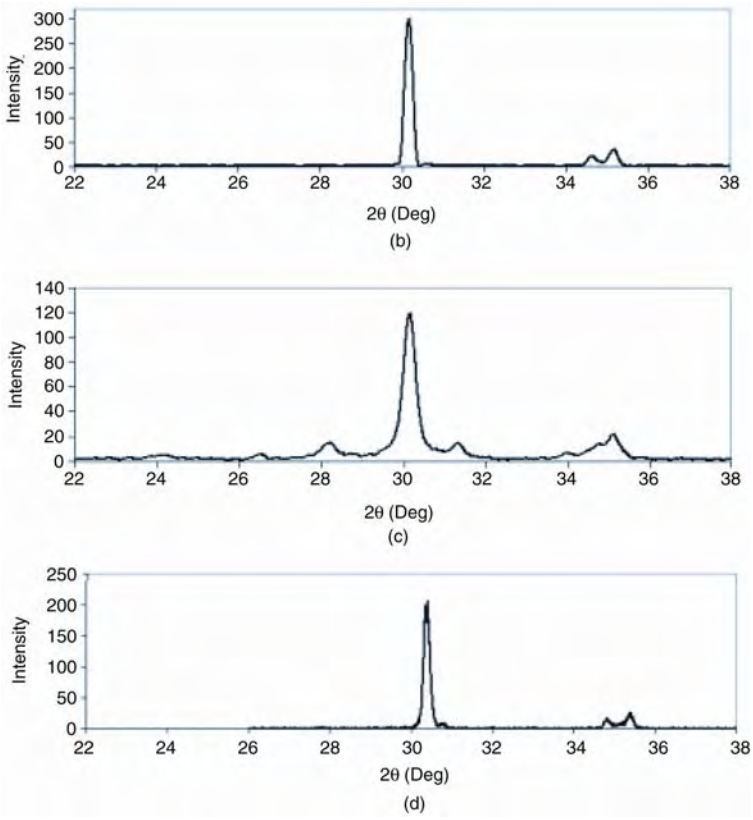


Figure 8 XRD patterns of (a) unstabilised zirconia powder; (b) sintered Tosoh disc; (c) Tosoh powder and (d) sintered Technox disc (continued)



From XRD analysis, unstabilised zirconia powder showed a classic monoclinic pattern (Figure 8(a)). The Tosoh disc after sintering (Figure 8(b)) was shown to be wholly tetragonal. The splitting of the (110) and (002) peak at 2Θ (~35º) was a clear indication of the presence of tetragonal phase (Ghosh et al., 2006). The Technox powder was very similar and also shown to be tetragonal after sintering (Figure 8(d)). The powder sample of Tosoh (Figure 8(c)) revealed the presence of some monoclinic phase, that is, secondary peaks are observed at ~28º and ~31.5º. This phase is then transformed to tetragonal during sintering, leading to an increase in density. After sintering, the pycnometry–generated value of 5.98 g/cm^3 would then no longer be valid as a reference density from which to calculate percentage theoretical density. Density, Vickers hardness and fracture toughness measurements were carried out on green and sintered discs, the results of which are summarised in Table 1. From Table 1 it is clear that the Tosoh powder sintered very readily. The Technox powder needed higher temperatures to yield % Dth greater than 99%. This was as expected, since earlier, dilatometry analysis data showed that the maximum densification rate of Technox powder occurred at approximately 100ºC higher than for Tosoh powder. Hardness values ranged from 11 to 12.5 GPa across all samples tested. Piconi and Macauro suggest typical Vickers hardness of 12 GPa for TZP ceramics used in biomedial applications (Piconi and Macauro, 1991).

Table 1 Density, hardness and fracture toughness values for Tosoh and Technox samples

Sintering Temp (°C)	*Green Density % D_{th} Tosoh*	*Sintered Density % D_{th} Tosoh*	*Green Density % D_{th} Technox*	*Sintered Density % D_{th} Technox*	*Vickers Hardness Tosoh (GPa)*	*Vickers Hardness Technox (GPa)*	*Fracture Toughness Tosoh K_{IC} (MPa $m^{1/2}$)*	*Fracture Toughness Technox K_{IC} (MPa $m^{1/2}$)*
1350	40.11	97.40	40.75	94.67	11.67 ± 0.30	10.94 ± 0.34	5.49 ± 0.34	5.14 ± 0.25
1400	41.38	98.95	41.98	96.89	12.54 ± 0.23	11.48 ± 0.21	4.88 ± 0.28	5.08 ± 0.23
1450	40.94	99.44	40.99	97.57	12.30 ± 0.24	12.37 ± 0.37	4.97 ± 0.25	4.82 ± 0.26
1500	40.96	99.31	40.88	98.05	12.57 ± 0.17	11.97 ± 0.39	4.20 ± 0.38	5.47 ± 0.34
1550	–	–	40.68	99.11	–	12.19 ± 0.31	–	5.20 ± 0.26

For Tosoh samples, the fracture toughness was highest (5.49 ± 0.34 MPa.$m^{1/2}$) for lower sintering temperature and gradually decreased with increasing temperature. For the Technox samples no definite pattern was observed with increasing temperature. Technox samples reached a maximum fracture toughness of 5.47 ± 0.34 MPa.$m^{1/2}$ for a sintering temperature of 1500ºC. Pedzick et al. investigated slow crack propagation using 3Y-TZ Tosoh powder (Pedzich and Wajler, 2006). They reported a fracture toughness value of 5.0 ± 0.5 MPa.$m^{1/2}$ by Vickers indentation. Chung et al. reported a fracture toughness value of 4.8 ± 0.2 MPa $m^{1/2}$, using 3Y-TZ Tosoh powder, for samples sintered at 1600°C for 3 hr in air (Chung et al., 1997). Basu et al. investigated a simple but innovative route based on the mixing and hot pressing (under identical conditions) of 3Y-TZ Tosoh powder (Basu et al., 2004b). The experimental results yielded a fracture toughness of 3.3 ± 0.3 MPa $m^{1/2}$ using 30 kg indentation load.

Almost full density was achieved by using isothermal ramping and single dwell time sintering. However, such an approach is rarely optimal in terms of grain size. Chen and Wang pioneered two-step sintering, which is by now a widely accepted approach to achieve full densification, while maintaining fine grain sizes (Chen and Wang, 2000). Barba et al. also advocate two-step sintering and claim that when relative density has reached critical values (~90%), temperature should be decreased and dwell time increased, to maximise the potential for complete densification (Barba et al., 2004). In the case of the Technox powder being studied here it was felt that 1380°C as a dwell temperature would be optimal if employed in two-step sintering as it was the temperature of maximum densification rate, as seen in Figure 7 Polotai et al. produced a fine grained barium titanate ceramic with a % D_{th} of 99.7% using two-step sintering combined with rate controlled sintering (Polotai et al., 2005). The first sintering step was employed to produce and freeze in place a uniform pore microstructure while minimising grain growth. The diffusion distance was thus minimised during constant grain-size sintering which maximised densification kinetics leading to an almost fully dense ceramic. Polotai et al. reported a grain growth factor of twelve for two-step sintering, which was five times smaller than that observed for conventional sintering. Wang et al. applied two-step sintering to 200 nm Y_2O_3 powder and reported a coarsening ratio of two, from powder particle size to dense ceramic grain size (Wang et al., 2006b). The ratio was six for 10 nm powders, which is considerably lower than for conventional sintering. A two-step sintering approach was employed for the Technox powder based on the dilatometry data from Figure 7. As can be seen from Table 2, density increased with increasing hold time at 1380ºC.

Table 2 Sintered density and hardness of two-step sintered Technox discs

Holding time at 1380°C (hr)	*Sintered Density % Dth*	*Vickers Hardness (R_A)*	*Fracture Toughness K_{IC} (MPa $m^{1/2}$)*
4	96.06	11.28 ± 0.20	5.48 ± 0.36
8	97.40	12.53 ± 0.33	4.84 ± 0.37
12	98.47	12.87 ± 0.19	4.96 ± 0.25
16	98.58	12.87 ± 0.29	6.12 ± 0.46

Fracture toughness reached a maximum value of 6.12 ± 0.46 MPa $m^{1/2}$ for a holding time of 16 hr. Hardness increased with increasing hold time, reaching 12.87 GPa for a holding time of 16 hr.

Elastic modulus values of 194 and 153 GPa were recorded for the conventionally sintered Tosoh and Technox samples, respectively. The densities of the test specimens were 99.44 and 98.05 g/cm^3, respectively. The lower density of the Technox sample is suggested as a reason for the lower value of elastic modulus recorded.

Basu et al. and Ceilli et al. reported values for 3Y-TZ of 194 and 201 GPa, using a resonant frequency method and a four point bending apparatus equipped with extensometer, respectively (Basu et al., 2004b; Celli et al., 2003). Tuan et al. measured elastic modulus of alumina-zirconia composite discs of 25.4 mm diameter using an ultrasonic technique (Tuan et al., 2002). According to Tuan et al. the elastic modulus measurement can provide information about the interior of the composites, such as indicating the presence of cracks and porosity, which will cause a reduction in the modulus. In their study, a good correlation was found between the measured modulus values and those calculated from the rule of mixtures. Moraes et al. used a rule of mixtures approach to calculate elastic modulus of alumina-zirconia composites, justifying it based on the fact that their samples were of high density and free of defects (Moraes et al., 2004). Tan et al. measured elastic modulus of sintered Al_2O_3-ZrO_2 ceramics by measuring compression and shear velocities through the materials (Tan et al., 1997). According to Tan et al. the acoustic impedance of a sample will be a function of porosity, microcracks and different phases. In their study they found that increasing the compacting pressure on the green sample resulted in a corresponding increase in Young's Modulus. However, modulus values measured for Al_2O_3 were approximately half the value quoted in the literature which is difficult to understand, that is, 195 GPa as opposed to 396 GPa, as recorded by Tuan et al.

4 Conclusions

Two different grades of 3Y-TZP nano powders were investigated. Both were found to be heavily prone to agglomeration in water. Thermal analysis of these powders revealed that binder burn-off behaviour was a function of the type of atmosphere used. Dilatometry analysis of bar-shaped samples made from the powders revealed that the point of maximum densification rate occurred at an elevated temperature for the powder of greater particle size. Sintered discs exhibited densities >99% theoretical, and no evidence of a $T \rightarrow M$ transformation was detected. For both powders, hardness increased with increasing sintering temperature. The fracture toughness of Tosoh discs decreased almost

linearly with increasing sintering temperature. Two-step sintering when applied to Technox powder led to a maximum in fracture toughness.

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