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Sintering, microstructure and mechanical properties of commercial Y-TZPs

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The sintering behaviour of Y-TZP ceramics, their resulting microstructures and properties are influenced not only by the characteristics of the raw materials but also were found to be dependent on the thermal history during the fabrication process. It is generally understood that fracture toughness increases as grain size increases up to a certain limit but in the present investigation, the results obtained challenge this view. The work is concerned with grain size dependence on the mechanical properties, in particular on the fracture toughness. Two commercially available powders based on two different processing techniques (i.e. coated and co-precipitated) were studied. It has been found that both materials exhibited different fracture toughness trends. Smaller grains of coated Y-TZP resulted in high fracture toughness > 12 MPa $m^{1/2}$ while the opposite effect was seen in the co-precipitated material which showed enhanced fracture toughness with increasing grain size above a certain lower limit from a nonconventional heat treatment.

1. Introduction

Yttria tetragonal zirconia polycrystalline ceramics (Y-TZP) are promising materials owing to their excellent mechanical and thermal properties. The improved properties combined with excellent biocompatibility, wear resistance, high chemical and corrosion resistance make this material one of the best candidates for many components including orthopaedic prostheses as a replacement for metallic materials [1]. Furthermore, the ability of these materials to behave superplastically [2, 3] has widened their applications.

It is well documented [4–8] that the properties of sintered materials are mainly dependent on the initial powder properties. Variables such as the amount of yttria content and the fabrication route in particular determine the degree of homogeneity (i.e. yttria distribution), the particle sizes and impurity contents in the powder. For unagglomerated particles of submicron size, the addition of SiO_2, Al_2O_3 and transition metal oxides can be tolerated, leading to the fabrication of ceramics with improved characteristics and structural reliability.

The high strength and fracture toughness exhibited by this ceramic are attributed mainly to the martensitic stress-induced change from the metastable tetragonal (t) to monoclinic (m) phase. While the monoclinic phase is a thermodynamically stable polymorph at room temperature, the tetragonal structure can be retained at room temperature provided that the grain size is below some critical value [9–11]. Above this critical size, spontaneous transformation will occur on cooling from the sintering temperature, accompanied by deterioration of the mechanical properties.

The critical grain size varies depending on the processing history of the powder, the amount and type of stabilizers. It has been suggested [9] that the chemical free energy change associated with the t-to-m phase transformation is dependent on these parameters (i.e. increasing the amount of stabilizer will eventually reduce the chemical free energy) subsequently affecting the critical grain size. For example a critical grain size of about 3 μm was reported in the case of CeO_2 [12] and 0.38 μm for Er_2O_3 [13] stabilizers. In contrast, Lawson [14] failed to show a definite grain size dependence in Y-TZP ceramics and therefore does not support the critical grain size theory as being the only limiting parameter in the retention of high tetragonal phase. Other characteristics such as amounts of additive, stabilizer distribution, sintering programme, fired density and grain size are all interrelated. In general, the decrease in the volume fraction of the metastable t-phase in any TZP system will reduce the transformation toughening.

The yttria distribution in the ZrO_2 grains is another factor believed to contribute to enhanced fracture toughness in Y-TZP ceramics [14]. It is well known that Y-TZP ceramics are susceptible to low temperature (i.e. 65–500 °C) ageing in humid atmospheres and to hot aqueous media [15–18], resulting in property degradation. The exact mechanism has not been fully explained but this phenomenon is recognized to be associated with the t-to-m transformation which starts from the surface of the component [19].

It has previously been postulated that a homogeneous distribution of yttria in the ZrO_2 grains is vital for preventing this martensitic transformation with its accompanying micro and macro-cracking. However, it has been shown that an inhomogeneous stabilizer distribution is in fact beneficial [20, 21] and this is one reason why yttria-coated plasma produced ZrO_2 powders possess excellent fracture toughness at lower sintering temperatures and superior resistance to the ageing-induced phase changes compared to co-precipitated powders [22].

The objectives of the present work were to compare the sintering behaviour of both coated (2.5 mol % Y_2O_3) and co-precipitated (2.5 and 3 mol % Y_2O_3) zirconia powders focusing mainly on the effect of increasing grain size on the fracture toughness for each composition by altering the sintering temperature or soaking period.

2. Experimental procedures

In the preliminary investigations a 'standard' Tioxide 2.5Y-TZP (YZ860) was compared with Tosoh 2.5 and 3Y-TZP materials sintered over a wide temperature range in order to obtain ceramics with different grain sizes. Fig. 1 shows typical as-manufactured agglomerates of each starting material.

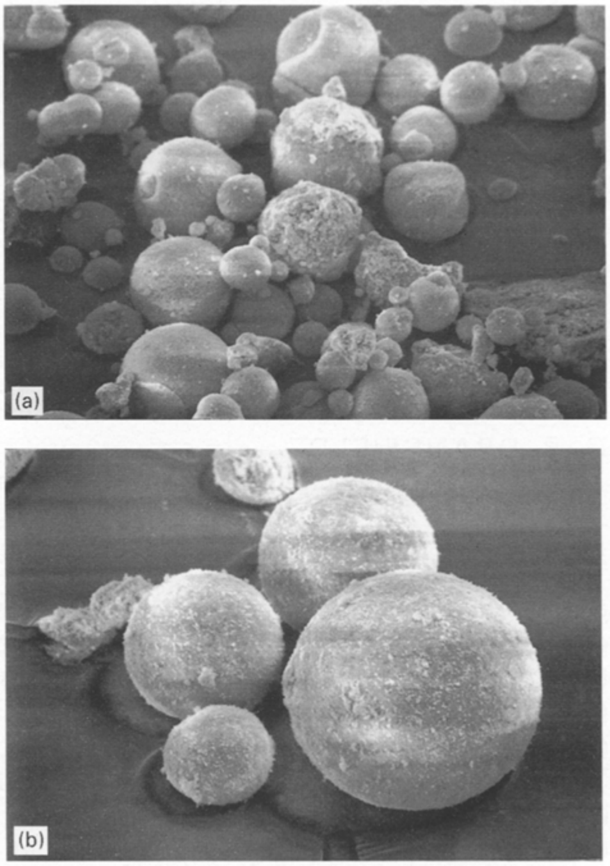

Figure 1 Typical as-manufactured agglomerates of (a) coated Tioxide powders and (b) co-precipitated Tosoh powders (TZ-3Y). (Magnification = ×414.)

The powder mixtures were die-pressed into discs (3 g, 19 mm diameter) and rectangular bars (8 g, 6 mm × 5 mm × 100 mm) samples. Tioxide disc samples were die-pressed at 70 MPa while a lower pressure of 21 MPa was employed for Tosoh materials due to problems of lamination at higher pressures. All disc samples were then cold isostatically pressed at 200 MPa. However, lamination problems were not encountered during uniaxial pressing of the bar samples at 60 MPa. The green disc compacts were sintered in air at a furnace ramp rate of 10 °C min^{-1} to between 1350 and 1600 °C, maintained at the soak temperatures for 2 h and then cooled in the furnace while the bar samples were fired at 1450 °C. The cooling rate for all samples was 10 °C min^{-1}.

The bulk densities of the sintered samples were measured using a water immersion technique. All discs were polished to a 1 μm surface finish on one face using a diamond paste prior to testing. The bar samples were used to determine Young's modulus of each type of Y-TZP material by using a flexural-resonant frequency technique [23]. Phase identification was by X-ray diffraction (XRD) using $\{1\,1\,1\}$ peaks and the fraction of monoclinic phase in the as-sintered body was evaluated using the relationship developed by Toraya *et al.* [24]. Fracture toughness (K_{1c}) and microhardness (H_v) were measured on polished samples using the Vickers indentation method. In all cases the load of the indenter was kept constant at 300 N and the values of K_{1c} were computed using the equation derived by Niihara *et al.* [25]. Three measurements were made for each sample and average values were obtained. In addition, the microstructural evolution under the various sintering conditions was examined using scanning electron microscopy (SEM). The grain size was determined on thermally etched specimens from scanning electron micrographs using the line intercept analysis of Mendelson [26].

3. Results and discussion

3.1. Sintered tetragonal phase

The influence of sintering temperature on the tetragonal phase retention of the Y-TZP ceramics is shown in Fig. 2. The results show that both of the Tosoh Y-TZP bodies were 100% (tetragonal + cubic) regardless of the sintering temperature. Tioxide samples on the other hand, contained very small quantities of monoclinic phase at the lower sintering temperatures (< 1400 °C).

At higher sintering temperatures (> 1400 °C), SEM micrographs for the coated material revealed that grain growth had occurred. This similar trend was observed by Lawson *et al.* [27] in other grades of coated Y-TZP ceramics.

It should be pointed out that evidence of the cubic phase present in each material is clearly revealed by SEM (see Fig. 3). This observation is also in good agreement with the predicted phases present in the ZrO_2–Y_2O_3 phase diagram of Scott [28] for the present sintering regime. In addition the SEM

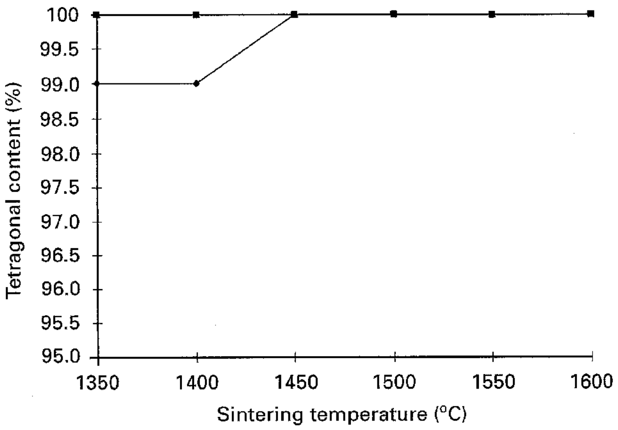

Figure 2 The effect of sintering temperature on the phase retention in Y-TZP ceramics. Key: -◆- YZ860; -■- TZ-2.5Y; -▲- TZ-3Y.

examination of both materials revealed that the fraction of cubic phase increased with heat treatment temperature but at a different rate, i.e. quicker with coated Y-TZP. At this stage, the different observations in both Y-TZP materials reported here, are attributed to the effects of the powder processing route and the purity of the starting material.

3.2. Density measurement

The densification curves as functions of sintering temperatures are shown in Fig. 4. It can be seen that on the whole Tosoh 3Y-TZP exhibited $>98\%$ of theoretical density regardless of firing temperature. The measured bulk density varied from 6.01–6.09 Mg m^{-3}.

The Tosoh 2.5Y-TZP showed an initial increase in the bulk density with fluctuations between 1400 and 1500 °C after which there was a slight decrease. The maximum measured density for this composition was 6.03 Mg m^{-3} at 1500 °C.

The Tioxide Y-TZP, however, showed considerable sensitivity to sintering temperature. The density increased up to a maximum of 6.02 Mg m^{-3} at 1400 °C and then decreased at higher temperatures. However, it should be mentioned here that other sintering cycles can also be employed for coated Y-TZP to produce highly dense bodies and these will be described elsewhere [29].

The grain sizes as a function of sintering temperature for the different processing routes for Y-TZP ceramics are presented in Fig. 5. As can be seen the grain size slowly increases at the higher sintering temperatures for both materials but at different rates. The graph shows that TZ-3Y samples generally have a smaller average grain size compared to TZ-2.5Y samples, which may explain the higher densities attained in the former. However, in the case of coated Y-TZP, the average grain sizes increased drastically beyond 1400 °C mainly due to the growth of cubic and to some extent, the tetragonal grains.

An attempt to correlate the grain size and density obtained for coated Y-TZP is presented in Fig. 6. It can be seen, as the grain size increased from 0.3 to 1 μm, there was a sharp decrease in density. Above 1 μm, no further decrease was observed.

From the above results, the decrease in bulk densities can be attributed mainly to the inhomogeneous distribution of Y_2O_3 in the ZrO_2 grains which is responsible for the development of cubic grains, in turn aiding the nucleation of monoclinic by promoting thermal expansion mismatch stresses in the structure. The present results showed that smaller grained materials had high density for coated Y-TZP.

3.3. Vickers hardness (H_v) and fracture toughness (K_{1c})

Fig. 7 shows the relation between Vickers hardness and sintering temperature. The coated Y-TZP attained a maximum hardness value of 13.2 GPa when fired at 1400 °C, before decreasing and levelling off with increasing sintering temperature.

For the Tosoh (TZ-2.5Y), the hardness value increased to a maximum value of 13.9 GPa at 1400 to 1500 °C and decreased linearly up to 1600 °C, whereas for Tosoh TZ-3Y, the hardness value remained constant between 1350 and 1450 °C at 13.9 GPa then decreased slightly becoming constant for firing temperatures for 1500 to 1600 °C. Both the Tosoh ceramics attained identical maximum hardnesses between 1400–1450 °C. In all cases the hardness and density changes with sintering temperature were similar.

Fig. 8 shows the relationship between fracture toughness of the samples and sintering temperature. The K_{1c} values for Tioxide Y-TZP gradually decreased as the sintering temperature increased from 1350 to 1450 °C. At higher sintering temperatures, further decrease in fracture toughness was not observed and instead a more constant trend was exhibited. The decrease in K_{1c} can be attributed to homogenization over the stabilizer within the ZrO_2 grains and the growth of cubic grains. The maximum K_{1c} value obtained for this Y-TZP was 12.2 MPa m$^{1/2}$ at 1350 °C.

Both the co-precipitated Y-TZP materials exhibited a constant K_{1c} with increasing grain size, but with the lower yttria content material having slightly higher fracture toughness, which is consistent with the results of other researchers [30–32]. However, the literature states that K_{1c} increases as the sintering temperature or grain size increases. The present results clearly show that the fracture toughness of the Tosoh materials is relatively insensitive to the sintering temperature and schedule used.

The unusual trend exhibited by coated Y-TZP ceramics can be attributed to the stabilizer distribution within the powder resulting in yttria enrichment at the grain boundaries of the sintered bodies. It has been suggested [27] that the enhanced transformability of the core structure, due to the very slow diffusion of yttria into the tetragonal grains at lower temperatures (<1400 °C), is responsible for the high fracture toughness of coated Y-TZP. Sintering at higher temperatures will increase the mobility of yttria, reducing the inhomogeneity and resulting in more stable grains with less transformability.

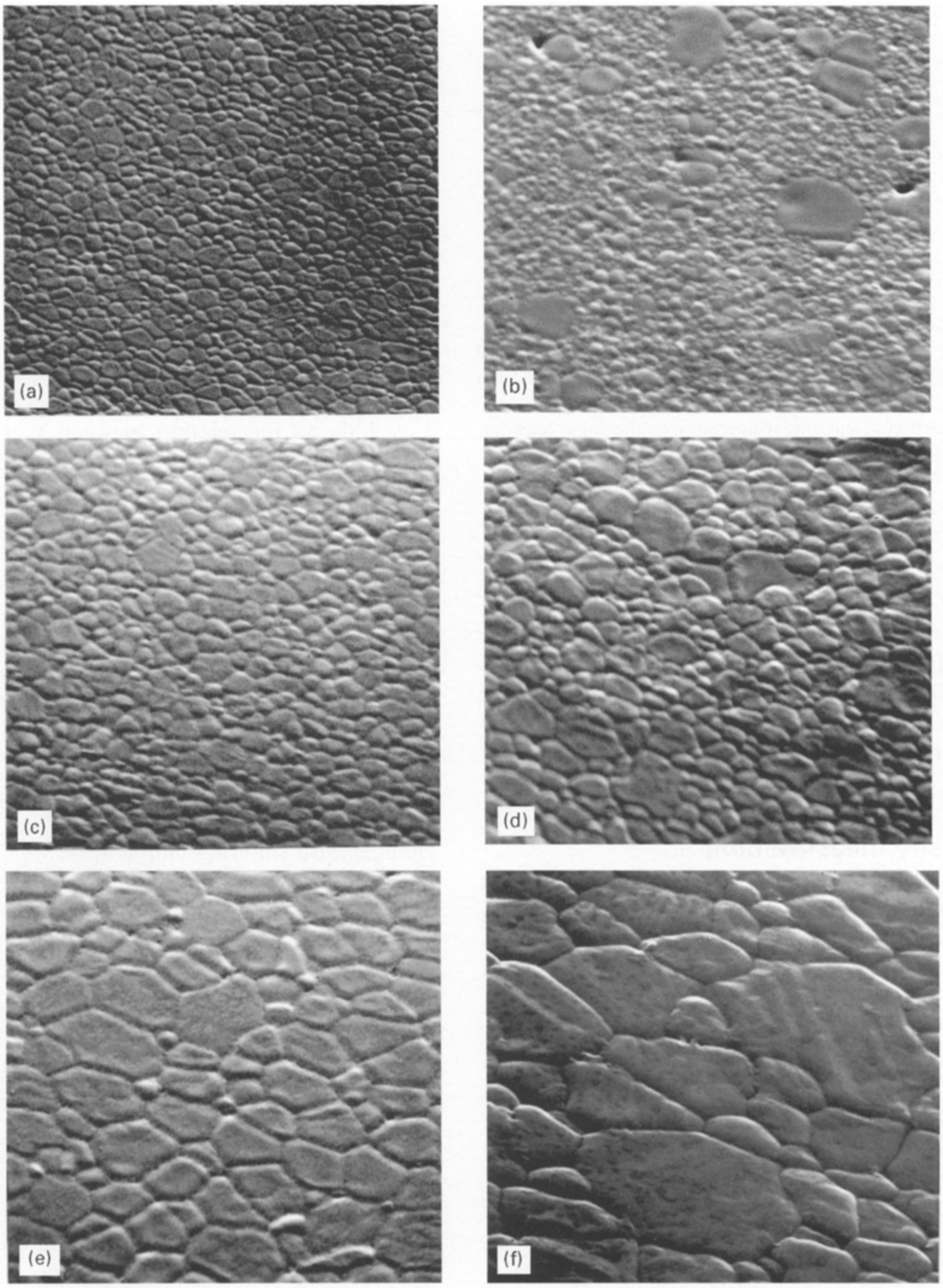

Figure 3 Microstructural evolution of co-precipitated TZ-2.5Y (a, c, e) and coated Y-TZP (b, d, f) ceramics at several temperatures. (a) and (b) 1350 °C, (c) and (d) 1450 °C and (e) and (f) 1600 °C. (Magnification = × 10 000.)

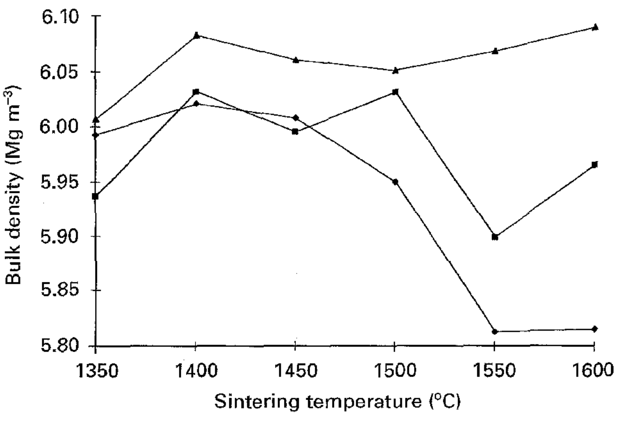

Figure 4 Bulk density as a function of sintering temperature for Y-TZP ceramics. Key: -◆- YZ860; -■- TZ-2.5Y; -▲- TZ-3Y.

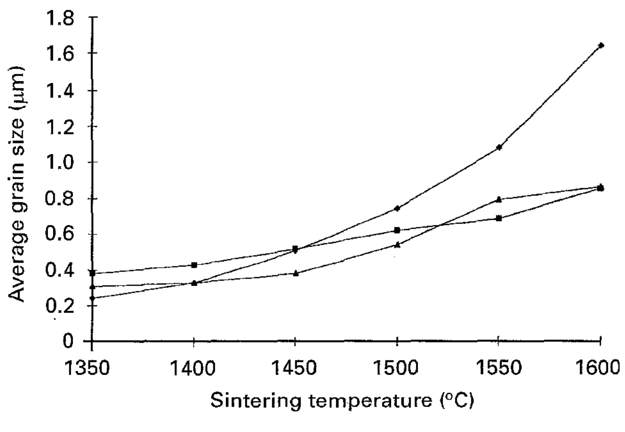

Figure 5 The effect of sintering temperature on average grain sizes of Y-TZP materials. Key: -◆- YZ860; -■- TZ-2.5Y; -▲- TZ-3Y.

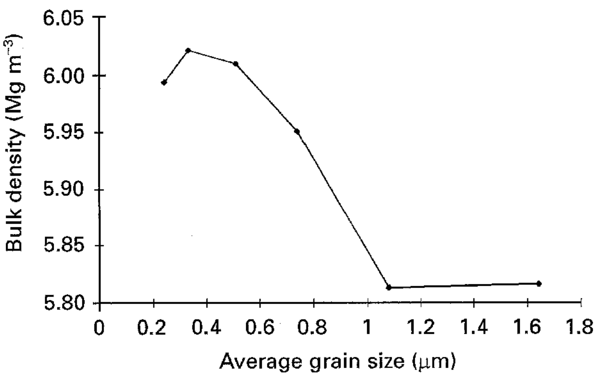

Figure 6 The effect of grain growth on the sintered bulk density of Tioxide Y-TZPs. Key: -◆- YZ860.

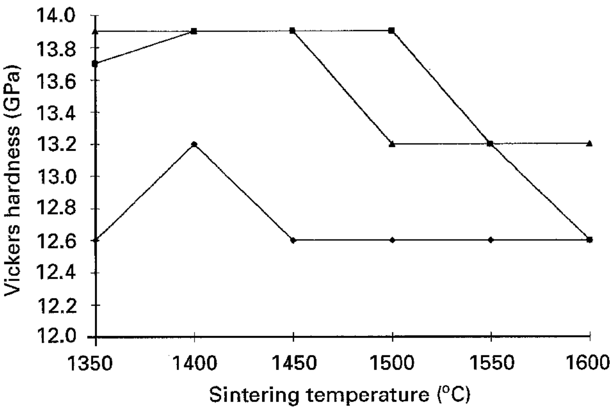

Figure 7 The effect of sintering temperature on the Vickers hardness of Y-TZPs. (Indentation load was 300 N.) Key: -◆- YZ860; -■- TZ-2.5Y; -▲- TZ-3Y.

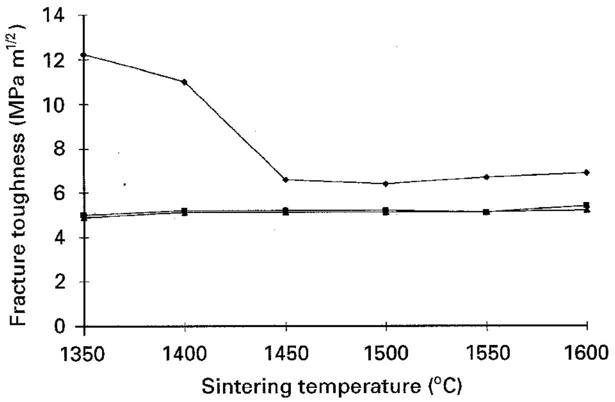

Figure 8 The effect of sintering temperature on the indentation fracture toughness of Y-TZPs. (Indentation load was 300 N.) Key: -◆- YZ860; -■- TZ-2.5Y; -▲- TZ-3Y.

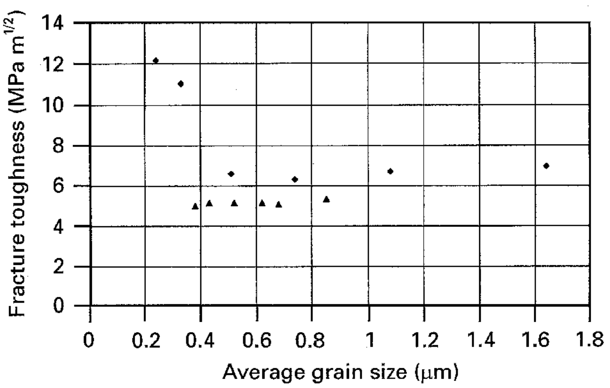

Figure 9 The grain size effect on the fracture toughness of Y-TZP ceramics. Key: ◆ YZ860; ■ TZ-2.5Y.

Fig. 9 shows how the fracture toughness changed with grain size for coated (YZ860) and co-precipitated (TZ-2.5Y) sintered bodies. It can be observed for YZ860 that in a narrow grain size range (0.24 to 0.51 μm) a considerable decrease in K_{1c} (from 12 to 6 MPa m$^{1/2}$) occurred and beyond that grain size range no significant changes in K_{1c} were observed. It is generally thought that an increase in grain size up to a certain limit will increase the transformability and therefore increase the fracture toughness; the reverse is observed for coated Y-TZPs. As for the Tosoh Y-TZP samples, no significant changes in fracture toughness could be observed over the grain sizes used in the present study.

To fulfil one of the objectives of this work, Tosoh Y-TZP samples were fabricated and fired at the optimum sintering temperature (1500 °C) for various times (up to 50 h) to enable grain growth to occur. Table I shows the as-sintered average properties of the resulting ceramics.

It can be seen from Table I, that the properties of both co-precipitated materials obtained from the sintering cycle with a 2 h hold and those shown with that obtained for up to 21 h holding time were quite similar. These results show that increasing the sintering time up to 21 h, had little effect on the bulk density and resulted in increased grain size.

The fracture toughness of both ceramics, on the other hand started to increase as the grain size increased beyond 0.8 μm with the lower yttria content having a higher value. The increase in fracture toughness for ceramic bodies having average grain sizes above 0.8 μm (or > 21 h sintering times) in this study was due to transformation toughening. In contrast, at lower sintering times (or < 0.8 μm), since the starting powder was homogeneous, the sintered microstructure consisted of fine tetragonal grained material (see Fig. 3) which was relatively stable and did not easily undergo the stress induced phase transformation. Since the K_{1c} equation derived by Niihara *et al.* [25] is a function of the l/a ratio (i.e. the ratio of the Palmqvist crack length to the indentation half diagonal), Fig. 10 shows the interdependence of this parameter and the average grain sizes for the 2.5Y-TZP ceramics.

The graph shows distinctively that both materials revealed a different (l/a) ratio trend. In the coated material, the (l/a) ratio is approximately proportional to the average grain size while it is almost inversely proportional in the case for co-precipitated powders. From the present results, it is hypothesized that a lower grain size limit phenomenon was influencing the transformability of the tetragonal grains hence the fracture toughness of both Y-TZP materials;

(a) In co-precipitated powder, below a certain grain size (e.g. 0.8 μm), a transformation toughening mechanism was not active mainly due to the high

TABLE I The properties of the co-precipitated samples after sintering at 1500 °C for long holding times

Holding time (h)	Bulk density ($\mathrm{Mg\,m^{-3}}$)	K_{1c} ($\mathrm{MPa\,m^{1/2}}$)	H_v (GPa)	$t + c$ phase (%)	Average grain size (μm)
Tosoh (2.5Y-TZP) $E = 171$ GPa at 1450 °C/2 h ($\rho_t = 6.1\ \mathrm{Mg\,m^{-3}}$)					
2	6.03	5.2	13.9	100	0.62
10	5.95	5.1	11.5	100	0.66
21	6.02	5.5	12.6	100	0.84
50	5.97	10.2	12.0	98.7	0.98
Tosoh (3Y-TZP) $E = 170$ GPa at 1450 °C/2 h ($\rho_t = 6.1\ \mathrm{Mg\,m^{-3}}$)					
2	6.05	5.1	13.2	100	0.54
10	6.10	5.1	12.6	100	0.66
21	6.08	5.3	12.6	100	0.72
50	6.07	8.3	12.6	99.2	0.98

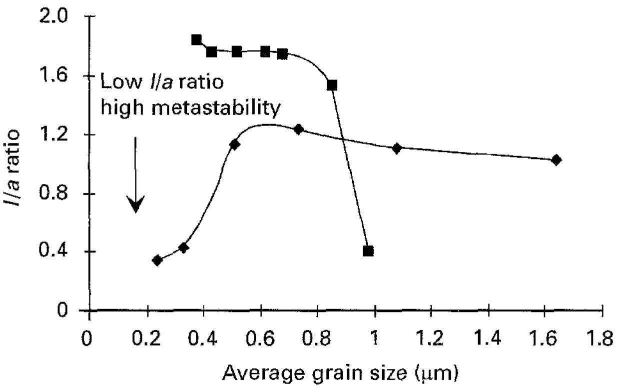

Figure 10 The (l/a) ratio as a function of average grain size for the 2.5Y-TZP ceramics. Key: -◆- coated Y-TZP; -■- co-precipitated TZ-2.5Y.

homogeneity of the powder. Conversely, when the grain size was greater than 0.8 μm but less than a critical size, an increase in K_{1c} occurred.

(b) In contrast for coated material, the effect was opposite. Below a certain lower grain size limit (say 0.5 μm) enhanced fracture toughness resulted. Above this grain size 0.5 μm, no further decrease in K_{1c} took place. This phenomenon is attributed to the inhomogeneous nature of the starting material.

3.4. Microstructural development

Fig. 3 shows typical microstructures of several co-precipitated and coated 2.5Y-TZP samples sintered at various temperatures. At lower temperatures, it was difficult to distinguish the t and c phases in the TZ-2.5Y material due to a very uniform microstructure and distribution of equiaxed fine grains indicating the high degree of homogeneity of the starting powder. However as the sintering temperature increased, grains corresponding to the cubic phase were larger than those of the tetragonal grains (see Fig. 3e and f). In contrast, abnormally large grains corresponding to cubic phase in all the coated materials were evident even at low sintering temperatures (Fig. 3b). The more bimodal grain size consisting of fine equiaxed tetragonal grains and larger cubic grains inherited by coated Y-TZP ceramics can be attributed to the processing technique of the powders [33].

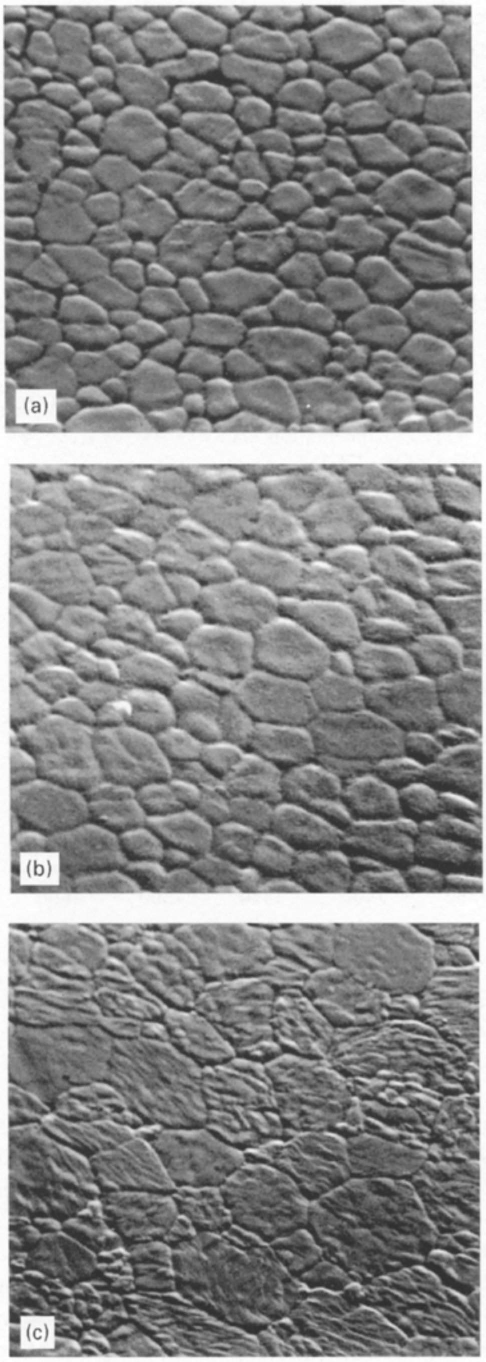

Figure 11 Effect of holding time on the microstructure of co-precipitated 2.5Y-TZP. The sintering temperature was 1500 °C. Holding times (a) 10 h (b) 21 h and (c) 50 h. (Magnification = × 10000.)

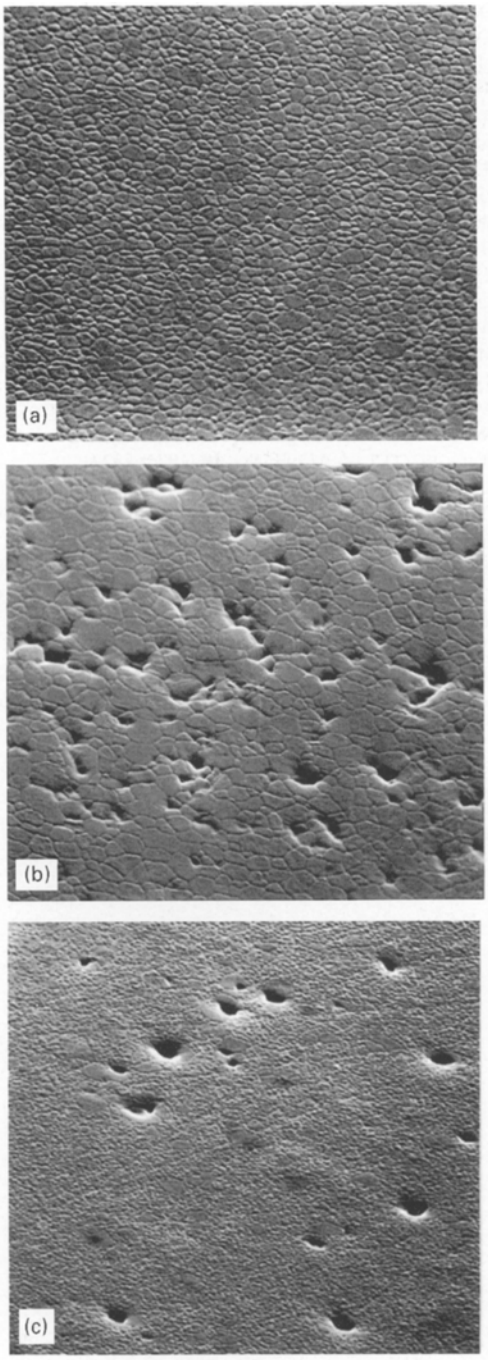

Figure 12 The development of porosity in Y-TZP ceramics. (a) TZ-3Y (1500 °C/21 h), (b) TZ-3Y (1500 °C/50 h) and (c) YZ860 (1400 °C/2 h). (Magnification = × 3000.)

In addition, evidence of tetragonal precipitates embedded within the cubic grains that were believed to have occurred during cooling from the sintering temperature is shown in Fig. 3f, as tiny spots.

Fig. 11 shows the influence of holding time on the grain morphology of co-precipitated powder. There is a minimal difference in grain size between the 10 and 21 h holding time samples. However, excessive partitioning within the tetragonal grains was noticed for the 50 h holding time samples. This could then account for the increase in K_{1c} since the tetragonal grains are highly unstable.

The development of porosity exhibited by both coated and co-precipitated Y-TZP as shown in Fig. 12 is still not fully understood. At lower magnifications (× 3000) all the SEM micrographs of coated samples revealed a certain amount of intergranular porosity, e.g. Fig. 12c. In the co-precipitated ceramics, the development of porosity was only observed for the 1500 °C/50 h sintering as shown in Fig. 12b. However at this stage, this porosity phenomenon is still unclear.

4. Conclusions

1. In the present study, the results showed that the processing history of the starting powder is a crucial factor influencing the sintered microstructure and hence the mechanical properties of Y-TZP ceramics.
2. The characteristics and properties of coated Y-TZP were dependent on the heat treatment temperature. One of the consequences of the coating technique was the development of cubic phase even at low sintering temperature.
3. In contrast, the properties of co-precipitated Y-TZP ceramics were relatively insensitive to the sintering regime employed. A sintering cycle with long holding times was necessary to enhance the fracture toughness of these ceramics.
4. The higher yttria content of co-precipitated powder (TZ-3Y), resulted in smaller grain sizes coupled with higher densities, consistent with that reported in literature.
5. The decrease in density with increasing temperature in coated Y-TZP ceramics was attributed to the growth of the cubic grains in the structure and to some extent, the presence of residual porosity.
6. The transformability of the tetragonal grains for both Y-TZP ceramics were manifest by a lower grain size limit. The fracture toughness trend of coated material contradicted the vast body of reported literature concerning fracture toughness theory, which states that fracture toughness should increase with increasing grain size and transformability. On the other hand, the fracture toughness of co-precipitated material started to increase at alower grain size limit via a nonconventional sintering cycle.

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