

Low-temperature sintering and prolonged holding time on the densification and properties of zirconia ceramic

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In the present work, the effect of low temperature sintering, focusing on varying the sintering holding times on the mechanical properties, microstructure and low temperature degradation behavior of undoped and MnO₂-doped Y-TZP ceramics were investigated. Green samples were sintered at temperatures ranging from 1100 to 1250 °C at varying holding times ranging from 12 min. to 480 min. The sintered bodies were characterized in terms of bulk density, Vickers hardness, fracture toughness, phase stability and grain size. The results indicated that the relative density of above 95%, Vickers hardness of 14 GPa and fracture toughness of 5 MPam^{1/2} were obtained when sintered at lower sintering temperature (below 1250 °C) and longer sintering times for MnO₂-doped Y-TZP samples. Grain growth was marginal and the average grain size of all samples ranged between 0.14 and 0.28 µm. The results indicated that the grain growth kinetics was influenced mainly by the sintering temperature and not by the sintering holding time. The addition of MnO₂ was found to be beneficial in enhancing densification and mechanical properties of Y-TZP particularly at low sintering temperature of 1100 °C and low holding time of 12 min. The low-temperature degradation experiment conducted in superheated steam indicated that all the samples did not transformed to the monoclinic symmetry, attributed mainly to the lower grain size sintered at relatively low sintering temperatures.

Key words: Low temperature sintering, prolonged holding times, Y-TZP, Mechanical properties, Low temperature degradation.

Introduction

Zirconia based ceramic in particular, yttria-tetragonal zirconia polycrystals (Y-TZP) display high strength and toughness, suitable for a range of applications ranging from household appliances such as kitchen knives to aggressive/mechanical components such as chemical filters, piston rings, extrusion dies, cutting tool inserts, etc. Recently zirconia ceramics have received great response in biomedical applications especially for dental restoration owing to their excellent bio-compatibility as well as good esthetic appearance. The high strength and fracture toughness of stabilized zirconia are attributed to the ability of the ceramic to absorb energy from propagating crack which causes the surrounding tetragonal grains to spontaneously transform to the monoclinic symmetry and preventing further crack propagation into the bulk material; a phenomenon known as transformation toughening [1].

One of the major limitation of Y-TZP is the undesirable low temperature degradation (LTD) or hydrothermal ageing when exposed to steam environment at temperatures ranging from 60 to 500 °C, which result in a spontaneous tetragonal to monoclinic phase transformation [2, 3]. When this phase transformation occurs, it spread inwards from the surface causing compressive stresses built up due to the transformed grains, resulting in the formation of micro and macro cracks thus leading to failure of the ceramic. The mechanism of LTD still remains controversial, but many believed that the presence of water vapour facilitates LTD by accelerating the kinetic reaction of the monoclinic phase transformation [4-6].

There are several factors that have direct influence on the LTD of Y-TZP ceramics such as the amount and distribution of stabilizer, grain morphology and presence of secondary phases [7-10]. It is also been reported that the room-temperature phase stability, strength and toughness of Y-TZP depend strongly on a critical grain size [11, 12]. For instance, lowering of the grain size has a positive impact in enhancing the strength, however in contrast, the fracture toughness was found to increased gradually with increasing grain size and peaked at a critical grain size before decreasing with further

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increased in the grain size [7-9]. The critical grain size in 3 mol% Y-TZP has been reported vary from 1 to 6 μm , depending on the processing condition of the starting powders and consolidation methods [13, 14]. Nevertheless, improvement in LTD resistance for most Y-TZPs requires the critical grain size of the ceramic to be below 0.25 μm [15].

The sintering conditions (e.g. sintering condition, soaking temperature and holding time) are one of the predominating factors which determines the properties of the Y-TZP ceramic [16]. In most cases for commercial Y-TZP powders, sintering temperature at 1400-1500 °C and holding time of 2-4 hrs are required via the common pressureless sintering approach [17, 18]. In addition, it has been observed that a decreased in bulk density and grain growth proceed during high temperature sintering and the use of prolonged sintering times [14, 19-22]. Furthermore, higher sintering temperatures promote the formation of large cubic grains which lowers the fracture toughness of the sintered body [23-28].

A viable method frequently being used to suppress grain growth in Y-TZP ceramic is by lowering the densification temperature through the use of suitable sintering additives [2]. Many workers have shown that the addition of small amount of dopants such as SiO_2 , Al_2O_3 , Fe_2O_3 , CuO and MnO_2 were beneficial in refining the grain structure and promoting densification at lower sintering temperatures. For example, Wu et al. [29] reported that addition of 0.25 wt% Al_2O_3 could effectively retard the LTD in 3Y-TZP [11]. Guo [30] successfully produced high densities (> 95%) sintered bodies with an average grain size of < 0.20 μm at 1150 °C when doped with up to 2 mol% Fe_2O_3 . On the other hand, Ramesh [31] discovered that high relative densities (> 97.5%) could be obtained at < 1300 °C with the addition of 0.5 wt% MnO_2 .

The present work was aims at investigating the LTD behaviour and microstructural development of commercial 3 mol% Y-TZP with and without the aid of MnO_2 additive by pressureless sintering at low temperature (1100-1250 °C). The study also explores at prolong sintering (12-480 minutes) on the microstructure and properties of the Y-TZP.

Experimental Procedures

The samples were manufactured from high purity commercial available 3 mol% yttria-stabilized zirconia powder (Kyoritsu, Japan). In this work, two MnO_2 -doped Y-TZP containing 0.5 and 1.0 wt% were prepared via mechanical milling using ethanol as the mixing medium. The doped powders were dried in oven and sieved to obtain ready to pressed powders. The green samples in the form of discs (20 mm diameter) and rectangular bars (4 mm $\times$ 13 mm $\times$ 32 mm) were cold isostatically pressed at 200 MPa. The green samples were pressureless

sintered under ambient condition using a box furnace (Carbolite, UK) at four different temperatures (1100, 1150, 1200 and 1250 °C) for 5 sintering holding times (12, 60, 120, 240 and 480 min.) with standard heating and cooling rates of 10 °C/min. The as-sintered disc was ground on one surface by using SiC papers followed by diamond polishing to a 1 μm surface finish before testing.

Bulk density of the sintered samples was measured by Archimedes method using distilled water as medium and the relative density was obtained by taking the theoretical density of Y-TZP as 6.10 g/cm³. Young's Modulus measurement by sonic resonance was determined for rectangular bar sample using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer; the vibrations are physically induced in the sample by tapping. The Young's Modulus was calculated using the experimentally determined resonant frequency [32]. Vickers hardness (H_v) and fracture toughness (K_{Ic}) were measured on polished disc samples using the Vickers indentation method. The value of K_{Ic} was computed using the equation derived by Niihara et al. [33]. For each sample, five measurements were made and the average values were obtained.

The phases present in the powders and sintered samples were determined by X-ray diffraction (XRD) using Cu-K α as the radiation sources operating at 40 kV and 40 mA within 2θ range 27-33 ° with 0.02 ° step size. The monoclinic (m) phase present in the ceramic matrix was determined using the method proposed by Toraya et al. [34].

Hydrothermal ageing or LTD experiment was performed in an autoclave containing distilled water and heated for 180 °C/10 bar for periods up to 120 hrs. The monoclinic phase changes as a function of ageing time of 0, 3, 6, 12, 24, 48 and 120 hrs were monitored. The microstructure of the specimens was observed by field emission scanning electron microscope (FE-SEM) and the average grain size measurement was calculated using the line intercept analysis of Mendelson [35].

Results and Discussion

The relative density of the undoped, 0.5 wt% MnO_2 -doped- and 1 wt% MnO_2 -Y-TZPs sintered at various temperature and periods are shown in Fig. 1. Overall, the relative density of the samples displaced an increasing trend with increasing sintering temperature and holding times, with the former being more dominant than the latter. The dopant was found to be beneficial in enhancing the densification of Y-TZP to a certain extend. For instance, sintering at 1200 °C showed that for the undoped Y-TZP to achieve above 90% relative density requires a minimum holding time

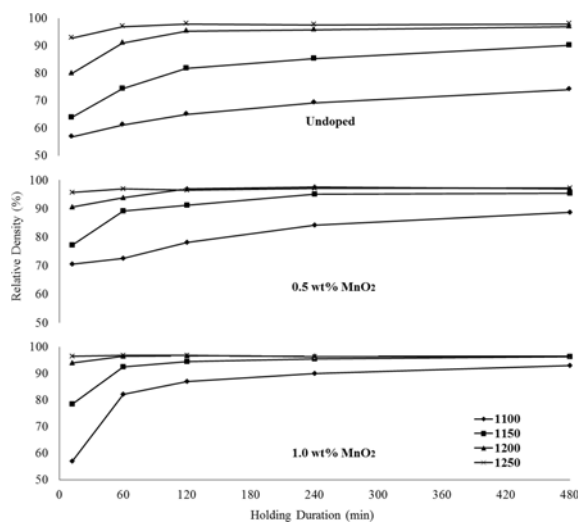


Fig. 1. Effect of sintering temperature and holding time on the relative density of Y-TZPs.

of 120 min. while both the MnO_2 doped samples required only 12 min. holding time to achieved similar density. Nevertheless, at low sintering temperature of 1100 °C, the 1.0 wt% MnO_2 -doped samples obtained similar density with longer holding time of 240 min. Sintering at 1250 °C resulted in the relative density remained constant for all samples at ~97% regardless of holding time except for the undoped Y-TZP which exhibited slight improvement (93 to 97%) when the holding time was extended beyond 12 min. The effect of dopant in promoting high densification of Y-TZP at low temperature sintering was in agreement with reported literatures [31, 36]. Zhou et al. [37] suggested that the diffusion activation energy was reduced as the result of Mn^{4+} substitution in the crystal structure of zirconia. The results also indicated that higher amount of MnO_2 dopant (1.0 wt%) was beneficial in aiding densification of Y-TZP ceramics at low temperature with longer holding time at temperatures of 1100–1150 °C but not effective for high temperature (> 1200 °C) sintering.

The variation of the fracture toughness of the zirconias with increasing sintering holding times and temperatures is shown in Fig. 2. Sintering at higher sintering temperatures (1200 & 1250 °C), the K_{Ic} of the undoped and 0.5 wt% MnO_2 -doped Y-TZPs did not vary significantly, between 4.9 and 5.6 $\text{MPa m}^{1/2}$, with increasing sintering holding time. On the other hand, the toughness of all Y-TZPs sintered at lower sintering temperature (1100 & 1150 °C) was enhanced (1.6 to 5.2 $\text{MPa m}^{1/2}$) with increasing holding times. In order to achieved $K_{Ic} > 5 \text{ MPa m}^{1/2}$ at 1150 °C, the holding time for undoped Y-TZP was 480 min, while the holding time for MnO_2 (0.5 and 1.0 wt%) doped Y-TZPs requires a shorter duration of 60 min. In comparison to the undoped Y-TZP, a longer holding times (240 and 480 min) was needed for both the MnO_2 -doped Y-TZPs

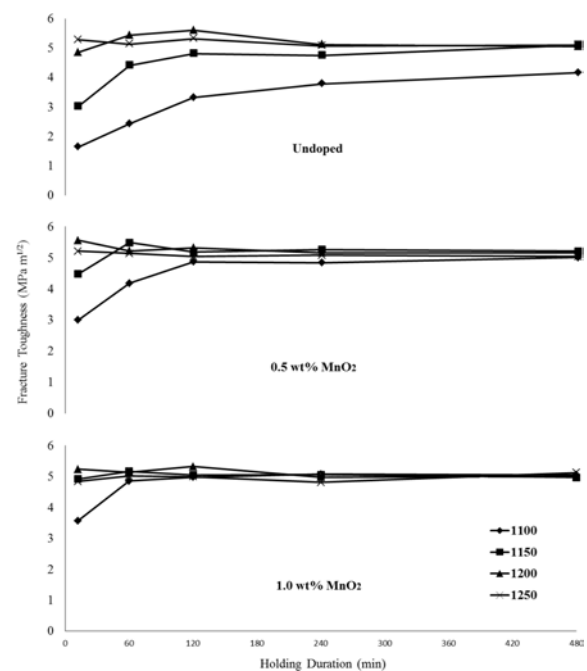


Fig. 2. Fracture toughness variation as a function of sintering temperature and holding time.

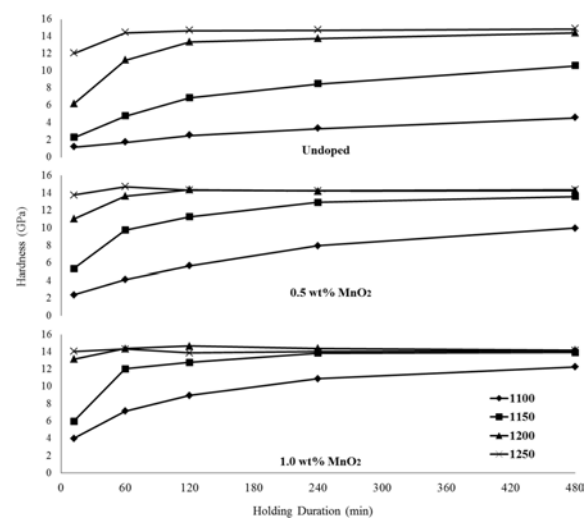


Fig. 3. Effect of sintering temperature and holding time on the Vickers hardness of zirconias.

sintered at 1100 °C to attain a K_{Ic} of above 5 $\text{MPa m}^{1/2}$. In general, at sintering temperatures of 1200–1250 °C, all the Y-TZPs exhibited a constant toughness despite increasing holding time which is likely to be attributed to the homogeneous distribution of stabilizer within the zirconia grains and thus resulting in a stable tetragonal grain with less transformability [38]. Therefore, it can be inferred that the stability of the tetragonal grains of Y-TZP was not affected with the addition of manganese oxide when sintered using the current sintering profile as all the samples did not exhibited the presences of monoclinic phase.

The Vickers hardness trend (Fig. 3) of the Y-TZPs

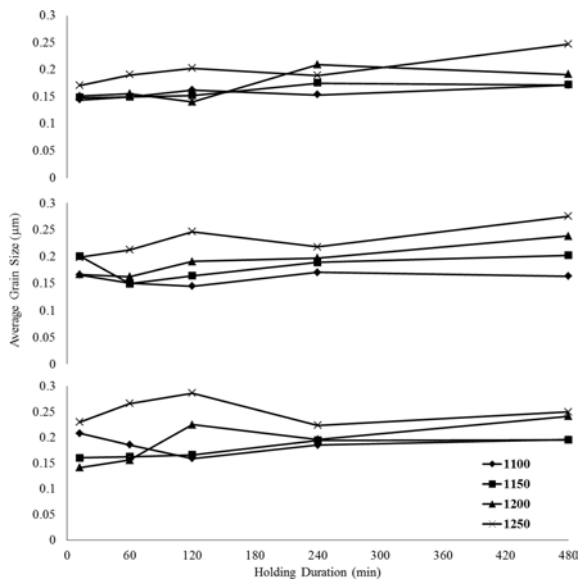


Fig. 4. Average grain size variation as a function of sintering temperature and holding time.

was in good agreement with that of relative density variation with sintering temperature and holding time. In general, the hardness was found to increase with sintering temperature and holding times up to 120 min. In the present work, high hardness of > 14 GPa was obtained for the doped samples sintered at 1250°C

with 12 min. and 60 min. holding times. For the 1 wt% MnO_2 -doped Y-TZP, the Vickers hardness was found to fluctuate marginally between 13 and 14 GPa regardless of holding time employed. All the Y-TZPs sintered at low temperatures of 1100 and 1150°C could hardly achieve hardness above 14 GPa, albeit long holding times coupled and with the aid of sintering additive.

The mechanical properties (e.g. hardness and toughness) of the ceramic for structural application can be correlated with the densification and the grain size of the sintered body. Based on Figs. 1 and 3, hardness of the Y-TZP when sintered at low temperatures of 1100 and 1150°C was relatively low mainly due to the low density of the ceramic. It was not the case for MnO_2 -doped Y-TZP sintered at 1250°C where the hardness showed a slight dropped compared to the undoped sample and further declined for the 1 wt% MnO_2 -doped Y-TZP. Higher amount of dopant believed to create porosity resulting to a reduction in densification [39] and this seemed to be the trend observed in present work. The FE-SEM investigation also revealed that the formation of cubic grain of relatively lower density as compared to tetragonal grain was not possible as there was no sign of exaggerated large grains, believed to be of the cubic type, that usually exist at elevated sintering temperatures [14, 20].

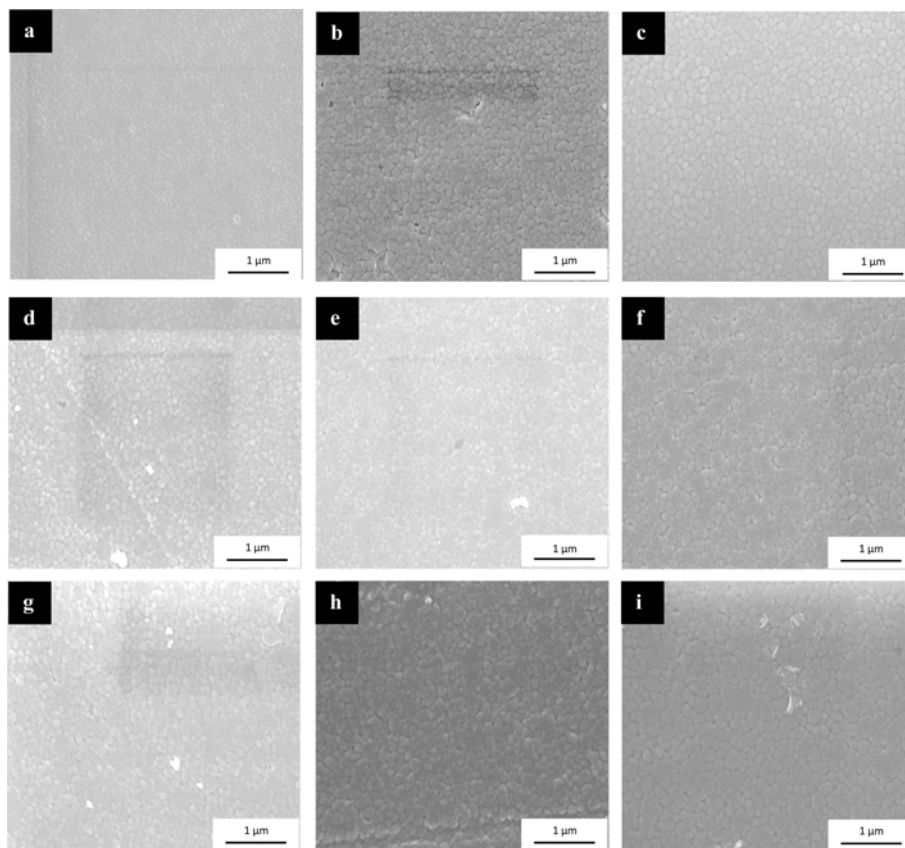


Fig. 5. Microstructure evolution of Y-TZPs sintered at 1250°C with various holding time for: undoped - (a) 12 min., (b) 120 min. & (c) 480 min.; 0.5 wt% MnO_2 -(d) 12 min., (e) 120 min. & (f) 480 min., and 1 wt% MnO_2 -(g) 12 min., (h) 120 min. & (i) 480 min.

Selected FE-SEM micrographs of polished Y-TZP surfaces are shown in Fig. 4. In general, a uniform equiaxed fine grain microstructure was observed for all samples. The grain sizes varied from 0.14 to 0.28 μm . The average grain size was observed to fluctuate between 0.15 and 0.20 μm for samples sintered at 1100–1150 $^{\circ}\text{C}$, where majority of the samples grain size are more prone to the lower limit. Within the same sintering temperature range, the effect of sintering duration on the grain growth of the Y-TZP ceramics was marginal. However Y-TZP ceramics sintered at 1200–1250 $^{\circ}\text{C}$, larger grains was evident which range between 0.20 and 0.25 μm . It was also found that longer sintering time promoted grain growth for the undoped samples but the doped samples exhibited higher growth rate especially for samples doped with 1 wt% MnO_2 .

The effect of hydrothermal ageing on the tetragonal phase stability of the sintered Y-TZP was studied by exposing in superheated steam for up to 120 hrs and the XRD patterns are shown in Fig. 5. The peaks corresponding to the monoclinic phase was not detected in the undoped and MnO_2 -doped Y-TZPs sintered at various temperature profiles even after exposure in superheated steam for up to 120 hrs.

In terms of ageing resistance, it is well established in many research that grain size factor is one of the indicators used to measure the stability of the tetragonal grain during hydrothermal ageing test. Y-TZP ceramic is susceptible to LTD when the grain sizes are above a critical size [40, 41]. The current work revealed that all the ceramics were resistant to ageing-induced phase transformation and the average grain sizes of all the samples varied between 0.14 to 0.29 μm , which is less than the critical size of 0.3 μm as reported in earlier work [42]. According to Schmauder and Schubert [43], the stresses originated from thermal expansion anisotropy is lower for smaller grains if compared to the larger grains. In addition, the grain shape also plays a part, for instant, spherical or grains with rounded edges have less stresses as observed in the present Y-TZP. Several workers have shown that improvement in ageing resistance was plausible with the addition of dopants and relates the enhancement to suppression of grain growth in the sintered Y-TZP resulting from low temperature sintering and grain boundary modification [29, 32, 36, 44, 45].

Conclusions

The influence of sintering temperature, sintering holding times and sintering additives on the densification and properties of Y-TZP have been investigated. It was found that MnO_2 -doped Y-TZP ceramics exhibited a relative density of above 95% when sintered at low temperature of 1150 $^{\circ}\text{C}$ and holding time of 240 min.

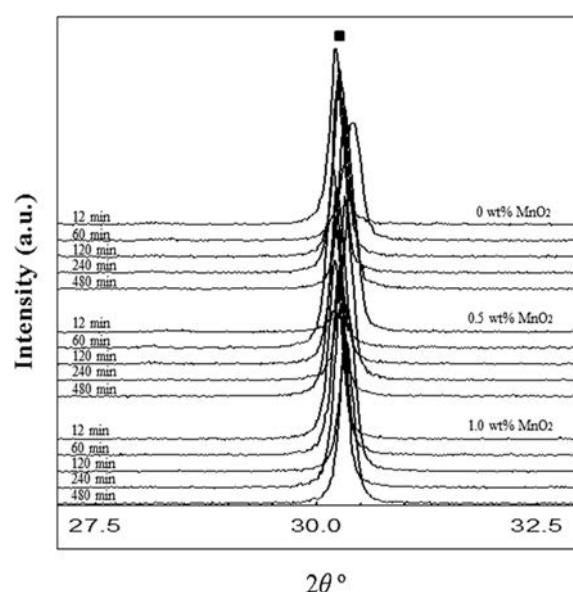


Fig. 6. XRD of Y-TZPs sintered at 1250 $^{\circ}\text{C}$ after hydrothermal ageing for 120 hrs, revealing the presences of tetragonal phase (■).

while undoped samples required higher sintering temperature of 1200 $^{\circ}\text{C}$ but shorter holding time of 120 min. to achieve similar density. Vickers hardness of above 14 GPa was achieved with sintering temperature and holding time of 1150 $^{\circ}\text{C}$ and 240 min, respectively for Y-TZP ceramic doped with 1 wt% MnO_2 compared to undoped ceramic which required a higher sintering temperature of 1250 $^{\circ}\text{C}$. The fracture toughness of about 5 $\text{MPa}\cdot\text{m}^{1/2}$ could only be achieved for undoped Y-TZP ceramic when sintered at 1150 $^{\circ}\text{C}$ at a long holding time of 480 min. whereas a shorter holding time of 60 min. was sufficient to achieved similar toughness for the manganese oxide doped ceramics. The average tetragonal grain size of all the samples varied between 0.14 and 0.28 μm , and grain coarsening was not observed for all samples even with the use of long holding times. The results showed that the holding time has marginal effect on the grain growth but higher growth rate was prevalent with increasing sintering temperature. Finally, all the zirconias exhibited excellent resistant to LTD without any formation of monoclinic phase when exposed to superheated steam for periods up to 120 hrs.

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