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Ceramics International 34 (2008) 1603–1608
CERAMICS INTERNATIONAL
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Effect of manganese oxide on the sintered properties and low temperature degradation of Y-TZP ceramics

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Received 4 January 2007; received in revised form 27 February 2007; accepted 2 April 2007
Available online 2 June 2007

Abstract

The sinterability of yttria-tetragonal zirconia polycrystals (Y-TZP) containing small amounts of MnO_2 as sintering aid was investigated over the temperature range of 1250–1500 °C. Sintered samples were evaluated to determine bulk density, Young's modulus, Vickers hardness and fracture toughness. In addition, the tetragonal phase stability of selected samples was evaluated by subjecting the samples to hydrothermal ageing in superheated steam at 180 °C/10 bar for up to 24 h. The results showed that the addition of MnO_2, particularly ≥0.3 wt% was effective in aiding densification, improving the matrix stiffness and hardness when compared to the undoped Y-TZP sintered at temperatures below 1350 °C. On the other hand, the fracture toughness of Y-TZP was unaffected by MnO_2 addition except for the 1 wt% MnO_2-doped Y-TZP samples sintered above 1400 °C. The hydrothermal ageing resistance of Y-TZP was significantly improved with the additions of MnO_2 in the Y-TZP matrix.

Keywords: Manganese oxide; Sintering additives; Ageing; Y-TZP; Zirconia

1. Introduction

Yttria-tetragonal zirconia polycrystals ceramics (Y-TZP) possessed excellent physical and mechanical properties, thus making it an attractive candidate for a host of engineering applications [1,2]. One of most successful applications of Y-TZP ceramics is found in orthopedics, with femoral heads for total hip replacement [3,4]. The excellent mechanical properties of Y-TZP can be attributed to a remarkable phenomenon known as transformation toughening [5]. In this mechanism, the stress at the tip of a propagating crack will be absorbed by the metastable tetragonal grain and causing it to transform into the monoclinic symmetry which is accompanied by about 4% volume expansion. As a result, compressive strain is generated at the crack tip thus making it difficult for further crack advancement. Typically, Y-TZP exhibits strengths and toughnesses of more than 1 GPa and 6–10 MPa $m^{1/2}$, respectively [6].

However, one of the major limitations of Y-TZP ceramic is its susceptibility to ageing-induced tetragonal (t) to monoclinic (m) phase transformation when exposed in steam environment. Kobayashi et al. [7] was the first to observe that Y-TZP ceramics exhibited a slow (t) to (m) phase transformation, starting at the free surface followed by the formation of microcracking and strength degradation. Many other workers have since reported the ageing phenomenon in Y-TZP and attempted to suppress this devastating effect of ageing [8–11] although the underlying mechanism that governs ageing has not been unequivocally resolved [12]. Nevertheless, many studies were devoted towards grain boundary modification by the use of sintering additives or dopants since it has been perceived that during ageing monoclinic nucleation starts at grain boundary regions and propagate inwards into the grain [4,13,14].

In general, small or even minute amounts of dopants can promote densification and substantially control the microstructure as well as to enhance the mechanical properties of the sintered Y-TZP body [15–22]. For instance, studies carried out by Kenellopoulous and Gill [22] revealed that doping Y-TZP with copper oxide (CuO) enhances the densification of the ceramics through a mechanism involving liquid phase due to

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0272-8842/$34.00
doi:10.1016/j.ceramint.2007.04.012

the low melting point of CuO in ZrO_2 matrix. Therefore, the inclusion of transition metal oxides such as manganese oxide (MnO_2) is likely to affect hydrothermal ageing resistance if they aid densification at relatively low temperatures, below 1350 °C.

In this present work, the beneficial effect of MnO_2 doping on the densification and mechanical properties of commercial 3 mol% Y-TZP is reported. In addition, the effect of MnO_2 in suppressing the ageing-induced phase transformation is highlighted.

2. Materials and methods

2.1. Sample preparation

The as-received 3 mol% yttria-stabilized zirconia powder supplied by Kyoritsu, Japan had a total impurity concentration of about 0.1 wt%, with SiO_2, Fe_2O_3, TiO_2 and Al_2O_3 as the major impurities. The Y-TZP powder (standard grade KZ-3YF) had a specific surface area of 12 m^2/g and a mean particle diameter of 0.3 μm. Varying amounts of high purity manganese oxide (MnO_2: 0.05, 0.1, 0.3, 0.5 and 1 wt%, BDH, UK) was mixed with the Y-TZP powders by wet milling, using zirconia balls as the milling media and ethanol as the mixing medium. The slurry was oven dried and sieved to obtain soft, ready-to-press powders.

Disc (20 mm diameter) and rectangular bar (4 mm × 13 mm × 32 mm) green samples were compacted at 0.3 MPa and cold isostatically pressed at 200 MPa. Consolidation of the particles by pressureless sintering was performed in air using a rapid heating furnace (ModuTemp, Australia), at various temperatures ranging from 1250 to 1500 °C, maintained at the soak temperature for 2 h before cooling to room temperature. The sintered samples were ground on one face by SiC papers of 120, 240, 600, 800 and 1200 grades successively, followed by polishing with 6 and 1 μm diamond paste to produce an optical reflective surface.

2.2. Characterization

The bulk density of the sintered samples was measured based on Archimedes' principle using an electronic balance retrofitted with a density determination kit (Mettler Toledo, Switzerland). The Young's modulus by sonic resonance was determined for rectangular samples 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 modulus of elasticity or Young's modulus is calculated using the experimentally determined resonant frequency [23] and the values were found be consistent regardless of the number of test performed for each samples. Fracture toughness (K_{Ic}) and Vickers hardness measurements (Future Tech., Japan) were made on polished samples using the Vickers indentation method. The indentation load was kept constant at 98.1 N and a loading time of 10 s was employed. The values of K_{Ic} were computed using the equation derived by Niihara et al. [24]. For each test, five measurements were made and the error was found to be less than 1%. As such, average values were used for the analysis.

Phase analysis by X-ray diffraction (XRD: Geiger-Flex, Rigaku Japan) of the powders and solid samples were carried out under ambient conditions using Cu K α as the radiation source operating at 35 kV in step mode with a 0.02° 2θ step and a count time of 0.5 s per step over the 2θ range 27–36° which covers the monoclinic (m) and tetragonal/cubic (t, c) related {1 1 1} peaks. The fraction of the monoclinic (m) phase present in the ceramic matrix was determined using the method of Toraya et al. [25]. In order to determine if the dopant promoted the formation of cubic (c) phase in the Y-TZP structure, high angle diffraction analysis was performed on all sintered samples. For this purpose, a 0.02° 2θ step and a count time of 35.5 s per step over the 2θ range 72–76° which covers the cubic related {0 0 4} peaks were used. The volume fraction of the cubic phase was then estimated by using the relationship of Garvie et al. [5] which was modified by Paterson and Stevens [26]. In addition, microstructural evolution under the various sintering temperatures was examined using scanning electron microscopy (SEM). The samples were polished to 1 μm surface finish using diamond paste and subsequently thermally etched to delineate the grain boundaries. The average grain size was determined from scanning electron micrographs using the line intercept analysis [27].

The hydrothermal ageing experiment was performed in an autoclave containing superheated steam (180 °C/10 bar) for up to 24 h. The extent of surface monoclinic development was evaluated by XRD analysis.

3. Results and discussion

The XRD results of the as-received Y-TZP powder indicated the presence of ∼20% monoclinic (m) phase and ∼80% tetragonal (t) phase content. Similar phase ratios were also found in all the doped powders, thus indicating that the dopant had negligible effect on the phase content of the starting zirconia powder.

Upon sintering up to 1500 °C, samples containing up to 0.5 wt% MnO_2 exhibited a fully tetragonal phase whereas the tetragonal grains in the 1 wt% MnO_2-doped ceramic started to become unstable when sintered above 1450 °C. This was evident with the detection of about 3% surface monoclinic content when fired at 1500 °C. In addition, the XRD analysis conducted at higher diffraction angle for all the samples indicated the presence of cubic (c) phase in the 1 wt% MnO_2-doped Y-TZPs throughout the sintering regime employed. The cubic phase was not detected in all other samples. The measured cubic phase in the 1 wt% Mn-doped Y-TZP was found to increase with increasing sintering temperature as shown in Table 1. Further sintering at 1600 °C, however was detrimental as the 1 wt% MnO_2-doped developed high amounts of (m) phase, i.e. ∼48% and this was accompanied by severe cracks on the sample surfaces.

The average tetragonal grain sizes determined from SEM micrographs for polished and thermally etched Y-TZP samples

Table 1
Phase analysis of 1 wt% MnO_2-doped Y-TZP sintered at various temperatures

	Phase content (%)						
	1250 °C	1300 °C	1350 °C	1400 °C	1450 °C	1500 °C	1600 °C
(m)-ZrO_2	0	0	0	0	0	3.3	48.3
(t)-ZrO_2	96.1	95.6	95.1	94.5	91.9	86.9	0
(c)-ZrO_2	3.9	4.1	4.9	5.5	8.1	9.8	51.7

Table 2
Influence of MnO_2 on the average tetragonal grain sizes (μm) of Y-TZPs sintered at various temperatures

MnO_2 content (wt%)	Sintering temperature		
	1250 °C	1350 °C	1500 °C
0 (undoped)	0.24	0.27	0.51
0.05	0.23	0.28	0.49
0.1	0.22	0.28	0.48
0.3	0.24	0.27	0.49
0.5	0.22	0.28	0.5
1	0.23	0.29	0.5

sintered at 1250, 1350 and 1500 °C are presented in Table 2. In general, the addition of MnO_2 to Y-TZP did not affect the average tetragonal grain size when compared to the undoped ceramic sintered at the same sintering temperature as typically shown in Fig. 1 for 1350 °C sintering.

The bulk density variation with sintering temperature for undoped and Mn-doped Y-TZPs is shown in Fig. 2. The density of Y-TZPs sintered below 1400 °C was significantly improved by the addition of up to 0.5 wt% manganese oxide. In particular, Fig. 2 shows that Y-TZP samples containing ≥0.3 wt% MnO_2 exhibited ∼98% theoretical density (the theoretical density of Y-TZP was taken as 6.1 Mg m^{-3}) if compared to the undoped ceramic (∼91% theoretical density) when sintered at 1250 °C. The bulk density of the undoped, 0.05 and 0.1 wt% MnO_2 doped exhibited a similar trend with increasing sintering temperature, i.e. the bulk density increases to a maximum at 1350 °C for both the doped samples and at 1450 °C for the undoped ceramic before remaining almost constant with further increase in temperature.

In contrast, the bulk density variation of the 1 wt% MnO_2-doped Y-TZP exhibited an opposite trend with increasing sintering temperature above 1300 °C as shown in Fig. 2. In

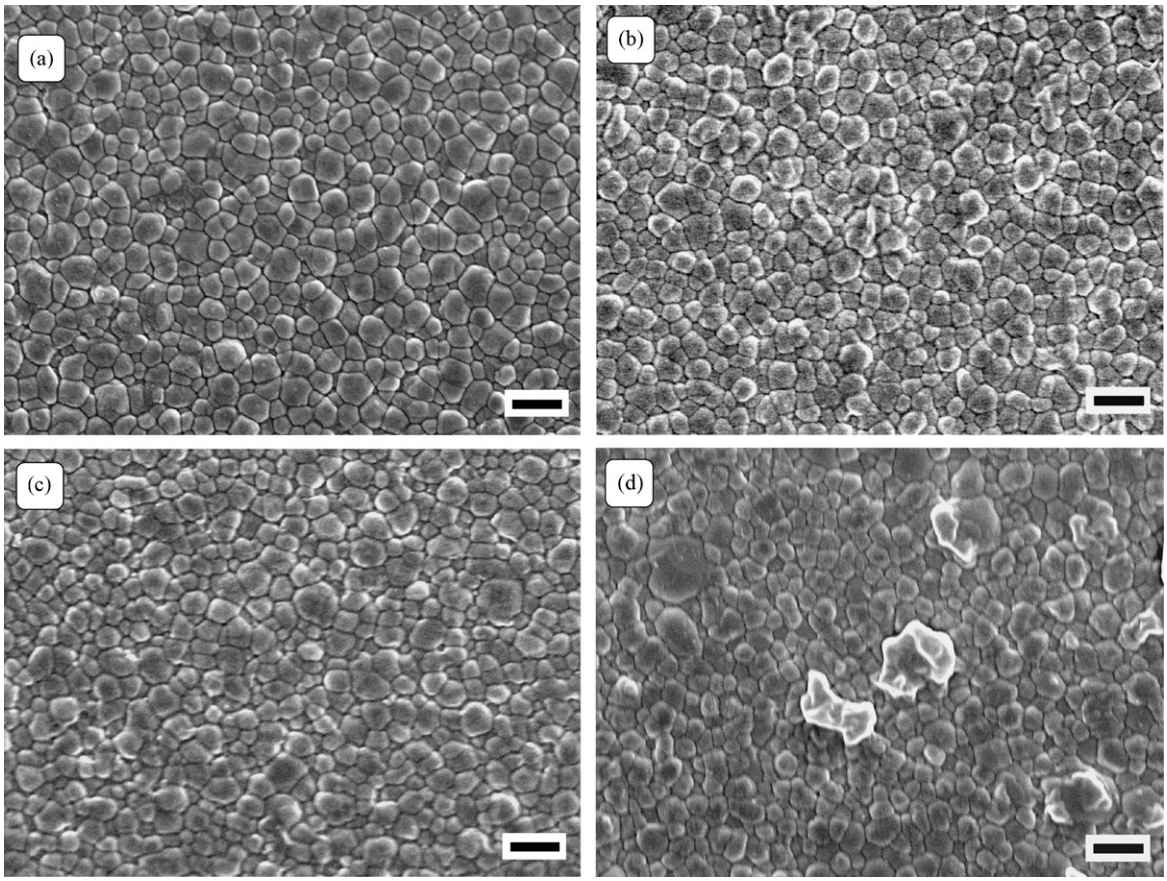

Fig. 1. SEM microstructure of samples sintered at 1350 °C. (a) Undoped Y-TZP and, (b) 0.05 wt%, (c) 0.1 wt% and (d) 1 wt% MnO_2-doped Y-TZP, respectively (bar = 0.5 μm).

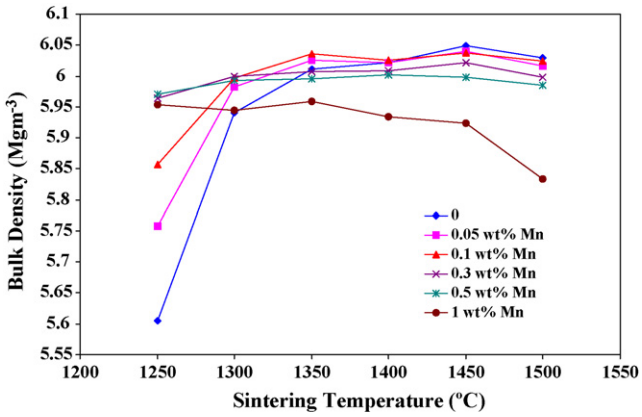

Fig. 2. Effect of sintering temperature and MnO_2 addition on the bulk density of Y-TZP.

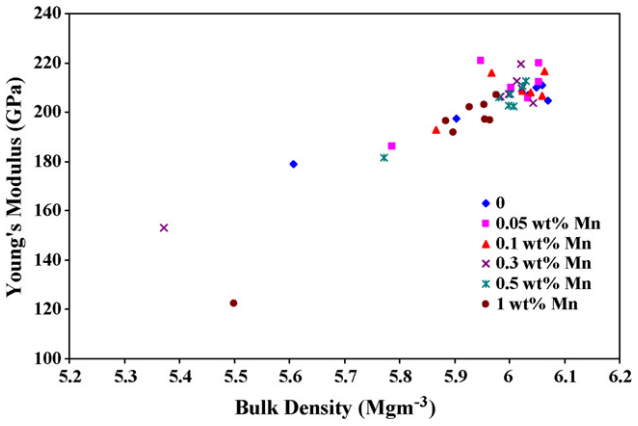

Fig. 4. Young's Modulus varied linearly with increasing bulk density.

general, the lower bulk density exhibited by the 1 wt% MnO_2-doped Y-TZP throughout the sintering regime employed as depicted in Fig. 2 could be attributed to the development of cubic phase in the tetragonal matrix.

The variation of Young's Modulus (E) of sintered samples with increasing sintering temperature is shown in Fig. 3. The beneficial effect of MnO_2 in enhancing the matrix stiffness of Y-TZP can be observed particularly when sintered at low temperature of 1250 °C. The E value of the undoped Y-TZP was low (<180 GPa) when sintered at 1250 °C as compared to >200 GPa for Y-TZP containing ≥0.3 wt% MnO_2 as shown in Fig. 3. However, as the sintering temperature was increased, the E value of the undoped material started to increase slowly and reached a maximum of ∼208 GPa at 1450 °C. Samples containing 0.05 and 0.1 wt% MnO_2 exhibited E values >200 GPa when sintered ≥1300 °C, whereas the E values of samples containing 0.3 and 0.5 wt% MnO_2 were generally above 200 GPa regardless of sintering temperature. In contrast, the Young's modulus of the 1 wt% MnO_2-doped Y-TZP was high (∼205 GPa) when sintered at 1250 °C but as the sintering temperature was increased, this was accompanied by a decreased in the E value to below that of the undoped ceramics. In general, the Young's modulus of all the Y-TZPs studied correlated well with the sintered bulk density, i.e. the E value varied linearly with increasing density as shown in Fig. 4.

The effect of sintering temperatures and MnO_2 additions on the room temperature Vickers hardness of Y-TZPs is shown in Fig. 5. The results revealed the beneficial effect of MnO_2 in improving the hardness of Y-TZP at low sintering temperatures (i.e. below 1350 °C). The hardness of the undoped Y-TZP was at its lowest (∼9.7 GPa) when sintered at 1250 °C and soon increases rapidly to ∼12.8 GPa at 1300 °C before reaching a maximum of ∼13.7 GPa at 1400 °C. The hardness of these samples, however decreased slightly with further sintering, down to ∼13.2 GPa at 1500 °C. In comparison, the hardness of all the MnO_2-doped samples was higher than the undoped material when sintered at 1250 and 1300 °C as shown in Fig. 5. The hardness trend of the 0.05 and 0.1 wt% MnO_2-doped samples was similar, i.e. increased rapidly from ∼11.3 and ∼12.0 GPa, respectively when sintered at 1250 °C to attained values of above 13 GPa at 1300 °C. However, for sintering beyond 1300 °C, the hardness trend of both doped materials was in agreement with that of the undoped ceramic.

Similar observation was noted for the hardness trend of 0.3 and 0.5 wt% MnO_2-doped Y-TZPs with increasing sintering temperature. Both materials exhibited very high hardness of ∼13.2 GPa (0.3 wt%) and 13.6 GPa (0.5 wt%) when sintered at 1250 °C. As the sintering temperature increased to 1300–1350 °C, both the 0.3 and 0.5 wt%-doped ceramics attained similar hardness value of 13.5 GPa. However, sintering beyond

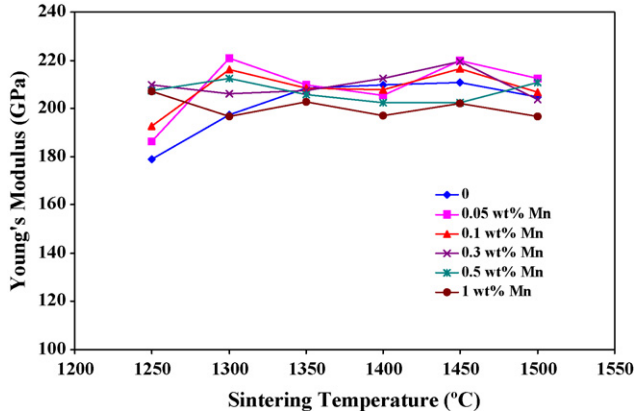

Fig. 3. Effect of MnO_2 additions on the Young's modulus of Y-TZPs.

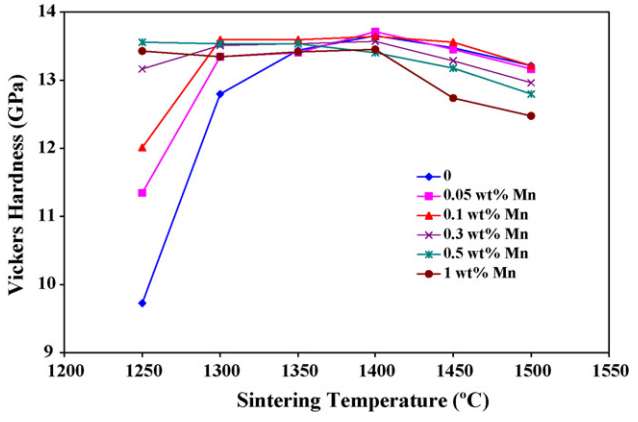

Fig. 5. Variation of Vickers hardness of Y-TZPs as a function of sintering temperature.

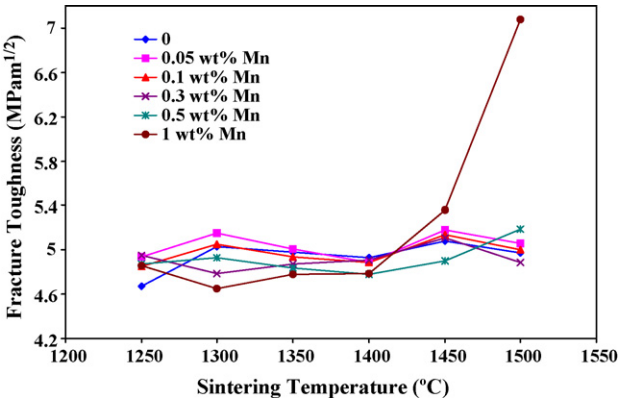

Fig. 6. Effect of MnO_2 on the fracture toughness of Y-TZPs.

1350 °C was detrimental as the hardness of both ceramics decreased, with the 0.5 wt% MnO_2 being more affected as shown in Fig. 5.

In contrast, the hardness of the 1 wt% MnO_2-doped Y-TZP did not change significantly for sintering up to 1400 °C. The hardness of the sample was observed to fluctuate between 13.3 and 13.4 GPa when sintered between 1250 and 1400 °C, before decreasing rapidly with further sintering. The 1 wt% MnO_2-doped Y-TZP exhibited the lowest hardness for sintering above 1400 °C as shown in Fig. 5 and this can be associated with the relatively low bulk density exhibited by the samples as depicted in Fig. 2 and also to the increased in cubic phase content for samples sintered above 1450 °C. Nevertheless, the hardness of 1 wt% MnO_2-doped ceramics was higher than the undoped Y-TZP when sintered at 1250–1300 °C.

The variation in the fracture toughness of undoped and MnO_2-doped Y-TZPs is shown in Fig. 6. It has been found that the fracture toughness of the undoped and up to 0.5 wt% MnO_2-doped Y-TZPs did not vary significantly with increasing temperatures and the K_{Ic} values fluctuated between 4.6 and 5.2 MPa $m^{1/2}$. Since the transformation toughening mechanism is related closely with the transformability of the (t) grains [6], the fracture toughness can be used as an indication of the state of stability of the tetragonal grains in the zirconia matrix. In general, a high fracture toughness would indicate that the (t) grain was in a metastable state and responded immediately to the stress field of a propagating crack, such as induced during the indentation test [18]. In the present work, Y-TZP containing up to 0.5 wt% MnO_2 did not show any indication of enhance toughness which suggest that the (t) grains were stable. However, in the case of the 1 wt% MnO_2-doped samples, the fracture toughness was found to increased from 4.8 MPa $m^{1/2}$ at 1400 °C to 5.3 MPa $m^{1/2}$ at 1450 °C and then rapidly to >7 MPa $m^{1/2}$ when sintered at 1500 °C as depicted in Fig. 6.

The present work shows that the tetragonal phase stability was not disrupted in Y-TZP containing up to 0.5 wt% MnO_2 and for sintering of up to 1450 °C. However, for the 1 wt% MnO_2-doped Y-TZP and for sintering above 1450 °C, spontaneous phase transformation was observed upon cooling from sintering to room temperature. Based on this observation, it is plausible that the high MnO_2 content (>0.5 wt%) could have reacted with yttria at temperatures above 1450 °C. As a result of the dissolution of yttria in the zirconia matrix, the minimum amount of stabilizer required for stabilization of the (t) phase was reduced. This in turn could have caused some of the tetragonal grains to undergo the spontaneous phase transformation to the (m) phase upon cooling to room temperature as observed in the 1 wt% MnO_2-doped samples sintered above 1450 °C. Furthermore, the fact that the fracture toughness of the 1 wt% MnO_2-doped Y-TZP increased from 5.3 MPa $m^{1/2}$ at 1450 °C to >7 MPa $m^{1/2}$ at 1500 °C, indicates that the tetragonal grains was in the metastable state and therefore responded immediately to the induced stresses resulting from indentation, i.e. enhanced transformation toughening effect. Further evidence on the effect of MnO_2 on yttria dissolution is being sorted and will be reported in subsequent paper.

In order to study the effect of hydrothermal ageing on the tetragonal phase stability, samples sintered at 1350 °C were exposed to superheated steam for periods ranging up to 24 h. For this experiment, the 1 wt% MnO_2-doped ceramic was not tested due to the overall poor performance exhibited by this material. Fig. 7 shows that the undoped Y-TZP exhibited the worst ageing resistance as indicated by the rapid rate of phase transformation observed within few hours of exposure. The (m) phase increased rapidly with exposure time and attained about 92.6% content after ageing for 24 h. In contrast, the MnO_2-doped Y-TZPs exhibited improved ageing resistance when compared to the undoped ceramic. In particular, the 0.5 wt% MnO_2-doped samples did not undergo phase transformation throughout the ageing experiment. The 0.3 wt% MnO_2-doped samples started to age slowly when the ageing time exceeded 6 h and attained about 14% (m) content after exposure for 24 h. Both the 0.05 and 0.1 wt% MnO_2-doped ceramics exhibited a similar ageing trend. These samples started to age after exposure for 3 h and the ageing kinetics increased at a steady pace with further ageing and attained ~57–58% monoclinic content after 24 h of exposure. These observations clearly demonstrate that the addition of MnO_2 was beneficial in suppressing the ageing-induced (t) to (m) phase transformation in Y-TZP ceramics. The actual role of MnO_2 in the ageing mechanism is still to be resolved but it is believed that the formation of manganese-rich compounds could have prevented

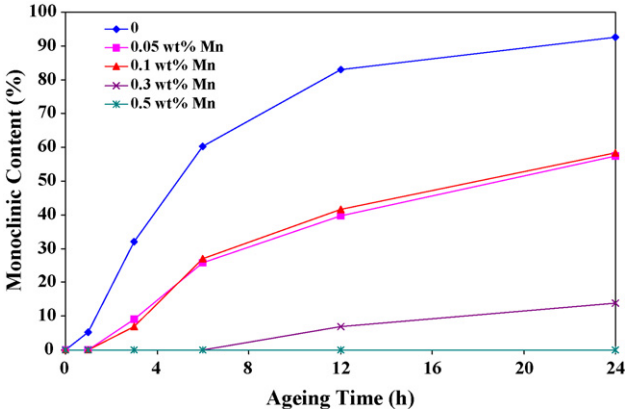

Fig. 7. The effect of hydrothermal ageing on the monoclinic phase development in Y-TZPs sintered at 1350 °C.

hydroxyl reaction with zirconia near grain boundary regions [28].

4. Conclusions

The present work shows that the addition of manganese oxide was beneficial in aiding sintering of Y-TZP ceramics, particularly when sintered at low temperatures, below 1350 °C. More specifically, a high relative density of ∼98% of theoretical value and exceptionally high hardness (>13 GPa) and high elastic modulus (>200 GPa) were measured for Y-TZPs containing ≥0.3 wt% MnO_2 when sintered at 1250 °C. The research also found that the addition of MnO_2 had a negligible effect on the grain size of the tetragonal grains.

The tetragonal phase stability of the zirconia matrix was not disrupted by the addition of up to 0.5 wt% MnO_2 throughout the sintering regime employed. In contrast, the tetragonal grains of the 1 wt% MnO_2-doped Y-TZP started to become unstable when sintered above 1450 °C. Although the fracture toughness of the Y-TZP at this stage was found to increased, the high dopant concentration promoted the development of cubic phase in the tetragonal matrix regardless of sintering temperature and resulted in the spontaneous tetragonal to monoclinic phase transformation in samples sintered ≥1500 °C.

The beneficial effect of MnO_2 doping in suppressing the hydrothermal degradation of Y-TZP ceramics has been revealed. In particular, the addition of 0.5 wt% MnO_2 was found to be most effective in hampering the ageing-induced (t) to (m) phase transition.

Acknowledgements

The authors would like to thank the Ministry of Science, Technology and Innovation of Malaysia (MOSTI) for providing the financial support under the IRPA grant No. 09-99-03-0043 EA001. In addition, the support provided by UNITEN, TNB Research and SIRIM Berhad in carrying out this research is gratefully acknowledged.

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