

The effects of sintering additives on the mechanical properties and microstructure evolution of 3 mol% Y-TZP

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The current work investigates the effects of sintering additives, particularly focused on 0.5 wt% manganese oxide (MnO₂) and 0.1 wt% alumina (Al₂O₃), and co-doping both additives together (i.e. MnO₂ + Al₂O₃), on the microstructure and mechanical properties of 3 mol% Y-TZP. The doped powders were prepared by attrition milling and subsequently green samples were sintered in air at temperatures ranging from 1250 to 1550 °C with 2 hrs holding time. The results showed that the dopants have not disrupted the tetragonal phase stability. All the dopants aided sintering at 1250 °C but with MnO₂ being most effective in promoting densification with samples, recording about 97.6% relative density. Similar improvement in the mechanical properties was also observed for the doped zirconia. Young's modulus, Vickers hardness and fracture toughness as high as 192 GPa, 13.6 GPa and 4.6 MPam^{1/2}, respectively were obtained for both, the MnO₂-doped and co-doped Y-TZPs, when sintered at low temperature of 1250 °C. Microstructural examination, however revealed that the MnO₂ dopant promoted exaggerated grain growth when sintered at higher temperatures.

Key words: Alumina, Manganese oxide, Co-doped, Y-TZP, Mechanical properties.

Introduction

Yttria tetragonal zirconia polycrystals (Y-TZP) ceramic is one of the most demanding material over metals for biomedical applications because it possesses an overall best combination of strength above 800 MPa [1, 2], high fracture toughness (> 10 MPam^{1/2}) [3, 4], biocompatibility and aesthetic properties. In addition, the basic color of Y-TZP is opaque to white allowing more natural appearance especially in dental restoration. This attractive material is widely used in dentistry and orthopedics because of its high purity which enables more precise control of properties during manufacturing and its availability in the market [5]. The extraordinary mechanical properties of Y-TZP can be attributed to transformation toughening, a mechanism that provides resistance to crack propagation by externally applied stress as a consequence of phase transformation from tetragonal to monoclinic at room temperature [6].

However, a major drawback of this ceramic is that when it is exposed to water or steam at temperatures of 100 to 300 °C, the Y-TZP experience a spontaneous

tetragonal to monoclinic phase transformation, a phenomenon known as low temperature degradation (LTD) or ageing, resulting in surface cracking [7, 8]. For instance in 2001, Clarke et al. reported that LTD played a major role in the fracture of high number of Y-TZP femoral heads shortly after implementation [9–11]. Therefore, it is important to develop a reliable Y-TZP that has immunity against LTD over longer periods (15 to 20 years) without compromising on the fracture toughness especially for orthopedic application [12]. The LTD phenomenon has received much attention over the years and numerous researcher found that grain boundary modification via adding selective sintering additive or dopant is one of the most economical method in suppressing this ageing-induced tetragonal to monoclinic phase transformation of Y-TZP [13, 14].

The selection of dopants is important since it plays different roles in improving the zirconia ceramic. For instance, Ramesh et al. [15] revealed that the addition of up to 0.5 wt% MnO₂ to Y-TZP was beneficial in enhancing the mechanical properties especially in promoting densification [15]. Another attractive dopant for Y-TZP is alumina. It has been reported by Nogiwa-Valdez et al. [16] that the addition of 0.1 wt% Al₂O₃ to Y-TZP resulted in improved resistance to ageing without affecting the mechanical properties especially

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fracture toughness when sintered at 1450 °C. Alternatively, the addition of ternary dopant has also been shown to be effective in retarding the LTD rate [17-19].

Therefore, the primary objective of this work was to investigate the combine effect of co-doping 0.1 wt% of Al₂O₃ and 0.5 wt% of MnO₂ on the mechanical properties and microstructure development of 3 mol% Y-TZP ceramics sintered at different temperatures of 1250 to 1550 °C.

Experimental Procedures

The starting powder was a commercially available 3 mol% yttria-stabilized zirconia (TZ-3YB, Tosoh Corporation, Japan). The co-doping was accomplished by mixing 0.5 wt% of MnO₂ and 0.1 wt% of alumina simultaneously with the Y-TZP powder. For comparison purpose, the dopant were also added separately with the Y-TZP powder. The powder mixtures were subjected to attrition milling for 30 minutes at 550 rpm using ethanol as the mixing medium and 5 mm diameter zirconia milling balls as the grinding medium. The resulting slurry was dried in an oven for 24 hrs. The dried cake was crushed and sieved to obtain the doped Y-TZP powders. Disc samples (diameter 20 mm, each weighing 2.5 g) and rectangular bar samples (4 × 13 × 32 mm, each weighing 3 g) were compacted in steel die by uniaxial pressing at 3 MPa using hydraulic bench press. The green bodies were subsequently cold isostatic pressed (Shanxi Golden Kaiyuan CO. LTD. China) at 200 MPa. The samples were pressureless sintered in air at four different temperatures i.e. 1250, 1350, 1450 and 1550 °C with a 2 hrs holding time each. The samples were sintered in a box furnace at a ramp rate of 10 °C/min with normal cooling process. Prior to body characterization, sintered disc samples were ground using silicon carbide (SiC) papers and subsequently polished using 6 μm and 1 μm diamond paste to obtain an optical reflective surface.

The bulk density of samples was determined using water immersion technique based on Archimedes principle using an electronic balance (Shimadzu AY220, Japan) retrofitted with a density determination kit. The relative density was determined by taking the theoretical density of Y-TZP as 6.09 g/cm³. Fracture toughness (K_{Ic}) and Vickers hardness (H_v) were determined on polished samples using the Vickers indentation method (Mitutoyo AVK-C2, USA). For this purpose, the indentation load was kept constant at 10 kgf and loading time of 10 sec was used. The value of K_{Ic} was computed using the equation derived by Niihara et al. [20]. For each sample, five measurements were made and the average values were obtained. Young's Modulus (E) 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 [21].

The microstructural evolution of the polished sintered Y-TZP samples was observed using the field emission transmission electron microscope (FE-SEM). For this purpose, the polished samples were thermal etched at a temperature 50 °C below their respective sintering temperature at a heating rate of 10 °C/min for 30 min to delineate the grain boundaries. The average tetragonal grain size was determined from FE-SEM micrographs using the line intercept analysis [22].

Phase analysis by X-ray diffraction (XRD) (PANalytical Empyrean, Netherlands) of the solid samples were carried out under ambient condition using Cu-Kα 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. [23].

Results and Discussion

The XRD analysis of all the samples revealed that the dopant additions as well as the sintering temperatures have not disrupted the tetragonal phase stability and all samples regardless of the type of dopant used revealed the presence of a fully tetragonal structure after sintering.

The effects of sintering temperature on relative density of un-doped and doped Y-TZP samples are as shown in Fig. 1. The results revealed that addition of dopants was beneficial in enhancing the densification of Y-TZP at low temperature. In particular, sintering at 1250 °C resulted in highest relative density of 97.6% as compared to 92.9% for the un-doped sample. However, as the sintering temperature increased to 1350 °C, the co-doped and 0.5 wt% MnO₂ doped Y-TZP did not show any improvement in the relative density. The addition of 0.1 wt% Al₂O₃ was also effective in aiding

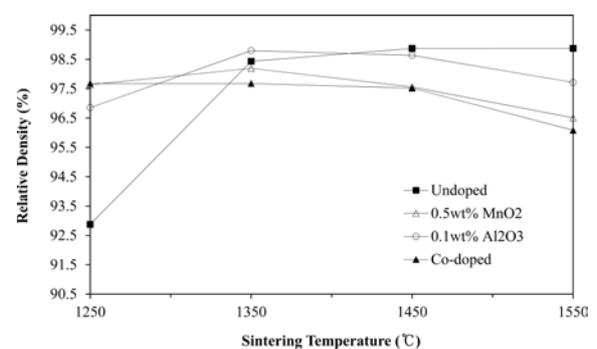


Fig. 1. Effect of dopants and sintering temperatures on the relative density of Y-TZP.

densification and the samples achieved relative density of 98.8% as compared to 98.4% for un-doped ceramic when sintered at 1350 °C. In contrast, as sintering proceeded beyond 1350 °C, all the dopants did not exhibit much effect in promoting densification as shown in Fig. 1. On the contrary, the relative density of the un-doped Y-TZP was found to increase gradually with increasing sintering temperature and attained a maximum of 99% when sintered at 1550 °C.

The variation in Young's Modulus (E) for the Y-TZP with sintering temperature and dopants are shown in Fig. 2. In agreement with the relative density trend, the addition of dopants was effective in enhancing the stiffness of the tetragonal zirconia matrix when sintered below 1450 °C. The results indicated that co-doped samples had lower E value when compared to single dopants regardless of sintering temperature employed. It was found that, the addition of 0.5 wt% MnO_2 achieved the highest E value of 194 ± 2 GPa at 1250 °C while the addition of Al_2O_3 gave the highest E value of 200 ± 1.5 GPa at 1350 °C. In agreement with the bulk density trend, the E value of the undoped Y-TZP increased gradually with increasing temperature and reached a maximum of 203 ± 2 GPa at 1450 °C before declining slightly to 197 ± 1.5 GPa at 1550 °C.

The influence of sintering temperature and dopants addition on the Vickers hardness of the Y-TZP are

shown in Fig. 3. It was found that the hardness of co-doped Y-TZP was relatively high when sintered at 1250 °C and 1350 °C. The highest hardness achieved by this sample was about 14.6 GPa at 1350 °C when compared to 12.7 GPa for the un-doped sample. The 0.1 wt% Al_2O_3 -doped Y-TZP samples exhibited similar trend and have almost similar hardness values as that of the co-doped Y-TZP. In all cases, the trend of hardness for the doped sample declined with further sintering beyond 1350 °C while un-doped samples declined beyond 1450 °C. This observation is consistent with other researchers where they found that the hardness gradually increased to maximum at certain sintering temperature followed by a decreased with further sintering [25-28].

The variation in the fracture toughness of un-doped and doped samples with sintering temperatures is shown in Fig. 4. The optimum K_{Ic} value of $6 \text{ MPam}^{1/2}$ was achieved with 0.5 wt% MnO_2 -doped Y-TZP and followed up by co-doped samples which recorded a value of $5.3 \text{ MPam}^{1/2}$ when sintered at 1550 °C. This high fracture toughness could be associated with the transformation toughening effect which is a unique attribute of tetragonal zirconia. Lawson et al. [7] have emphasized that the K_{Ic} value could be used to demonstrate the stability of the tetragonal grains in the zirconia matrix. According to these authors, a high K_{Ic} indicates that the transformation toughening mechanism was in operative since the tetragonal grains were retained in the metastable state and hence responded instantly to the stress field of a propagating crack during the Vickers indentation test.

The microstructures of un-doped and doped Y-TZPs sintered at 1250 °C and 1550 °C are shown in Fig. 5. At low sintering temperature of 1250 °C, residual pores are generally visible as shown in Figs. 5(a) and 5(c) for the un-doped and 0.1 wt% Al_2O_3 -doped Y-TZP, respectively. This observation is consistent with the low bulk density measured at this temperature for these samples. In comparison, the 0.5 wt% MnO_2 -doped (Fig. 5(b)) and the co-doped Y-TZPs (Fig. 5(d)) revealed dense microstructure when sintered at 1250 °C. In general, it

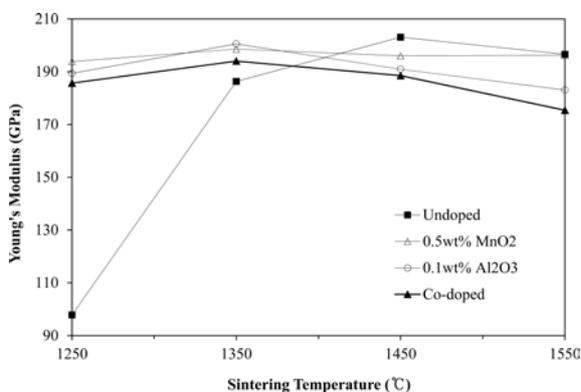


Fig. 2. Young's modulus variation with dopant addition and sintering temperatures.

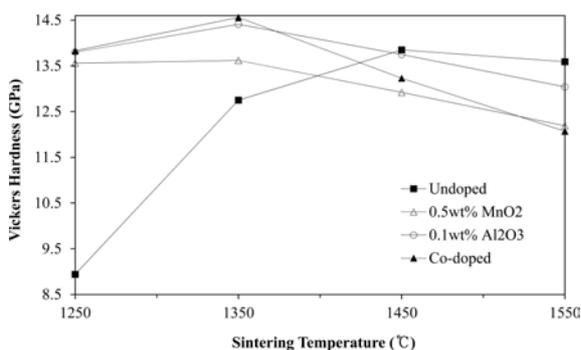


Fig. 3. Effect of dopants and sintering temperatures on the Vickers hardness of Y-TZP.

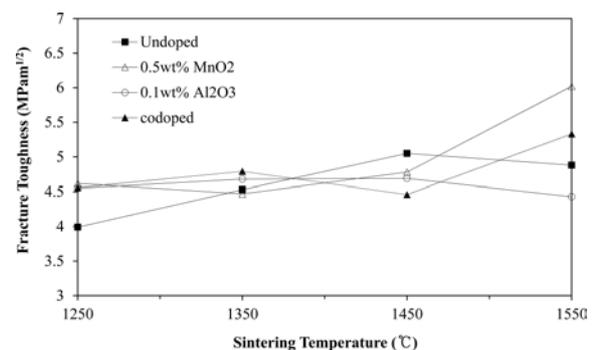


Fig. 4. Variation in fracture toughness as a function of dopant addition and sintering temperatures.

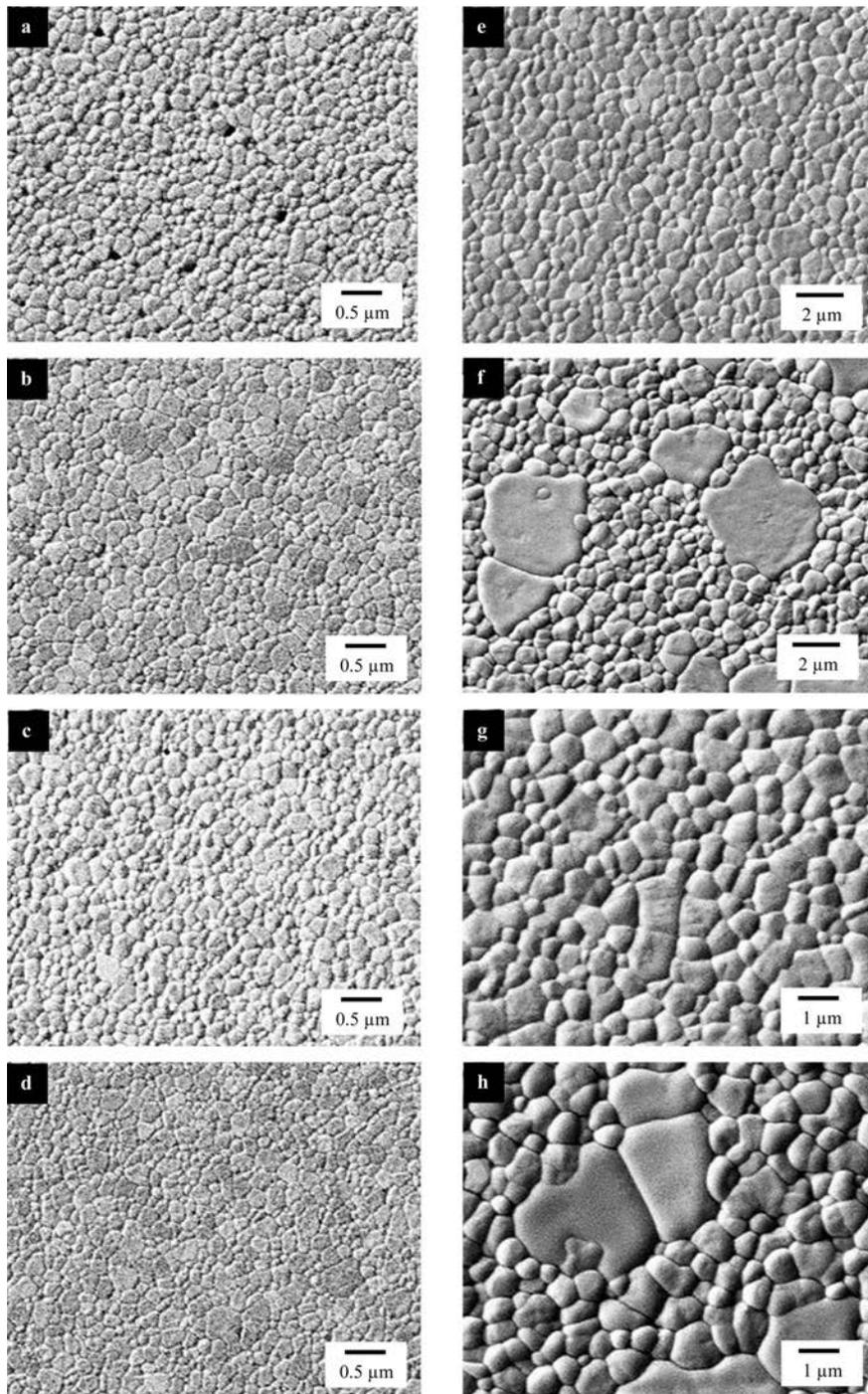


Fig. 5. Microstructural development for Y-TZP sintered at 1250 °C [(a) un-doped, (b) 0.5 wt% MnO₂-doped, (c) 0.1 wt% Al₂O₃-doped and (d) co-doped Y-TZP] and 1550 °C [(e) un-doped, (f) 0.5 wt% MgO₂-doped, (g) 0.1 wt% Al₂O₃-doped and (h) co-doped Y-TZPs].

was difficult to distinguish the tetragonal and cubic grains due mainly to the very uniform microstructure and distribution of equiaxed fine grains particularly for the un-doped and the 0.1 Al₂O₃-doped Y-TZPs. In contrast, a more bimodal microstructure comprising of fine tetragonal grains and relatively large abnormal grains believed to be of the cubic type [29] was clearly observed for the 0.5 wt% MnO₂-doped Y-TZP (Fig. 5(f)) and the co-doped samples (Fig. 5(h)) when sintered at 1550 °C. Such microstructural feature was not seen for

Table 1. Average grain size (μm) of Y-TZPS sintered at different temperatures.

Dopants	Sintering temperature (°C)			
	1250	1350	1450	1550
Un-doped	0.20	0.32	0.54	0.78
0.5 wt% MnO ₂	0.20	0.27	0.44	1.08
0.1 wt% Al ₂ O ₃	0.21	0.25	0.42	0.80
Co-doped	0.21	0.30	0.48	1.17

the un-doped and Al₂O₃-doped Y-TZPs. It is envisaged that during sintering, the MnO₂ could have aided densification through forming a transient liquid phase that facilitated particle rearrangement and could help in accelerating densification. As sintering proceeded, coalescence of tetragonal grains could have taken place resulting in the formation of abnormally large grains as that observed in the present work. This process, could possibly cause the adjacent smaller grains to suffer yttria depletion thus making the grains metastable and hence promoting transformation toughening effect as evident from the high fracture toughness measured for the 0.5 wt% MnO₂-doped samples sintered at 1550 °C as shown in Fig. 4. The average tetragonal grain size for the Y-TZPs are presented in Table 1. In general, it was found that the average grains size varied from 0.20 µm to 1.17 µm with increasing temperature from 1250 °C to 1550 °C.

Conclusions

In this present work, the influence of 0.1 wt% Al₂O₃, 0.5 wt% MnO₂ and co-doping (0.1 wt% Al₂O₃ + 0.5 wt% MnO₂) on the mechanical properties and microstructural development of 3 mol% Y-TZP were investigated. The results revealed that the dopants have not disrupted the tetragonal phase stability throughout the sintering regime employed. The optimum sintering temperature for the co-doped Y-TZP was at 1350 °C, with sintered body exhibiting maximum H_v of 14.6 GPa and K_{1c} of 4.8 MPam^{1/2}. The result also indicated that the Al₂O₃ dopant was effective in enhancing the densification and mechanical properties of Y-TZP when sintered below 1450 °C without inducing grain coarsening. In contrast, the incorporation of 0.5 wt% of MnO₂ promoted the development of a bimodal microstructure comprising of fine tetragonal grains and relatively large abnormal grains in the Y-TZP matrix.

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