

INFLUENCE OF MANGANESE ON THE SINTERING PROPERTIES OF TETRAGONAL ZIRCONIA

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The influence of small additions of MnO₂ (up to 1 wt. %) on the sintering behaviour of yttria-stabilized zirconia sintered over the temperature range from 1250°C to 1500°C was investigated. It was found that the mechanical properties of Y-TZP were dependent on the dopant amount and sintering temperature. The results revealed that relative densities above 97.5 % of theoretical (i.e. > 5.95 Mg m⁻³) could be obtained in Y-TZPs sintered at low temperatures, 1250°C and 1300°C, with the additions of ≥ 0.3 wt. % MnO₂. In comparison to the undoped samples, the additions of up to 1 wt. % MnO₂ and for sintering up to 1350°C was found to be beneficial in enhancing the Vickers hardness of the ceramic. The fracture toughness of Y-TZP however, was found to increase only in the 1 wt. % MnO₂-doped samples when sintered above 1400°C. The relation between the measured mechanical properties is discussed with the emphasis on the role of the manganese oxide.

INTRODUCTION

Yttria Tetragonal Zirconia Polycrystalline ceramics (Y-TZP) have become an important commercial material due to its excellent combination of high mechanical and thermal properties, biocompatibility, high wear resistance, good chemical and corrosion resistance. Typically, Y-TZP are being used for adiabatic diesel engine parts, as thermal barrier coatings, oxygen sensors, fuel cells, heating elements, polymer processing dies, extrusion dies, grinding media, orthopedic femoral head implants and cutting tools [1-4].

It is well documented that the mechanical properties and microstructure of sintered Y-TZP ceramics are mainly dependent on the initial powder properties [5, 6]. 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. In general, fine, uniform grain structure with full densification is required for engineering ceramics to achieve good mechanical properties.

One of the major limitations of Y-TZP ceramics as engineering materials is the undesirable surface-initiated phase transformation from the (t) to (m) symmetry accompanied by property degradation during exposure to low temperature water or aqueous solutions; a phenomenon subsequently known as low-temperature

degradation (LTD) or ageing. The underlying LTD mechanism is still not resolved but it is understood to be associated with hydroxyl ion incorporation in the zirconia lattice, which subsequently destabilizes the tetragonal phase [7, 8].

In order to suppress LTD in Y-TZP, the inclusion of sintering additives such as TiO₂, SiO₂, Al₂O₃, CuO, MgO, Fe₂O₃, etc. have been investigated by many researchers since this is the most effective and simplest way to achieve a dense body at low temperature sintering. In most cases, the additives were found to segregate at grain boundary and form a grain boundary glassy phase in combination with Y₂O₃ and ZrO₂ [9-15]. For instance, Duh and Hwung [10] observed that a small amount of MgO increased the densification rate for Y-TZP. It was suggested that MgO may act to aid sintering in Y-TZP by decreasing the surface diffusion coefficient and the reducing pore mobility would retard the degree of particle coarsening during sintering. In another research, Kenellopoulos & Gill [16] reported that the doping of CuO enhances the densification of Y-TZP material through a mechanism involving liquid phase due to the low melting point of CuO in ZrO₂ matrix. Therefore, the inclusion of transition metal oxides such as manganese oxide (MnO₂) is likely to affect hydrothermal ageing resistance if they aid sintering at relatively low temperatures (i.e. ≤ 1300 °C) and result in densification without grain growth.

The aim of the present work was to study the influence of adding small amounts of manganese oxide (up to 1 wt. %) on the densification and mechanical properties of yttria-stabilized zirconia.

EXPERIMENTAL

The base powder, a co-precipitated sprayed dried 3 mol. % yttria-zirconia (Y-TZP) was manufactured and supplied by Kyoritsu Japan. Varying amounts of high purity MnO_2 (0.05, 0.1, 0.3, 0.5 and 1 wt. %, BDH, UK) doped Y-TZP powders were prepared by a wet colloidal method, 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 powder. Disc (20 mm diameter) and rectangular bar ($4 \times 13 \times 32$ mm) green samples were compacted at 0.3 MPa and 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°C 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 μm and 1 μm diamond paste to produce an optical reflective surface. 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 (E) 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 was calculated using the experimentally determined resonant frequency [17]. Fracture toughness 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.* [18]. Average values were taken from five measurements.

Phase analysis by X-ray diffraction (Geiger-Flex, Rigaku Japan) of the powders and sintered samples were carried out under ambient conditions using Cu-K α as the radiation source. The fraction of the monoclinic (m) phase present in the ceramic matrix was determined using the method of Toraya *et al.* [19]. The morphology of the powders and microstructural evolution of the sintered samples were studied by using a Scanning Electron Microscope (Philips XL30 ESEM).

RESULTS AND DISCUSSION

The morphology of the as-received sprayed-dried granule (spherical shape) of the starting yttria-stabilized powder is shown in Figure 1. The XRD analysis of the powders revealed that the monoclinic content in the undoped powder was $\sim 18\%$ and did not varied significantly with dopant addition as shown in Figure 2.

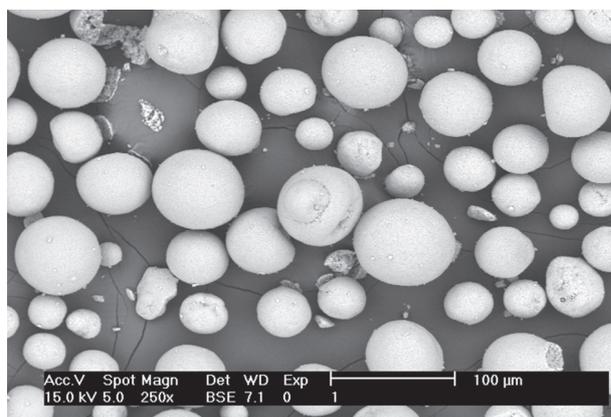


Figure 1. SEM picture of the as-received yttria-stabilized powder.

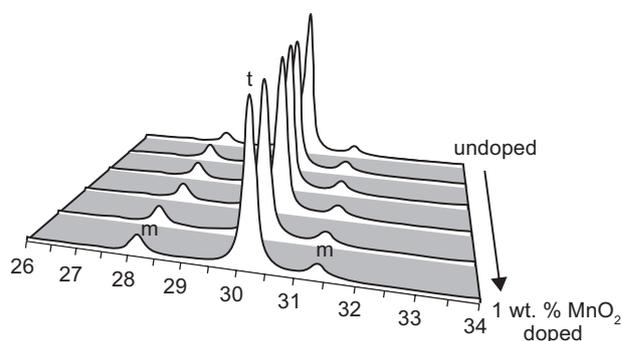


Figure 2. XRD plot of the undoped and MnO_2 -doped powders revealing a dual phase mixture comprising that of monoclinic (m) and tetragonal (t) symmetries.

The XRD results of the undoped and up to 0.5 wt. % MnO_2 -doped Y-TZPs exhibited 100 % tetragonal (t) phase regardless of sintering temperatures. The results indicated that the additions of up to 0.5 wt. % manganese oxide did not interrupt the tetragonal (t) phase stabilization of the zirconia matrix during cooling from the sintering temperature. All sintered bodies were intact and did not exhibit any cracking or shape distortion after pressureless sintering. In contrast, the tetragonal phase stability of the 1 wt. % MnO_2 -doped Y-TZP was disrupted when sintered at 1500 °C, with the formation about 3 % monoclinic (m) phase in the zirconia matrix and this figure was found to increase to about 55 % when sintered at 1600 °C. This change is clearly depicted in the bulk density and fracture toughness measurements.

The bulk density variations with sintering temperatures for the undoped and MnO₂-doped Y-TZPs are shown in Figure 3. The beneficial effects of MnO₂ in enhancing the consolidation process of Y-TZP at low temperatures have been revealed. In particular, the graph shows that Y-TZP samples containing ≥ 0.3 wt.% MnO₂ exhibited ~ 97.5 % of theoretical density (the theoretical density of Y-TZP is taken as 6.1 Mg.m⁻³) when sintered at 1250°C as compared to 91.8 % for the undoped ceramic. The bulk density of the undoped, 0.05 wt. % and 0.1 wt. % MnO₂-doped Y-TZP exhibited a similar trend with increasing sintering temperature, i.e. the bulk density increases to a maximum at 1350°C for both the MnO₂-doped samples and at 1450°C for the undoped material as shown in Figure 3 before remaining almost constant with further increased in temperature.

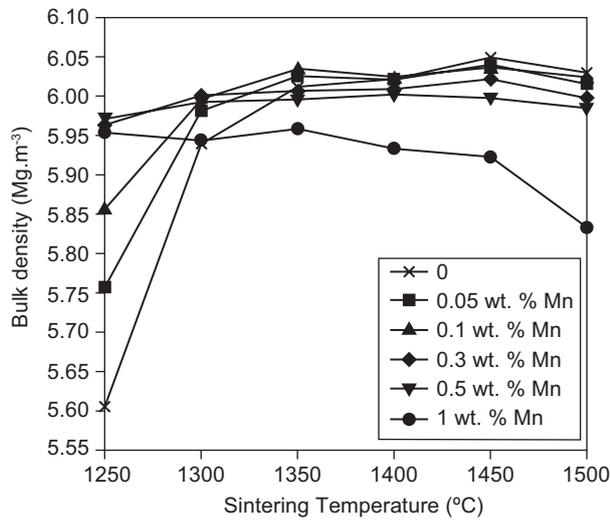


Figure 3. Effect of sintering temperature and MnO₂ on the bulk density of Y-TZP.

The bulk density of Y-TZP containing 0.3 wt. % and 0.5 wt. % MnO₂ was found to increase monotonically with increasing temperature, with the latter exhibiting a higher bulk density for all sintering temperatures. On the other hand, the addition of 1 wt. % MnO₂ did not aid the densification of Y-TZP when sintered beyond 1300°C. The bulk density was observed to decrease slowly from 5.95 Mg m⁻³ when sintered at 1250°C to ~ 5.9 Mg m⁻³ when sintered at 1450°C, and then rapidly decline to 5.85 Mg m⁻³ when sintered at 1500°C. This decrease in density is in agreement with the formation of (m) phase as detected by XRD in samples sintered at 1500°C.

The variation in Young's modulus (*E*) for the Y-TZPs with sintering temperature and dopant concentrations is shown in Figure 4. In agreement with the bulk density results, the additions of ≥ 0.3 wt. % MnO₂ was effective in enhancing the stiffness of the zirconia matrix when sintered at 1250 - 1300°C. For instance, *E* values > 200 GPa was measured for samples containing ≥ 0.3 wt. % MnO₂

when compared to 175 GPa for the undoped samples when sintered at 1250°C. The undoped Y-TZP required a higher sintering temperature of 1350°C to attain an *E* value of 200 GPa. Sintering beyond 1350°C resulted in a slight increase in the modulus, with a maximum of about 210 GPa was obtained for the undoped Y-TZP when sintered at 1400 - 1450°C.

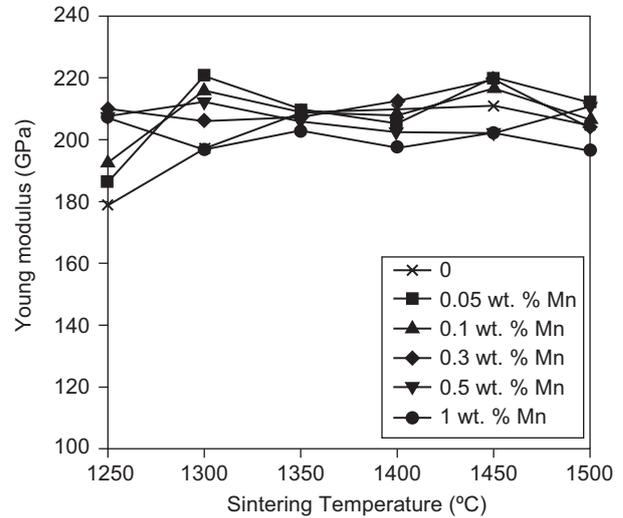


Figure 4. Effect of sintering temperature and sintering additives on the Young's modulus of Y-TZPs.

The present work also revealed that the matrix stiffness varies linearly with the bulk density of the sintered Y-TZP body as shown in Figure 5. It was found that Young's modulus of the sintered body increased linearly up to a maximum of > 200 GPa with increasing bulk density up to > 6 Mg m⁻³, regardless of dopant additions.

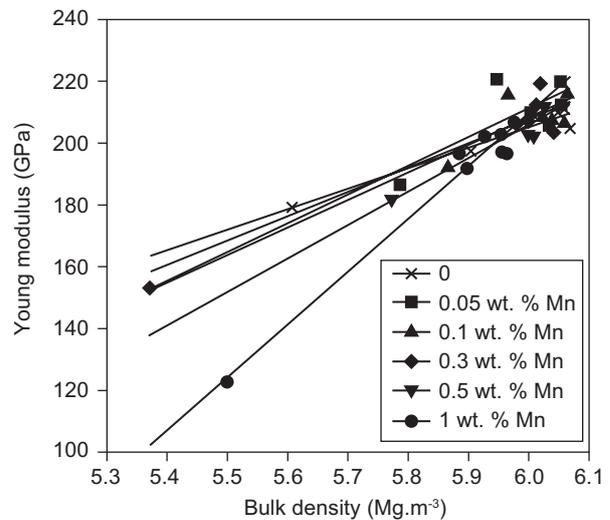


Figure 5. A linear relationship exists between the Young's modulus and bulk density of Y-TZP regardless of MnO₂ additions.

The variation in the fracture toughness of undoped and MnO₂-doped Y-TZPs is shown in Figure 6. It has been found that the fracture toughness of the undoped and up to 0.5 wt. % MnO₂-doped Y-TZPs fluctuated within the range of 4.6 to 5.2 MPa m^{1/2} and did not vary significantly with increasing temperatures. Since the transformation toughening mechanism is related closely with the transformability of the (t) grains, the fracture toughness can be used as a means of 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 is in a metastable state and will respond immediately to the stress field of a propagating crack, such as one induced during an indentation test. In the present work, Y-TZP containing up to 0.5 wt. % MnO₂ did not show any indication of enhanced toughness which supports the theory that the dopant could not have disrupted the tetragonal stability. On the other hand, in the case of the 1 wt. % MnO₂-doped samples, the fracture toughness was found to increase 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. This result is in agreement with the small amount of (m) phase (~3 %) detected in this sample by XRD technique.

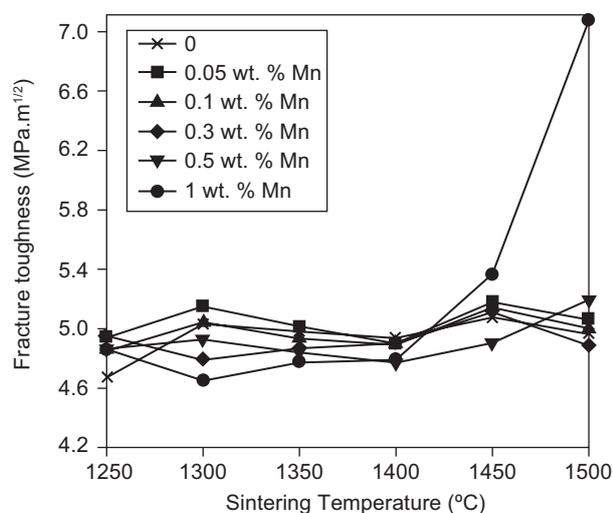


Figure 6. The influence of MnO₂ on the fracture toughness of Y-TZPs sintered at various temperatures.

The present work shows that the tetragonal phase stability was not disrupted in Y-TZP containing up to 0.5 wt. % MnO₂ and for sintering of up to 1450°C. Above these regimes, spontaneous phase transformation was observed upon cooling from sintering to room temperature. Based on this observation, it can be hypothesized that the presence of high MnO₂ dopant (> 0.5 wt.%) could have reacted with yttria at temperatures above 1450°C to form a Mn-rich glassy phase. As a result of the dissolution of Y₂O₃ in the zirconia matrix, the minimum amount of stabilizer required for

stabilization of the (t) phase was reduced, resulting in spontaneous phase transformation to the (m) phase upon cooling as evident in the present work for the 1 wt. % MnO₂-doped samples sintered above 1450°C. This is also in agreement with the fracture toughness results which indicated that the tetragonal grains of the 1 wt. % MnO₂-doped Y-TZP sintered at 1500°C was in the metastable state and responded immediately to induced stresses resulting from indentation, i.e. enhanced transformation toughening effect, as evident from the high K_{Ic} value measured for this sample (> 7 MPa.m^{1/2}) as compared to the 1450°C sintered sample (~5.3 MPa.m^{1/2}).

The effect of sintering temperatures and MnO₂ additions on the room temperature Vickers hardness of Y-TZPs is shown in Figure 7. The results clearly show the beneficial effect of MnO₂ in improving the hardness of Y-TZP at low sintering temperatures. 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 the samples, however, decreases slightly with further sintering, down to ~3.2 GPa when sintered at 1500°C. In comparison, the hardness of all the MnO₂-doped samples was higher than the undoped material when sintered at 1250°C and 1300°C as shown in Figure 7. The hardness trend of the 0.05 and 0.1 wt. % MnO₂-doped samples was similar, i.e. increases rapidly from ~11.3 GPa 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. % MnO₂-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. %) at 1250°C. As the sintering temperature

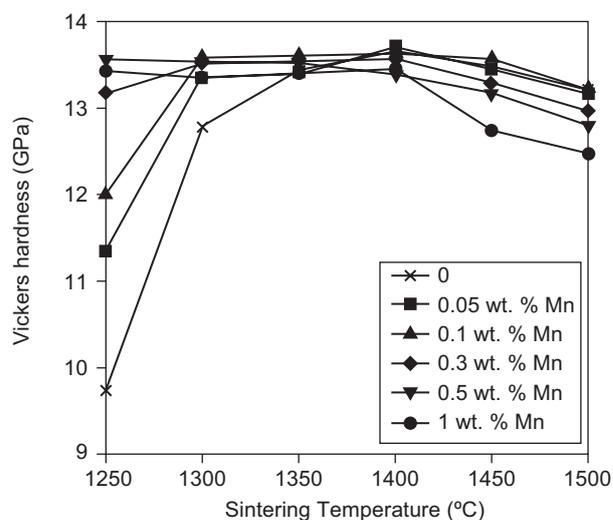


Figure 7. The influence of MnO₂ on the Vickers hardness of Y-TZPs sintered at various temperatures.

increases to 1300 - 1350°C, both materials exhibited similar hardness of 13.5 GPa. However, sintering beyond 1350°C was detrimental as the hardness of both this doped ceramics declined, with the 0.5 wt. % MnO₂-being more affected as shown in Figure 7.

In contrast, the hardness of the 1 wt. % MnO₂-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 - 13.4 GPa when sintered between 1250 - 1400°C, before decreasing rapidly with further sintering. The 1 wt. % MnO₂-doped Y-TZP exhibited the lowest hardness for sintering above 1400°C as shown in Figure 7 and this can be associated with (m) phase development detected in such samples sintered at 1450°C and 1500°C.

CONCLUSIONS

The sinterability of MnO₂-doped yttria-tetragonal zirconia polycrystals ceramics was investigated. The results indicated that the additions of MnO₂ was effective in enhancing densification and mechanical properties of Y-TZP, particularly at low temperatures < 1300°C. A linear relationship was observed between the Young's modulus and the bulk density, regardless of dopant additions. The tetragonal phase stability of the zirconia matrix was not disrupted in the presences of up to 0.5 wt. % MnO₂ throughout the sintering regime employed. On the other hand, the (t) phase stability of the 1 wt. % MnO₂-doped ceramic was sensitive to the sintering temperature and the Y-TZP matrix started to lose its stability when the temperature increased above 1400°C. This changes was accompanied by a decline in bulk density and Vickers hardness, and a concomitant increased in the fracture toughness.

Acknowledgments

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