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Characterization of Manganese Doped Y-TZP for Biomedical Applications

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Abstract

The densification behaviour and mechanical properties of manganese oxide doped yttria tetragonal zirconia polycrystals (MnO_2-doped Y-TZP) were studied. Green samples containing varying amounts of MnO_2 (0.05 to 1 wt%) were prepared using the wet colloidal technique. A pressure less sintering technique was used to sinter the specimens at temperatures varying between 1150°C to 1600°C. Sintered bodies were characterized to determine the bulk density, tetragonal content, Young's Modulus, hardness and fracture toughness. The results showed that the sintered bulk density and Young's Modulus was enhanced by the addition of up to 0.1 wt% MnO_2. On the other hand, fracture toughness of the material was further improved and more prominent for dopant addition of up to 0.3 wt% but for the 0.5 wt% addition of MnO_2, an initial decrease in trend was observed, which after a sintering temperature of 1350°C, a drastic increase in properties was observed. As for the hardness of the material, addition of all wt% of dopant exhibited an improvement up to a sintering temperature of 1400°C. In addition to that, hydrothermal ageing - induced phase transformation of Y-TZP sintered at 1300°C for samples containing 0.5 and 1.0 wt% of MnO_2 was suppressed.

Keywords: Sintering temperature; Manganese oxide; Mechanical properties; Characterization.
PACS: 81.20.Ev; 75.47.Lx; 62.25.-g; 81.07.-b.

1. Introduction

Zirconia based materials, in particular yttria-doped tetragonal zirconia polycrystalline (Y-TZP) ceramics, exhibit very high strength and high toughness at room temperature [1, 2]. Many of these ceramics are typically very fine grained, with grain size less than 1μm. Their very high modulus, high compressive strength, unique combination of mechanical properties: high wear resistance, low coefficient of friction, very good biocompatibility and the good compromise they represent between fracture resistance, crack resistance and wear behaviour makes this material one of the best candidates for many components including orthopaedic prostheses as a replacement for metallic materials [3]. The increase in crack resistance is attributed to phase transformation toughening, which

increases its crack propagation resistance. The stress-induced phase transformation involves transformation of metastable tetragonal grains to the monoclinic phase at the crack tip, which, accompanied by volume expansion, induces compressive stresses [4].

The objective of the present work is to study the effect of manganese on the densification behaviour and mechanical properties of commercial 3 mol% Y-TZP (Kyoritsu, Japan) and manganese powders of 99.9% purity (Kyoritsu Japan) powder prepared via wet colloidal technique.

2. Materials and Methods

The starting powders used were as-received commercial 3 mol% Y-TZP (Kyoritsu, Japan) and manganese oxide powders of 99.9% purity (Kyoritsu, Japan). Six batches of MnO_2-doped Y-TZP powder mixtures were prepared with the following manganese oxide content: 0 (undoped), 0.05, 0.1, 0.3, 0.5 and 1 wt%, respectively. Mixing of the powder was accomplished using the wet colloidal process whereby the mixture was milled using zirconia balls for 1 hour. The slurry was subsequently dried and sieved. The green samples i.e. rectangular shape (4 x 13 x 32mm) and disc (20mm) in diameter was prepared by uniaxial pressing at 10 kN using hardened steel mould and die assembly. The green compacts was subsequently cold isostatically pressed at 200 MPa (Riken Seiki, Japan). Consolidation of particles by pressureless sintering was performed in air using a rapid heating furnace (ModuTemp, Australia) at various temperatures ranging from 1150°C to 1600°C, maintained at the soak temperature for 2 hours before cooling to room temperature.

The bulk density of the sintered samples was measured by Archimedes' method, with distilled water as the immersion media 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 resonance 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 (ASTM E1876-97). Fracture toughness and Vicker hardness measurements (Matsuzawa, Japan) were made on polished samples using the Vicker's 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 [5]. Average values were taken for five measurements.

3. Results and Discussion

3.1 Bulk Density measurement

The densification curve as a function of sintering temperatures is shown in Fig. 1. In general, the bulk density variation of all composition studied exhibited a similar trend with increasing sintering temperature; a gradual upward trend as the sintering temperature increased. However, the sample that had 1 wt% MnO_2, exhibited a reverse trend; the bulk density decreased with increasing sintering temperature. The bulk density of samples sintered beyond 1250ºC onwards was significantly improved by additions of MnO_2. It was evident that the doped samples recorded densities well above the undoped sample density of 5.605 Mgm^{-3} All the samples attained above 98% of theoretical density, when sintered

above 1300°C but after that point, at a temperature of 1450°C onwards, a gradual decrease in bulk density was observed for all doped samples.

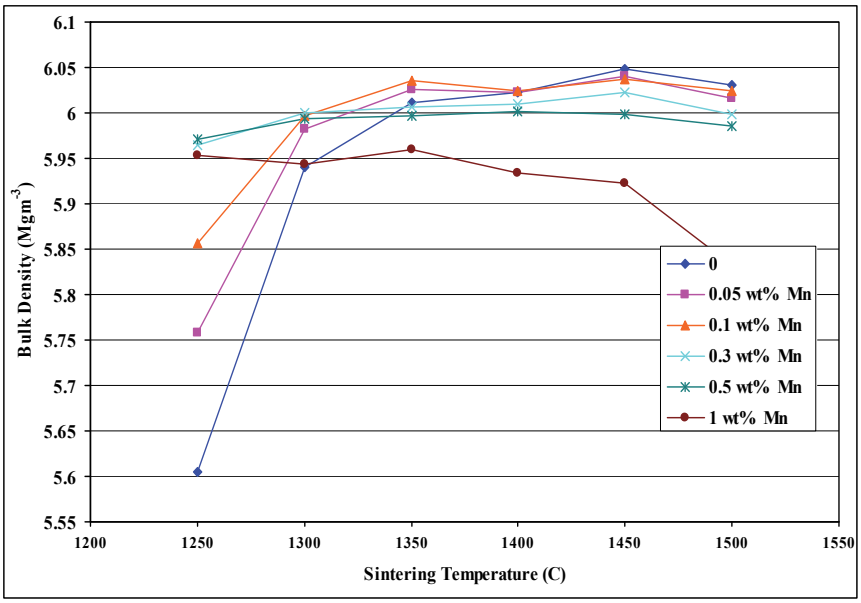

Fig 1: Effect of MnO_2 addition on the bulk density of the MnO_2 doped Y-TZP sample with respect to sintering temperature

The results also indicated that the addition of MnO_2 initially showed a drastic effect in enhancing the bulk density of the samples, but upon addition of 0.3 wt% of MnO_2 onwards a slight decrease in bulk density was observed. However, the density of 1wt% MnO_2, unlike other additions, exhibited a gradual drop from 5.959 Mgm^{-3} as the sintering temperature increased above 1350°C.

Another distinct observation that was made from the present work is the influence of the dopant on the densification of the Y-TZP samples. As can be noted from Fig. 4, the bulk density trend of the Y-TZP did not change very much with increasing dopant concentration.

3.2 Young's Modulus (E) measurement

The relationship between the Young's Modulus (E) of the sintered body, sintering temperature and MnO_2 addition is shown in Fig. 5. The variation in the Young's Modulus with sintering temperature of all composition studied is in good agreement with the variation in bulk density shown in Figure 2. It was found that the Young's modulus of the sintered body increased up to a maximum of > 200 GPa with increasing bulk density up to > $6Mgm^{-3}$, except for sample that had 1 wt% dopant addition, which portrayed an inconsistent trend. Furthermore, Ramesh et al. [6] have shown that the stiffness of engineered ceramic body is governed by bulk density and not significantly affected by grain growth.

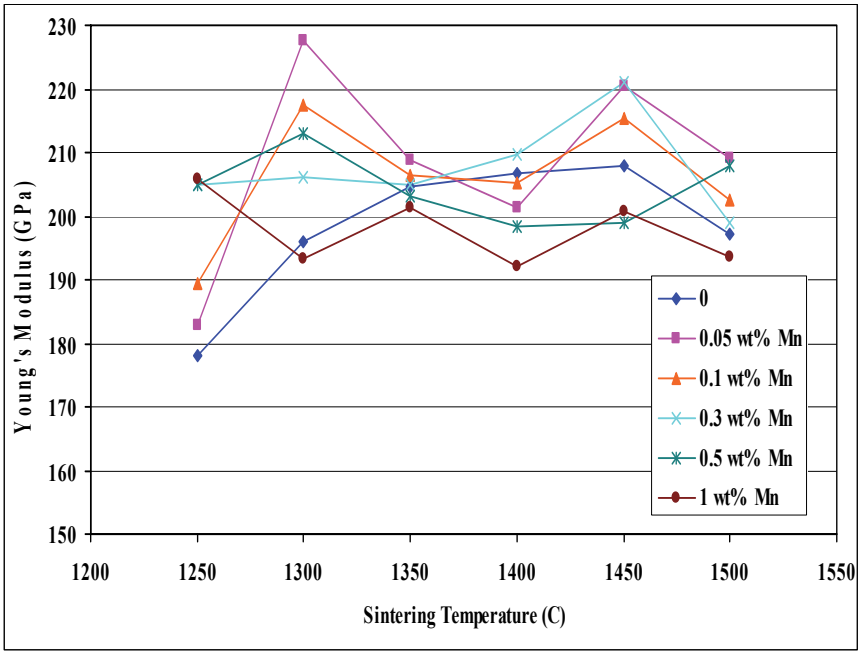

Fig 2: The Effect of MnO_2 addition on the Young's Modulus of the MnO_2 doped Y-TZP sample with respect to sintering temperature

The MnO_2 addition was found to have marginal effect on the Young's Modulus. For example, at a sintering temperature of 1350°C, an undoped sample had an E value of 204.5 GPa as compared to a sample doped with 0.3 wt% MnO_2 which recorded an E value of 205 GPa. Such behaviour was also observed for other monolithic ceramics. It has been reported in literatures, (Vleugels et al., [7], Xu et al., [8], Lin et al., [9], Duh et al., [10]) that the Young's modulus/stiffness of the material is hardly influenced by the dopant content.

3.3 Vickers Hardness measurement

The Vickers Hardness of MnO_2 doped Y-TZP and undoped Y-TZP is shown in Fig. 3. All samples exhibited a similar trend, whereby, the hardness increased rapidly as sintering temperature increase up to 1400°C, and then gradually decreased as sintering temperature is further increased. However, it is obvious that the addition of a dopant has played an effective role in the hardness of the material. Referring to a sintering temperature of 1250°C, an undoped sample exhibited a hardness of 9.73 GPa while a sample having 1 wt% dopant exhibited a hardness of 13.43 GPa.

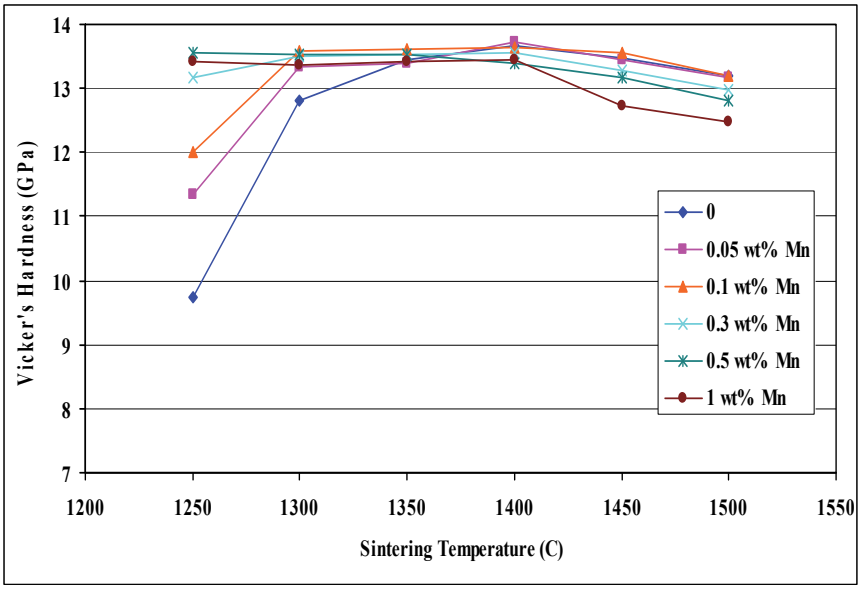

Fig 3: Effect of MnO_2 addition on the Vicker's Hardness of the MnO_2 doped Y-TZP sample with respect to sintering temperature

A close correlation was also observed between the hardness and the bulk density of the sample. For example, the hardness of the 0.05 wt% MnO_2-doped Y-TZP increases (from 11.35 GPa to 13.71 GPa) with increasing bulk density up to 1400°C and thereafter decreases (to 3.17 GPa) with increasing sintering temperature. However, the relative density of the sample did not change much with increasing sintering temperature and the percentage of the relative density was rather high (between 94%-98%).

Xu [11] highlighted that this hardness trend could be attributed to a reduced residual porosity. As the relative density increases, the sample attains a much denser structure, therefore the hardness increases relatively. Once maximum density and hardness is attained, the hardness is seen decreasing with increasing sintering temperature. This phenomenon could be attributed to grain growth and spontaneous transformation and eventually the formation of micro cracks.

3.4 Fracture Toughness measurement

Results of the fracture toughness for the MnO_2 doped Y-TZP specimens are shown in Figure 4. The fracture toughness was measured by the indentation technique. The fracture toughness of all compositions, except the 1 wt% MnO_2, exhibited similar trends. This trend is also in good agreement with the variation in the Vickers hardness. In general, an inverse relationship was observed between the hardness and the fracture toughness of the material. For example, referring back to the fracture toughness trend, taking into account 0.1 wt% MnO_2, there was a slight increase in toughness until a sintering temperature of 1300°C was achieved, meanwhile, a decrease in hardness was observed. Above 1300°C, a decrease in toughness was observed as the sintering temperature increased but an increase in the hardness was observed instead. These results are in good agreement with Chen [12], whereby he stated that the relationship between fracture toughness and hardness exhibits an inverse dependence of fracture toughness on hardness.

It was also found that most of the values of fracture toughness fell in the range of 4.95 ± 0.20 MPam$^{1/2}$ and 7.08 MPam $^{1/2}$. The latter value is the maximum K_{Ic} attained for the 1wt% MnO_2 doped Y-TZP sintered at 1500ºC. The minimum value of fracture

toughness obtained for the MnO_2 doped Y-TZP was in agreement with values reported in the literature for Y-TZP sintered up to 1450ºC [1, 7, 11, 313]. In general, the maximum K_{Ic} for most doped Y-TZP reported in the literature varied between 6.2 and 6.7 $MPam^{1/2}$.

However, for samples possessing 1wt% MnO_2, sintered at above 1400°C, a drastic increase in fracture toughness strength was observed. At a sintering temperature of 1500°C, a fracture toughness of 7.08 $MPam^{1/2}$ was recorded.

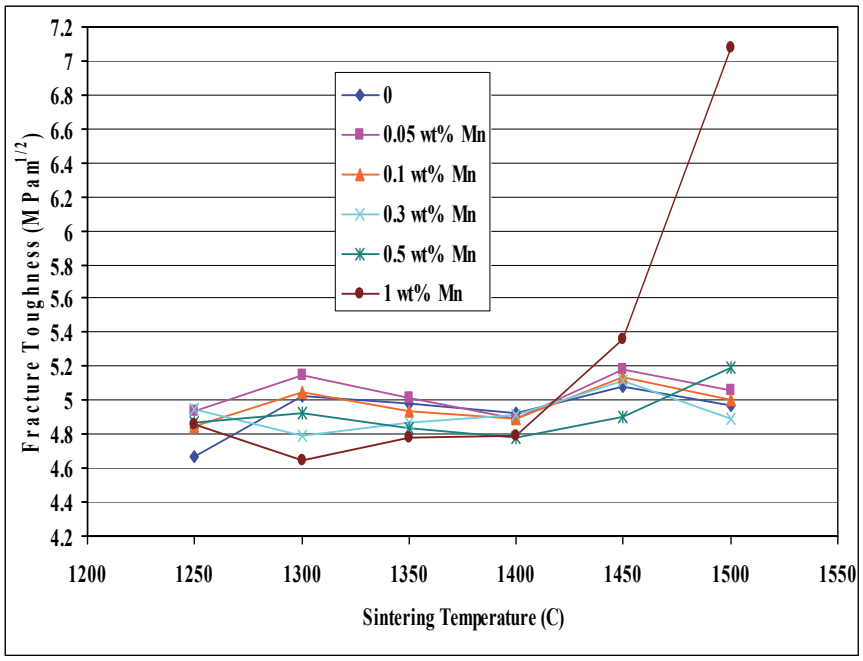

Fig 4: The effect of MnO_2 addition on the fracture toughness of MnO_2 doped Y-TZP sample with respect to sintering temperatures.

4. Conclusion

(i) Vickers hardness of MnO_2-Y-TZP is dependent on the sintering temperature. The hardness increases with the increase of sintering temperature up to 1400°C and subsequently decreases from there on. A reduced residual porosity may be a contributing factor to this phenomenon. A further decrease in hardness may be an effect attributed to grain growth and the spontaneous transformation and eventually the formation of micro cracks.

(ii) The correlation of hardness and toughness of MnO_2 - Y - TZP displays an inverse relationship. For a 0.1 wt% MnO_2, there was a slight increase in toughness until a sintering temperature of 1300°C was achieved, meanwhile at the same time period, a decrease in hardness was observed. It can be deduced that the addition of a dopant has played an effective role in the hardness of the material.

(iii) It can also be deduced that very high values of fracture toughness value was attained (7.08 $MPam^{1/2}$) for 1wt% MnO_2 doped Y-TZP sintered at 1500ºC. The presence of monoclinic phase was also detected at this time. At the same time, an inverse relationship was also observed between the hardness and the fracture toughness of the material.

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