Examining the impact of MnO_2 and CeO_2 on Mechanical Properties, Degradability, and the Microstructure of Zirconia

R. Dinesh, S. Meenaloshini, G. Mohsen, U. Sankar

Abstract*: The effect of CeO_2 and MnO_2 additions (up to 1 wt%) on the sintering behaviour of yttria-stabilized zirconia sintered from 1250ºC to 1450ºC was investigated. From the findings, mechanical properties are likely to improve via the addition of 0.2 wt% CeO_2 and 0.8 wt% MnO_2 with Y-TZP. This composition increased the density of Y-TZP. The value of density achieved was about 6.04 g/cm3, approximately 98% of the theoretical density of Y-TZP. The mechanical properties (i.e. hardness and strength) of the material were significantly increased as well. Besides that, the 0.2 wt% CeO_2 and 0.8 wt% MnO_2 composite displayed higher elasticity of 211 GPa compared to pure Y-TZP with a theoretical value of 200 GPa. Sintering over 1450 ºC is expected to degenerate the composite's physical and mechanical properties. Sintering at higher temperatures (>1350 °C) would affect the properties of the composite, due to a bigger grain size obtained at high temperature.

***Index Terms*: CeO_2, MnO_2, Microstructure, Degradation**

I. INTRODUCTION

Generally, Y-TZP is used in application such as biomedical implant, sandblasting nozzles, sharp edges of scissors and knifes, and metal cutting tools [1- 8].

Whereas Y-TZP exhibits favorable features, it continues to be associated with unfavorable low temperature ageing phenomenon. The situation is compounded by the presence of humid conditions [9-11]. To address this problem, small amounts of additives can be used because they are responsible for the densification and control of microstructures, as well as to enhance the mechanical properties of the material. The benefit of transition metal oxide in suppressing the ageing-induced (t) to (m) phase transformation has been reported by several researchers [12]. In particular, the addition of MnO_2 and CuO to Y-TZP was seen to enhance sinterability, finer grain sizes and higher fracture toughness. These effects were reported by [13-16].

It has been reported that improved Y-TZPs with optimized mechanical properties and ageing resistant could be obtained by the addition of more than one stabilizer to zirconia [17]. It was found that the CeO_2 addition to Y-TZP could prevent ageing, while retaining fracture toughness between 7–9MPam$^{1/2}$. This study strived to investigate the impact of manganese oxide and cerium oxide on the mechanical properties and densification of Y-TZP.

II. MATERIALS AND METHODS

Varying amounts of CeO_2 and MnO_2 (0.05, 0.1, 0.3, 0.5 and 1 wt%, Sigma Aldrich) doped Y-TZP powders were prepared by a wet colloidal method. The mixing medium was ethanol while the milling media involved zirconia balls. To obtain the ready-to-press and soft slurry powder, the slurry was oven dried before compacting bar samples and discs. 0.3 MPa and isostatically pressed at 200 MPa. These tests were in accordance with [19] and [20]. The values of KIc were computed using the equation derived by [21]. Five measurements aided in achieving average values.

RESULTS

A. Bulk Density

Different sintering temperatures were used to investigate the bulk density of the composites, hence their densification behaviur. Other parameters that supported this investigation included MnO_2 and CeO_2. Figure 1 illustrates the contents.

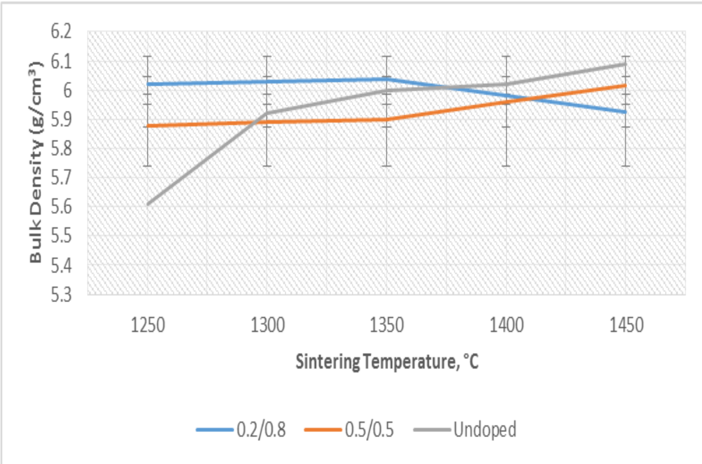

Fig. 1: Influence of sintering temperature

B. Hardness

Fig. 2 illustrates the correlation between temperature and manganese oxide, as well as cerium oxide. From the results, it is evident that when manganese oxide and cerium oxide are added, zirconia exhibits a significant improvement in hardness, especially if sintered at a lower temperature (i.e. 1250ºC) compared to result obtained at 1450°C. It was observed in Fig. 2 that the highest hardness value of approximately 9.4GPa was achieved for the 0.2wt% of CeO_2 and 0.8wt% of MnO_2 composition for samples sintered at 1250ºC. However, as the sintering temperature increased, the 0.2wt% CeO_2/0.8wt% MnO_2 composition displayed a decreasing trend up to 1450°C. In

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contrast the undoped and 0.5wt% CeO_2/0.5wt% MnO_2 composition samples showed a gradual increase-to-constant value trend with increasing sintering temperature.

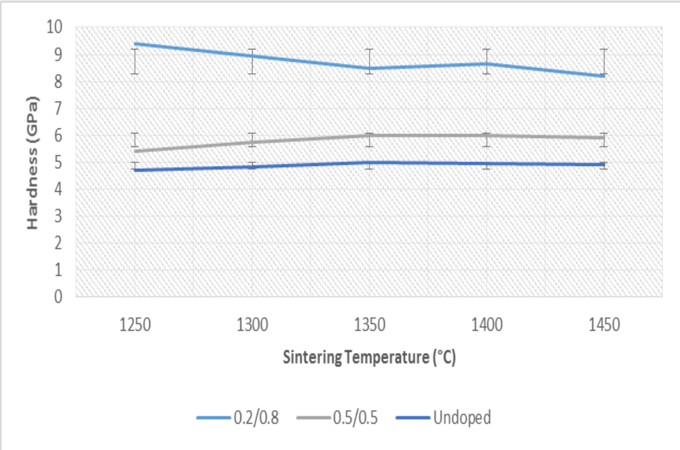


Fig. 2 Influence of sintering temperature on the Vickers hardness of the CeO_2/MnO_2-Y-TZP composites

C. Flexural Strength

From Fig. 3, it was evident that the addition of CeO_2 and MnO_2 to Y-TZP yielded an increase in flexural strength, with a big increase at 1350°C. Besides that, the strength of the composites continued to increase gradually as the sintering temperature increased to 1450°C. This observation was seen for all specimens. In particular, the sample consisting 0.2wt% CeO_2/0.8wt% MnO_2 recorded highest value of strength.

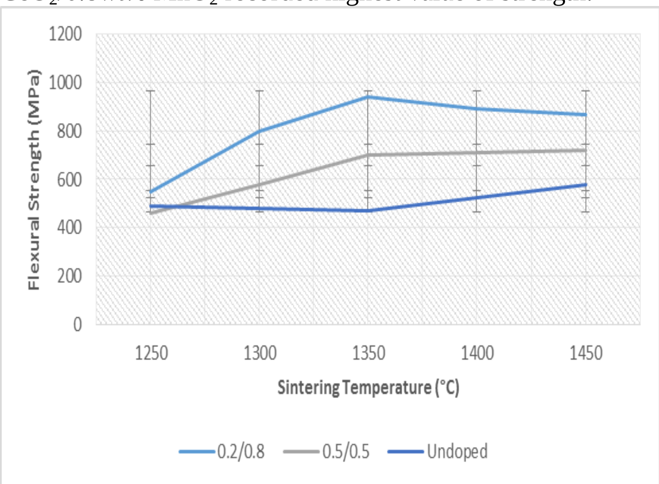


Fig. 3 Influence of sintering temperature on the Flexural strength of the CeO_2/MnO_2-Y-TZP composites

Similar results were reported whereby a strength value of 880MPa and 1226MPa respectively was obtained and the authors also speculated that the cause for high bending strength could be associated with the size of the Y-TZP grains as well as porosity [26, 27]. The diffusion-controlled transformation of zirconia strongly depends on its grain size. A larger grain size would result in a detrimental effect to the Y-TZP ceramics due to the formation of microcracks and the accumulation of tensile residual stresses which could lead to a decrease in strength with progressing t→m transformation [28].

D. Young's Modulus

The effect of cerium oxide and manganese oxide doped Y-TZP on the Young's modulus is seen in Fig. 4. It was observed that the Young's modulus of Y-TZP increased gradually as the sintering temperature increased. The major effect of CeO_2 and MnO_2 in enhancing the matrix stiffness of Y-TZP can be seen particularly when sintered at 1350ºC, whereby all composite samples stiffness increases significantly. It was found that the 0.2wt% CeO_2 /0.8wt% MnO_2 samples achieved the highest E value of 220GPa at 1350ºC, slightly higher than theoretical value of the Young's modulus of pure Y-TZP (200GPa).

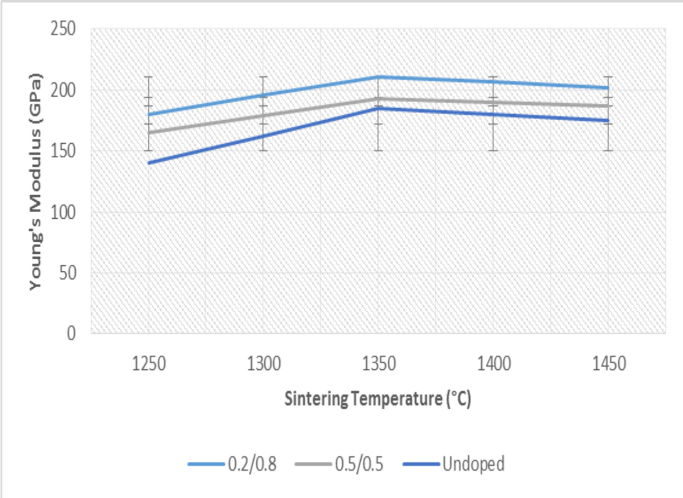
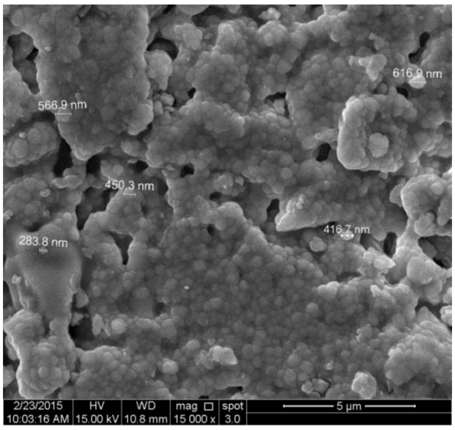


Fig. 4 Influence of sintering temperature

However, as the samples were sintered above 1350°C, the Young's Modulus of all samples began to display a decrease in elasticity. This decrease could be due to increased porosity with increasing sintering temperature [29, 30]. However, previous researchers had suggested that the addition of ceria does not induce any defect to the surface or cracks that could affect the elastic modulus [31].

E. Microstructural Evaluation

The morphology and grain size of the two best compositions (i.e. 0.2wt% CeO_2/0.8wt% MnO_2 and 0.5wt% CeO_2/0.5wt% MnO_2) was investigated. The significant increase in grain size of the 0.5wt% CeO_2/0.5wt% MnO_2 could be due to the phase transformation from t→m. A larger grain size could have been formed due to microcracks of the intergranular boundaries caused by sintering at a higher temperature [32].



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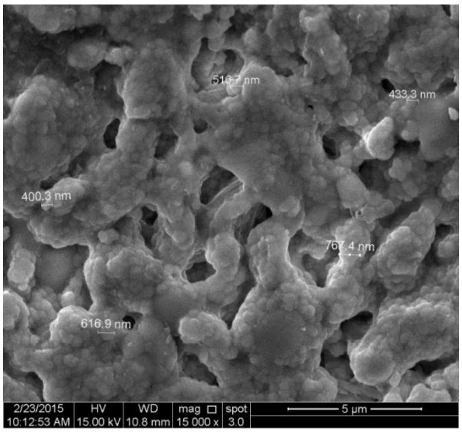
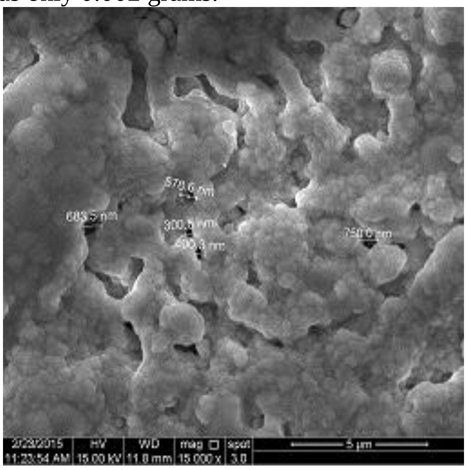


b)

Fig. 5 a) The SEM image for 0.2wt% CeO_2/0.8wt% MnO_2 and b) 0.5wt% CeO_2/0.5wt% MnO_2 specimens

F. Hydrothermal Degradation

The results show that the undoped Y-TZP exhibited the worst ageing resistance and the tetragonal grains transformed to the monoclinic symmetry within few hours of exposure [33]. The undoped ceramic attained about 92.6% m content after ageing for 1 hour. In the current research, the maximum weight loss was seen to be 0.004 and 0.008 grams. The higher weight loss could probably be attributed by the preparation technique, the presence of impurities and also the sintering temperature. The overall weight loss in this study is slightly higher (0.004g) than the weight loss of the Y-TZP ball head observed by [34], which was only 0.002 grams.



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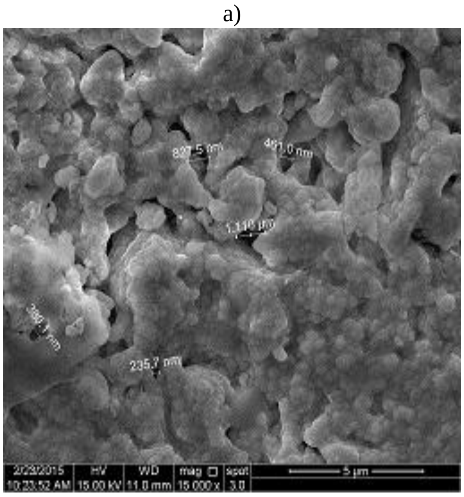

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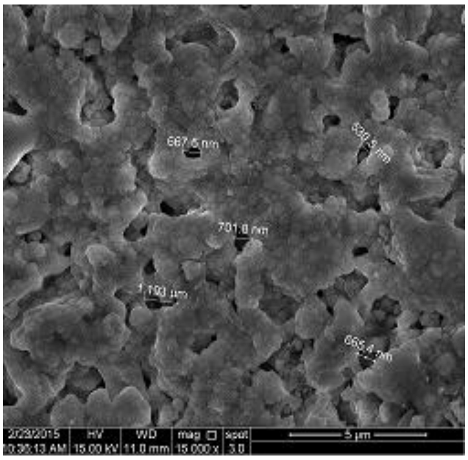

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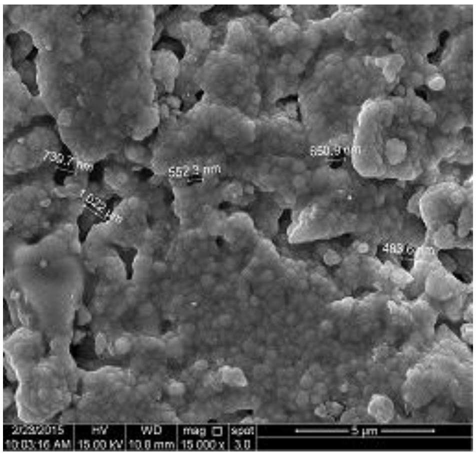

d)

Fig. 6 SEM image

III. CONCLUSION

From the findings, mechanical properties are likely to improve via the addition of 0.2 wt% CeO_2 and 0.8 wt% MnO_2 with Y-TZP. This composition increased the density of Y-TZP. The value of density achieved was about 6.04 g/cm3, approximately 98% of the theoretical density of Y-TZP. The mechanical properties (i.e. hardness and strength) of the material were significantly increased as well. Besides that, the 0.2 wt% CeO_2 and 0.8 wt% MnO_2 composite displayed higher elasticity of 211 GPa compared to pure Y-TZP with a theoretical value of 200 GPa. Sintering over 1450 ºC is expected to degenerate the composite's physical and mechanical properties. Sintering at higher temperatures (>1350 °C) would affect the properties of the composite, due to a bigger grain size obtained at high temperature.

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