Densification Behavior and Mechanical Properties of Cerium Oxide and Manganese Oxide-doped Yttria Tetragonal Zirconia Polycrystals Ceramics for Dental Applications

G. Sankar, S. Meenaloshini, R. Dinesh

Abstract*: This research work focuses on the mechanical properties and microstructural behavior of high-purity CeO_2 and MnO_2-doped Y-TZP. The compositions were varied with different weight percentage i.e from 0.5 to 1.5wt%. The samples were homogenously mixed using wet milling and ball milling operations. Then, the samples were shaped into circular discs and rectangular bars by uniaxial pressing at 200 MPa and then pressure less-sintered at various temperatures between 1250˚C and 1450˚C. 1h holding time was applied before cooling down. The results have shown, that the addition of dopant and sintering temperature has significantly contributed towards the enhancement of the mechanical properties of Y-TZP. The mechanical properties in relation to bulk density, Young's modulus, Vickers hardness, and flexural were measured. The best mechanical property values for the CeO_2 and MnO_2-doped Y-TZP ceramics were 5.67 Mgm^{-3} and 8.46 GPa for density and Vickers hardness, respectively. The best flexural strength and Youngs modulus values obtained from the experiment were ~900 MPa and 210 GPa respectively. These results indicate that the addition of dopants have reinforced the densification parameters and toughened the samples. These results were obtained for the composition of 0.5wt% MnO_2 and 0.5wt% CeO_2 sintered at 1350˚C.

***Index Terms*: CeO_2, MnO_2, Mechanical Properties, Microstructure**

I. INTRODUCTION

Zirconia is known for excellent mechanical properties; hence it holds a unique place amongst all oxide ceramics. Zirconia impart transformation toughening, because zirconia maintains strength and chemical inertness. Besides, Yttria-stabilised tetragonal zirconia polycrystalline ceramics (Y-TZP) has been a very popular engineering material, as the mechanical properties is outstanding. Y-TZP has been widely used in many applications like engine parts, valves, cutting tools, and moulds. This is due to their good fracture toughness, high strength, elastic modulus, and wear resistance [1-3].

Because of its stabilizing effect of yttria, Y-TZP ceramic is possible to be processed in the metastable tetragonal (t) structure. This process is crucial as the retention of the (t) phase at ambient temperature allows it to transform to the monoclinic (m) structure under external applied stress [4-5].

On the other hand, in humid condition, especially temperatures ranging from 20°C to 500°C, the Y-TZP ceramics exhibit an obvious low temperature ageing phenomenon. This phenomenon is also known as low temperature degradation (LTD) or hydrothermal ageing [6-7]. Despite the many favorable characteristics of Y-TZP such as excellent mechanical properties and wear properties, there is this drawback that is caused by the Y-TZP. LTD happens when tetragonal (t) to monoclinic (m) phase transformation, takes place rapidly in the samples.

Therefore, different experiments have been performed to study the micro mechanism of (t) to (m) phase transformation, to curb the LTD phenomenon, to mitigate the microcrack expansion [8-16]. Based on research findings, the addition of ceramic oxides (MgO, Al_2O_3, ZnO, CaO, and CeO_2) help overcome if not prevent the low temperature degradation occurrence in Y-TZP ceramics [17-21]. CeO_2 is generally used to stabilize the tetragonal phase of zirconia and is also known to increase the sintering of glass ceramics and strength and thermal stability. This work presents effect of different parameter on the surface morphology and particle distribution.

II. MATERIALS AND METHODS

In this research the main powder used was, a co-precipitated sprayed dried 3mol% yttria-zirconia (Y-TZP). This powder was manufactured and supplied by Kyoritsu Japan. At the same time, different amounts of high purity CeO_2 and MnO_2 (undoped, 0.5, 1.0 and 1.5wt% doped Y-TZP) powders were prepared using a wet colloidal method. The zirconia balls and ethanol were used as the milling and mixing medium in the ultrasonic machine. Upon the mixing operation, the slurry obtained was oven dried at 60˚C for 12 hours. The dried sample was then sieved, and the powder was readied for pressing operation.

Then, the powder was formed into circular discs and rectangular bars, which were compacted at 0.3 MPa and pressed iso-statically at 200 MPa. To further harden the samples, the pressed samples were pressureless sintered in air using a heating furnace, ModuTemp.

Revised Manuscript Received on May 05, 2019.

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The samples were fired at temperatures ranging from 1250˚C to 1450˚C. The holding time was maintained at 1h before cooling to room temperature. The sintered samples were then, ground on SiC papers of 120, 240, 600, 800 and 1200 grades successively, followed by polishing with 6 µ diamond paste. This grinding and polishing processes were carried out to produce a smooth and reflective surface.

The mechanical properties test was conducted by calculating bulk density for the sintered samples. Archimedes principle was used to obtain the bulk density. This was done using an electronic balance retrofitted with a density determination kit (Mettler Toledo, Switzerland).

The instrument (GrindoSonic: MK5 "Industrial", Belgium) was used to determine the Young's modulus (E), using sonic resonance. This instrument determines the resonant frequency of a sample through the vibrational harmonics of the sample using a transducer. Through tapping, the vibrations are physically induced in the sample. The Young's modulus or also known as the modulus of elasticity was calculated using the experimentally determined resonant frequency (ASTM, 1998) [22].

The Vickers hardness measurements (Future Tech., Japan) was performed using the polished samples which is called the Vickers indentation method. A loading time of 10 s was employed while the indentation load was kept constant at 98.1 N. The equation derived by Niihara et al used to compute the values of KIc [23].

The microstructure of the samples was evaluated by JSM-6310 scanning electron microscopy (SEM). The test was conducted to investigate the microstructure and morphology of the best sintered samples with excellent mechanical properties.

III. RESULTS

A. Bulk Density

Fig. 1 shows the bulk density results against sintering temperatures for undoped and CeO and MnO doped Y-TZP. The bulk density of doped Y-TZPs has shown significant change through the addition of 0.5, 1.0, 1.5 wt% CeO and MnO as compared to the undoped Y-TZP. The bulk density of the undoped and 1.0 wt% CeO and MnO doped samples obtained similar trend with the increase of sintering temperature where the bulk density increased in the beginning (1250°C to 1350°C) and decreased when the sintering temperature was increased to 1450°C. For the 0.5 wt% CeO and MnO doped Y-TZP, the trend started with a decrease of bulk density from temperatures 1250°C to 1350°C and then increased when sintered at 1450°C. Addition of CeO_2 and MnO_2 were found to be most beneficial between 1350°C to 1450°C as the samples were almost completely dense as compared to the undoped Y-TZP. The Y-TZP sample with 1.5 wt% CeO and 1.5 wt% MnO obtained the highest bulk density value of 5.7611 Mgm^{-3} sintered at 1450°C, about 95% of theoretical density of Y-TZP (6.09 g/cm^3). The Y-TZP sample with 0.5 wt% CeO and 0.5 wt% MnO also obtained high bulk density value of 5.6709 Mgm^{-3} sintered at 1450°C, about 94% of theoretical density of Y-TZP (6.09 g/cm^3). This portrays that excellent bulk density can be achieved by sintering samples at high temperature. This is due to high diffusion ability of dopants in Y-TZP matrix. Similarly, the obtained results also show a trend matching with other researchers who have carried out work using CeO_2 and MnO_2 as sintering additives in Y-TZP [24-25].

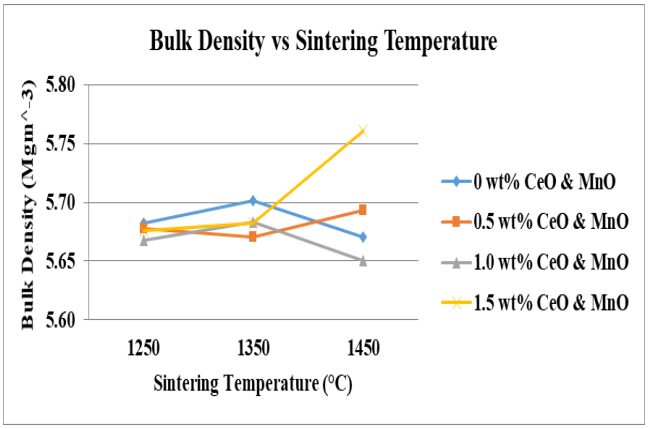

Fig. 1 Effect of sintering temperature on the bulk density of the MnO_2/CeO_2-Y-TZP composites

B. Vickers Hardness

Fig. 2 shows the effect of sintering temperature against CeO_2 and MnO_2 addition, towards the Vickers hardness of Y-TZP composites. Based on the results obtained, the addition of CeO_2 and MnO_2 were beneficial in enhancing the hardness of zirconia when sintered at lower sintering temperature (i.e. 1250˚C) as compared to the results obtained at 1450°C. It was observed in Fig. 2 that the highest hardness value of approximately 8.46 GPa was achieved for the 0.5 wt% of CeO_2 and 0.5 wt% of MnO_2 composition for samples sintered at 1350˚C. However, with the increase in sintering temperature, 1450°C, the 0.5% CeO_2 and 0.5wt% MnO_2 composition displayed a drastic decrease in hardness. The decrease in hardness could be due tetragonal to monoclinic phase transformation of ZrO_2 for 0.5 wt% CeO_2 and 0.5 wt% MnO_2 composition. On a contrary, the increase in hardness occurs as the number of micro-cracks occurring within the ceramic, during the measurement of Vickers's hardness is reduced [26]. Generally, good hardness values were obtained at lower sintering temperature.

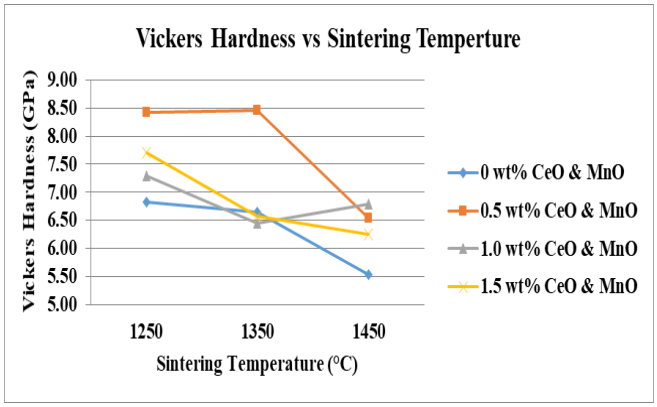

Fig. 2 Effect of sintering temperature on the Vickers hardness of the CeO_2/MnO_2-Y-TZP composites

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C. Flexural Strength

From Fig. 3, the strength of Y-TZP composites was responsive towards the sintering temperature, as it gradually increased from 1250°C to 1350°C and dropped at 1450°C. It was evident that the addition of CeO_2 and MnO_2 to Y-TZP yielded an increase in flexural strength, with a relatively high rate of increase at 1350°C. The 0.5wt% CeO_2/0.5wt% MnO_2 composition was the best as compared to other compositions. In particular, the sample consisting 0.5wt% CeO_2/0.5wt% MnO_2 has shown the highest flexural strength values; increasing from ~800 MPa at 1250˚C to ~900 MPa at 1350°C. This result exceeded the theoretical value of flexural strength for Y-TZP of 900 MPa [27]. Hence, this shows the grain size contributes significantly towards the diffusion-controlled transformation of zirconia. A larger grain size would result in a detrimental effect to the Y-TZP ceramics. Decrease in strength happens because of the propagation of microcracks and the growth of tensile residual stresses, whereas in this composition it conforms that the crack propagation was mitigated [28].

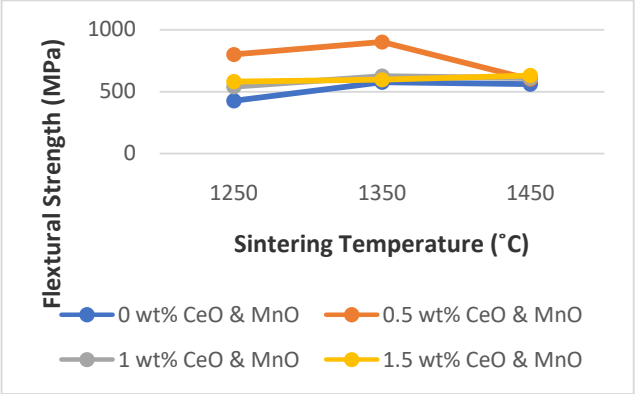

Fig. 3 Effect of sintering temperature on the Flexural strength of the CeO_2/MnO_2-Y-TZP composites

D. Youngs Modulus

Fig. 4 shows the effect of the addition of cerium oxide and manganese oxide doped Y-TZP on the Young's modulus. The results showed similar trend like the flexural strength where the Young's modulus of Y-TZP too increased gradually from 1250˚C to 1350˚C and dropped at 1450˚C. The major effect of CeO_2 and MnO_2 when sintered especially at 1350˚C, has enhanced the matrix stiffness of Y-TZP. It is notable that the 0.5wt% CeO_2/0.5wt% MnO_2 samples achieved the highest Young's modulus value of 210GPa at 1350˚C, which is slightly higher than the theoretical Young's modulus value which is 200GPa. However, the samples sintered above 1350°C, showed a decrease in Young's modulus for all samples which illustrates a decrease in elasticity. The decrease in Young's modulus is due to the increasing porosity with increasing sintering temperature [29-30]. On a contrary, the addition of ceria does not cause any defect to the surface or form micro-cracks that could affect the Young's modulus as reported by other researcher [31].

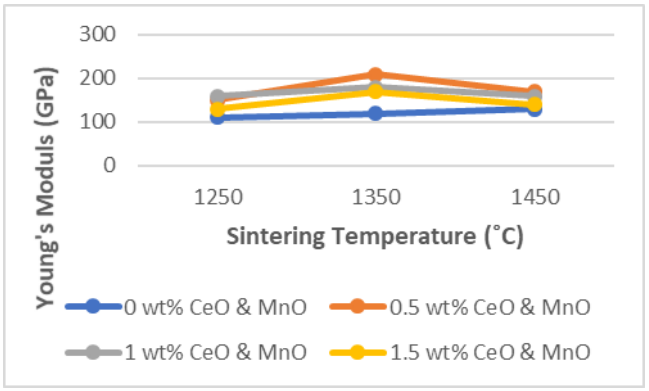

Fig. 4 Effect of sintering temperature on the Youngs Modulus of the CeO_2/MnO_2-Y-TZP composites

E. Microstructure Evaluation

The addition of CeO_2 and MnO_2 also contributed towards the transformation toughening mechanism. Thus, the microstructure and the morphology of the samples were analyzed using the Scanning Electron Microscope (SEM). The samples were coated with a layer of platinum before the SEM imaging was performed. This is to avoid the occurrence of charging. The morphology and grain size of the best compositions 0.5wt% CeO_2/0.5wt% MnO_2 was investigated. This sample displayed an average grain size value of approximately 464.92nm. The SEM micrograph for this sample is depicted in Fig. 5. The significant increase in grain size of the 1.0wt% CeO_2/1.0wt% MnO_2 could be due to the phase transformation from tetragonal to monoclinic. A larger grain size could have been formed due to microcracks of the intergranular boundaries which may be due to sintering at high temperature [32]. LTD which is known as the transformation from tetragonal to monoclinic phase, happens in biomedical applications, through the propagation of martensite, and this leads to hydrothermal ageing [33]. Hence, this transformation is highly sensitive to mechanical and chemo-mechanical stresses. It can be said, this transformation is the contributing factor towards fracture toughening in stabilized zirconia [34]. Hence, the results obtained for the flexural strength in this research was relatively high for 0.5wt% CeO2/0.5wt% MnO_2 composition sintered at 1350˚C which is an excellent contribution factor towards mechanical properties of biomedical applications.

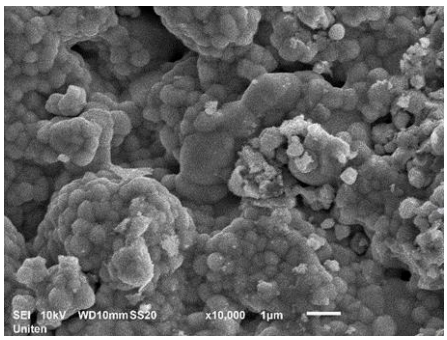

Fig. 5 The SEM image for 0.5wt% CeO_2/0.5wt%MnO_2

IV. CONCLUSION

The results from this research show that the mechanical properties of the compositions have been enhanced by the addition of 0.5wt% CeO_2 and 0.5wt% MnO_2 with Y-TZP. The results portrayed excellent density achievement, i.e 5.67 g/cm^3, which is about 94% of the theoretical density of Y-TZP. Besides, mechanical properties (i.e. Vickers hardness, Young's Modulus and flexural strength) also experienced significant results. In addition to that, the 0.5wt% CeO_2 and 0.5wt% MnO_2 composite displayed higher Young's modulus of 200GPa. Sintering above 1450˚C has shown degeneration in the composite's physical and mechanical properties. Sintering at higher temperatures (>1350°C) had affected the mechanical properties of the composite, due to bigger grain size obtained at higher temperature.

ACKNOWLEDGMENT

With immense pleasure the authors would like to thank the FRGS for providing the financial support under the grant no. 20160114FRGS. In addition, the authors also highly appreciate the support provided by UNITEN, in carrying out this research to achieve its success.

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