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Research Article

The Influence of Manganese Oxide on the Densification and Mechanical Properties of 3Y-TZP Ceramics

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Abstract
With outstanding integration of mechanical performances and biocompatibility, 3 mol% of yttria stabilised tetragonal zirconia polycrystals (3Y-TZP) ceramic are extensively fabricated as biomedical implants. Conventional sintering (CS) was generally employed to produce 3Y-TZP bodies with promising densification, which resulted in grain coarsening and mechanical properties deterioration due to elevated sintering temperatures (> 1500°C). The main weakness of 3Y-TZP ceramic is the spontaneous tetragonal to monoclinic phase transformation under humid environment, which is known as low-temperature degradation (LTD). In present work, undoped and MnO_2 (0.3 and 0.5 wt%) doped 3Y-TZP green bodies were prepared and subjected to CS at 1200–1500°C for an hour of dwelling time. It was found that the optimum concentration of MnO_2 dopant was 0.5 wt%. Reasonable toughness values of 5–7 MPa.$m^{1/2}$ revealed the tetragonal phase stability of 3Y-TZP grains was not altered by doping of MnO_2. Moreover, outstanding density level of > 96% of 0.5 wt% MnO_2 doped 3Y-TZP ceramics demonstrated the superb Young's modulus of > 200 GPa and Vicker's hardness of >13 GPa. Fabrication of 3Y-TZP by doping MnO_2 had reduced the total processing time by ~ 9% and sintering temperature by up to 150°C when compared to undoped 3Y-TZP ceramics sintered at 1400°C.

Keywords: Manganese oxide, 3Y-TZP, Zirconia, Doping, Sintering

1 Introduction

With 3 mol% yttria stabilisation, tetragonal-only phase zirconia (3Y-TZP) ceramics are facing increasing demand due to their promising mechanical performances, high resistance to corrosion and lightweight that make the material a promising candidate to cover miscellaneous applications, for example, biocompatible structural ceramics, which include the area of biomaterials prosthesis implant [1]. In the field of orthopaedics, 3Y-TZP has successfully led the way towards good implant designs that were impossible with alumina, which is more fragile. The primary application of this bioceramic is in the fabrication of ball heads to replace the worn

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joints for total hip replacements [2]. There was an estimation of 500,000 zirconia femoral head being implanted since 1985 [3]. The characterisation of 3Y-TZP ceramics with excellent wear resistance, strength and fracture resistance are owing to the metastability of (t) phase at room temperature associated with the transformation toughening mechanism [4].

However, the distribution of zirconia ceramic as orthopaedic artificial implant had been suspended and recalled in 2001 due to the occurrence of LTD [5]. With ongoing research, in the field of dentistry, 3Y-TZP has been used for prosthetic rehabilitation as a core material for resin-bonded fixed partial dentures (FPDs) since 2004 [6]. By replacing titanium alloy, zirconia endosseous implants act as the revolution of modern restorative dentistry [7]. As a consequence of its outstanding fracture toughness, strength and excellent aesthetic properties that enables it to mimic the natural tooth colour and translucency, ZrO_2 ceramic is considered to be the most appropriate dental material for bridge and crown restoration [8].

Commonly, in order to fabricate 3Y-TZP bodies with promising relative densities (> 95%) for structural applications conventional sintering (CS) is adopted. However, high firing temperature of > 1500°C was needed for fabrication which causing undesirable grain enlargement that is detrimental to the physical properties, mechanical performances and LTD resistance of sintered 3Y-TZP bodies as reported by previous researchers [9].

Therefore, the usage of dopants or sintering additives to modify the grain boundary of undoped 3Y-TZP had been studied recently. Based on previous findings, the addition of MnO_2 enabled 3Y-TZP ceramics to achieve promising densification and enhanced mechanical properties at much lower firing temperatures between 1250°C to 1300°C [10], [11]. The enhanced densification is likely owing to the MnO_2 dissolution in the matrix of Y-TZP by Mn-rich formation at grain boundaries of 3Y-TZP, thus increasing the Zr^{4+} ionic mobility across and within the regions of grain boundaries. The grain boundary diffusivity is significantly activated, promoting the particles consolidation in shorter duration and at lower firing temperatures when compared to undoped 3Y-TZP [12].

The main purpose of current work is to focus on producing undoped and MnO_2 (0.3 and 0.5 wt%) doped 3Y-TZP samples with lower firing temperature without influencing the mechanical properties. The undoped and MnO_2 doped 3Y-TZP samples were compared in terms of densification behaviour and mechanical performances.

2 Methodology

2.1 *Sample preparation*

Commercial undoped 3 mol% yttria-stabilised zirconia (3Y-TZP) powder (Kyoritsu Ltd., Japan) that consisted of primary impurities about 0.1 wt% of Fe_2O_3, SiO_2, TiO_2, and Al_2O_3 was used. Besides, Manganese (IV) oxide (MnO_2) powder (Merck, Germany) was adopted, which contained around ≤ 0.1 wt% of SO_4, ≤ 1.0% with Ba and Ca and 1.5% with Fe. MnO_2 doped powder was synthesised via co-precipitation method. The undoped and doped 3Y-TZP powder was pressed into discs (2.5 g each) and bars (3.0 g each) uniaxially under a pressure of 0.3 MPa by using a mould and dies set. The green bodies were afterwards subjected to cold isostatic pressing (CIP) for 60 s at pressure of 200 MPa. The cold isostatically pressed green bodies were sent for single-stage pressureless sintering at different firing temperatures between 1200°C to 1500°C by adopting Carbolite furnace. The green bodies were sintered from ambient temperature to the maximum desired sintering temperatures at rates of 10°C/min and dwelled for an hour before cooling to room temperature. Disc-shaped sintered bodies were ground by silicon carbide (SiC) papers with 180, 240, 600, 800, and 1200 grits and polished by using diamond pastes of 3 μm to 1 μm together with diamond polishing cloth to ensure the attainment of mirror reflective surface.

2.2 *Material characterization*

Water immersion technique was employed by using a standard Vibra HT and density measurement kit to obtain the bulk density of the sintered 3Y-TZPs based on the Archimedes principle with distilled water as the immersion medium. Theoretical densities of 3Y-TZP (6.10 g/cm^3) were taken to obtain the relative densities of sintered samples. The density tests were repeated five times for each sintered sample and average values were taken. The commercial instrument used for testing of material's elasticity is GrindoSonic: MK5 "Industrial" Beldium. Physical vibrations were induced

by tapping the bar samples. The electromagnetic transducer was used to transmit the mechanical vibration and received by the amplifier. The experimentally obtained resonant frequencies were used to calculate the Young's Modulus (E) of sintered samples. Five readings of resonant frequencies were taken for each bar sample. Vicker's hardness (H_v) and fracture toughness (K_{Ic}) determinations were performed on polished disc samples by adopting Vicker's indentation test with 10 kgf of constant load and 10 s of holding time. Then, a Palmvisk crack was formed after the load was released. There were at least three indentations made for each polished sample and result was taken averagely. The fracture toughness (K_{Ic}) were conducted based on equation generated by Niihara *et al*. [13].

3 Results and Discussion

The effect of firing temperatures on the bulk densities of 3 types of sintered bodies (undoped, 0.3 and 0.5 wt% MnO_2 doped) is shown in Figure 1. The relative densities of both undoped and doped 3Y-TZP specimens possessed similar trends of increment with the elevating sintering temperatures. The relative density of undoped 3Y-TZP sintered at 1500°C was decreased, which might be attributed to oversintering which was highlighted by Jiang *et al*. [14]. It is obviously depicted that 3Y-TZP ceramics doped with MnO_2 (0.3 and 0.5 wt%) were able to attain > 95% of relative densities at 1250°C whereas only 92.45% were achievable by undoped 3Y-TZP bodies. It is in agreement with some findings that highlighted the addition of MnO_2 facilitated the densification of 3Y-TZP ceramics in much lower sintering temperature (1250°C to 1300°C) [10], [15]. This phenomenon is attributed to the dissolution of MnO_2 in the matrix of 3Y-TZP by Mn-rich formation at grain boundaries hence promoting the Zr^{4+} ionic mobility across and within the grain boundaries regions [12]. In addition, MnO_2 doped 3Y-TZP samples exhibited slight relative densities increment up to 97.79% with increasing temperatures, but the relative densities of undoped 3Y-TZP increased significantly up to 1300°C and experienced minor densification enhancement up to 1400°C. The slowing down of the densification rate at the final sintering stage of undoped 3Y-TZP was most likely owing to grain growth [16]. It is significant to fabricate 3Y-TZP with high-density level as a less dense body with open

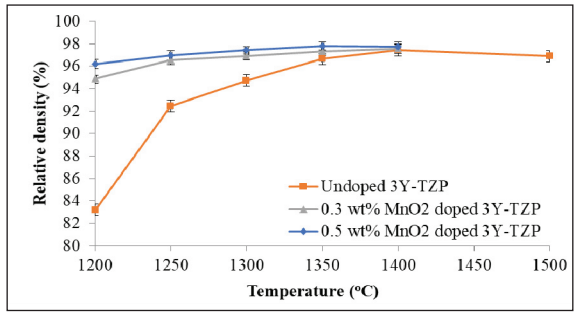

Figure 1: Changes of relative densities attained by undoped and MnO_2 (0.3 and 0.5 wt%) doped conventional sintered 3Y-TZP with various sintering temperatures.

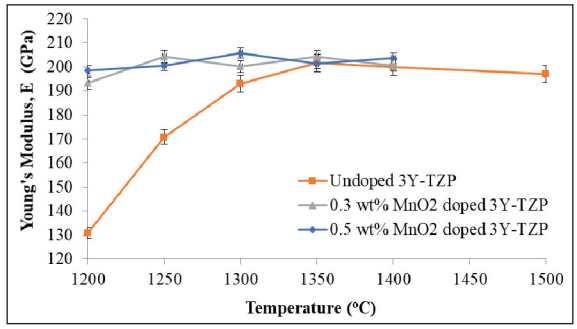

Figure 2: Changes of Young's modulus attained by undoped and MnO_2 (0.3 and 0.5 wt%) doped conventional sintered 3Y-TZP with various sintering temperatures.

pores allows smoother water molecules penetration to its bulk causing LTD to occur at the material surface an on the entire internal. The loss of material's cohesion could be harmful to its mechanical properties [17].

The role of firing temperatures on Young's modulus (E) of the undoped and doped (0.3 and 0.5 wt% MnO_2) 3Y-TZP ceramics is displayed in Figure 2. It is notable that, for all cases, E increased with increasing firing temperatures. The E values of doped 3Y-TZP varied slightly between 193.18 GPa to 205.78 GPa throughout the firing regime. At 1250°C, doped samples were able to achieve > 200 GPa of E values. This phenomenon could be attributed to the higher relative densities achieved by MnO_2 doped 3Y-TZP than that of undoped 3Y-TZP at the similar sintering temperature. The inclusion of MnO_2 that provide better mechanical interlock will led to firmer fixation of doped 3Y-TZP matrix and therefore

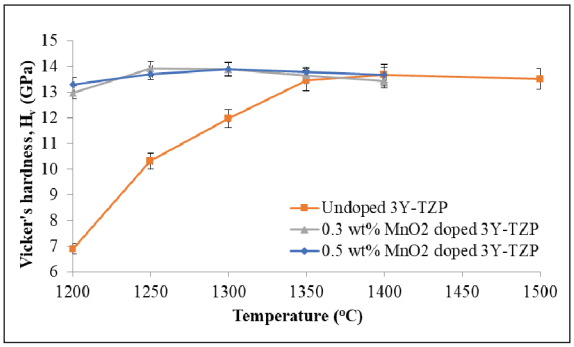

Figure 3: Changes of Vicker's hardness attained by undoped and MnO_2 (0.3 wt% & 0.5 wt%) doped conventional sintered 3Y-TZP with various sintering temperatures.

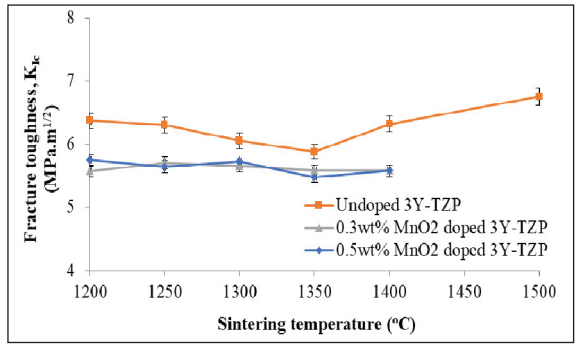

Figure 4: Changes of fracture toughness attained by undoped and MnO_2 (0.3 and 0.5 wt%) doped conventional sintered 3Y-TZP with various sintering temperatures.

enhancing Young's modulus at lower sintering temperature. The E values obtained by doped samples in this work were outstanding as the E value for biomaterial application should be ≥ 200 GPa based on ISO 13356:2015 [18]. For doped samples, the fluctuation of E values (> 200 GPa) throughout the sintering regime regardless of sintering temperatures was observed by previous findings as well [19]. For the case of undoped 3Y-TZP, there was an improvement of E significantly from 130.88 GPa to 193 GPa between firing temperatures between 1200°C to 1300°C. With further firing processes, undoped 3Y-TZP attained the peak value of 201.59 GPa at 1350°C. The gradual E values increment reflected the density improvement and the residual pores reduction of undoped 3Y-TZP ceramics.

The influence of firing temperatures on the Vicker's hardness (H_v) of 3 kinds of fired zirconia samples (0, 0.3 and 0.5 wt% MnO_2) has been illustrated in Figure 3. The H_v trends climbed to reach a peak then declined slightly with further sintering corresponded to other findings [19]. For undoped 3Y-TZP, hardness increased with elevating firing temperatures between 1200°C to 1400°C from 6.9 GPa to the maximum hardness value of 13.66 GPa. There was not much effect on improving hardness with further temperature increment. Conversely, MnO_2 (0.3 and 0.5 wt%) doped sintered samples were able to attain ~13 GPa at firing temperature as low as 1200°C. The trends of doped 3Y-TZP ceramics did not vary much throughout the firing regime. The maximum hardness values achieved by 0.3 and 0.5 wt% MnO_2 doped ceramics were 13.91 GPa at 1250°C and 13.88 GPa at 1300°C respectively. For 0.5 wt% doped 3Y-TZP, the hardness values obtained were more than 13 GPa regardless of sintering temperatures. Based on the results of current research, MnO_2 was able to promote hardness development at lower firing temperatures (1200–1350°C) which agrees to the previous findings [10], [12], [18]. Vicker's hardness of 3Y-TZP is related to porosity and grain size. At low sintering temperature, MnO_2 doped 3Y-TZP sintered bodies with dense and fine microstructure will ensure the close pack of bimodal grain distribution and hence provided higher tendency to allow matrix dislocation motion [20].

The relationship between the firing temperatures and the fracture toughness, K_{Ic}, of 3 compositions (0, 0.3 and 0.5 wt% MnO_2) of 3Y-TZP sintered bodies is shown in Figure 4. It is obvious to note the inverse relationship between the crack lengths generated around the indentation with the K_{Ic} of the material. With crack lengths obtained, the K_{Ic} was calculated. For undoped 3Y-TZP ceramics, the K_{Ic} value dropped from 6.37 MPa.m$^{1/2}$ to 5.88 MPa.m$^{1/2}$ from 1200°C to 1350°C, and climbed gradually to obtain 6.75 MPa.m$^{1/2}$ at 1500°C. These phenomena indicate that firing temperatures and dopant had a negligible influence on K_{Ic} of sintered 3Y-TZP. The results obtained by current result agrees with findings by previous research which mentioned that K_{Ic} values between 2.5 to 14 MPa.m$^{1/2}$ with H_v values ranging from 11 to 13.5 GPa were attained when firing processes were conducted in the range of temperatures from 1400–1500°C [21]. Furthermore, for doped 3Y-TZP samples, fluctuating

trends of K_{Ic} were noticeable regardless of sintering temperatures adopted. The K_{Ic} varied between 5.58 MPa.$m^{1/2}$ to 5.75 MPa.$m^{1/2}$. The insignificant change of K_{Ic} values indicated that the (t) phase stability was not disturbed by the doping of MnO_2 up to 0.5 wt% throughout the firing regime applied. Identical results were attained previously [10], [11]. The reasonable toughness values obtained was hypothesized due to proper grain boundary formed after sintering process that enable the metastable tetragonal grains to respond instantly so that propagating stress field could be successfully absorbed during the Vicker's hardness test [15]. The slightly lower K_{Ic} values obtained by doped 3Y-TZP ceramics when compared to that of undoped 3Y-TZP might be attributed to less (t) grains available for transformation toughening mechanism [22].

4 Conclusions

This research implicated the substantial role of opting the doping of MnO_2 up to 0.5 wt% in fabricating 3Y-TZP samples for orthopaedic application with the exceptional relative density of > 96%, excellent Vicker's hardness of > 13 GPa, outstanding Young's modulus of > 200 GPa and good fracture toughness of 5–7 MPa.$m^{1/2}$. MnO_2 doped samples sintered at 1250°C were able to achieve comparable mechanical properties and density level with undoped samples sintered at temperature > 1400°C. It was found out that with further increment of sintering temperatures (>1250°C), the effect of MnO_2 was insignificant. For future work, the LTD resistance of 3Y-TZP doped with different MnO_2 concentration will be determined by hydrothermal ageing test and the ageing behaviour of the sintered samples will be reported based on XRD analysis.

Acknowledgments

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