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Influence of sintering profile on the mechanical properties of manganese oxide doped 3Y-TZP

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Abstract. Zirconia ceramic has been identified as one of the advanced ceramic material with great mechanical properties which is used as engineering and implant materials. However, the great potential of the ceramic is hindered by low temperature degradation (LTD) where the ceramic experiencing t-m phase transformation that weakens the properties of 3Y-TZP in the presence of moisture. Two-step sintering was found to be effective in producing fully resistance 3Y-TZY but very long holding time is required. Manganese Oxide (MnO₂) is reported as good densification aid at low sintering temperature for 3Y-TZP but the LTD issue is not fully resolved. In this study, the effects of different sintering profiles and dwell time on 3Y-TZP added with 0.5 wt.% of MnO₂ were studied in order to improve the resistance towards LTD without affecting the intrinsic properties of the ceramic. The effects of adding 0.5 wt.% of manganese oxide (MnO₂) into 3 mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP) were studied using different sintering profiles and dwell time. The samples were sintered at 1400°C and 1250°C with varying dwell time of 1 min and 2 hours for single step sintering and a combination of 1 min and 30 min, 2 hours and 25 hours for two step sintering. The optimal sintering profile was Profile C2 where doped 3Y-TZP undergone two step sintering with dwell time of 1 minute at 1400°C and 1250°C for 30 minutes. At this optimal sintering conditions, the doped 3Y-TZP samples exhibited 98.5% relative density, with Young's Modulus of 206.66 GPa and Vicker's Hardness of 14.35 GPa.

Keywords: Sintering, 3Y-TZP, Mechanical Properties, Manganese Oxide,



1. Introduction

Zirconia (ZrO_2) is an advanced ceramic material that has caught many researchers' attention over the years due to its excellent mechanical properties. In the late sixties, the need of metal free material resulted zirconia to become more profound in the medical industry as zirconia was considered as the replacement material for steel. This is mainly due to its excellent biocompatibility and enhanced aesthetics properties. Zirconia is used in orthopaedics as a new material for hip head replacement instead of titanium or alumina prostheses. Ron Garvie discovered the transformation of toughening mechanism in zirconia ceramic in 20th century where it presents in three different forms at different temperature range namely cubic, monoclinic and tetragonal crystal structures. The transformation from tetragonal phase (t-phase) to monoclinic phase (m-phase) occurs when there is an external stress stimulated which contributes to the toughening effect [1].

Zirconia ceramic is an unstable material that tends to transform from its tetragonal (t) metastable phase which has good properties to monoclinic (m) phase that is stable but with poorer properties. Yttria is added into zirconia to stabilize the phase by retaining tetragonal phase at room temperature. It has been found that doping manganese oxide into Y-TZP had produced significant effect in assisting the sintering process in aiding densification, improving the matrix stiffness and hardness as compared to undoped sample when single step was sintered at temperature below 1350°C. However, transformations of tetragonal to monoclinic phase in hydrothermal ageing condition that degrades the material's properties are yet resolved [2].

Two-step sintering method is an improvement from the conventional pressure-less single step sintering method. Two-step sintering increases the density of the sintered body without grain growth and improves the mechanical properties of 3Y-TZP. Two-step sintering process helps to attain the critical density at the initial temperature and followed by further consolidation process at the second holding temperature. One drawback of the second holding temperature is that it often takes longer period to achieve good properties [3]. In recent work, when the two-step sintered body was aged in a super-heated steam for 100 hours, the samples had no sign of degradation and remained intact. Two-step sintering process resists the transformation of t-phase to m-phase by having great tetragonal phase stability and thus not affecting the mechanical properties of the samples [6]. However, there is still lack of study in identifying the optimal sintering profiles that prevents degradation in 3Y-TZP. Moreover, the effects of various sintering parameters such as sintering technique, temperatures and holding time on the properties of the material is of great interest.

As such, the aim of this current research is to compare and contrast single step and two-step sintering process while investigating the effects of MnO_2 as dopant on the properties of the material at varying sintering profiles.

2. Experimental

Commercially available tetragonal zirconia polycrystals stabilized with 3 mol % of yttria, 3Y-TZP (TOSOH, Japan) were used as the precursor powder and manganese oxide (MnO_2) was used as dopant. The powder of 3Y-TZP and MnO_2 were mixed through ultrasonification and ball milling process with 150ml of ethanol. The mixed mixture of 3Y-TZP and 0.5wt.% of MnO_2 was subjected to ultrasonification using ultrasound probe with a pulse of 28-35k Hz for 45 minutes. The mixture was then ball milled for 1 hour at 400 rpm in 175ml of ethanol solution along with 2mm diameter zirconia milling balls. The slurry mixture was separated from the grinding media and it was evenly spread on a tray and dried at 70°C overnight in drying oven to ensure residual ethanol evaporated. The dry residues were then sieved by using a 250 μ m mesh stainless steel sieve and the powder was obtained. Two batches of powder were obtained, undoped pure 3Y-TZP and 3Y-TZP doped with MnO_2 powder samples.

The two batches of powder were then uniaxially pressed at 3 MPa at 2 different shapes. One is rectangular bar with a dimension 30x10x10 mm and weighted 3 grams and another disc shaped with a dimension of 20 mm diameter and 5 mm thickness weighing 2.5 grams. These prepared samples then undergo cold isostatic pressing (CIP) at 200 MPa. Two types of sintering method were employed, i.e. one-step and two-step sintering method. Referring to Table 2.1, the green bodies in profile A and B will be sintered using single step sintering technique whereas the green bodies in profile C, D and E will be

sintered using two-step sintering technique. Single-step sintering was carried out at 1400°C under ambient air temperature with a constant heating rate of 10°C/min. The specimens were then isothermally held with dwell time varied at 1 minute for specimens under profile A and at 2 hours for specimens under profile B. Specimens from both profiles were then cooled down with similar cooling rate of 10°C/min. Two-step sintering was carried out by heating the sample up to 1400°C as the first stage sintering step. The first temperature, T1 was carried out at constant ramp rate of 10°C/min. The samples were then held at a constant temperature for a short period of 1 minute. Then, for the second step, the specimens were cooled to 1250°C at a constant rate of 10°C/min which was T2. At T2, the specimens were held isothermally with dwell time varied where it was 30 minutes for profile C, 2 hours for profile D, and 25 hours for profile E. After the dwell period, the specimens were all cooled down with similar cooling rate of 10°C/min.

Table 1: Details of each sintering profile and dopants content

Sintering Profile Abbreviation	Sintering temperature(°C)	Dwell Time	Additives
A1	1400	1 min	Undoped
A2	1400	1 min	Doped 0.5 wt.% MnO ₂
B1	1400	2 hours	Undoped
B2	1400	2 hours	Doped 0.5 wt.% MnO ₂
C1	1400 & 1250	1 min & 30 mins	Undoped
C2	1400 & 1250	1 min & 30 mins	Doped 0.5 wt.% MnO ₂
D1	1400 & 1250	1 min & 2 hours	Undoped
D2	1400 & 1250	1 min & 2 hours	Doped 0.5 wt.% MnO ₂
E1	1400 & 1250	1 min & 25 hours	Undoped
E2	1400 & 1250	1 min & 25 hours	Doped 0.5 wt.% MnO ₂

3. Results and Discussion

Figure 1 shows the effects of the sintering profile on the relative density of doped and undoped 3Y-TZP. Most samples achieved relative density more than 95% based on theoretical density of 6.1 gcm⁻³. Density for non-doped samples are increasing with holding time where the highest relative density is obtained by profile B1 at 99.10%. While the lowest relative density is 94.31% by profile A1 when sintered with single step sintering profile.

For two steps sintering, the relative density of the non-doped samples is also enhanced from 97% to 98.90% when holding time increases from 30 min to 25 h respectively. All doped samples attained relative density beyond 98% except A2 with 97.78%. However, the dopant has null effect on density of the doped samples with increasing holding time for both sintering methods.

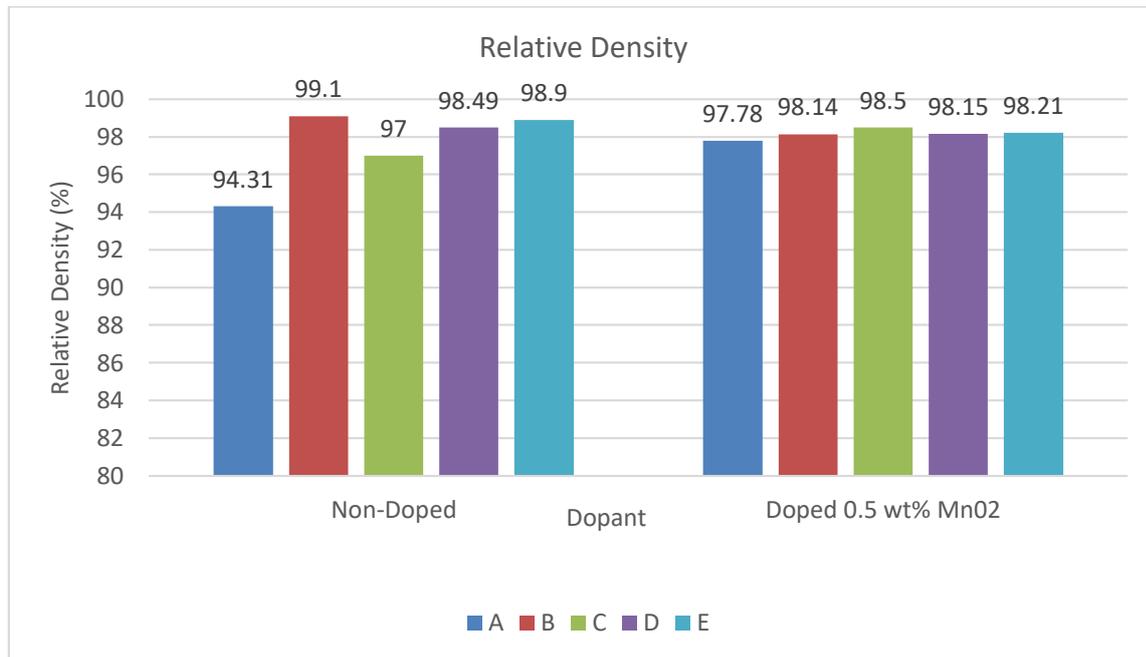


Figure 1: Bar Chart of Relative Density by different sintering profiles

Figure 2 shows the effect of different sintering profiles and dopants on the Young's Modulus, E. The highest E value was obtained by profile B1 with 210.82 GPa. Whereby the lowest E value was of profile A1 with 198 GPa. Overall comparison of Young's Modulus of doped and undoped sample shows that doped samples have better improvement in matrix stiffness when they are sintered with two-step sintering technique. The undoped sample has the best Young's modulus when they are sintered with longer sintering time (profile B) using single step sintering method. Addition of MnO₂ is beneficial in obtaining higher stiffness when shorter dwelling time is considered.

The average Young's modulus will be in the range of 200 GPa regardless of their sintering technique, except for sample A1. Sample A2 with dopant addition could achieve 203 GPa when sintered as dopant addition enhanced the densification process. The addition of dopant is beneficial when single step sintering is in context, however, dopant has little to no effect on samples that are sintered using two step sintering process as all samples achieve >200 GPa value.

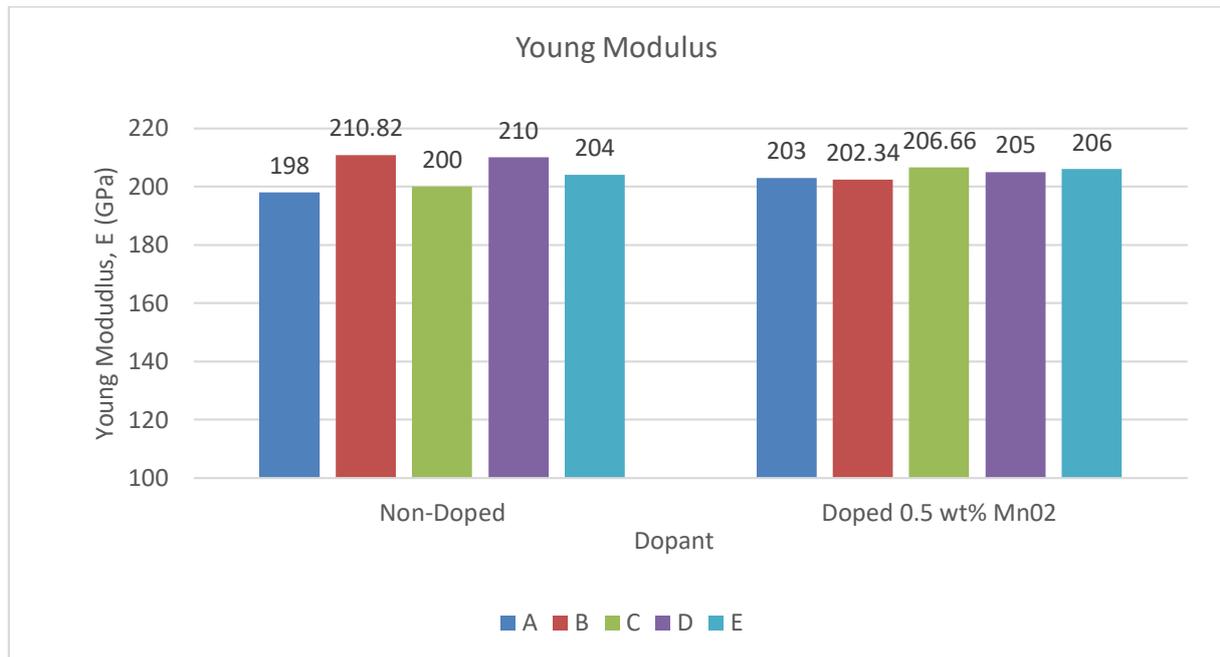


Figure 2: Bar Chart of Young's Modulus of samples sintered by different sintering profile.

The development of Vickers hardness of 3Y-TZP samples is depicted in Figure 3. The hardness increases significantly with holding time especially for the undoped samples. The highest Vickers hardness value was obtained by sample under profile E1 with the value of 14.52 GPa while the lowest Vickers hardness is obtained by sample under profile A1 recorded at 12.93 GPa. Overall, the undoped sample has better hardness values when they are sintered with two step sintering and longer dwell time. This finding aligns with researchers done in the past where the hardness values of undoped samples were higher than that of doped samples [4].

Doped samples using two step sintering process, profile C's sample with shorter holding time is able to achieve hardness value close to that of longer holding time. Hence, hardness of two step sintered doped samples are all comparable regardless of their holding time, all in the range of 14.3 to 14.4 GPa. It also proved that hardness value correlates well with the relative density of 3Y-TZP samples.

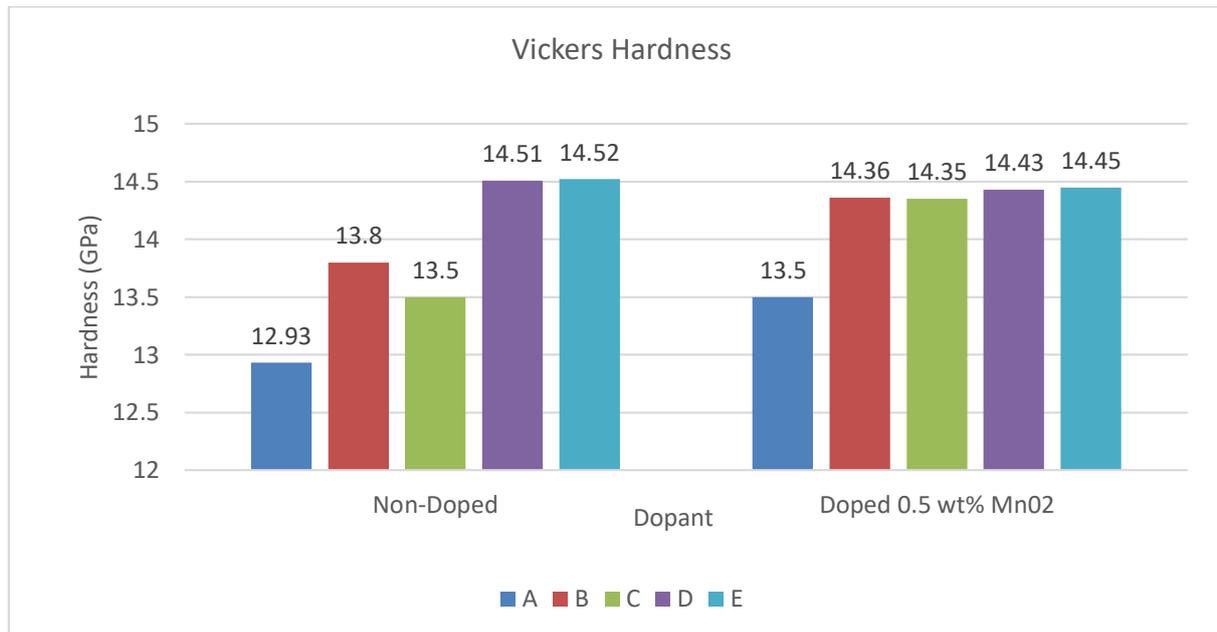


Figure 3: Bar Chart of Vickers Hardness of undoped and doped sample sintered by different sintering profiles.

4. Conclusion

In conclusion, the addition of MnO₂ as a dopant did play a substantial role in assisting the samples to achieve higher densification at short holding time. The mechanical properties such as, matrix stiffness and Vicker's hardness can be enhanced with the addition of dopant especially when they are two-step sintered with shorter sintering time. For instance, MnO₂ doped sample when subjected to two-step sintering process at 1400°C for 1 minute and 1250°C for 30 minutes (profile C2), could achieve >98% relative density, ~206GPa Young's Modulus and ~14.3GPa of Vicker's hardness. This value is comparable to that of two-step sintered at longer holding period. Although sample E1 produced highest Vickers hardness value of 14.52GPa and high relative density of >98%, it required longer holding time of 25 hours. All the values obtained through profile C2 achieves the minimum requirement of structural engineering ceramics that allows it to be used in real application.

5. Future Work

The current work shall be further explored to identify the hydrothermal aging resistance properties to prove the properties and benefits of two step sintering process using 0.5 wt.% manganese at short sintering time to curb the monoclinic content from forming due to hydrothermal aging. By identifying the monoclinic content, the optimal sintering time and process could be identified that would prevent aging with good mechanical properties.

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