The Effects of Sintering Additives on the Sintering of 3Y-TZP Ceramic

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Abstract. The influence of 0.5 wt.% of manganese oxide (MnO₂) addition as dopant into 3 mol% yttria stabilized tetragonal zirconia polycrystals (3Y-TZP) were studied in comparison to undoped 3Y-TZP using different sintering profiles. Samples were sintered at 1200°C, 1300°C and 1400°C with holding time of 1 min, 12 min, 2 hours and 20 hours all for single step sintering. The optimal sintering profiles are A4 and C2 where 3Y-TZP doped with 0.5% wt. MnO₂ sintered at 1400°C for 12 minutes and 1200°C for 20 hours respectively. At these sintering parameters, the MnO₂ doped 3Y-TZP sample exhibited relative density of ~97%, Vicker’s Hardness value of ~13 GPa, Fracture toughness value of ~4 MPa m¹/² and Young’s modulus of ~210 GPa.

1. Introduction

Zirconia is known as an oxide ceramic that is present with crystal structure transition properties when its subjected to increasing temperature. Zirconia at room temperature adopts monoclinic crystal structure and slowly transitions to tetragonal and cubic phase at temperature up to 1170°C and 2370°C respectively. Tetragonal phase structure particularly possesses great properties such as high flexural strength, excellent chemical and thermal stability and great biocompatibility. In the early seventies, medical industry had the necessity for metal free material to be used as replacement for titanium steel that were widely used for hip head replacement. In 20th century, a research work identified a mechanism in zirconia ceramics known as transformation toughening where the material transforms from tetragonal phase (t-phase) to monoclinic phase (m-phase) in the presence of external stress which in return contributes to toughening effect. [1]

One of the major drawbacks of this material is that this material is unstable and has the tendency to alter from its tetragonal (t) structure that is also a metastable phase which has great properties to monoclinic (m) phase that is stable but with weaker properties. Through research it was found that by
adding Yttria, particularly 3 mol% helps to alleviate the phase by retaining tetragonal phase structure at normal room temperature. Doping manganese oxide into yttria stabilized tetragonal zirconia polycrystals, Y-TZP, had been substantial in assisting pressureless sintering process. [2] This is as undoped 3Y-TZP requires longer dwell time to achieve desired mechanical properties and hydrothermal aging behaviour. Where, it was concluded that the addition of >0.3 wt.% of MnO₂ was effective in improving densification, material’s matrix stiffness and also the hardness when they are single step sintered at temperature below 1350°C as compared to undoped Y-TZP samples. Particularly it was found 0.5 wt.% of manganese oxide has improved the mechanical properties when sintered below 1350°C using the conventional sintering method. This is where the tetragonal structure phase stability in zirconia ceramic’s matrix remains undisrupted at that dopant weight percentage addition. [2] [5] There are many works in past that have discussed the effects of MnO₂ addition as dopants in enhancing the properties of 3Y-TZP. [6] [7]

However, the optimal sintering parameter using 0.5 wt.% of manganese oxide as dopant produced for structural application by enhancing the densification while not losing its mechanical properties of 3Y-TZP were not proposed. Thus, the objective of this study is to identify the optimal sintering profile to fabricate the 3Y-TZP doped 0.5 wt.% of manganese oxide with relative density >95% at varying sintering parameters whilst comparing it to undoped 3Y-TZP samples.

2. Experimental
2.1. Sample Preparation
The precursor powder used was 3Y-TZP (TOSOH) Japan also known as tetragonal zirconia polycrystals stabilized with 3 mol % of yttria, along with manganese oxide (MnO₂) as dopant. Both the material, 3Y-TZP and MnO₂ were then mixed through ultra-sonification process for 45 minutes using an ultrasound probe that remits pulse of 29-36k Hz. The mixture then continued with ball milling process with 200ml of ethanol for 60 minutes at 450rpm. 2mm diameter zirconia milling balls were added to the mixture to assist milling process. The slurry media prepared was separated from the zirconia milling balls and was poured evenly on a tray before drying them in a pre heated drying oven at 70°C overnight to ensure all ethanol evaporates. Once dried, the residue is sieved using a 250 µm stainless steel mesh sieve and the mixed powder was collected. Two different batches of powder prepared, undoped 3Y-TZP and 0.5 wt.% of MnO₂ doped 3Y-TZP powder samples. All of the samples from different batches were uniaxially pressed at 3 MPa to rectangular bar and disc shape with dimensions, 30x10x10 mm weighing 3 grams and 20mm diameter, 5mm thickness weighing 2.5 grams, respectively. All pressed green samples then subjected to cold isostatic pressing (CIP) at 210 MPa.

2.2. Sintering Method
Single step sintering method deployed for all samples. Referring to the Table 1, three temperature range sintering carried out starting from 1200°C, 1300°C and 1400°C at four dwell periods of 1 min, 12 min, 2 hours, and 20 hours. The single step sintering (SSS) process was carried out at with a constant heating rate of 10°C/min using carbolite furnace from room temperature and once dwell period was completed it was cooled down with similar cooling rate of 10°C/min.

| Sintering Profile | Sintering Time | Sintering Temperature (°C) | Sintering Profile Dopants |
|-------------------|----------------|---------------------------|--------------------------|
| a1                | 1 min          | 1200                      |                          |
| a2                | 12 mins        | 1300                      |                          |
| a3                | 2 hours        |                           |                          |
| a4                | 20 hours       |                           |                          |
| b1                | 1 min          | 1300                      |                          |

Table 1: Listed are the sintering profiles and additives.
3. Result and Discussion

3.1. Relative Density

Figure 1 represents relative density of varying sintering profiles in comparison to doped and undoped 3Y-TZP samples. All doped samples achieve relative density of >95% when sintered with dwell time of above 2 hours at 1200°C, 1300°C and 1400°C. Undoped samples however achieve relative density >95% when sintered at 1200°C at longer dwell time of 20 hours. Relative density of 3Y-TZP that are more than 95% are accepted as a criterion for structural engineering ceramics applications. Whereby, this aligns with a research done in 2013 where the addition of >0.3 wt.% manganese and sintered at low temperature helps the consolidation process of 3Y-TZP that improves the densification of the material.

At lower sintering temperature, longer dwell time needed to achieve densification >95% for undoped samples a4. Whereas for 0.5 wt.% manganese oxide doped A3 samples, when sintered at 1200°C, the hardness value reaches 13 GPa range only when sintered with dwell time of >2 hours. However, when it was sintered at temperature 1300°C, doped B1 sample achieves relative density of >95% when held for 1 minute, where undoped sample needed 12-minute dwell time. Nevertheless the additive has no apparent densification effect with longer sintering holding time at sintering temperature above 1400°C.

3.2. Vicker’s hardness

The effects of varying sintering profiles are shown in Figure 2. The hardness of undoped samples increases with increasing dwell time especially at lower sintering temperature of 1200°C. For 0.5 wt.% manganese oxide doped samples, when sintered at 1200°C, the hardness value reaches 13 GPa range only when sintered with dwell time of >2 hours. However, when it was sintered at temperature 1300°C and 1400°C, hardness was hovering around 13 GPa at all dwell time before reducing to 12.88 GPa when sintered at 1400°C, for 20 hours.

The peak hardness value attained through undoped sample that was sintered at 1200°C for 20 hours, recording value at 15.26 GPa, while the lowest value was 3.13 GPa that of sintered at 1200°C for 1 minute. Through the conventional single step sintering process, it shows that longer sintering time
required when sintered at temperature 1200 °C, and similar hardness value can be achieved when samples are sintered at temperature >1300 °C, for both doped and undoped samples.

Figure 1 Bar Chart of Relative Density with varying sintering profile

Figure 2 Bar Chart of Vicker’s Hardness with varying sintering profiles

3.3. Young’s Modulus

The varying Young’s Modulus (E) for doped 3Y-TZP and undoped 3Y-TZP are depicted as bar chart in Figure 3. The doped samples are in correlation with the relative density where the dopants addition have improved the tetragonal zirconia matrix stiffness when sintered at temperature above 1200 °C at dwell time of more than 2 hours, 1300 °C at dwell time more than 12 min and 1400 °C at dwell time more than 1 minute. All these samples at these parameters are able to achieve Young’s modulus of >200GPa. The addition of dopant has been significant in enhancing the elastic modulus of 3Y-TZP as compared to the undoped samples. The highest E value of 207.1 GPa obtained through 0.5 wt.% MnO2 doped 3Y-TZP sintered at 1300 °C for 20 hours followed by a slight drop to 206.6 GPa for
sample sintered at 1400 ℃ for 20 hours.

Figure 3 Bar Chart of Young’s Modulus with varying sintering profiles

4. Conclusion

In conclusion, MnO₂ as dopant addition to 3Y-TZP are important in improving the matrix stiffness of 3Y-TZP to achieve increased densification at low sintering temperature or short holding time. Through conventional pressureless sintering method, the mechanical properties can be enhanced with higher temperature at shorter holding period. Sample C2, sintered at 1400 ℃ and 12 minutes dwell time achieves Vicker’s hardness value of ~13 GPa, with relative density of >97% and Young’s Modulus of ~206 GPa. On the other hand, similar properties are achieved for sample A4 with 20 hours of holding time at 1200 ℃. Both samples A4 and C2 comply within the requirement of structural application engineering ceramics material.

5. References

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