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MECHANICAL PROPERTIES OF NIOBIUM OXIDE DOPED Y-TZP FOR BIOMEDICAL APPLICATIONS

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ABSTRACT

The influence of small additions of Nb_2O_5 (up to 1 wt%) on the sintering behaviour of yttria-stabilized zirconia sintered over the temperature range from 1200 ºC to 1500 ºC was investigated. It was found that the mechanical properties of Yttria-tetragonal Zirconia Polycrystals ceramic (Y-TZP) were dependent on the dopant amount and sintering temperature. Fracture toughness increased as the Nb_2O_5 content increased, which indicated that the annihilation of oxygen vacancies in 3Y-TZP was responsible for the instability of the t-ZrO_2 lattice. The results also revealed that there was no significant influence of the Nb_2O_5 doping on the sintered density of the Y-TZP. The relation between the measured mechanical properties is discussed with the emphasis on the role of the niobium oxide.

Keywords: Niobium oxide; Zirconia; Mechanical Properties;

INTRODUCTION

Zirconium dioxide (ZrO_2) or commonly known as zirconia is a form of oxide ceramic, a subset of the broad ceramic and glasses classification materials. Zirconia-based materials are increasingly being considered in engineering applications as alternatives to other ceramic materials due to their relatively high fracture toughness and bending strengths. Values of fracture toughness of greater than 12 MPa $m^{1/2}$ and tensile strengths of 1000–1500 MPa have been observed for 2.5 mol% yttria-stabilised zirconia [1,2] comparing with alumina [3] which did not exhibit a good fracture toughness (<5 MPa $m^{1/2}$) and a low bending strength (<600 MPa).

The specialty of Yttria-tetragonal zirconia polycrystals ceramics (Y-TZP) compared to other monolithic materials is its microstructural ability to absorb energy from propagating crack, which prevents further crack development. This phenomenon is subsequently known as transformation toughening [4]. In this mechanism, the energy absorbed by the zirconia matrix in the vicinity of the propagating crack is consumed by the tetragonal (t) grains to transform to the monoclinic (m) symmetry which is accompanied by approximately 3 to 4% volume expansion [5].

However, there are limitations in the use of Y-TZP ceramic in many engineering applications, as its susceptibility to ageing-induced tetragonal (t) to monoclinic (m) phase transformation when exposed in steam environment. It has been observed by researches that Y-TZP ceramics exhibited slow (t) to (m) phase transformation, starting from the surface leading to the formation of microcracking and strength degradation. Desirable mechanical properties have been offset by poor resistance of the material to the effects of humid atmospheres at temperatures ranging from 60 to 500 °C [6].

Zirconia is well known for its great properties which deposit high strength, high fracture toughness, high hardness, wear resistance, good frictional behavior, non-magnetic, electric insulation, low thermal conductivity, corrosion resistance in acids and alkalis, modulus of elasticity similar to steel and coefficient of thermal expansion similar to iron which grant them the name of 'ceramic steel'. In addition to that, the performance of zirconia is way better than the metal base material where zirconia can withstand higher temperature, corrosion resistance and others.

Particularly, Y-TZP has been used in vast applications ranging from household appliances such as knives, scissors and cutters to aggressive/mechanical environment such as chemical filters, piston rings, extrusion dies, cutting tool inserts, etc [7].

EXPERIMENTAL DETAILS

Two typeS of powders were prepared where both of these are commercial type powder, the 3 mol% of yttria-stabilised zirconia powder Zirconium Oxide (ZrO_2-3Y dopped) powder which was manufactured by Nanostructured and Amorphous Materials Inc., USA, as main powder and niobium oxide (Nb_2O_5) as dopant, manufactured by Wako Pure Chemical Industries Ltd, Japan.

Six different amounts of niobium oxide compositions were prepared. i.e undoped, 0.05 %wt, 0.1 %wt, 0.3 %wt, 0.5 %wt, and 1 %wt. Compositions were prepared by ball-milling with zirconia balls as milling media and ethanol as mixing medium. After milling, the slurry was oven dried and sieved with 212 µm mesh stainless steel sieve. The dried samples were then uniaxially pressed (3 discs and 1 bar for each profile) at 0.3 MPa. Each circular disc weighed 2.5 g and each rectangular bar weighed 3.0 g. The samples were also cold isostatically pressed at 200 MPa. The samples were then sintered in a furnace under atmospheric condition at 10 °C/min ramp rate, temperatures ranging from 1200 °C to 1500 °C while maintaining the soak temperature for 2 h before cooling to room temperature.

The sintered samples were ground on one face by SiC papers of 120, 240, 600, 800 and 1200 grades successively, followed by polishing with 6µm and 1µm diamond paste in order to obtain the optical reflective surface [8].

The bulk density of the sintered samples was measured by Archimedes' Technique with water immersion method with the Standard Mettler Toledo Balance AG204 densimeter. Vicker's hardness (Hv) fracture toughness (K_{IC}) were measured on polished samples using Vicker's indentation method [9,10]. A constant specific load of 100 N was applied for 10 seconds to the polished samples. At least three indentations were made for each sample. Vicker's hardness, Hv was calculated using the empirical relationship according to Evans and Charles [11].

$$H_v = \frac{1.854}{d_{ave}} \qquad (1)$$

A few equations are available to calculate the K_{IC} according to Niihara and Antis [12,13]. The K_{IC} was computed according to the equation derived by Antis et.al. which was recently modified by (Kaliszewski, et al. 1994) [14].

$$K_{IC} = 0.019\ (E/H)^{½} / C^{3/2} \qquad (2)$$

where P is the indentation load, E is the Young's Modulus, H is the Vicker's hardness, d_{ave} is the length of indent diagonal, C is the crack dimension measured from the center of the indent impression (c = d/2 + l) and l is the average crack length. Three measurements were made for each sample and average values were obtained.

The Young's modulus test was conducted on the rectangular bar samples by impulse excitation technique using the commercial testing instrument (GridoSonic: MK5"Industrial", Belgium). By monitoring and evaluating the vibration harmonics induced by tapping on the rectangular bar, the resonant frequency of the sample can be measured using a transducer. Thus, Young's Modulus will be calculated by flexural-resonant frequency technique [15]. The Young's modulus of the sample can be calculated using the standard test method (ASTM E1876-97) [16].

Phase analysis by X-ray diffraction of polished samples was carried out at room temperature using Cu-Kα as the radiation source. The fraction of surface monoclinic content was evaluated using the method of Toraya, Yoshimura and Somiya [17]. The hydrothermal ageing experiment was performed in an autoclave containing superheated steam (180 °C/10 bar) for up to 5 h. The fraction of surface monoclinic content was then evaluated using the method of Toraya, Yoshimura and Somiya, 1984 [17].

RESULTS AND DISCUSSION

The variation of bulk density for 3Y-TZPs with different amounts of Nb_2O_5 sintered at temperatures 1200 ^oC – 1500 ^oC is shown in Figure 1. It shows that all the Y-TZP compositions including the undoped 3Y-TZP shared a common densification trend. The bulk density of all compositions gradually increased with increasing sintering temperature and started to decline after 1400 °C. The density range between 1300 ^oC to

1400 °C were found to be the most profound sintering temperature as all samples sintered at this temperatures showed remarkable densities which were close to the theoretical density. It is clearly seen that at 1400 °C, all samples exhibited density value ~ 98% of the theoretical density [18].

Furthermore, it has been observed that the addition of dopant has reduced the sintering temperature required for achieving full densification. Although at 1400 °C it exhibited convincing density value but with further increase in the sintering temperature resulted in a decline of the bulk density. This can be due to the over-stabilized phase condition where the phase takes the transformation from tetragonal to cubic.

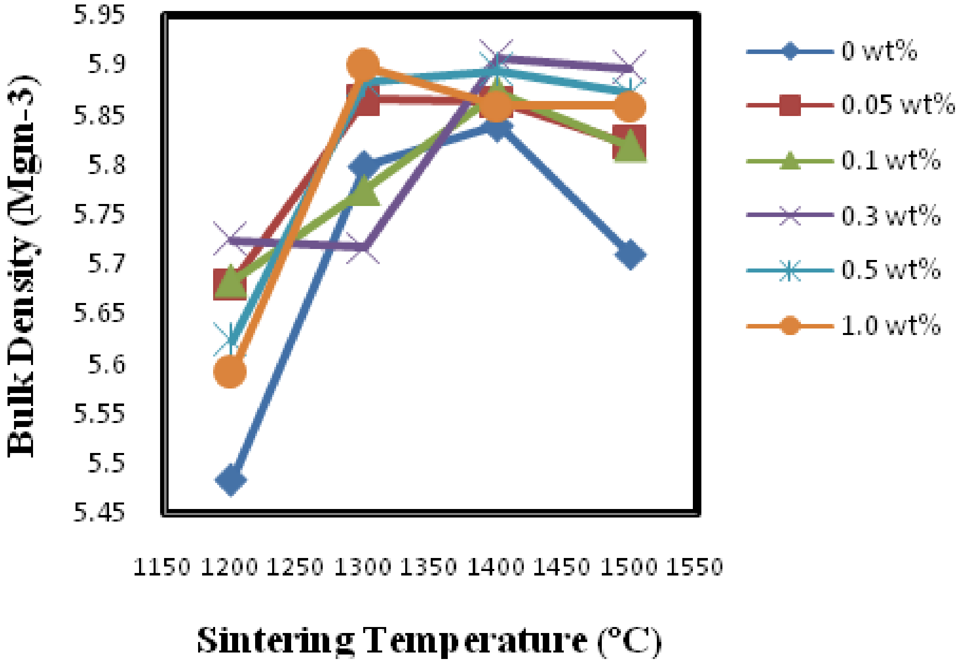

Figure 1: Effect of sintering temperature and Nb_2O_5 addition on the Bulk Density of Y-TZPs

The variation of Young's Modulus (*E*) of sintered samples with increasing sintering temperature is shown in Figure 2. The major effect of Nb_2O_5 in enhancing the matrix stiffness of Y-TZP can be seen particularly when sintered at low temperature, 1300 ºC, where 0.05 wt% and 0.1 wt% samples reached almost the theoretical value of the Young's modulus. Referring to Figure 2, it shows that an *E* value of above 200 GPa was achieved at sintering temperature ≥ 1300 °C.

In comparison, the Young's modulus of the undoped 3Y-TZP started low at ~190 GPa when sintered at 1200 °C but soon raised to a maximum of ~205 GPa when sintered at 1400 °C and 1500 °C. In contrast, the Young's modulus of 0.05 wt% Nb_2O_5-doped Y-TZP increased gradually as the sintering temperature increased but started to drop after

1400 ºC, to below that of the undoped ceramics. In common, the Young's modulus of all samples studied correlated well with the sintered bulk density as the E value varied linearly with increasing density. According to the data obtained in the experiment, it can be said that with ≤ 0.3 wt% of Nb_2O_5 the *E* value was enhanced at the temperature of 1300 ºC.

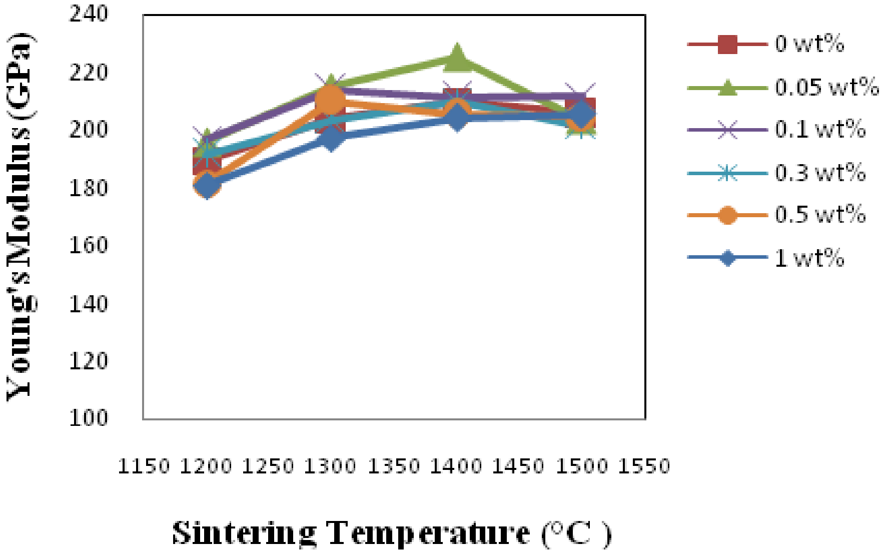

Figure 2: Effect of sintering temperature and Nb_2O_5 addition on the Young's modulus of Y-TZPs

Figure 3 shows the effect of fracture toughness of the Nb_2O_5-doped and undoped samples where it has been found that the fracture toughness of the undoped samples increased gradually with increasing sintering temperatures. On the other hand, it was clearly seen that the additions of niobium oxide have an effect on the fracture toughness of 3Y-TZP. There was a remarkable enhancement in fracture toughness of the Nb_2O_5-doped samples compared to the undoped samples sintered at 1200 ºC. The undoped sample only reached the fracture toughness value of 6.05 $MPam^{1/2}$ while the other samples with various amount of niobium oxide achieved the toughness range between 7.01 $MPam^{1/2}$ to 7.13 $MPam^{1/2}$.

It can also be deduced from the graph that, doping niobium oxide into 3Y-TZP can increase the fracture toughness but not with increasing sintering temperature. As transformation toughening mechanism is closely related with the transformability of the tetragonal grains [19], the fracture toughness can be used as an indication of the state stability of the tetragonal grains in the zirconia matrix. Generally, high fracture toughness would indicate that the (t) tetragonal grain was in a metastable state and responded immediately to the stress field of propagating crack, such as induced during the indentation test [2].

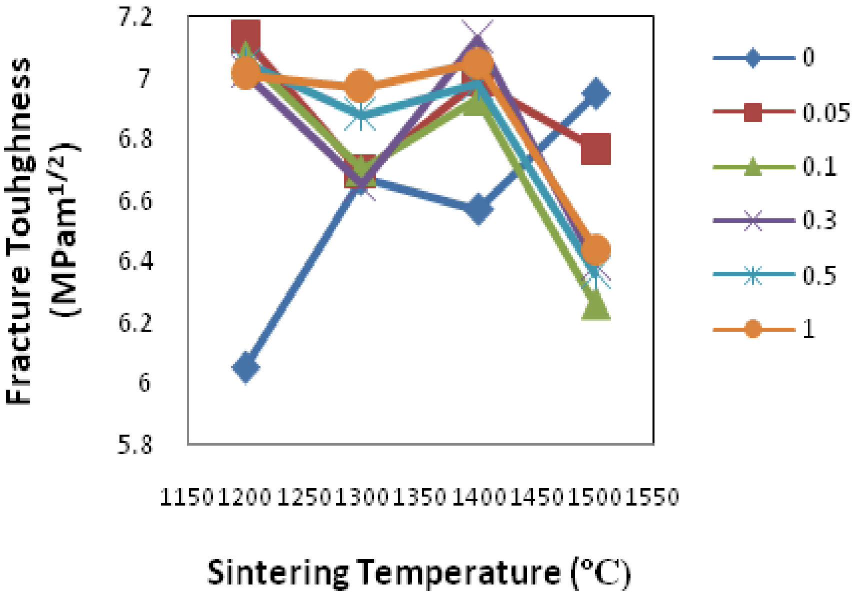

Figure 3: Effect of sintering temperature and Nb_2O_5 addition on the fracture toughness of Y-TZPs

The effect of sintering temperatures and Nb_2O_5-doped samples on the room temperature Vickers hardness of Y-TZPs is shown in Figure 4. The lowest value of the undoped 3Y-TZP hardness was around 12.7 GPa when sintered at 1200 °C which reached the theoretical hardness value while the other doped samples also showed good hardness values. Generally, all samples showed a similar trend with increasing sintering temperature profiles. The hardness values increased gradually till 1400 ºC and dropped significantly upon further firing at 1500 ºC.

Although all the samples showed a similar trend in the graph but most of the hardness of Nb_2O_5-doped samples were higher than the undoped samples when sintered between 1200 °C and 1400 °C as shown in Figure 4. The material hardness of the 0.05 wt%, 0.1 wt%, 0.3 wt%, 0.5 wt% and 1.0 wt% dropped upon sintering at 1500 ºC yet the hardness values were still within the range of acceptance. The hardness of all the doped materials was in agreement with the undoped ceramic at between ~13.2 GPa to ~13.3 GPa sintered after 1300 ºC.

From Figure 4, it is seen that the samples sintered at 140 °C obtained the highest hardness value for both doped and undoped ceramics. Generally, good hardness values were obtained at lower sintering temperature.

The resistance towards phase transformation between tetragonal to monoclinic, ageing experiment with fifty hours were carried out with the intervals of 1, 3, 6, 9, 12, 24 and 50 hours. In this study, only samples that were sintered at 1300 °C and 1500 ºC were taken for the ageing experiment. Phase transformation from tetragonal (*t*) to monoclinic (*m*) when exposed to low temperature water or aqueous solutions is the major limitation of Y-TZP ceramics as engineering materials.

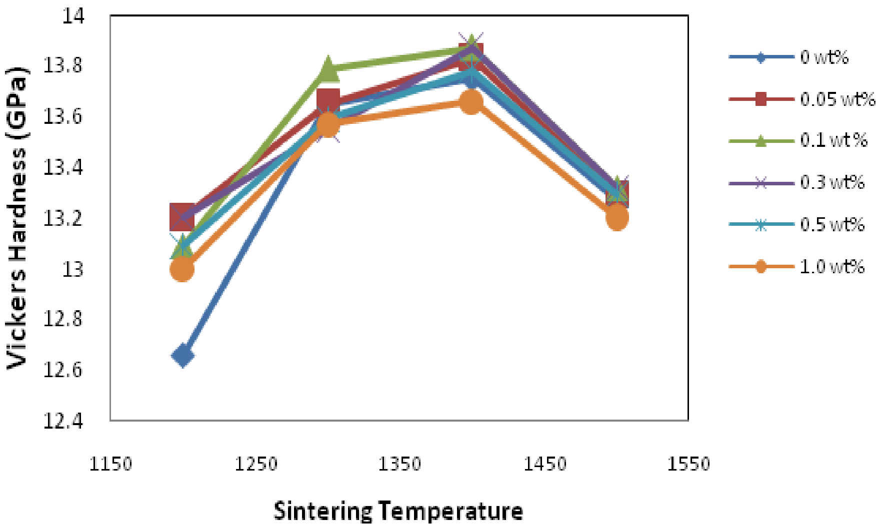

Figure 4: Effect of sintering temperature and Nb_2O_5 addition on the hardness of Y-TZPs

Figure 5 shows the ageing behavior of the undoped and doped samples with increasing ageing hours for various amounts of dopants. Generally, the x-ray diffraction (XRD) analysis showed no monoclinic phase was observed and all the sintered samples were fully in tetragonal phase after the ageing experiment.

In the first hour of the experiment, there is no significant changes in phase for the 1300 ^{o}C sintered samples except the samples with 1 wt% of Nb_2O_5 which exhibited gradual increase in the monoclinic phase. The monoclinic phase content reached 30 % after 50 hours of ageing which still indicated that phase is not fully disrupted.

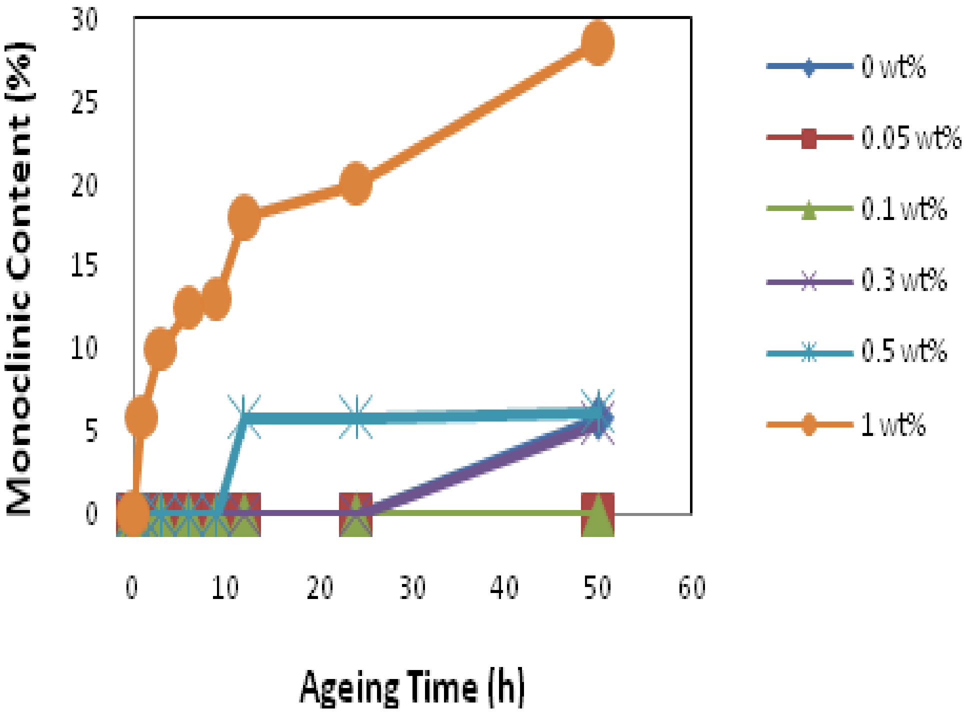

Figure 5: Effect of hydrothermal ageing on the monoclinic phase development in Y-TZPs sintered at 1300 °C

Meanwhile, the sintered samples for 1500 ^{o}C showed an increasing trend in the monoclinic phase content with increasing Nb_2O_5 content. Based on the ageing experiment, the samples sintered at 1500 ^{o}C reached approximately 90% of the monoclinic phase as depicted in Figure 6. Apart from that, all samples sintered at 1500 ^{o}C have fully degraded after 20 hours of ageing.

In short, increasing the amount of Nb_2O_5 has accelerated the LTD rate which was in accordance to D.J. Kim *et al.* who stated that the amount of *t*→*m* transformation increases with increasing Nb_2O_5 content [18]. At the same time, sintering temperature for the samples affects the phase transformation as well. The rate of phase transformation from *t*→*m* is proportional to the sintering temperature. Higher sintering temperature resulted in earlier phase transformation of tetragonal phase to monoclinic phase.

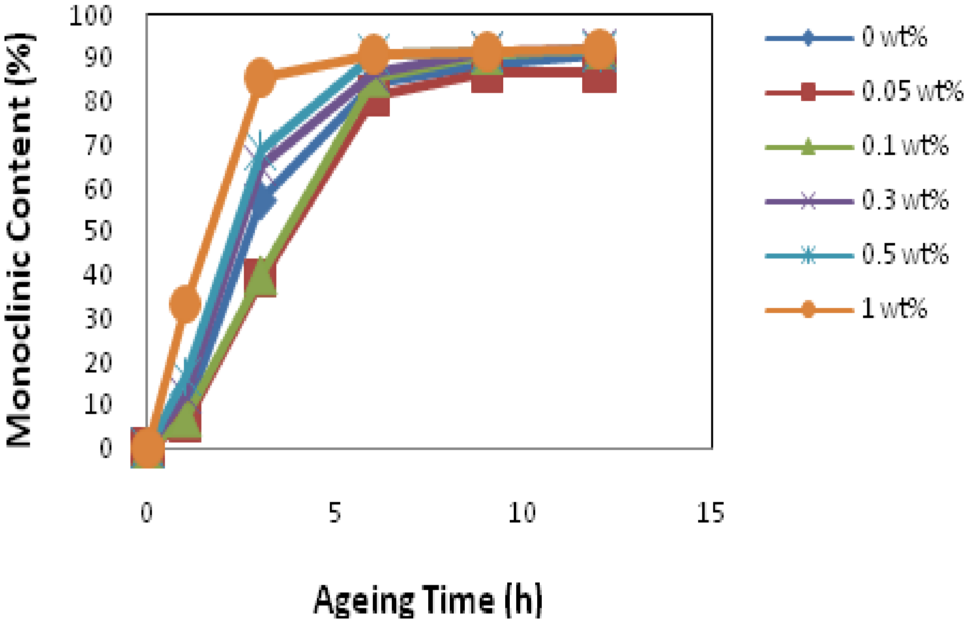

Figure 6: Effect of hydrothermal ageing on the monoclinic phase development in Y-TZPs sintered at 1500 °C

CONCLUSION

The current work has shown that the addition of niobium oxide up to 1 wt% with Y-TZP ceramics was found to be beneficial as a sintering aid especially when sintered at 1400 ºC. Generally, better results of mechanical properties of the doped samples were obtained compared to the undoped. Doping Nb_2O_5 into 3Y-TZP especially enhanced the fracture toughness and hardness. More specifically the bulk density was improved to ~5.9 Mgm^{-3} (~98% of the theoretical density), Young's modulus was enhanced to ~205 GPa, fracture toughness was increased to ~7.2 $MPam^{1/2}$ and the hardness was increased to ~13.8 GPa for Y-TZPs containing 0.3 wt% Nb_2O_5.

The tetragonal phase stability of the zirconia matrix was not disrupted by addition of Nb_2O_5. The experiment showed that samples which were sintered at 1300 ^{o}C survived the hydrothermal degradation test. The rate of LTD was affected by two factors which were the sintering temperature and the content of Nb_2O_5. Higher sintering temperature and higher amount of Nb_2O_5 resulted in earlier phase transformation from *t*→*m* took place. Experimental results do not support previous researches which reported that the best sintering temperature would be the range of 1500 ^{o}C to 1550 ^{o}C. The reason for this is due to the starting powders which have very high agglomeration rate and affect the experiment during the green body preparation.

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