DENSIFICATION BEHAVIOR AND PROPERTIES
OF IRON OXIDE DOPED Y-TZP CERAMICS

SIVA KUMAR S.[1], TEOW H. L.[2,*], NIAKAN A.[3], JEFFREY K. C. L.[1]

[1]School of Engineering, Taylor's University, Taylor's Lakeside Campus, No. 1 Jalan
Taylor's, 47500, Subang Jaya, Selangor DE, Malaysia
[2]School of Engineering, INTI International College Subang, No. 3, Jalan SS15/8, 47500,
Subang Jaya, Selangor DE, Malaysia
[3]Department of Mechanical Engineering, University of Malaya, 50603,
Kuala Lumpur, Malaysia
*Corresponding Author: hsienloong.teow@newinti.edu.my

Abstract

The effect of small addition of Fe2O3 (up to 1 wt%) on the densification behaviour and mechanical properties of commercially available 3 mol% Yttria Tetragonal Zirconia Polycrystals (Y-TZP) sintered from 1250°C to 1500°C was investigated. Tests were carried out in order to determine the bulk density, Vickers hardness, Young's Modulus and fracture toughness of the sintered samples. Based on the work carried out, it is revealed that the amount of dopants and sintering temperature influences the mechanical properties of Y-TZP. The results showed that even sintering at low temperature at 1250°C, relative bulk density ~98% of theoretical density could be achieved with the addition of 0.3 wt% Fe_2O_3. The additions of small amounts of Fe_2O_3 from 0.05 wt% to 1.0 wt% was found to be beneficial in enhancing the matrix stiffness and hardness of the sintered bodies when compared to the undoped counterpart sintered at same temperature. However, the fracture toughness was found to be unaffected by the additions of small dopant amounts except for the case of 0.5 and 1 wt% Fe_2O_3 when sintered above 1400°C.

Keywords: Y-TZP, Zirconia, Iron Oxide, Densification, Mechanical Properties.

1. Introduction

Yttria Tetragonal Zirconia Polycrystalline, also known as Y-TZP, has become an important advanced material as it exhibits excellent combination of mechanical properties, thermal properties and high wear resistance. Zirconia has been used in various applications. Such applications include the use of zirconia to strengthen the silicon carbide ceramics [1] fuel cell's oxygen sensor, heating elements and

extrusion dies [2-5]. Besides zirconia has been widely used in the biomedical field as orthopaedic femoral head implant and as a replacement tooth due to its biocompatibility [6].

There are three polymorphs that are known to exist in pure zirconia which are the monoclinic (m), tetragonal (t) and cubic (c) [7]. Pure undoped zirconia exhibits the following phase transition depending on the temperature as shown in Fig. 1.

$$(\text{m-}ZrO_2) \underset{1170°C}{\overset{950°C}{\rightleftharpoons}} (\text{t-}ZrO_2) \overset{2370°C}{\rightleftharpoons} (\text{c-}ZrO_2) \overset{2680°C}{\rightleftharpoons} \text{liquid}$$
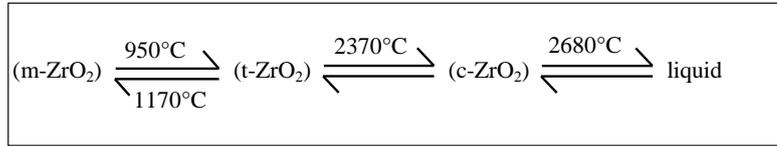
Fig. 1. Phase transition of a pure undoped Zirconia [7].

The (t)→(m) phase transformation in zirconia is a reversible isothermal martensitic transformation and there will be large temperature hysteresis approximately 200 K are involved in this transformation. In addition, this (t)→(m) transformation is also accompanied by 4-5% volume change and a shear strain of 14-15% [6-7]. Large amount of stress are induced by this transformation hence lead to destruction of pure zirconia when it is sintered above 1170°C [8]. In the last few decades, there have been many researches focusing on manufacturing structural ceramics with excellent mechanical properties such as high toughness combined with high strength [9].A few authors has suggested that one of the main issues in developing a high toughness ceramics is the microstructural design. One of the main features of zirconia is the phenomenon called transformation toughening [10].

Higher zirconia's fracture toughness can be achieved by enhancing its microstructure through introducing a non-linear crack shielding zone crack tip [10] or by stopping or delaying the motion of the crack front. These sequences of events leads to a phenomenon known as the stress induced transformation toughening. Transformation toughening involves zirconia's phase transformation from the metastable (t) phase to the stable (m) phase around an advancing crack. As the phase transformation involves 4-5% volume expansion, a net compressive stress is introduced in the process zone around the crack tip as shown in Fig. 2. In order to obtain optimum results from transformation toughening, it is best to retain maximum amount of metastable (t) phase at room temperature or at the application temperature. According to various transformation toughening literature, the terms transformability usually refers to the easiness at which the t-ZrO_2 transforms to m-ZrO_2 around the crack tip stress field [11-15].

Although Y-TZP has excellent mechanical properties, it also has an Achilles heel. When there is (t)→(m) transformation due to propagating crack, the results will be transformation toughening. However, when the free surface is exposed to moist temperature usually around 100°C to 600°C, the Y-TZP will suffer properties degradation due to the autocatalytic surface-initiated transformation from the metastable (t)-ZrO_2 phase to the stable (m)-ZrO_2 phase counterpart [16]. The autocatalytic transformation is also known as the low temperature degradation or LTD and this phenomenon has been extensively studied for three decades. The underlying LTD mechanism is still yet to be resolved [17-18].
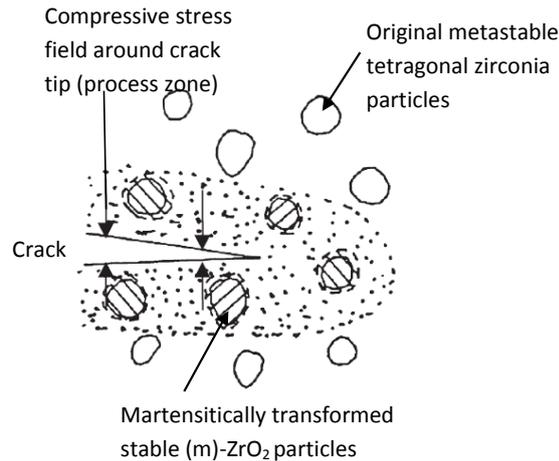
Fig. 2. Schematic diagram showing stress induced transformation in the compressive stress field of a propagating crack. [7].

Researches has been done by many authors [19-25] to study the effect of doping transition metal oxides such as Nb_2O_5, SiO_2, Al_2O_3, CuO, Nd_2O_5 and MnO_2 in improving the LTD properties. In most of the cases, with the addition of the transition metal oxides as sintering additives, it was revealed that the additives would segregate at the grain boundary forming a Y_2O_3 and ZrO_2 rich grain boundary glassy phase [19-26]. For instance, Kenellopous & Gill [27] has reported that Y-TZP doped with CuO exhibits enhanced densification due to the liquid-phase sintering mechanism due to the low melting point of CuO in the ZrO_2 matrix. In addition, Golieskardi et. al.,[16] has also reported that with small addition of Al_2O_3 and CeO_2 would improve Y-TZP densification and also improving its mechanical properties. The authors have attributed it to the presence of glassy phase that could have suppressed the grain growth and also sealed the grain boundary. Therefore, doping transition metal oxides such as Fe_2O_3 are likely to influence the LTD properties if the dopant is able to aid sintering at low temperature (i.e., 1250°C) resulting in densification without significant grain growth.

It is known that in transformation toughened ceramics the stress-induced (t) to (m) phase transformation that occurs around a propagating crack is responsible for increase in fracture toughness [28-30]. As a result, the degree of toughening is governed by the amount of tetragonal grains available which are able to undergo the transformation (Vf) and also transformation zone depth (h). The toughness of the ceramic has been related to these parameters by McMeeking and Evans [31,32]. The theoretical equation which derived by McMeeking and Evans [31] relating toughness increment and transformation toughening is as shown in Eq. (1).

$$K_{IC} = K_{IC}^m + \frac{\eta \cdot V_f \cdot \Delta V \cdot E \cdot (h)^{1/2}}{(1-\mu)} \qquad (1)$$

where K_{IC} and K_{IC}^m are the true fracture toughness and the fracture toughness of the matrix without transformation toughening respectively, η is a constant determined by the nature of the transformation, V_f is the fraction transformed tetragonal phase, ΔV is the volume expansion associated with the transformation, E is the Young's modulus, h is the half width of the transformation zone depth

and μ is the Poisson's ratio of the material. Generally, the toughness can be optimised by optimising both the V_f and $(h)^{1/2}$ parameters as enhanced toughness requires large transformation zone and high fraction transformable (t) phase.

The aim of this research is to study the effect of small amounts of iron oxide (from 0.05 wt% to 1 wt%) on the densification and mechanical properties of commercially available 3 mol% Y-TZP.

2. Experimental Setup

3 mol% Y-TZP powder, supplied by Kyoritsu Japan, manufactured through the co-precipitated method was used. This powder had a total impurity concentration of approximately 0.1 wt%. The major impurities were found to be SiO_2, Fe_2O_3, TiO_2 and Al_2O_3. High purity iron oxide powder manufactured by Sigma-Aldrich, US with weight concentrations (wt%) of 0.05, 0.1, 0.3, 0.5, and 1 wt%, was doped with Y-TZP powders. The dopants were introduced through wet milling methods, employing zirconia balls and ethanol as the milling media and the mixing medium respectively. The resulting slurry was dried in an oven and subsequently sieved to obtain soft, ready-to press powders. Green samples consisting of discs with 20 mm diameter and rectangular bars sized 4 mm × 13 mm × 32 mm were compacted at 0.3 MPa before undergoing cold isostatic pressing at 200 MPa. Pressureless sintering was chosen as the method to consolidate the powder in air using a rapid heating furnace manufactured by ModuTemp, Australia. Pressureless sintering was performed at various temperatures ranging from 1250 to 1500°C with 2 hours holding time before subsequently cooling down to ambient temperature. As-sintered specimens were subjected to grinding on one face by silicon carbide papers ranging from grades 120 to 1200. Post grinding, these specimens were polished with diamond paste of 6 μm and 1 μm. This procedure a shiny surface is obtained on one face of all specimens.

Densities of as-sintered samples were determined using Archimedes's principle. Rectangular bars were used to determine Young's Modulus by physically tapping the samples. The tapping physically induced vibration with a frequency that was detected and measured by a commercially available testing instrument (GrindoSonic: MK5 "Industrial", Belgium) using [33]. The values of Young's modulus obtained through this method were been found to be consistent and independent from the number of tests performed for each samples.

Vickers indentation method was performed by a machine manufactured by Future tech, Japan and was used on polished samples to determine the Vickers hardness of the samples. The values obtained from the hardness measurements were then subsequently used to obtain the fracture toughness (K_{IC}). During the hardness measurements, indentation load was kept constant at 98.1 N with a 10 s loading time. Fracture toughness' values were computed using the equation derived by Niihara et al., [34]. Average values were taken from five measurements. X-ray diffraction (Geiger-Flex, Rigaku Japan) was used for phase analysis of the powders. The phase analysis measurement was conducted under ambient conditions using Cu-Kα as the radiation source. The amounts of monoclinic (m) phase present in the ceramic matrix were determined using the method proposed by [35]. Micro-scale changes in the structure and morphology were examined using scanning electron microscopy (Phenom ProX).

3. Results and Discussion

The XRD results of the undoped (0 wt%) to 0.3 wt% Fe_2O_3 doped Y-TZPs shows that the samples consists of 100 % tetragonal (t) phase regardless of the sintering temperature employed. This is an indication that tetragonal phase stability of the zirconia matrix are unaffected by the addition of dopant up to a maximum limit of 0.3 wt% Fe_2O_3. However, the tetragonal phase stability of 0.5 wt% and 1 wt% Fe_2O_3-doped Y-TZP was affected when sintered at 1450°C with the formation of 2.6 % monoclinic (m) phase in the zirconia matrix and this monoclinic (m) phase was found to increase up to 4.5 % for the case of 1 wt% Fe_2O_3.

The effect of varying sintering additives (0 to 1 wt%) on the variation between bulk density and sintering temperature for undoped and Fe_2O_3-doped Y-TZP are shown in Fig. 3. Assuming the theoretical density (T.D.) of Y-TZP as 6.1 Mgm^{-3}, it is revealed that Y-TZP samples containing ≥ 0.3 wt% Fe_2O_3 exhibited higher relative densities ~97 % of the T.D. when sintered at 1250°C as compared to the undoped Y-TZP which achieved only 92.2 % of the T.D. when sintered at same temperature. The bulk densities of the 0.5 and 1 wt% were found to increase slightly from 97.87% to 98.36% and from 97.30% to 97.60% respectively when sintered within a temperature range of 1250°C to 1400°C, before reducing to 98.52% and 96.20% respectively at 1500°C. The bulk densities of all other samples (undoped, 0.05 and 0.1 wt%) all followed a similar trend which may be describe as a significant increase between a temperature range of 1250°C to 1350°C. Subsequently the density of these samples were found to fluctuate between (98.03% to 98.69%) in the temperature range of 1350°C to 1400°C before steadily decreasing with an increase in the temperature up to 1500°C.
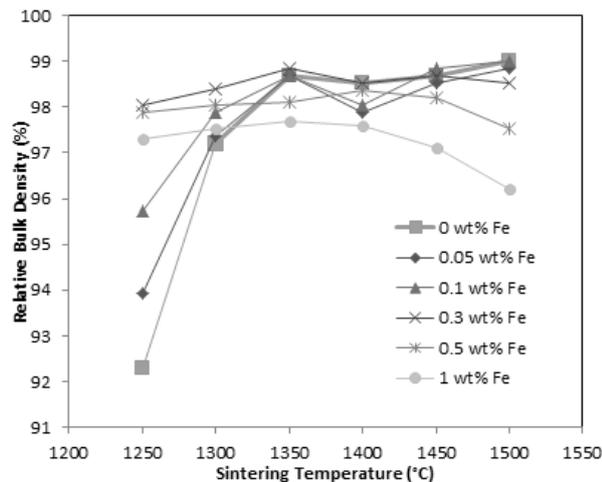
Fig. 3. Effect of sintering temperature and Fe_2O_3 on the bulk density of Y-TZP sintered at various temperatures.

The bulk density of Y-TZP containing 0.3 wt% sintered at 1250°C was among the highest in all samples as it achieved ~98% of the T.D. Subsequently the bulk density increased from 98.03% to 98.85% with increasing sintering temperature up to 1350°C before reducing to 98.52% at 1500°C. In the case of 1 wt%, the addition of sintering additives does not aid the densification of Y-TZP when sintered above 1350°C. The relative bulk density was observed to be around

97.3% T.D. when sintered at 1250°C, increasing to a maximum value of 97.7% T.D. at 1350°C before decreasing gradually when sintered at 1400°C and finally undergoing significant reduction from 97.6% to 96.2% T.D. when sintered at 1500°C. The significant reduction of density when sintered at 1400°C to 1500°C may be attributed to the formation of cubic grains. This phenomenon is in agreement with the works of [36].

The effects of iron oxide addition on the Young's modulus of Y-TZP are shown in Fig. 4. In agreement with the results obtained for bulk density, it is found that the additions of 0.3 wt% Fe_2O_3 was beneficial in improving the stiffness of the zirconia matrix when sintered at 1250°C to 1300°C. Using the results obtained for 1250°C, samples with 0.3 wt% Fe_2O_3, exhibited a Young's modulus of 212 GPa which is 12.8% higher when compared to the corresponding Young's modulus value of 188 GPa for the undoped sample. Based on Fig. 4, undoped Y-TZPs require sintering at higher temperatures *i.e.* 1350°C in order to achieve values of E >200 GPa.
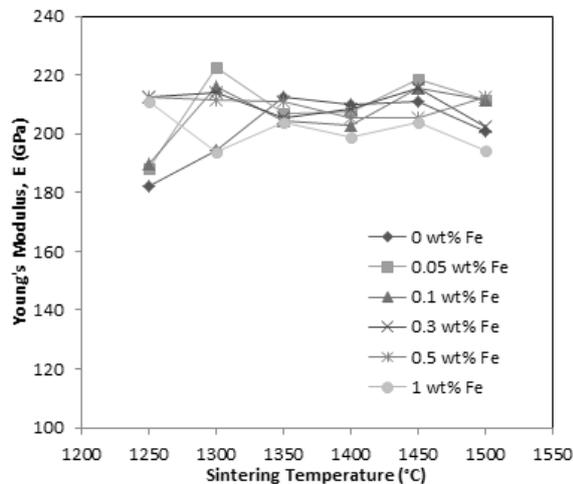
Fig. 4. Effect of sintering temperatures and Fe$_2$O$_3$ on the Young's modulus of Y-TZP sintered at various temperatures.

Based on the current work, it is also revealed that there is a linear relationship between the Young's modulus and the bulk density of the sintered Y-TZP bodies as shown in Fig. 5. It was revealed that regardless of the amount of dopants employed, the sintered body exhibited Young's modulus of more than 200 GPa when the relative bulk density was more than 98 % T.D. Therefore, it can be inferred that the matrix stiffness deeply influences the bulk density.

Figure 6 shows the effect of iron oxide as dopants on the fracture toughness of Y-TZP sintered bodies. It has been revealed that up to 0.3 wt% Fe_2O_3, sintering additives had negligible effect on the fracture toughness as the values of fracture toughness fluctuated in the range of 4.54 to 5.03 MPam$^{1/2}$. Since the transformation toughening mechanism is dependent on the phase stability of the (t) grains, the values of fracture toughness can be used as an indicator for the degree of stability of the (t) grains in the zirconia matrix. Generally, a high value of fracture toughness would indicate that the (t) grains are in a metastable state.

Based on the current work, up to 0.3 wt% Fe_2O_3, there is no sign of fracture toughness enhancement. This is in agreement with the theory that the tetragonal phase stability is not affected by the dopant concentration [7]. However, for the case of 0.5 wt% and 1 wt% Fe_2O_3-doped Y-TZP, at temperature above 1400°C, there is an increase in fracture toughness of these sintered bodies. In the case of 0.5 wt% Fe_2O_3, there is an increase in fracture toughness from 5.01 to 5.1 when sintered at 1450°C followed by rapid increase to 5.81 when sintered at 1500°C whereas for the 1 wt% Fe_2O_3, the fracture toughness increased from 5.02 to 5.72 MPam$^{1/2}$ when sintered at 1450°C followed by significant increase to 7.34 MPam$^{1/2}$ when sintered at 1500°C. The results obtained are in agreement with the XRD phase analysis where small amount of monoclinic (m) phase about ~4.5 % were detected in this sample.

Based on these observations, it can be inferred that there might be a mechanism that is triggered $_{causing}$ yttria segregation in the Y-TZP matrix. The mechanism suggested is as described in the following. During sintering, large amounts of yttria surround particular tetragonal grains hence causing the tetragonal grains to be over-stabilised leading to significant grain growth. Due to the non-uniform segregation of yttria, a number of tetragonal grains which lack yttria would undergo a spontaneous (t) to (m) phase transformation upon cooling to room temperature. This is in agreement with the data obtained from the XRD phase analysis where small amounts of monoclinic phase was detected in the 1 wt% Fe_2O_3 samples when sintered at 1500°C. On the other hand, tetragonal grains which have the optimum amount of yttria required for transformation toughening would remain in a metastable state. These tetragonal grains would readily undergo transformation toughening when stress is induced resulting in higher values of fracture toughnesses as shown in Fig. 6.
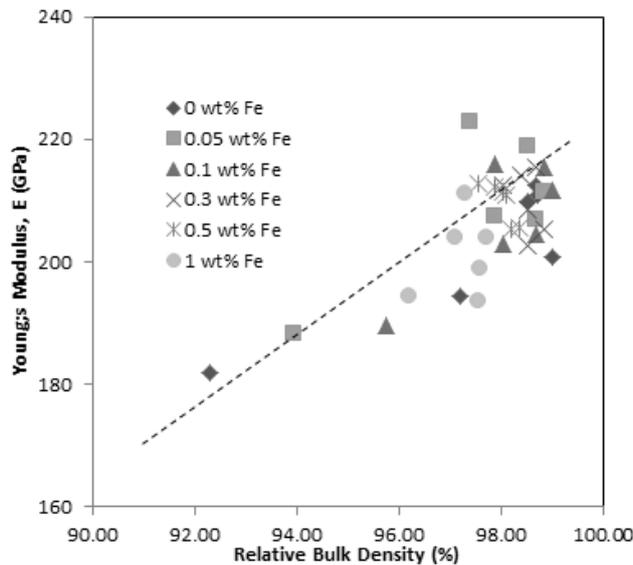
Fig. 5. Linear relationship exists between the Young's modulus and bulk density of Y-TZP regardless added amounts of Fe_2O_3.
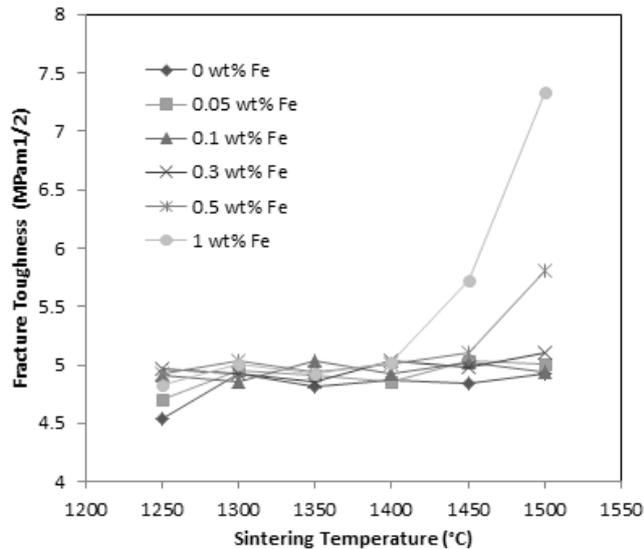
**Fig. 6. Effect of Fe$_2$O$_3$ on the fracture toughness
of Y-TZPs sintered at various temperatures.**

The effect of sintering temperatures and additions of Fe$_2$O$_3$ on the Vickers hardness of Y-TZPs are as shown in Fig. 7. It may be shown that addition of Fe$_2$O$_3$ on Y-TZP has beneficial effect on the Vickers hardness of Y-TZPs especially at low temperature sintering such as 1250°C. The undoped Y-TZP exhibits the lowest hardness at ~9.5 GPa when sintered at 1250°C then followed by rapid increase to ~12.8 GPa when sintered at 1300°C before reaching a maximum hardness of ~13.7 GPa when sintered at 1400°C. However, as the sintering temperatures increases beyond 1400°C, the hardness for these samples reduced to ~13.1 GPa when sintered at 1500°C. On the other hand, at low temperature sintering of 1250°C and 1350°C, all the Fe$_2$O$_3$ samples exhibited higher hardness as compared to the undoped samples. Similar trend were observed for Y-TZPs doped with 0.05 wt% and 0.1 wt% Fe$_2$O$_3$. The hardness of these samples starts out low when sintered at low temperature of 1250°C. As the sintering temperature increase, the hardness of these samples increases rapidly from 11.4 and 12.6GPa to 13.3 and 13.4 GPa respectively when sintered at 1300°C. When the samples were sintered beyond 1300°C, these samples exhibit hardness trends which were quite similar to the hardness trend for the undoped Y-TZP.

The hardness trend of 0.3, 0.5 and 1 wt% Fe$_2$O$_3$ were found to be similar. These samples show very high hardness at low temperature sintering of 1250°C. As the temperature increases from 1300°C to 1350°C, these samples have almost the same hardness ~13.3 GPa except for 0.5 wt% Fe$_2$O$_3$ which was found to be around 13.6 GPa. As the sintering temperature increases further to 1400°C, it is found that the hardness value decreased rapidly with a decrement that was more evident in the 1 wt% Fe$_2$O$_3$-doped samples from. The hardness value decreased from ~13.4 GPa to ~11.7 GPa when sintered at 1400°C and 1500°C respectively. The rapid decrease in the hardness value when the sintering temperature was increased from 1450°C to 1500°C for these samples may be attributed that the formation of monoclinic (m) phase detected in these samples.
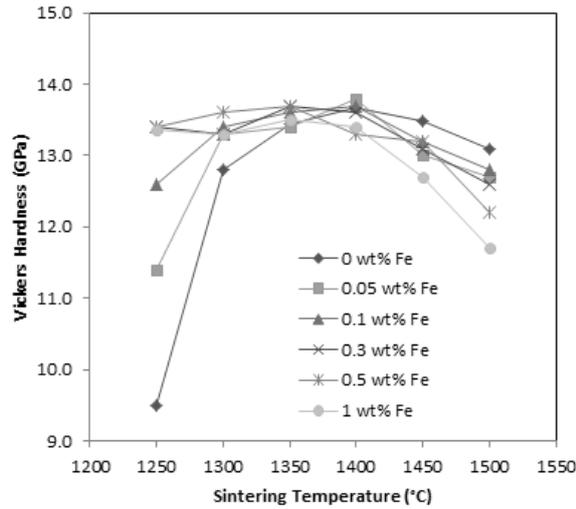
**Fig. 7. Effect of Fe$_2$O$_3$ on the Vickers hardness
of Y-TZPs sintered at various temperatures.**

In this present work, an attempt was made to compute the values of transformation zone size, V_f $(h)^{1/2}$ based on the equation (1) derived by McMeeking and Evans. Using the calculated values of K_{IC} in Fig. 6, values of E presented in Fig. 4 and parameters employed by Wang et al. [37] i.e. $\eta = 0.23$, $\Delta V = 0.05$, $\mu = 0.3$ and $K_{IC}^m = 3$ MPam$^{1/2}$, the transformation zone size V_f $(h)^{1/2}$ was computed and plotted against fracture toughness as shown in Fig. 8.

Based on Fig. 8, it can be observed that the K_{IC} versus V_f $(h)^{1/2}$ i.e. the product of transformable tetragonal phase and square root of the transformation zone depth adjacent to the propagating crack, perfectly fits a linear relationship regardless the amount of dopant. This observation is in agreement with the work of Wang et al. [29] and Swain [37], and thus also confirming the theoretical predictions of McMeeking and Evans regarding the relationship between K_{IC} and transformation zone size.
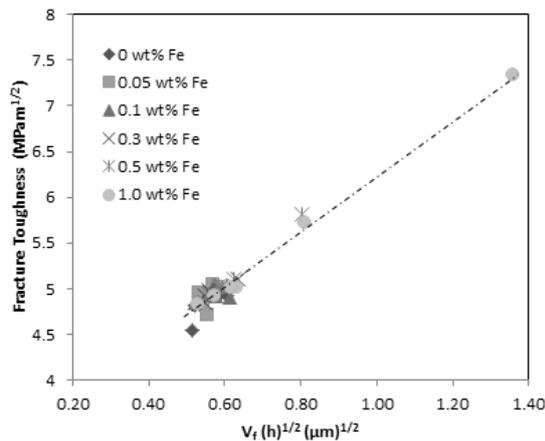
Fig. 8. Relationship between K_{IC} and transformation zone size, V_f $(h)^{1/2}$.

4. Conclusions

The densification behaviour of Fe_2O_3-doped yttria tetragonal zirconia polycrystals and the effect on the mechanical properties of Y-TZP has been investigated. Based on the results obtained, the following has been revealed.

- Small additions of Fe_2O_3 was effective in promoting densification and also enhancing Y-TZPs mechanical properties especially when sintered at low temperature of 1250°C.

- The Young's modulus and bulk density has been shown to have a linear relationship regardless of dopant additions.

- Up to 0.3 wt% Fe_2O_3, the tetragonal phase stability was unaffected by the addition of Fe_2O_3. On the other hand, the Y-TZP matrix started to lose its stability when sintering temperature increased above 1400°C. This phase instability is associated with the decrement in the bulk density and the Vickers hardness, but caused an increase in the fracture toughness. In addition, the transformation zone depth adjacent to the propagating crack is also revealed to perfectly fits a linear relationship regardless of dopant content.

References

1. Eric, W.N.; Gregory, E.H.; and William, G. F. (2013). Mechanical Behavior of Zirconium Diboride–Silicon Carbide Ceramics at Elevated Temperature in Air. *J. Eur. Ceram. Soc.*, (33), 15-16.

2. Masaki, I.; and Kobayashi, K.; (1998). High Toughened PSZ. In Saito S. (Ed.), Advanced Ceramics, (pp. 210-226). Oxford Uni. Press, UK.

3. Stevens, R. (1986). An Introduction to Zirconia Ceramics. (113). Magnesium Elektron, Ltd., UK.

4. Piconi, C.; Burger, W.; Richter, H.G.; Cittadini, A.; Maccauro, G.; Covacci, V.; Bruzzese, N., Ricci, G.A.; and Marmo, E. (1998). Y-TZP Ceramics for Artificial Joint Replacements. *Biomaterials*, (19), 1489.

5. Ramesh, S.; Gill, C.; Lawson, S.; and Dransfield, G. P. (1996). Sintering, Microstructure and Mechanical Properties of Commercial Y-TZPs. *J. Mater. Sci.* (31), 6055.

6. Seyed, A. A.; Suma, K.; Mangala, D. and Ranjana, M.; (2014). Zirconia: Properties and Applications – A review, *Pakistan Oral & Dental Journal* (34), 178-183.

7. Basu, B; and Balani, K. (2011). Advanced Structural Ceramics. New York, John Wiley & Sons.

8. Rosler, J.; Harders, H.; and Baker, M. (2007). Mechanical Behaviour of Engineering Materials: Metals, Ceramics, Polymers, and Composites. Springer Science & Business Media.

9. Basu, B. (2005). Toughness Tailoring of Yttria – Stabilised Tetragonal Zirconia Ceramics. *Int. Mater. Rev.* (50), 239-256.

10. Chevalier, J.; Laurent, G.; Anil, V.V. and David, R.C. (2009). The Tetragonal- Monoclinic Transformation in Zirconia: Lessons Learned and Future Trends. *J. Am. Ceram. Soc.* (92), 1901-1920.

11. Ruhle, M. and Evans, A.G. (1989). High toughness ceramic and ceramic. *Prog. Mater. Sci.* (33), 85 .

12. Garvie, R.C.; Hannink, R.H. and Pascoe, R.T. (1975). Ceramic steel? *Nature* (258), 703.

13. McMeeking, R.M. and Evans, A.G. (1982) Mechanics of transformation - toughening in brittle materials. *J. Am. Ceram. Soc*. 65 (5), 242- 246.

14. Burke, D.P. and Rainforth, W.N. (1997) . Intermediate rhombohedral (r – ZrO$_2$) phase formation at the surface of sintered Y - TZP's. *J. Mater. Sci. Lett.* (16), 883-885.

15. Heuer, A.H.; Chaim, R. and Lanteri, V. (1987). The displacive cubic $\rightarrow$ tetragonal transformation in ZrO$_2$ alloys. *Acta Mater.* 35 (3), 661 -666.

16. Golieskardi, M.; Satgunam. M.; Ragurajan, D. and Ansari, M.N.M. (2015). The Effect of Aluminum Oxide (Al2O3) and Cerium Oxide (CeO$_2$) on the Structural and Mechanical Properties of Yttria Tetragonal Zirconia Polycrystal (Y-TZP). *J. Aus. Ceram. Soc.*, 51 (1), 16-21.

17. Ramesh, S. and Gill, C; (2001). Environmental Degradation of CuO-doped Y-TZP Ceramics. *Ceramics International,* 27 (6), 705-711

18. Deville, S.; Chevalier, J. and Gremillard, L. (2006). Influence of Surface Finish and Residual Stresses on the Ageing Sensitivity of Biomedical Grade Zirconia. *Biomaterials,* (27), 2186-2192.

19. Nakatani, K.; Nagayama, H.; Yoshida, H.; Yamamoto, T. and Sakuma, T. (2003). The Effect of Grain Boundary Segregation on Superplastic Behavior in Cation-Doped 3Y-TZP. *Scripta Materialia*, (49), 791

20. Duh, J.G. and Hwung, J.J (1988). Synthesis and sintering behavior of Mgo-doped Yttria-Stabilized Tetragonal Zirconia Polycrystal (Y-TZP).*J. Mater. Chem. & Phys*. (20), 409

21. Maria, C.-L.; Scherrer, S.S.; Ammann, P.; Jobin, M. and Wiskott, H.W.A. (2011). Low Temperature Degradation of a Y-TZP Dental Ceramic. *Acta Biomaterialia* (7), 858.

22. Seidensticker, J.R. and Mayo, M.J. (1996). Thermal Analysis of 3-mol%-Yttria-Stabilized Tetragonal Zirconia Powder Doped with Copper Oxide. *J. Am. Ceram. Soc.* (79), 401.

23. Gremillard, L.; Epicier, T.; Chevalier, J. and Fantozzi, G. (2005). Effect of Cooling Rate on the Location and Chemistry of Glassy Phases in Silica-Doped 3Y-TZP ceramics. *J. Eur. Ceram. Soc.* (25), 875-882.

24. Sun, Y.-H.; Zhang, Y.-F.; and Guo, J.-K. (2003). Microstructure and Bending Strength of 3Y-TZP ceramics by Liquid-Phase Sintering with CAS Addition. *Ceram. Inter.* (29), 229.

25. Hodgson, S.N.B.; and Cawley, J. (2001). The Effect of Titanium Oxide Additions on the Properties and Behaviour of Y-TZP. *J. Mater. Proc. Tech.* (119), 112-116.

26. Ramesh, S.; Kelvin, C. W. J.; Tan, C. Y.; Purbolaksono, J.; Noor, A. M.; Hassan, M. A.; Sutharsini, U.; Satgunam, M. and Teng, W. D. (2013). Influence of Manganese on the Sintering Properties of Tetragonal Zirconia. *Ceramics-Silikaty* 57 (1),28-32.

27. Kanellopoulos, P.; and Gill, C. (2002). Hydrothermal Ageing of Yttria-Stabilised Zirconia, Sintered at 1300°C–1325°C: The Effects of Copper Oxide Doping and Sintering Time Variations. *J. Mater. Sci.* (37), 5075-5082.

28. Ruhle, M.; Claussen, N; and Heuer, A.H. "Microstructural Studies of Y_2O_3-Containing Tetragonal ZrO_2 Polycrystals (Y-TZP)," In *Advances in Ceramics*, Vol. 12, Claussen N., Ruhle M. & Heuer A.H. (eds.) (The Am. Ceram. Soc., Columbus, Ohio, 1984) pp. 352-370.

29. Wang, J.; Rainforth, M. and Stevens, R. (1989). The Grain Size Dependence of the Mechanical Properties in TZP Ceramics. *Br. Ceram. Trans. J.* (88), 1-6.

30. Claussen, N. (1985), Strengthening Strategies for ZrO2-Toughened Ceramics at High Temperatures. *Mater. Sci. and Eng.* (71), 23-38.

31. McMeeking, R.M. and Evans, A.G. (1982).Mechanics of Transformation-Toughening in Brittle Materials. *J. Am. Ceram. Soc.* (65), 242-246.

32. Evans, A.G. and Cannon R.M. (1986). Toughening of Brittle Solids by Martensitic Transformations. *Acta Metall.* (34), 761-800.

33. ASTM E1876-97, *Standard Test Method for Dynamic Young's Modulus, Shear Modulus and Poisson's Ratio by Impulse Excitation of Vibration*, Annual Book of ASTM Standards, 1998.

34. Niihara, K.; Morena, R.; and Hasselman, D.P.H. (1982). Evaluation of K_{IC} of Brittle Solids by the Indentation Method with Low Crack-to-Indent Ratios. *J. Mater. Sci. Letts.* (1), 13-16.

35. Toraya, H.; Yoshimura, M. and Somiya, S. (1984). Calibration Curve for Quantitative Analysis of the Monoclinic-Tetragonal ZrO_2 System by X-Ray Diffraction. *J. Am. Ceram. Soc.* (67), C-119 – C-121.

36. Sivakumar, S.; Ramesh, S.; Teow, H.L.; Yong, L.C. and Jeffrey, K.C.L., (2014). Effect of Short Time Sintering on the Mechanical Properties of Undoped Zirconia Ceramics. *Applied Mechanics and Materials*. (629), 420-425.

37. Swain M.V. (1985). Inelastic Deformation of Mg-PSZ and Its Significance for Strength-Toughness Relationship of Zirconia Toughened Ceramics. *Acta Metall*. (33), 2083-2091.