Research Article

Densification Behaviour and Mechanical Properties of Aluminium Oxide and Cerium Oxide-Doped Yttria Tetragonal Zirconia Polycrystal Ceramics Using Two-Step Sintering

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The densification behaviour, mechanical properties, and microstructure of high-purity Al_2O_3 and CeO_2-doped Y-TZP with different weight percentage varied from 0.3 to 1 wt% were investigated. The samples were pressed uniaxially at 200 MPa into rectangular bars and discs and pressureless-sintered at temperature ranging between 1250°C and 1450°C for 2 h while the microstructure was characterized with a scanning electron microscope (SEM). Two-step sintering process works well for temperature higher than 1400°C and it created most tetragonal phase arrangement for stable structure to delay ageing through phase transformation. The mechanical properties in terms of bulk density, Young's modulus, Vickers hardness, and fracture toughness were also measured. The results indicate that the addition of dopants accelerated the densification parameters and reinforced and toughened the obtained bodies. The maximum values for the mechanical properties of the Al_2O_3 and CeO_2-doped Y-TZP ceramics were 6.01, 220 GPa, 13.8 GPa, and 7 MPa for density, Young's modulus, Vickers hardness, and fracture toughness, respectively, which are higher than those of the doped samples.

1. Introduction

Yttria-stabilised tetragonal zirconia polycrystalline ceramics (Y-TZP) are becoming popular engineering materials due to their excellent mechanical properties, studied and used in many engineering applications, such as engine parts, valves, cutting tools, and moulds, due to their good fracture toughness, high strength, elastic modulus, and wear resistance [1–3].

In recent years, yttria-tetragonal zirconia polycrystals (Y-TZP), with their superior combination of mechanical properties and chemical inertness, have been employed in the biomedical field as an implant material [4–9]. In general, when a restricted number of ZrO_2 particles undergo the transformation during cooling from the sintering temperature, the accompanying volume expansion would cause the development of a fine distribution of microcracks in the ceramic matrix. These microcracks would increase the toughness by interacting with a propagating crack, causing deflection and blunting of the crack. Due to this nature,

the engineering application of pure ZrO_2 proves to be nonviable as the sintered body would crumble to pieces upon cooling from the sintering temperature [10, 11].

To overcome this undesirable phase transformation, stabilisers such as magnesia (MgO), calcia (CaO), ceria (CeO_2), and yttria (Y_2O_3) have been added in various quantities in zirconia. In general, alloying zirconia with these oxides reduces the change of chemical free energy, which in turn lowers the tetragonal to monoclinic transformation temperature to below ambient temperature [12–16]. Garvie et al. [17] highlighted the potential of increasing both the strength and toughness of zirconia through a mechanism involving the phase transformation of metastable tetragonal particles induced by the presence of the stress field ahead of a crack.

Kobayashi et al. [18] first discovered a serious limitation of Y-TZP ceramics for applications near 250°C in moist environment. Results revealed that the ceramic can suffer a slow, tetragonal to monoclinic phase transformation at the samples surface in a humid atmosphere, followed by microcracking and a serious loss in strength, a phenomenon

subsequently known as ageing or low temperature degradation (LTD). Ever since then, many researchers have experimented with Y-TZP with an attempt to understand the basic micro mechanisms of the ageing-induced (t) to (m) phase transformation and to suppress this LTD phenomenon [19–24]. Although the experimental observations of the ageing phenomenon are well understood, the actual mechanism responsible for the degradation has not been unequivocally explained. The effect of copper oxide (CuO) doping Y-TZP has been studied by Kanellopoulos and Gill [25–27]. It was found that mechanism involving liquid phase enhanced due to the low melting point of CuO in ZrO_2 matrix densification of the ceramics. The effect of TSS on the densification and grain growth of nanocrystalline 3Y-TZP ceramic was investigated by Mazaheri et al. [28]. From the results it was found that the grain growth rate of nanocrystalline 3Y-TZP in conventional sintering route is significantly lower than that of other ceramics such as ZnO and Al_2O_3; also full stabilized tetragonal zirconia (3Y-TZP) ceramic can be obtained at grain size <275 nm.

It has been reported that improved Y-TZPs with optimized mechanical properties and ageing resistant could be obtained by the addition of more than one stabiliser to zirconia. For instance, Xu et al. [29]. It was found that the addition of CeO_2 to Y-TZP could prevent ageing, while retaining relatively high fracture toughness of 7–9 MPam$^{1/2}$. Similar observation was made by Sato et al. [30, 31] who found that the ageing kinetics of 2, 3, and 4 mol% Y-TZP sintered at 1400°C to 1650°C decreased with increasing yttria content. Results also showed that increasing yttria content resulted in a reduction in the onset critical ageing temperature for phase transformation.

2. Materials and Method

The experiment was conducted from a starting Y-TZP powder containing 3 mol% yttria and cerium oxide-aluminium oxide powders of 99.9% purity as dopants manufactured by Kyoritsu Ltd., Japan. Three different compositions of CeO_2-Al_2O_3-doped Y-TZP powder mixtures (0.3, 0.5, and 1 wt%) and undoped Y-TZP sample were prepared. The ratio dopant to Y-TZP was 1 : 99, whereby, regardless of the percentage of dopant in each composition, the addition of both dopants will always be equal to 1 wt%. Each powder was weighed carefully and then underwent an ultrasonification process, whereby the base powder (Y-TZP) is first added with 150 mL of ethanol and left for 6 minutes, followed by the addition of the two dopants (Al_2O_3 and CeO_2), and further ultrasonification of 22 minutes follows. The powder was composed of primary particles with an average size of ~30 nm (Figure 1(a)) and spherical granules (Figure 1(b)). The powder was uniaxially compact in a standard procedure [32] at about 1 KN using hardened steel mold and die assembly. The powder was processed by cold isostatic pressing at 200 MPa, followed by pressureless sintering at temperature ranging from 1250°C to 1450°C in air. Unlike regular pressureless sintering, two-step sintering involves increasing the temperature to about 1000°C and is maintained for a period of one hour, before

further heating to 1250°C. The sintered samples were ground on one face by Silicon Carbide, SiC papers of 120, 240, 600, 800, and 1200 grades successively, followed by polishing with 6 μm and 1 μm diamond paste to produce an optical reflective surface. The Vickers indentation test performed using a load of 10 kn on polished surfaces in order to measure the hardness and indentation toughness. Bulk density of the specimens was determined by the Archimedes method using distilled water. The Young's modulus of the sample can be calculated using the standard test method (ASTM E1876-97) [33–35]. The microstructure of the samples was examined by JSM-6310 scanning electron microscopy (SEM).

3. Experimental Results and Discussion

3.1. Bulk Density. The variation of bulk density for Y-TZPs with different amounts of Al_2O_3 and CeO_2 sintered at temperatures 1250°C–1450°C is shown in Figure 2. All Y-TZP compositions including the undoped shared a common trend. Addition of Al_2O_3 and CeO_2 were found to be most beneficial at sintering temperatures of 1250°C to 1400°C. The results for undoped Y-TZP at low sintering temperature 1300°C shows that the relative density achieved was below 95%. In the case of the 0.5 wt% Al_2O_3 and CeO_2-doped ceramics, the two-step sintering at 1400°C was found to be beneficial in enhancing the densification of the ceramics. From the sintering regime employed, 1400°C was found to be the optimum sintering temperature as all Y-TZPs sintered at this temperature recorded densities that were close to 98%. In addition, for the 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP, maximum density of 6.01 Mgm^{-3} (i.e., 8% T.D.) was recorded at this temperature and further increase in the sintering temperature resulted in the decline of its bulk density. This phenomenon is probably attributed to a phase transformation from tetragonal to monoclinic zirconia that starts after 1400°C. During the phase transformation, a volume expansion of zirconia grains (i.e., expansion of the zirconia lattice) occurs and therefore a significant decrease in density is reported. Similar results have been reported by other researchers working on Al_2O_3 or CeO_2 as a sintering additive in Y-TZP [36, 37].

3.2. Young's Modulus. The effect of aluminium oxide and cerium oxide doped Y-TZP on the Young's modulus is shown in Figure 3. The addition of Al_2O_3 and CeO_2 was beneficial in enhancing the elastic modulus of Y-TZP, especially at low sintering temperatures of 1250°C and 1300°C when compared to the undoped Y-TZP.

Figure 3 shows that an E value of above 200 GPa could be achieved with the additions of ≥0.5 wt% Al_2O_3 and CeO_2 when sintered at 1350°C as compared to 197 GPa for the undoped Y-TZP. In comparison, the Young's modulus of the undoped Y-TZP started low, at 178 GPa when sintered at 1250°C; however, it soon increases with increasing sintering to reach a maximum of 202 GPa when sintered at 1400–1450°C. Both the additions of 0.5 and 0.1 wt% Al_2O_3 and CeO_2 exhibited the highest modulus (209–220 GPa) when
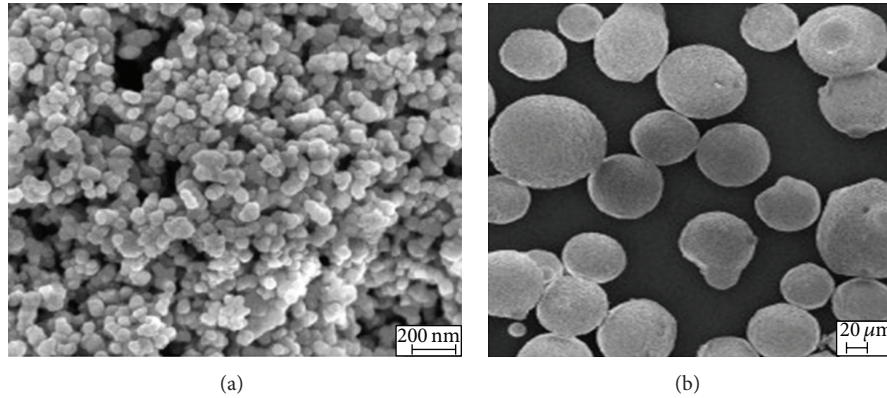
(a)

(b)

FIGURE 1: SEM micrographs show the particle morphology of Y-TZP: (a) primary particles; (b) spray-dried granules.
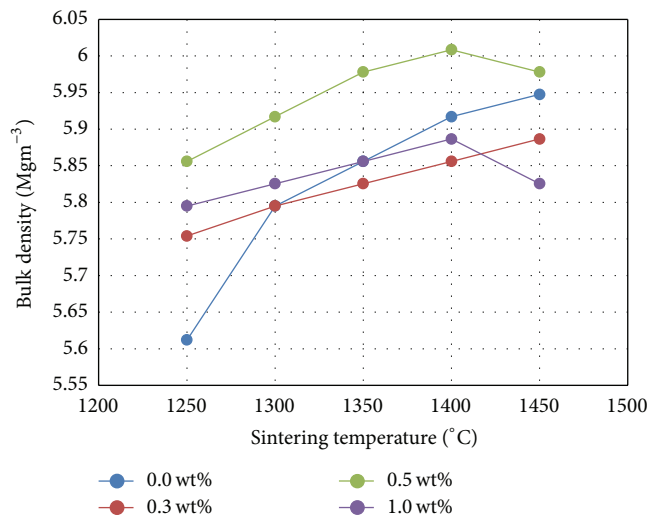

FIGURE 2: Effect of sintering temperature and sintering additives on the bulk density of Y-TZP.
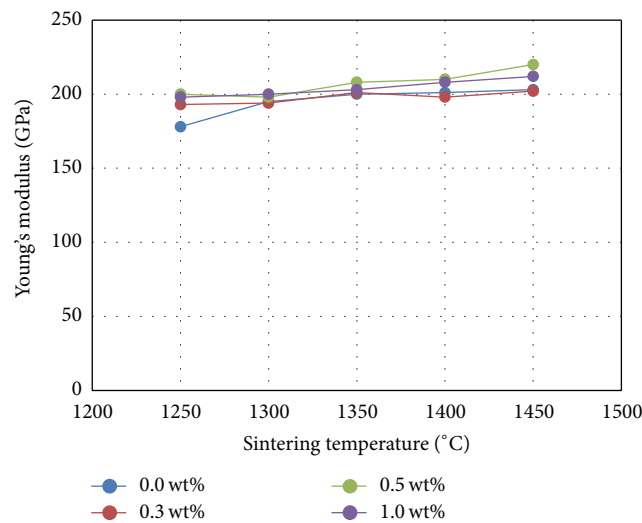

FIGURE 3: Effect of sintering temperature and sintering additives on the Young's modulus of Y-TZP.
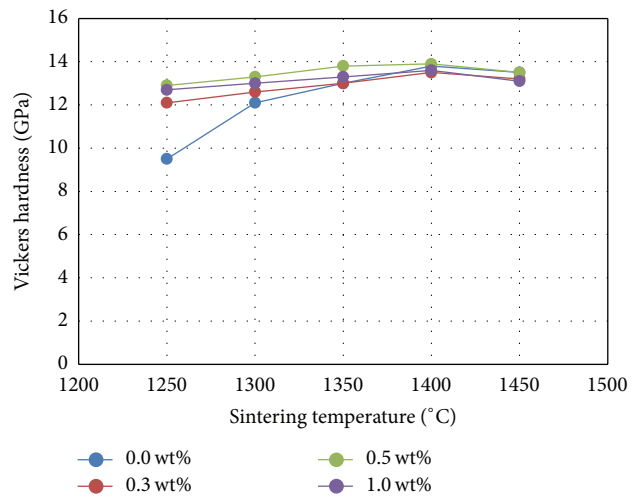

FIGURE 4: Vickers hardness variation of undoped and doped Al_2O_3 and CeO_2-doped Y-TZP.

sintered at 1400°C. Thereafter, the E values of these ceramics fluctuated slightly with increasing temperature.

3.3. Vickers Hardness. The effect of sintering temperature and Al_2O_3 and CeO_2 on the Vickers hardness of Y-TZP is shown in Figure 4. The results obtained in the present work confirmed that the Al_2O_3 and CeO_2 additions were beneficial in improving the hardness of zirconia when sintered at low sintering temperatures.

However, in the present work, bulk density is unlikely to be the governing factor for the decline of hardness observed from 1400°C to 1450°C because all Y-TZPs except for the 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP were more than 97% dense at these temperatures as shown in Figure 2. The decline of hardness could possibly be due to grain growth resulting from sintering at higher temperatures. The 1 wt% Al_2O_3 and CeO_2-doped Y-TZP display the lowest hardness for sintering above 1400°C as shown in Figure 4. Two possible explanations can be made for the decline in hardness of this sample when sintered above 1400°C; firstly, hardness was strongly
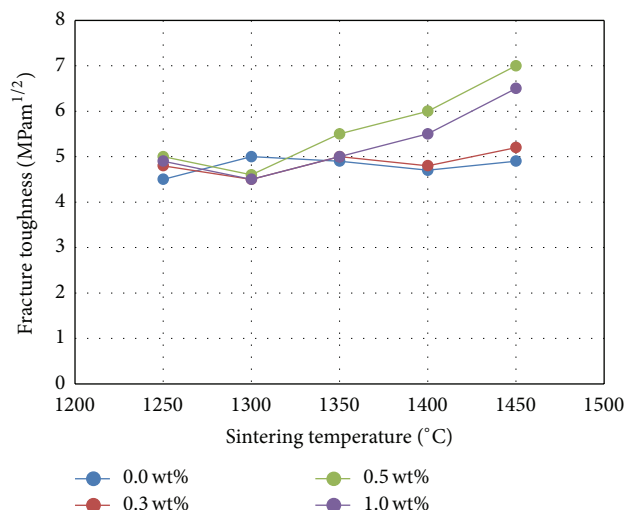
FIGURE 5: Variation of sintering temperature and Al_2O_3 and CeO_2 addition on the fracture toughness of sintered Y-TZP.

dependent on bulk density, which decreased considerably during the temperature range as shown in Figure 2 and, secondly, it can be associated with the reduction of tetragonal phase content and a concomitant increased in the cubic phase formation in the zirconia matrix with increasing temperature. The reduction of tetragonal phase content had been cited by Lawson et al. [38] and Liu and Chen [39] to be the reason for the lower hardness of Y-TZP doped with CuO and $Sr_2Nb_2O_7$, respectively.

3.4. Fracture Toughness. The effect of Al_2O_3 and CeO_2-doped Y-TZP and sintering temperature on the fracture toughness (K_{Ic}) is shown in Figure 5. In general, additions of up to 0.3 wt% Al_2O_3 and CeO_2 have negligible effect on the fracture toughness of Y-TZP for the entire sintering temperature investigated. The fracture toughness of these samples was found to fluctuate between 4.5 $MPam^{1/2}$ and 5.18 $MPam^{1/2}$. The fact that the K_{Ic} did not change significantly indicates that the additions of Al_2O_3 and CeO_2 below 0.3 wt% did not affect the tetragonal phase stability of Y-TZP. Higher Al_2O_3 and CeO_2 additions of 0.5 and 1 wt% also showed similar trend at sintering temperatures below 1300°C. However, sintering above 1300°C, the K_{Ic} of both Al_2O_3 and CeO_2-doped Y-TZP increased by increasing the temperature. This observation was more pronounced for the 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP, which exhibited a significant increase in K_{Ic} from 4.6 $MPam^{1/2}$ at 1300°C to 7.0 $MPam^{1/2}$ at 1450°C.

3.5. Microstructural and Phase Development. Scanning electron microscopic images of 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP sintered at 1450°C are presented in Figure 6(a). The analyses revealed that samples sintered at 1450°C showed particles that are nonspherical in shape and with little agglomeration and porosity. The surface topographies confirmed the presence of little agglomeration and porosity. For all of them, the zirconia appears agglomerated in light contrast

and the aluminium oxide and cerium oxide appear as dark background particles. The average particle size obtained from the particle size distribution analysis using the grain intercept method was 1.13 μm.

The SEM results are in good agreement with the density of the 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP sintered at 1450°C.

On the other hand, relatively rough surfaces were observed on surface sintered at 1250°C but no grains structures were clearly observed as depicted in Figure 6(b). The likely reason that 0.5 wt% Al_2O_3 and CeO_2-doped Y-TZP sintered at 1250°C did not have grain structure could be due to the presence of a glassy phase that suppressed the crystal growth and sealed the grain boundary.

It was also found that 1 wt% Al_2O_3 and CeO_2-doped Y-TZP sintered at 1450°C resulted in severe phase transformation which was also accompanied by networks of micro- and macrocracks on the surface as typically shown in Figure 7.

High angle XRD analysis performed on the 1450°C sintered sample revealed that very high percentage of cubic phase (up to 48%) was calculated in the zirconia matrix. This result indicated that sintering of 1 wt% Al_2O_3 and CeO_2-doped Y-TZP at 1450°C resulted in the formation of monoclinic and cubic phases in the zirconia matrix. The spontaneous phase transformation upon cooling from sintering and the development of the cubic phase was not observed for the 0.5 wt% Al_2O_3 and CeO_2-doped when sintered at 1450°C.

4. Conclusion

Sinterability and mechanical properties of Al_2O_3 and CeO_2-doped Y-TZP ceramics were studied in the present work. The beneficial effect of Al_2O_3 and CeO_2 in enhancing the densification of Y-TZP has been revealed. The Al_2O_3 and CeO_2-doped Y-TZPs achieved almost full density (>97% of theoretical density) at 1300°C. The study revealed that 1350°C was the optimum sintering temperature for all Y-TZPs to achieve >98% of theoretical density.

The variation of Young's modulus with sintering temperature of all composition studied was in good agreement with the variation in bulk density. In general, it was found that Y-TZPs containing above 0.5 wt% Al_2O_3 and CeO_2 attained E values above 200 GPa when sintered at temperature 1350°C.

In general, the hardness of all Al_2O_3 and CeO_2-doped Y-TZPs was higher than the undoped material when sintered at 1250°C and 1300°C. In particular, the addition of 0.3–1 wt% Al_2O_3 and CeO_2 was most effective in enhancing the hardness of Y-TZP. These doped samples exhibited hardness of >13 GPa as compared to ~9.7 GPa for the undoped ceramics sintered at 1250°C.

The additions of up to 0.3 wt% Al_2O_3 and CeO_2 were found to have negligible effect on the fracture toughness of Y-TZP throughout the sintering regime employed. The KIc of these samples was found to fluctuate between 4.67 $MPam^{1/2}$ and 5.18 $MPam^{1/2}$, which implied that the tetragonal phase stability of Y-TZP was not disrupted. However, as the temperature increased above 1400°C, an increasing KIc trend
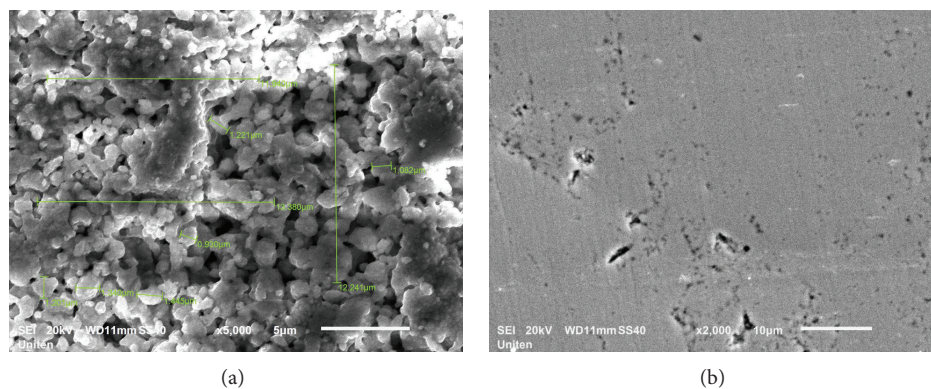
(a)

(b)

Figure 6: (a) SEM image showing lines intercepting on grain boundaries of sample at 1450°C. (b) SEM image showing lines intercepting on grain boundaries of sample at 1250°C.
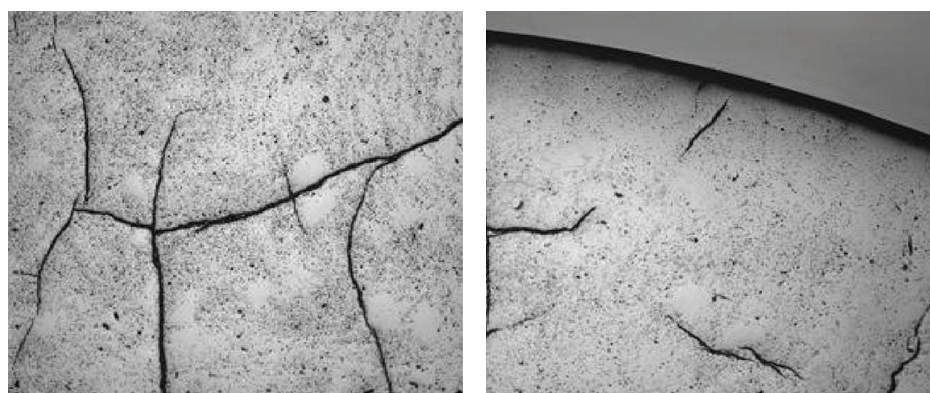

Figure 7: Effect of micro- and macrocracks on the surface of the 1 wt% Al_2O_3 and CeO_2-doped Y-TZP accompanying the (t) to (m) phase transformation upon cooling from sintering at 1450°C (mag. = ×50).

was noted for both ceramics. In particular, the 1 wt% Al_2O_3 and CeO_2-doped Y-TZP exhibited a significant increase in the fracture toughness, from 4.8 MPam$^{1/2}$ at 1400°C to 7.1 MPam$^{1/2}$ at 1450°C.

Conflict of Interests

The authors declare that there is no conflict of interests regarding the publication of this paper.

References

[1] R. Stevens, "Introduction to Zirconia," in *Zirconia and Zirconia Ceramics*, pp. 28–43, Magnesium Elektron, 1986.

[2] L. Gakovic, "Ceramic center pin for compaction tooling and method for making same," U.S. Patent no. 7,214,046, 2007.

[3] P. Christel, A. Meunier, M. Heller, J. P. Torre, and C. N. Peille, "Mechanical properties and short-term *in vivo* evaluation of yttrium-oxide-partially-stabilized zirconia," *Journal of Biomedical Materials Research*, vol. 23, no. 1, pp. 45–61, 1989.

[4] J. Chevalier and L. Gremillard, "Zirconia as a Biomaterial," *Comprehensive Biomaterials*, vol. 1, pp. 95–108, 2011.

[5] T. Kokubo and N. Masahiro, "Hard tissue repairing material," European Patent No. EP1225927, 2002.

[6] L. Gremillard, J. Chevalier, T. Epicier, and G. Fantozzi, "Improving the durability of a biomedical-grade zirconia ceramic by the addition of silica," *Journal of the American Ceramic Society*, vol. 85, no. 2, pp. 401–407, 2002.

[7] S. Deville, J. Chevalier, and L. Gremillard, "Influence of surface finish and residual stresses on the ageing sensitivity of biomedical grade zirconia," *Biomaterials*, vol. 27, no. 10, pp. 2186–2192, 2006.

[8] A. Sundh and G. Sjögren, "Fracture resistance of all-ceramic zirconia bridges with differing phase stabilizers and quality of sintering," *Dental Materials*, vol. 22, no. 8, pp. 778–784, 2006.

[9] A. Dakskobler, P. Jevnikar, Č. Oblak, and T. Kosmač, "The processing-related fracture resistance and reliability of root dental posts made from Y-TZP," *Journal of the European Ceramic Society*, vol. 27, no. 2-3, pp. 1565–1570, 2007.

[10] Y. Wang and P. Xiao, "The phase stability and toughening effect of 3Y-TZP dispersed in the lanthanum zirconate ceramics," *Materials Science and Engineering A*, vol. 604, pp. 34–39, 2014.

[11] M. Nawa, K. Yamada, and N. Kurizoe, "Effect of the t-m transformation morphology and stress distribution around the crack path on the measured toughness of zirconia ceramics: a case study on Ce-TZP/alumina nanocomposite," *Journal of the European Ceramic Society*, vol. 33, no. 3, pp. 521–529, 2013.

[12] Z. Wei, P. Cheng, L. Ming, B. Mingmin, and R. Pinggen, "Effect of notch depth on fracture toughness of Y-TZP and determination of its actual value," *Ceramics International*, 2014.

[13] Y. L. Zhang, X. J. Jin, Y. H. Rong, T. Y. Hsu, D. Y. Jiang, and J. L. Shi, "On the t → m martensitic transformation in Ce-Y-TZP ceramics," *Acta Materialia*, vol. 54, no. 5, pp. 1289–1295, 2006.

[14] I. Birkby and H. Hodgson, "Progress with zirconia ceramics," in *Proceedings of the 3rd European Symposium on Engineering Ceramics*, F. L. Riley, Ed., pp. 167–199, Elsevier Applied Science, 1991.

[15] C. F. Grain, "Phase relations in the ZrO_2-MgO system," *Journal of the American Ceramic Society*, vol. 50, pp. 288–290, 1967.

[16] E. Marcella, N. Denis, B. W. Susie, M. P. Ast, M. W. Timothy, and E. P. Douglas, "Zirconia phase transformation, metal transfer, and surface roughness in retrieved ceramic composite femoral heads in total hip arthroplasty," *The Journal of Arthroplasty*, vol. 29, pp. 2219–2223, 2014.

[17] R. C. Garvie, R. H. Hannink, and R. T. Pascoe, "Ceramic steel?" *Nature*, vol. 258, no. 5537, pp. 703–704, 1975.

[18] K. Kobayashi, H. Kuwajima, and T. Masaki, "Phase change and mechanical properties of ZrO_2-Y_2O_3 solid electrolyte after ageing," *Solid State Ionics*, vol. 3-4, pp. 489–493, 1981.

[19] L. Hallmann, P. Ulmer, E. Reusser, M. Louvel, and C. H. F. Hämmerle, "Effect of dopants and sintering temperature on microstructure and low temperature degradation of dental Y-TZP-zirconia," *Journal of the European Ceramic Society*, vol. 32, no. 16, pp. 4091–4104, 2012.

[20] M. Cattani-Lorente, S. S. Scherrer, S. Durual et al., "Effect of different surface treatments on the hydrothermal degradation of a 3Y-TZP ceramic for dental implants," *Dental Materials*, vol. 30, no. 10, pp. 1136–1146, 2014.

[21] S. Christian, R. Alexander, K. Christof, and K. Andreas, "Assessment of low-temperature degradation of Y-TZP ceramics based on Raman-spectroscopic analysis and hardness indentation," *Journal of the European Ceramic Society*, vol. 34, no. 16, pp. 4311–4319, 2014.

[22] S. Lawson, "Environmental degradation of zirconia ceramics," *Journal of the European Ceramic Society*, vol. 15, no. 6, pp. 485–502, 1995.

[23] L. Gremillard, J. Chevalier, T. Epicier, S. Deville, and G. Fantozzi, "Modeling the aging kinetics of zirconia ceramics," *Journal of the European Ceramic Society*, vol. 24, no. 13, pp. 3483–3489, 2004.

[24] S. Perko, A. Dakskobler, and T. Kosmac, "The densification and strength of porous Y-TZP materials with a bimodal particle size distribution for dental applications," *Journal of the European Ceramic Society*, vol. 32, no. 11, pp. 2633–2639, 2012.

[25] P. Kanellopoulos and C. Gill, "Hydrothermal ageing of yttria-stabilised zirconia, sintered at 1300°C–1325°C: the effects of copper oxide doping and sintering time variations," *Journal of Materials Science*, vol. 37, no. 23, pp. 5075–5082, 2002.

[26] S. Ramesh, M. Amiriyan, S. Meenaloshini et al., "Densification behaviour and properties of manganese oxide doped Y-TZP ceramics," *Ceramics International*, vol. 37, no. 8, pp. 3583–3590, 2011.

[27] L. Winnubst, S. Ran, E. A. Speets, and D. H. A. Blank, "Analysis of reactions during sintering of CuO-doped 3Y-TZP nano-powder composites," *Journal of the European Ceramic Society*, vol. 29, no. 12, pp. 2549–2557, 2009.

[28] M. Mazaheri, A. Simchi, and F. Golestani-Fard, "Densification and grain growth of nanocrystalline 3Y-TZP during two-step sintering," *Journal of the European Ceramic Society*, vol. 28, no. 15, pp. 2933–2939, 2008.

[29] T. Xu, J. Vleugels, O. van der Biest, and P. Wang, "Fabrication and characterization of (Nd,y)-TZP ceramics from stabilizer-coated nanopowder," *Materials Letters*, vol. 58, no. 26, pp. 3353–3357, 2004.

[30] T. Sato and M. Shimada, "Transformation of yttria -doped tetragonal ZrO_2 polycrystals by annealing in water," *Journal of the American Ceramic Society*, vol. 68, no. 6, pp. 356–359, 1985.

[31] T. Sato, S. Ohtaki, T. Endo, and M. Shimada, "Transformation of yttria-doped tetragonal ZrO_2 polycrystals by annealing under controlled humidity conditions," *Journal of the American Ceramic Society*, vol. 68, pp. 320–322, 1985.

[32] T. A. Egerton, E. J. Lawson, and P. W. Frost, "Stabilised zirconia," UK Patent Application GB 2 181 723 A, 1987.

[33] "Standard test method for dynamic young's modulus, shear modulus and poisson's ratio by impulse excitation of vibration," Annual Book of ASTM Standards ASTM E1876-97, 1998.

[34] R. C. Garvie and P. S. Nicholson, "Phase analysis in zirconia system," *Journal of the American Ceramic Society*, vol. 55, pp. 303–305, 1972.

[35] N. Kimura, S. Abe, J. Morishita, and H. Okamura, "Low-temperature sintering of Y-TZP and Y-TZP-Al_2O_3 composites with transitional metal oxide additives," in *Sintering '88*, S. Somiya, Ed., vol. 2, pp. 1142–1148, Elsevier Applied Science, 1988.

[36] N. Kimura, S. Abe, Y. Hayashi, J. Morishita, and H. Okamura, "Sintering behavior and anti-degradation property of MO_x-doped Y-TZP (M: Cu, Mn, Co, Ni, Zn)," *Sprechsaal*, vol. 122, no. 4, pp. 341–343, 1989.

[37] Y. Sakka, T. Ishii, T. S. Suzuki, K. Morita, and K. Hiraga, "Fabrication of high-strain rate superplastic yttria-doped zirconia polycrystals by adding manganese and aluminum oxides," *Journal of the European Ceramic Society*, vol. 24, no. 2, pp. 449–453, 2004.

[38] S. Lawson, C. Gill, and G. P. Dransfield, "The effects of copper and iron oxide additions on the sintering and properties of Y-TZP," *Journal of Materials Science*, vol. 30, no. 12, pp. 3057–3060, 1995.

[39] X. Q. Liu and X. M. Chen, "Microstructures and mechanical properties of $Sr_2Nb_2O_7$-toughened 3Y-TZP ceramics," *Ceramics International*, vol. 29, no. 6, pp. 635–640, 2003.