INFLUENCE OF PARTICLE SIZE AND PRE-SINTERING TEMPERATURE ON THE PROPERTIES OF ZIRCONIA BLOCK

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ABSTRACT: This study aimed to evaluate the influence of particle size and pre-sintering temperature on the mechanical properties of pre-sintered monolithic zirconia blocks. Zirconia blocks were fabricated using two types of zirconia 3YSZ powders: one with a particle size of 20-nm (20 nmZ) and another with a particle size of 60-nm (60 nmZ). The blocks were prepared through colloidal processing; shaped through slip casting and cold isostatic pressing; and partially sintered at 850, 900, and 950 °C for 2 h. The 20 nmZ and 60 nmZ blocks had diameters of 40 mm and thicknesses of 5 mm and 20 mm, respectively. Shrinkage, hardness and density properties of the blocks were later examined. The 20 nmZ blocks exhibited higher shrinkage, pre-sintered density, and Vickers hardness than the 60 nmZ blocks. The 20 nmZ blocks exhibited Vickers hardness values that ranged from 0.9 GPa to 1.27 GPa. These values are comparable with that of a commercial product. When sintered at the highest sintering temperature, the 20 nmZ and 60 nmZ blocks achieved 96.5% and 95.9% theoretical density, respectively. Results indicated that the mechanical properties of the pre-sintered monolithic zirconia blocks could be improved by controlling the initial particle size of the parent zirconia powder and pre-sintering the blocks at an appropriate temperature.

KEYWORDS: *Pre-Sintered Zirconia; Sintering; Colloidal Processing; Hardness; Zirconia Blank*

1.0 INTRODUCTION

Dental restorations, such as crowns, bridges, dentures, and implants, are commonly fabricated using zirconia given its excellent mechanical properties and biocompatibility. Zirconia used in dentistry applications is biomedical grade and contains 3 mol% yttria as a stabilizer [1-2]. The yttria stabilizer enhances the mechanical properties of zirconia and confers flexural strength with a value of up to 900–1200 MPa and fracture strength of approximately 7–10 $MPa \cdot m^{1/2}$ [3].

Zirconia-based dental restorations are usually fabricated by soft-machining a pre-sintered zirconia block or hard-machining a fully sintered zirconia block [4-5]. Pre-sintered zirconia block is usually soft-machined given the ease and rapidity of this method; in addition, soft-machining consumes minimal energy, provides a high material removal rate, and causes limited tool wear [6-7]. The properties and quality of dental restorations mainly depend on those of the fabricated zirconia block. Dense, homogeneous, nanostructured zirconia blocks with superior mechanical properties are required in dentistry applications to prolong the survival of dental restorations. Zirconia blocks are commercially produced via cold isostatic pressing (CIP) [8]. The agglomeration of oxide ceramic nanoparticles, however, is difficult to prevent in CIP.

A preliminary study has shown that the colloidal technique can be used to fabricate dense, homogenous, nanostructured zirconia blocks [9–11]. However, the feasibility of slip-casting a larger zirconia green body prepared through the colloidal technique remains unknown. The effects of processing parameters, such as the particle size of the parent zirconia powder and pre-sintering temperature, on the stability of the zirconia block have not yet been investigated. Thus, the present study aimed to investigate the effect of particle size and pre-sintering temperature on the mechanical properties of zirconia blocks.

2.0 METHODOLOGY

2.1 Materials

Two types of zirconia (3 mol% yttria-stabilized zirconia) powders with different particle sizes were used to fabricate zirconia blocks. One powder (Inframat Advanced Materials, USA) had a particle size of approximately 20 nm (20 nmZ). The other powder (Nabond Technologies, China) had a particle size of 60 nm (60 nmZ). In order to confirm the average particle size of each powder, both powders were characterized through transmission electron microscopy (TEM). The TEM images of each powder are shown in Figure 1.

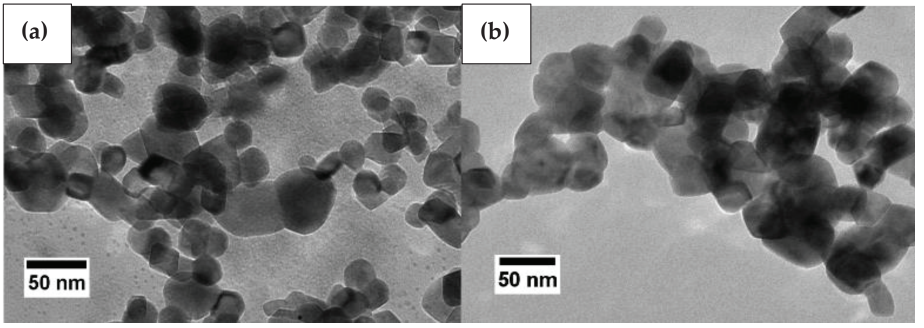

Figure 1: TEM images of (a) 20 nmZ and (b) 60 nmZ powders

2.2 Slurry Preparation

Suspensions were prepared from the 20nmZ and 60nmZ powders at solid loadings of 40 wt% and 50 wt%, respectively. Nitric acid was used to adjust the pH of both suspensions to pH = 2. The suspensions were stabilized with the addition of 0.5 wt% polyethelyneimene, which is a dispersant. The slurries were ball-milled to enhance particle homogeneity and break powder aggregates. Ball milling was performed in a zirconia jar with 10-mm zirconia balls as grinding media and at a rotational speed of 200 rpm for 1 h. The ball-to-powder ratio was 1:1.

2.3 Zirconia Block Consolidation

Each batch of zirconia slurry was poured into plaster moulds, which had cavities that were 40 mm in diameter and 25 mm in heights. The slurry was poured continuously into moulds until the desired thickness has formed. The slips were left to dry for two days and placed at room temperature under controlled moisture to prevent abrupt shrinkage. The slip-casted zirconia blocks were then subjected to CIP using a machine (Riken Seiki, Japan) at a pressure of 200 MPa for 1 min. Then, the green bodies were pre-sintered at 850 °C, 900 °C, and 950 °C in a furnace (VMK-1800, Linn High Germany). Figure 2 shows the sintering profile of the zirconia block. The blocks were heated to a specific pre-sintering temperature at a 3 °C/min heating rate and a soaking time of 2 h.

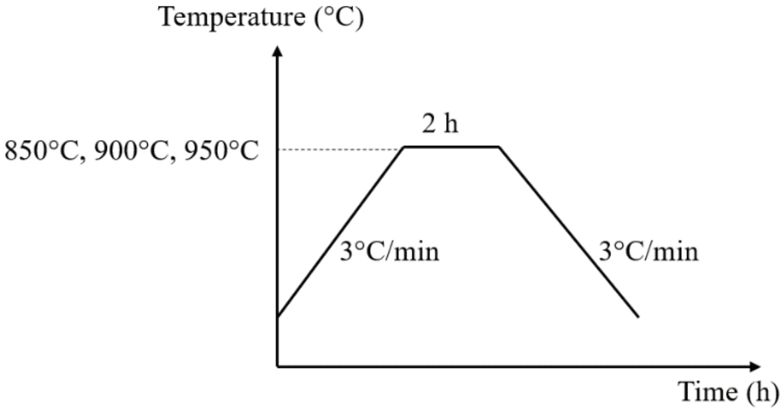

Figure 2: Sintering profile of the block samples

3.0 RESULTS AND DISCUSSION

3.1 Formability of Zirconia Block

Only block samples with thicknesses of less than 5 mm could be formed from 20 nmZ powder. Casting 20 nmZ slurry in moulds with thicknesses that exceeded 5 mm caused drastic shrinkage. Moreover, the final 20 nmZ disk exhibited numerous cracks after two days of drying. Therefore, as shown in Figure 3, the thicknesses of the 20 nmZ blocks were limited to ≤5 mm. Meanwhile, 60 nmZ blocks could be cast with a thickness of up to 20 mm without cracking or shrinking. In this study, it is important to obtain zirconia blocks with 20 mm thickness for milling into a dental crown. The standard thickness required for milling the zirconia block is in the range of 16 – 20 mm. If the block thickness is less than the specified range, the block cannot be milled into crown shape.

This difference in physical properties is attributed to the different particle sizes of the parent zirconia powders. Zirconia powders with small particle sizes have high specific surface areas that provide high surface charges. Upon dispersion in water during slurry preparation, there is ion adsorption with either H^+ or OH^- ions occurs on the large zirconia particle surface. The ion adsorption creates a high surface charge density on the particle surface that generates a strong repulsive force. H_2O molecules then bridged the particle adsorbed by OH^- ion with another particle surface charge of OH^- ion via hydrogen bond and developed large agglomerates. The existence of attractive van der Waals and repulsive electrostatic forces increased agglomeration in the 20 nmZ slurry than in the 60 nmZ slurry.

Small particles tend to agglomerate, thus considerably increasing slurry viscosity and subsequently adversely affecting the properties of the cast body [12]. Meanwhile, a low solid loading increases the distance between particles and decreases adsorption between particles, thus decreasing slurry viscosity and agglomeration. Therefore, the 20 nmZ slurry was prepared with a low solid loading (40 wt%) to enhance particle dispersion. Agglomeration was prevented through the addition of a dispersant and through pH adjustment.

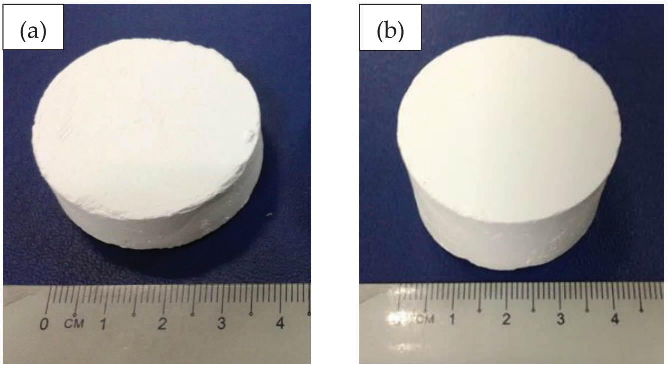

Figure 3: Zirconia blocks produced through slip casting and CIP: (a) 20 nmZ with thickness 5 mm and (b) 60 nmZ with thickness 20 mm

The cast 20 nmZ block shrank and cracked with prolonged drying time because more water content was removed during drying. A cast body with high water content is plastic enough to absorb dimensional changes without cracking. However, as the packing density increases because of water evaporation, the cast body becomes firmer and undergoes excessive shrinkage to generate cracks, which relieve stress. The traditional ceramic production method of slip casting may generate shrinkage because a packing factor gradient is introduced in the moulds during water evaporation [13].

3.2 Physical Properties of Pre-Sintered Zirconia Block

The volumetric shrinkage of the 20 nmZ and 60 nmZ blocks with 5 mm and 20 mm thickness respectively, were pre-sintered at different temperatures and the result is illustrated in Figure 4. The volumetric shrinkage of both blocks increased with increasing pre-sintering temperature. The 20 nmZ block drastically shrank when sintering temperature increased from 850 °C to 900 °C. Both types of zirconia blocks underwent nearly negligible shrinkage when pre-sintered at 850 °C given the absence of binder burnout. In this study, the zirconia blocks were prepared without the addition of binders. Thus, binder burnout did not occur.

The 20 nmZ block shrank more than the 60 nmZ block because of the low solid loading of the 20 nmZ slurry. A recent study revealed that ceramic blocks prepared from slurries with low solid loading exhibit drastic shrinkage because more water diffuses from the cast body, inducing compressive stresses from capillary tension that subsequently increase dimensional shrinkage [12, 14]. In addition, the 20 nmZ powder had a higher specific surface area than the 60 nmZ powder which was measured using the Brunauer–Emmett–Teller (BET) technique via N_2 gas adsorption as reported in a previous study [15]; this property has increased the driving force for diffusion [16]. This finding is closely related to the densification and mechanical properties of the 20 nmZ block and will be further discussed later.

When pre-sintered at 950 °C, the 20 nmZ block exhibited the highest theoretical density of 96.5%, which was slightly higher than that of the 60 nmZ block (95.9%) (Figure 5). This finding indicated that blocks cast from fine zirconia powders achieved high densification at low sintering temperatures. This advantageous behavior occurred because the large surface areas of the fine zirconia powders provided more contact points between particles and fewer diffusion paths during sintering. In addition, the particles of the fine zirconia powder were highly dispersed in the zirconia slurries prepared through the colloidal technique and achieved good packing density during sintering.

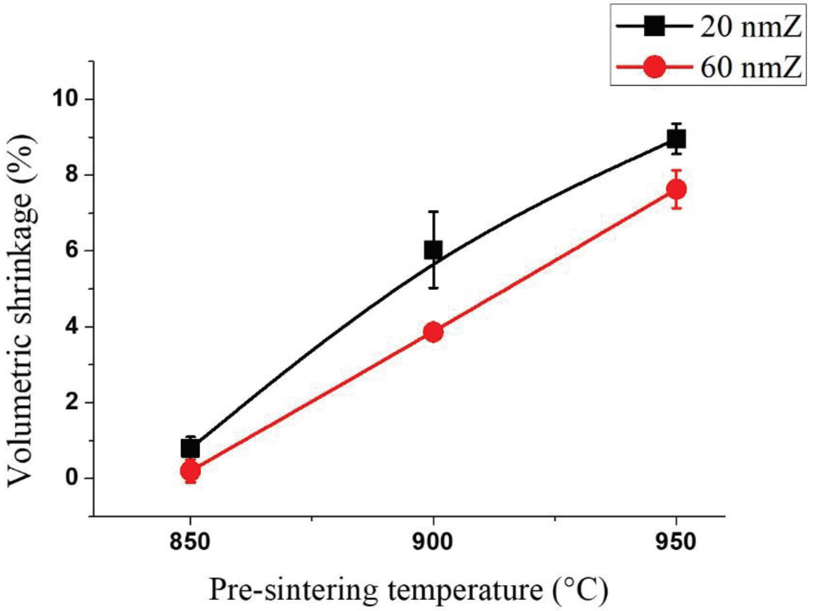

Figure 4: Volumetric shrinkage of zirconia block at different pre-sintering temperatures

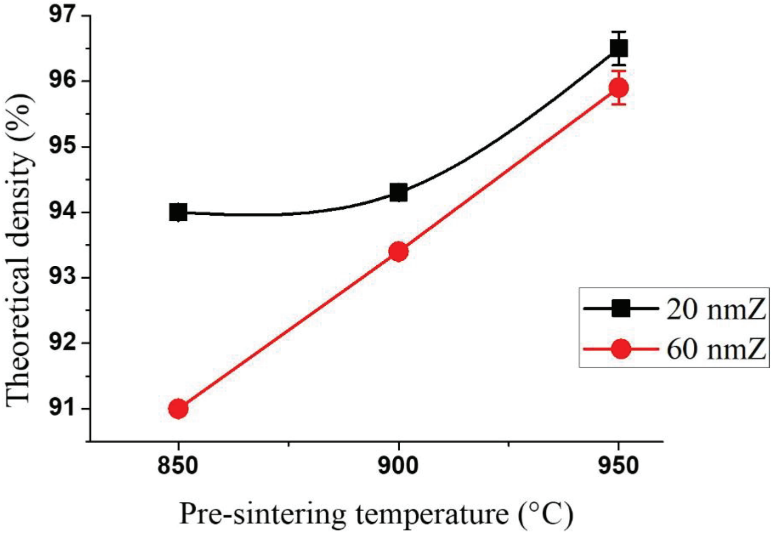

Figure 5: Theoretical density of zirconia block at different pre-sintering temperatures

Both experimental zirconia blocks achieve comparable theoretical density value with the commercial zirconia block. Zirconia block or blank are prepared commercially by pre-sintering at temperatures below 1500 °C to obtain a density of at least 95% of theoretical density [5]. Filser [8] investigated the pre-sintered zirconia that is developed using dry processing and found that the appropriate pre-sintering temperature of zirconia block with good densification is between 850 and 900 °C.

The densities of the 20 nmZ blocks that were pre-sintered at temperatures of 850 °C and 900 °C were slightly different but were significantly different from that of the 60 nmZ block that was pre-sintered at 850 °C. Compared with the large particles, which require high energy to diffuse, of the 60 nmZ powder, the fine particles of the 20 nmZ powder have higher driving force and can begin to densify at temperatures of as low as 850 °C. At the sintering temperature of 900 °C, the fine particles remained in the same state as that at 850 °C. At 850 °C, the pore system in the cast block was still being filled. Once the temperature increased to 950 °C, which is nearly 1000 °C, the particles likely began necking and fusing. However, necking and fusion did not completely occur because zirconia requires a higher temperature to achieve full densification. This result corresponded with the volumetric shrinkage of the blocks. Specifically, the highest volumetric shrinkage would result in the highest densification.

3.3 Mechanical Properties of Pre-Sintered Zirconia Block

The values for the Vickers hardness of pre-sintered block 20 nmZ and 60 nmZ with 5 mm and 20 mm thickness respectively, are shown in Figure 6. The 20 nmZ block was harder than the 60 nmZ block. The Vickers hardness values of both blocks consistently increased with increasing sintering temperature. This result is in accordance with the densification behavior of each block. Specifically, the hardness values are directly proportional to the density properties of both zirconia blocks. However, in contrast to the negligibly different shrinkage and density properties of the 20 nmZ and 60 nmZ blocks, the Vickers hardness values of the two blocks were significantly different. This result can be attributed to the limited shrinkage during sintering obtained by 60 nmZ blocks. The large particles of the 60 nmZ block might require higher sintering temperature to eliminate interparticle pores in the structure by atomic diffusion. The larger the particle size, the higher the activation energy required to induce the driving force for sintering, thus a high sintering temperature is preferred [17]. Due to longer diffusion distances of the larger particles compared to the finer particles, the larger particles were unable to eliminate the pores at a relatively low temperature as the finer particles. The blocks might require high sintering temperature, prolonged soaking time, or a low heating rate to complete diffusion and necking among particles to improve the mechanical properties of 60 nmZ block [18]. Moreover, colloidal stability of the slurry has to be enhanced by extending the duration of ball milling, adjusting the zirconia suspension to the appropriate pH, and adding the appropriate amount of dispersant to the slurry. This will create a homogeneous and dense green block with minimum porosity which will sinter well at lower temperatures.

High hardness facilitates the handling of brittle ceramics, such as zirconia, during machining. However, increasing hardness will affect the machinability of the blocks and increase tool wear [19]. The machining, including milling, grinding, and trimming, of hard blocks may introduce surface flaws and microcracks on the machined restoration framework and compromise the mechanical properties of the prepared dental restoration [5, 20]. Thus, an appropriate pre-sintering temperature is crucial to obtain blocks with the appropriate hardness for facile handling and milling.

The 20 nmZ block had Vickers hardness values that ranged from 0.9 GPa to 1.27 GPa. This range is within that of the commercial blank, IPS e.max ZirCAD (Ivoclar Vivadent), and of the commercial dental blanks used by Alao and Yin [7]. The results of this study showed that the mechanical properties of the 20 nmZ block are superior to those of the 60 nmZ block because of the homogenous, dense, fine particles of the parent 20 nmZ powder. The low solid loading of the 20 nmZ powder during colloidal processing induced the zirconia particles to disperse and homogenously pack. However, the 20 nmZ block could not be cast at a particular thickness. The 60 nmZ block was too soft and might not be suitable for machining. A morphological study must be conducted to identify the problem with grain structure that caused the low hardness of the 60 nmZ block. Nonetheless, the use of zirconia powders with small particle sizes could enhance densification kinetics during sintering at low temperatures and yield zirconia blocks with the appropriate density and hardness.

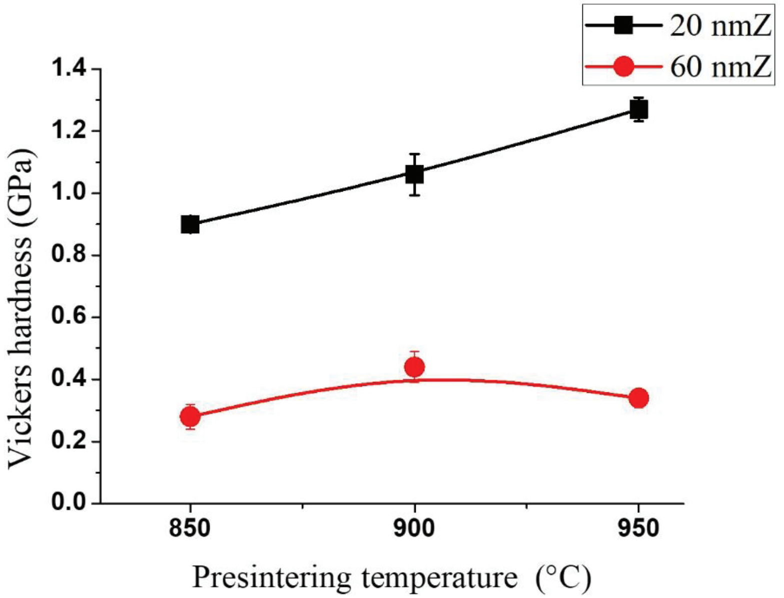

Figure 6: Vickers hardness of zirconia block at different pre-sintering temperatures

4.0 CONCLUSION

Colloidal suspensions with high solid loading could be prepared with 60 nmZ powder. The 60 nmZ blocks could be cast with high thicknesses of up to 20 mm. However, the pre-sintered 60 nmZ blocks exhibited low densification and hardness. In order to avoid shrinkage during casting, the 20 nmZ blocks should be cast with thicknesses of less than 5 mm. Nevertheless, the 20 nmZ blocks exhibited excellent density and hardness with the appropriate volumetric shrinkage when pre-sintered at 850 °C. The 20 nmZ zirconia blocks pre-sintered at 850 °C exhibited good densification and volumetric shrinkage comparable with the 20 nmZ block pre-sintered at 900 °C. In addition, the hardness of the 20 nmZ block was comparable with that of a commercial zirconia block and was suitable for machining.

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REFERENCES

[1] V. Lughi and V. Sergo, "Low temperature degradation -aging- of zirconia: A critical review of the relevant aspects in dentistry", *Dental Materials*, vol. 26, no. 8, pp. 807–820, 2010.

[2] A. Jemat, M.J. Ghazali, M. Razali, Y. Otsuka, and A. Rajabi, "Effects of TiO2 on microstructural, mechanical properties and in-vitro bioactivity of plasma sprayed yttria stabilised zirconia coatings for dental application", *Ceramics International*, vol. 44, no. 4, pp. 4271–4281, 2018.

[3] C. Piconi and G. Maccauro, "Zirconia as a ceramic biomaterial", *Biomaterials*, vol. 20, no. 1, pp. 1–25, 1999.

[4] I. Denry and J.R. Kelly, "State of the art of zirconia for dental applications", *Dental Materials*, vol. 24, no. 3, pp. 299–307, 2008.

[5] O.S. Abd El-Ghany and A.H. Sherief, "Zirconia based ceramics, some clinical and biological aspects: Review", *Future Dental Journal*, vol. 2, no. 2, pp. 55–64, 2016.

[6] A.R. Alao, R. Stoll, X.F. Song, T. Miyazaki, Y. Hotta, Y. Shibata and L. Yin, "Surface quality of yttria-stabilized tetragonal zirconia polycrystal in CAD/CAM milling, sintering, polishing and sandblasting processes", *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 65, pp. 102–116, 2017.

[7] A.R. Alao and L. Yin, "Nano-scale mechanical properties and behavior of pre-sintered zirconia", *Journal of the Mechanical Behavior of Biomedical Materials*, vol. 36, pp. 21–31, 2014.

[8] F.T. Filser, "Direct ceramic machining of ceramic dental restorations," Ph.D. dissertation, Department of Materials, Swiss Federal Institute of Technology, Zurich, Switzerland, 2001.

[9] N.F. Amat, A. Muchtar, M.J. Ghazali and N. Yahaya, "Suspension stability and sintering influence on yttria-stabilized zirconia fabricated by colloidal processing", *Ceramics International*, vol. 40, no. 4, pp. 5413–5419, 2014.

[10] C.H. Chin, A. Muchtar, C.H. Azhari, M. Razali and M. Aboras, "Optimization of pH and dispersant amount of Y-TZP suspension for colloidal stability", *Ceramics International*, vol. 41, no. 8, pp. 9939–9946, 2015.

[11] M. Aboras, A. Muchtar, C.H. Azhari, N. Yahaya and C.C. Hao, "Influence of processing on mechanical properties of 3Y-TZP for dental applications", *Jurnal Teknologi*, vol. 78, no. 11–3, pp. 7–12, 2016.

[12] A. Shafeiey, M.H. Enayati and A. Al-Haji, "The effect of slip casting parameters on the green density of MgAl2O4 spinel", *Ceramics International*, vol. 43, no. 8, pp. 6069–6074, 2017.

[13] K.S. Cho, J. Kim, S.Y. Lee, J.P. Oh and S. Il Park, "Shape forming of alumina by step pressure-vacuum hybrid slip casting", *Applied Mechanics and Materials*, vol. 217, pp. 1899–1902, 2012.

[14] I. Denry and R. Kelly, "Emerging ceramic-based materials for dentistry", *Journal of Dental Research*, vol. 93, no. 12, pp. 1235–42, 2014.

[15] N.F. Amat, A. Muchtar and M.J. Ghazali, "Effect of pH of suspension and mechanical treatment on nanosized zirconia dispersion", *Journal of Mechanical Engineering*, vol. SI 4, no. 3, pp. 10-19, 2017.

[16] A. Rafferty, A.M. Alsebaie, A.G. Olabi and T. Prescott, "Properties of zirconia-toughened-alumina prepared via powder processing and colloidal processing routes", *Journal of Colloid and Interface Science*, vol. 329, no. 2, pp. 310–315, 2009.

[17] L. Jiang, Y. Liao, Q. Wan and W. Li, "Effects of sintering temperature and particle size on the translucency of zirconium dioxide dental ceramic", *Journal of Materials Science: Materials in Medicine*, vol. 22, no. 11, pp. 2429–2435, 2011.

[18] M.Y. Zakaria, A.B. Sulong, M.I. Ramli, B. Ukwueze, W.S.W. Harun and R.L. Mahmud, "Fabrication of porous titanium- hydroxyapatite composite via powder metallurgy with space holder method", *Journal of Advanced Manufacturing Technology*, vol. 12, no. 1, pp. 37–48, 2018.

[19] R.G. Luthardt, M. Holzhuter, O. Sandkuhl, V. Herold, J.D. Schnapp, E. Kuhlisch and M. Walter, "Reliability and properties of ground Y-TZP-zirconia ceramics", *Journal of Dental Research*, vol. 81, no. 7, pp. 487–491, 2002.

[20] T.-H. Lan, C.-H. Wang, K.-K. Chen, M.-C. Wang, and H.-E. Lee, "Milling properties of low temperature sintered zirconia blocks for dental use", *Materials Science and Engineering: C*, vol. 73, pp. 692–699, 2017.