Microwave Sintering of Yttria-Stabilised Zirconia

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Abstract. 3mol% yttria-stabilised tetragonal zirconia polycrystal (3Y-TZP) ceramic is widely used as engineering material owing to its great strength. Recently, 3Y-TZP ceramic is receiving great response in dental restoration due to its bio-compatible properties and aesthetic appearance. To achieve high bulk density, high sintering temperature (> 1500 °C), low firing rate (10 °C/min) coupled with long dwelling period (2 hours) are required in conventional sintering (CS) to fabricate 3Y-TZP ceramic which resulted in high energy consumption. Therefore, non-conventional sintering technique with low energy consumption such as microwave (MW) sintering is worth to explore as almost 100 % of electromagnetic energy is converted into heat largely within the sample itself. The commercial available 3Y-TZP powder was MW fired from 1200 °C to 1400 °C. The 3Y-TZP ceramics fabricated via MW sintering was compared with those CS samples by assessing the densification and mechanical properties of the ceramics. It was revealed that the total sintering time was reduced by 75 % for microwave-sintered 3Y-TZP ceramics to achieve relative density of ~ 98 %, Young’s modulus of ~ 205 GPa, and Vicker’s hardness of 14.15 GPa at low sintering temperature (1200 °C) as compared to CS ceramic that required temperature above 1250 °C. However, the properties of both MW and CS-sintered ceramics are comparable when the sintering temperature exceeds 1250 °C.

1. Introduction

Among other biomaterials, 3Y-TZP ceramic possess several benefits in orthopaedics for knee and hip prosthesis including excellent corrosion resistance, excellent elastic modulus, outstanding fracture toughness, promising wear resistance, chemical inertness and high melting temperature [1,2]. Besides orthopaedic application, 3Y-TZP is widely used for restoration of bridge and crown due to their excellent mechanical properties and their aesthetic properties which make them able to mimic the natural tooth colour [3]. Normally, 3mol % of Yttria (Y₂O₃) is added to stabilize zirconia materials, which is identified as 3mol% yttria-stabilized tetragonal zirconia polycrystalline ceramic. The stabilized (t) phase is accountable for such optimized mechanical performance owing to the occurrence of transformation toughening mechanism [4]. Therefore, both strength and toughness of ceramics are improved by reason of the dissipation of energy from crack propagation both in overcoming the compressive stress owing to volume expansion [5]. Consequently, it is extremely imperative to ensure the material is thoroughly stabilized in the (t) phase.

In order to achieve high densification for structural application (> 95 %) and promising mechanical properties, CS required high sintering temperature (> 1500 °C), long dwelling time (2 h) and low ramp rate (10 °C/min) that usually causes grain coarsening in the specimen which leads to deterioration of physical, mechanical properties and ageing resistance [6]. It is even challenging to obtain fully densified materials for starting powder with nano range particles [7].

Hence, there are various routes available to manufacture 3Y-TZP, likewise the sintering additives usage [8], spark plasma sintering [9], pressure assisted sintering [10], colloidal powder processing...
with control of particle sizes distribution [11], and pulsed electric current sintering (PECS) [12]. However, due to complexity of the device and the use of expensive chemicals, it is labor intensive and difficult to implement these sintering approaches to fabricate ceramic materials.

Recently, concerning about the sintering time and energy consumption, as well as improvement of mechanical properties, numerous approaches in the area of sintering have arisen. For these reasons, there are growing interests in exploring the alternative sintering approaches for ceramic fabrication which are more time saving, commercially advantageous and environmental friendly. A new and straight-forward sintering approach using MW heating can be an alternative for zirconia ceramics consolidation. In several studies, homogenous fine-grained microstructure [13] of 3Y-TZP ceramic with improved densification [14] could be produced through MW sintering process at lower sintering temperatures, shorter dwell times and higher ramp rates [15, 16]. However, there is still lack of study on the influence of MW sintering parameters towards the fabrication process of 3Y-TZP ceramic. In addition, understanding on the effect of sintering parameters such as sintering temperature, heating rate and holding time of MW sintering towards the ceramic properties are of great interest.

The primary purpose of this research is to fabricate 3Y-TZP ceramics through MW sintering with various sintering temperatures. Comparisons were done between MV samples and CS samples from in terms of sintering time, densification and mechanical properties.

2. Experimental
The commercial 3Y-TZP powder manufactured by Kyoritsu in Japan, KZ-3YF that possessed approximately 0.1 wt% with TiO_2, SiO_2, and Al_2O_3 as the minor impurities, and Fe_2O_3 as the major impurities. The specific surface area and mean particle diameter of 3Y-TZP powder are 12 m²/g and 300 nm respectively. Powder was uniaxially pressed at 0.3 MPa into two forms including rectangular bars of 3 g per piece and discs of 2.5 g per piece. The green specimens were then subjected to cold isostatic pressing at 200 MPa with holding time of 60 seconds. Green bodies were fired via MW sintering at 1200 °C – 1400 °C with 1 min dwelling time and ramp rate of 20 °C/min in a multimode microwave furnace running 6kW and 2.45 GHz. Silicon Carbide (SiC) papers were used to grind discs samples with 180 (coarse), 240, 600, 800, and 1200 (fine) grades. Polishing was carried out to obtain optical reflective surface by using 1µm – 6 µm diamond paste respectively prior to characterization. The bulk densities of the sintered specimens were measured on the basis of Archimedes’ principle by water immersion. The relative densities were yielded by referring to the 6.07 g/cm³ as the density of 3Y-TZP theoretically. Mechanical testing for determination of Vicker’s hardness (H_v) with the indentation load of 10 kgf and held in place for 10 seconds, Young’s modulus (E) and fracture toughness (K IC ) with equation by Niihara et. al. [18] were done. The current experiment results were compared to the results of CS samples prepared from previous work [17].

3. Results and Discussion
As illustrated in Figure 1, MW was more useful in enhancing 3Y-TZP densification at a range of lower temperatures from 1200 °C to 1400 °C while compared to the CS. It is notable that 3Y-TZP sintered through MW possessed relative density > 97 % at 1200 °C while the relative density of 3Y-TZP from CS only achieved > 93 % at the similar temperature. As for CS method, densification occurs rapidly between the range of 1200 °C – 1250 °C and levels off up to 97.8 % as the temperature is further elevated. Both trends indicate that, the relative densities are increased with increasing firing temperatures with small increments after achieving the peaks. MW technique is able to enhance the ionic forward diffusion and hence speed up the firing process, consequently results in densification and grain coarsening in matrix. In fact, firing process consists of grain growth stage and densification stage [19]. Generally, if firing temperature exceeds the onset of densification temperature, there will be slight density increment attributed to the sintering final stage whereby less pores are eliminated and the grain coarsening begins [20].


As illustrated in Figure 2, it is observed that the E increases with increasing firing temperature. For both MW and CS sintered 3Y-TZP, the trends of E are quite similar to the density trends. Through MW sintering method, enhancement ceramics matrix stiffness can be achieved, predominantly as 3Y-TZP exhibited higher E values than CS method indicated by the attainment of consistent E value of approximately 208.09 GPa throughout the whole sintering regime. On the contrary, 3Y-TZP sintered through CS method could only achieve 178.32 GPa at 1200 °C and achieved E values of > 200 GPa at temperatures ranging between 1250 °C – 1500 °C.

Based on Figure 3, at 1200°C, 3Y-TZP sintered through CS could only achieve hardness (H_v) of 12.25 GPa whereas higher hardness, 14.15 GPa is attained by MW. When there was elevation of temperatures from 1200 °C to 1250 °C, H_v of CS 3Y-TZP improved due to increased bulk density. The H_v of all samples are in the tolerable range between 9 GPa to 15 GPa. MW-sintered 3Y-TZP achieved outstanding H_v of > 14 GPa throughout the whole sintering process. As for 3Y-TZP sintered by CS method, H_v values fluctuated between 13.28 GPa – 14.38 GPa between the firing temperatures of 1250 °C to 1400 °C. After reaching a peak, there is slight decrement of H_v for CS-sintered 3Y-TZP. The H_v decrement could be attributed to the grain growth. H_v of 3Y-TZP is also grain size dependent where
3Y-TZP with finer grain size was reported to attain increased $H_v$ [21]. Since the densities for CS-sintered 3Y-TZP sintered at 1400 °C and 1500 °C are nearly similar, then grain size seems to be the influential issue for the decrement of hardness.

![Figure 3](image3.png)

**Figure 3.** Relationship of firing temperature and Vicker’s hardness of 3Y-TZP between CS and MW sintering.

The influence of CS and MW firing techniques on the fracture toughness ($K_{ic}$) of YSZ was not very pronounced as shown in Figure 4. CS-sintered 3Y-TZP showed an elevating trend of fracture toughness with increasing firing temperature from 1200 °C at 4.68 MPa.m$^{1/2}$ up to 1350 °C and attained 5.07 MPa.m$^{1/2}$ of peak toughness. Any further sintering with higher temperature up to 1450 °C will cause deterioration of $K_{ic}$ before an elevation of $K_{ic}$ to 5.03 MPa.m$^{1/2}$ at 1500 °C. In general, $K_{ic}$ values of more than 4.9 MPa.m$^{1/2}$ were attained for the CS-fired bodies when sintering processes were carried out above 1350 °C. On the other hand, $K_{ic}$ of MW-sintered samples was able to attain 4.72 MPa.m$^{1/2}$ at 1200 °C. The $K_{ic}$ values obtained by MW-sintered samples were almost constant for all sintering temperatures which were from 4.7 MPa.m$^{1/2}$ to 4.8 MPa.m$^{1/2}$. $K_{ic}$ values were very much depending on the (t) grains stability [22]. The greater metastability and instantaneous response of (t) grains to oppose the propagating cracks during the indentation tests are indicated by higher $K_{ic}$ values.

![Figure 4](image4.png)

**Figure 4.** Relationship between firing temperature and fracture toughness of fired 3Y-TZP between CS and MW sintering.
From Table 1, total sintering time estimation based on various sintering methods is done. It is notable that, the sintering time is greatly diminished by ~75% when MW sintering technique is adopted. MW-sintered samples possess more promising mechanical performances than CS-sintered 3Y-TZP at lower temperatures, higher ramp rates, shorter dwelling times. As a result, the energy consumption and production time are reduced. These achievements can be beneficial in improving the productivity and cost saving for any ceramic product manufacturer by using MW sintering approach.

Table 1. Comparison between the sintering time of sintering approaches used in this work.

| Sintering method | Heat rate (ºC/min) | Starting temperature (ºC) | Firing temperature (ºC) | Holding time (min) | Time consumed | Time saving % |
|------------------|--------------------|--------------------------|------------------------|-------------------|---------------|---------------|
| Conventional     | 10                 | 26                       | 1400                   | 120               | ~ 4 h 18 min  | ~ 75%         |
| Microwave        | 20                 | 26                       | 1200                   | 1                 | ~ 1 hr        |               |

4. Conclusion
In current research, highly densed 3Y-TZP ceramics with promising mechanical properties had been successfully fabricated with processing cycle-time reduction of up to 75% at lower sintering temperature. In particular, as compared to CS-sintered samples, ceramics MW sintered at 1200 ºC attained high relative density of above 95%, Young’s modulus of ~ 205 GPa, hardness of 14.15 GPa and fracture toughness of 5.03 MPa.m$^{1/2}$. This study also revealed when sintering temperature exceeds 1250 ºC, the 3Y-TZP samples had null effects towards MW with the similar properties as those of CS.

References
[1] Piconi C and Maccauro G 1999 Zirconia as a ceramic biomaterial, Biomaterials 20 1–25.
[2] Soon G, Pingguan-Murphy B, Lai K W and Akbar S A 2016 Review of zirconia-based bioceramic: surface modification and cellular response, Ceram. Int. 42 12543–12555.
[3] Vaderhobli R and Saha S 2015 Microwave sintering of ceramics for dentistry: part 2, Dentistry, 5 1.
[4] Mecmeeking R M and Evans A G 1982 Mechanics of transformation-Toughening in brittle materials, J. Am. Ceram. Soc. 65 242–246.
[5] Piconi C and Acauro G M 1991 Zirconia as a ceramic biomaterial, Biomaterials 20 1-25.
[6] Ramesh S, Sara Lee K Y, Tan C Y and Tarlochan F 2018 Ceramics International 44 19639 – 19645.
[7] Anselmi-Tamburini U, Garay J E and Munir Z A 2006 Fast low-temperature consolidation of bulk nanometric-ceramic materials, Scripta Mater. 54 823–828.
[8] Kuang X, Carotenuto G and Nicolais L 1997 Review of ceramic sintering and suggestions on reducing sintering temperatures, Advanced Performance Materials. doi: 10.1023/A:1008621020555.
[9] Gao L, Hong J S, Miyamoto H, Torre S D D L 2000 Bending strength and microstructure of Al2O3ceramics densified by spark plasma sintering, Journal of the European Ceramic Society. doi: 10.1016/S0955-2219(00)00086-8.
[10] He Z and Ma J 2000 Grain-growth rate constant of hot-pressed alumina ceramics, Mater. Lett.
[11] Barringer E A and Bowen H K 1982 Formation, Packing, and Sintering of Monodisperse TiO2Powders, J. Am. Ceram. Soc.
[12] Zhou Y, Hirao K, Yamauchi Y, and Kanzaki S 2004 Densification and grain growth in pulse electric current sintering of alumina, J. Eur. Ceram. Soc.
[13] Demirskyi D, Agrawal D and Ragulya A 2013 Comparisons of grain size-density trajectory
during microwave and conventional sintering of titanium nitride, *J. Alloy. Comp.* 581 498–501.

[14] Monaco C, Prete F, Leonelli C, Esposito L, and Tucci A 2015 Microstructural study of microwave sintered zirconia for dental applications, *Ceram. Inter.* 41 1255-1261.

[15] Ai Y, Xie X, He W, Liang B and Chen W 2014 Microstructure and properties of Al₂O₃-ZrO₂ ceramics prepared by microwave sintering, *Key Eng. Mater.* 633 193–197.

[16] Presenda A, Salvador M D, Peñaranda-Foix F L, Moreno R and Borrell A 2015 Effect of microwave sintering on microstructure and mechanical properties in Y-TZP materials used for dental applications, *Ceram. Int.* 41 7125–7132.

[17] Ting C H, Ramesh S, Lwin N and Sutharsini U 2016 Sintering properties and low-temperature degradation behaviour of Y-TZP ceramics *J. Ceram. Proc. Res.* 17 1265-1269.

[18] Niihara K, Morena R and Hasselman D 1982 Evaluation of KIC of brittle solids by the indentation method with low crack-to-indent ratios, *J. Mater. Sci. Lett.* 1 13-16.

[19] Barba, Clausell C, Feliu C and Monzo M 2004 *Journal of the American Ceramic Society* 87(4) 571 – 577.

[20] Gibson I R, Ke S, Best S M and Bonfield W 2001 Effect of powder characteristics on the sinterability of hydroxyapatite powders. *J. Mater. Sci.: Mater.Med.* 12, 163-171.

[21] Ran S, Vleugels J, Huang S, Vanmeensel K, Blank D H A and Winnubst L 2010 Manipulating microstructure and mechanical properties of CuO doped 3Y-TZP nano ceramics using spark plasma sintering, *J. Eur. Ceram. Soc.* 30 899-904.

[22] Lawson S 1995 Environmental degradation of zirconia ceramics, *J. Eur. Ceram. Soc.* 15 485-502.