Effects of sintering profile on the densification behaviour of forsterite ceramics

S. Ramesh[a,]*, S.S. Tan[a], L.T. Bang[a], C.Y. Tan[a], J. Purbolaksono[a], S. Ramesh[b] and W.D. Teng[c]

[a]*Center for Advanced Manufacturing & Material Processing, Department of Mechanical Engineering, University of Malaya, Kuala Lumpur 50603, Malaysia*
[b]*Centre for Ionics University of Malaya, Department of Physics, Faculty of Science, University of Malaya, 50603 Kuala Lumpur, Malaysia*
[c]*Ceramics Technology Group, SIRIM Berhad, Shah Alam 40911, Malaysia*

The sintering behaviour of forsterite prepared by mechanical activation and heat treatment has been studied. The green compacts were sintered using two different sintering profiles. The first was based on the conventional sintering (CS) profile in which the powder compact was sintered at the desired temperature, holding for 2 hours and then cooled to room temperature. The second was based on a two-step sintering (TSS) profile in which the samples were sintered at a temperature T1 = 1400 ºC for 6 minutes and then continued sintering at a lower temperature T2 (i.e. 750 ºC, 850 ºC and 950 ºC) for 15 hours before cooling to room temperature. It was found that a minimum ball milling time of 7 h was necessary to completely eliminate secondary phases from developing in the forsterite matrix after sintering at 1400ºC. The sintering study indicated that the CS profile was effective in enhancing the fracture toughness of the sintered body when sintered at 1400 ºC but this was accompanied by exaggerated grain growth. In addition, it was found that sintering below 1400 ºC was not effective in preventing the formation of secondary phases in the sintered body. On the other hand, the TSS profile (T1 = 1400 ºC, T2 = 950 ºC) was found to be most beneficial in promoting densification and more importantly, to suppress grain coarsening of the forsterite body.

Key words: Forsterite, Sintering, Mechanical properties.

Introduction

Hydroxyapatite (HA) which comprise of 60% of main inorganic phase based bioceramic of human bone is an excellent choice for biomedical implant due to its superb biocompatibility in addition to strengthen the bone [1-3]. HA is proven to be able to provide a stable crystalline phase of calcuim phosphate (CaP) within body fluids. Nevertheless, the low fracture toughness of HA (0.7-1.2 MPam$^{1/2}$) compared to human cortical bone (2-12 MPam$^{1/2}$) [3] and femur bone (5.09 MPam$^{1/2}$) imposes a challenge to produce load bearing implants such as total hip replacement [4]. While many researchers have tried to improve the mechanical properties of HA by introducing additives into the synthesis process or reinforcing phase to make composite, the improved HA was never been reported to match the mechanical properties of human bone.

On the other hand, forsterite (Mg$_2$SiO$_4$) which belongs to the group of olivine [5], has a higher fracture toughness compared to HA. It was reported in the literature [6] that minerals such as magnesium and silicon are also essential elements in human body which promotes the development of human bones. Silicon is also one of the key minerals that influences the mineral metabolism, enhances estrogenic activity as well as insulin secretion which help in monitoring bone growth [6, 7]. Forsterite has been introduced as a potential biomaterial for implants due to its superior mechanical properties. Forsterite exhibits a relative high fracture toughness ranging from 2.4 MPam$^{1/2}$ to 5.16 MPam$^{1/2}$ [8-10] mimicking the human femur bone fracture toughness.

Further improvement in fracture toughness can be realized through careful processing of the ceramic to produce fine microstructure, in the nanometer range [10]. In addition, Webster et.al [11] reported that nano-structured bioceramic enhances osteoblast adhesion and improve the overall efficiency of the medical implant. However, synthesis of the pure dense nanostructure forsterite by using conventional sintering technique has been proven challenging. Different methods have been employed to synthesize forsterite including sol-gel method [9, 12, 13] and mechanical activation via ball milling [5, 10, 14, 15]. In the former method, the as-synthesized powders are normally subjected to long heat treatment cycles followed by sintering at high temperatures to obtain forsterite powders with good properties. On the other hand, the mechanical activation method has been widely used to synthesize nanocyrstalline forsterite due to the cascading motion

*Corresponding author:
 Tel : +603-7967-5209
 Fax: +603-7967-7621
 E-mail: ramesh79@um.edu.my

of the milling media which is effective in simulating chemical reactions between two or more phases [16].

The other issue often occur during sintering is the rapid grain growth which take place during the final-stage of the sintering process. To overcome this problem, Chen and Wang [17] proposed two-step sintering (TSS) technique to restrain the grain growth. The purpose of the TSS is to maintaining or controlling the grain growth while enabling the nanoparticle to obtain enough heat energy for the densification process. On the other hand, the conventional sintering (CS) involves sintering the compact from room temperatures to a desired temperature and hold for a certain soaking time to achieve densification. However, the high sintering temperatures and long duration in CS normally result in high density couple with abnormal grain growth [18].

The objectives of this research was firstly to optimize the mechanical activation process via ball milling method, focusing mainly on the milling duration, to promote phase-pure forsterite ceramic after sintering. Secondly, the sintering behaviour of optimized powder was evaluated by using two different sintering profiles i.e. the conventional sintering and a two-step sintering.

Experimental Procedure

Sample Preparation

Mechanical activation method was used to produce pure forsterite as described by several authors [8, 10, 19]. In the present work, magnesium oxide (97% purity, Merck) and talc ($Mg_3Si_4(OH)_2$; 99% purity, Sigma-Aldrich) was used at a weight ratio of Talc : MgO = 1.88 : 1 to produce stoichiometric composition of forsterite powder [8]. Ethanol was used as a mixing medium. The mixture was sonicated for 30 minutes to produce a homogeneous mixture. The mechanical activation was achieved by subjecting the resulting slurry to ball milling at a fixed rotation speed of 300 rpm for various durations of 3, 5 and 7 hours. The milling process was performed in a sealed plastic vials with 2 mm zirconia balls as the milling media. The as-milled powders were subsequently dried in an oven at 60 ℃ for 12 hours to evaporate the ethanol. The dried powders were sieved through a 212 μm sieve to remove any hard agglomerates.

The initial study was to determine the minimum ball milling duration to produce phase pure forsterite in the sintered body. To achieve this, it was decided to sintered the powders which were prepared from the 3, 5 and 7 hours ball milling at 1400 ℃. This temperature was chosen based on the work reported by Lee et al. [20] who found that forsterite sintered at 1400 ℃ yielded optimal mechanical properties. Once the minimum ball milling duration was established, more powders were subsequently prepared according to the steps described above for further study.

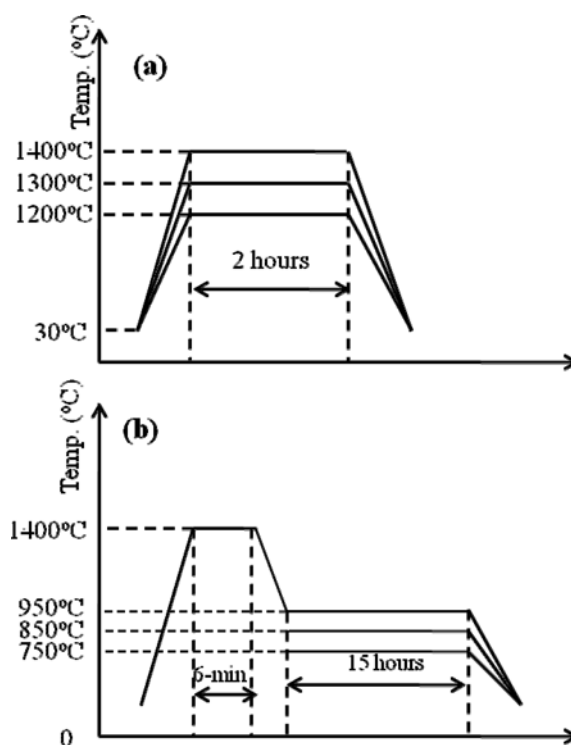For the sintering study, green compact was uniaxially

Fig. 1. The sintering profiles of (a) conventional sintering (CS) and (b) two-step sintering (TSS).

pressed using a bench-top hydraulic press to produce disc sample (20 mm in diameter) and rectangular bar sample (3 mm × 12 mm × 30 mm) followed by cold isostatic pressing at 200 MPa. The green samples were then sintered in air atmosphere based on two different sintering profiles. For the conventional sintering (CS) profile, the samples were sintered in a single step at a selected temperature (i.e. 1200 ℃, 1300 ℃ and 1400 ℃) using a ramp rate of 10 ℃/min., holding time of 2 hours and then cooling to room temperature. In the two-step sintering (TSS) profile, the green compacts were sintered at temperature T1 = 1400 ℃ for 6 minutes followed by continuing sintering at a lower temperature T2 (i.e. ranging from 750 ℃, 850 ℃ and 950 ℃) for 15 hours prior to cooling to room temperature. The temperature T1 was kept constant whereas the T2 varied. In all case, the sintering ramp rates were kept constant at 10 ℃/min. Fig. 1 illustrates both CS and TSS profiles used in this research. The sintered disc samples were ground and polished on one side for further characterization.

Characterization

The phase compositions of sintered samples were characterized using X-ray diffractometer (XRD: PANalytical Empyrean, Netherlands) operating at 45 kV and 40 mA with Cu-Kα as the radiation source. XRD patterns were recorded in the 2θ range of 20 ° - 60 ° at a step size of 0.02 ° and a scan speed of 0.5 °/min. The recorded XRD patterns were compared to

standard reference JCPDS-ICDD (Joint Committee of Powder Diffraction Standard-International Centre for Diffraction Data) files. The average crystallite size of the sintered samples was calculated by using the Scherrer's equation [21].

The relative density of sintered disc samples were measured by water immersion technique based on Archimedes's principle using electronic balance (Shimadzu AY220, Japan). The relative density of forsterite was calculated by taking the theoretical density of forsterite at 3.221 g/cm³. The micro-hardness (H_v) of the polished sintered compacts was measured using Vickers hardness tester (Mitutoyo AVK-C2, USA). A load of 1.96 N (0.2 kg) was applied for duration of 10 seconds to produce the indentation. The fracture toughness (K_{Ic}) was computed using the indentation crack length according to the equation derived by Niihara [22]. Five indentations were performed on each samples and the average value was taken. Young's Modulus of sintered rectangular bar samples was determined via sonic resonance method using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium) [23].

For the SEM observation, the polished samples were thermally etched at 50 °C below the sintered temperature, at a ramp rate of 10 °C/minute and a holding time of 30 minutes to delineate the grain boundaries. The microstructure of polished sample was characterized using a table-top scanning electron microscope (SEM: Hitachi TM3030 Tabletop Microscope, Japan) at an accelerating voltage of 15 kV. The average grain size was determined from the SEM images via the line intercept method [24].

Results and Discussion

The initial study was to determine the minimum ball milling duration to produce phase pure forsterite in the sintered body. The phase analysis of the powders produced at different milling durations and sintered at
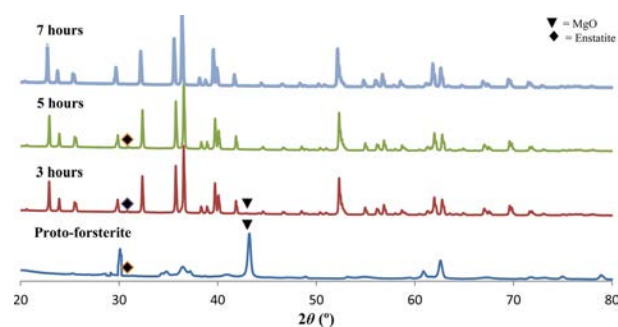

Fig. 2. The effect of ball milling duration on the phase present in the powder sintered at 1400 °C.
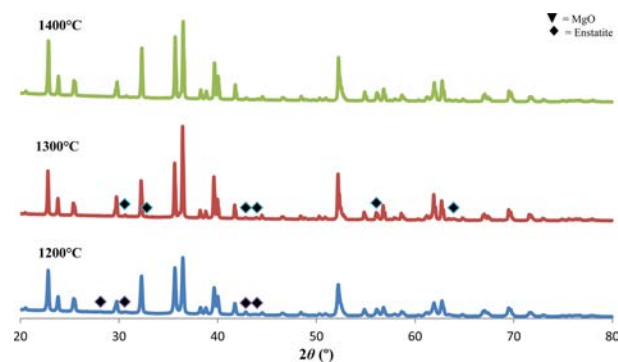

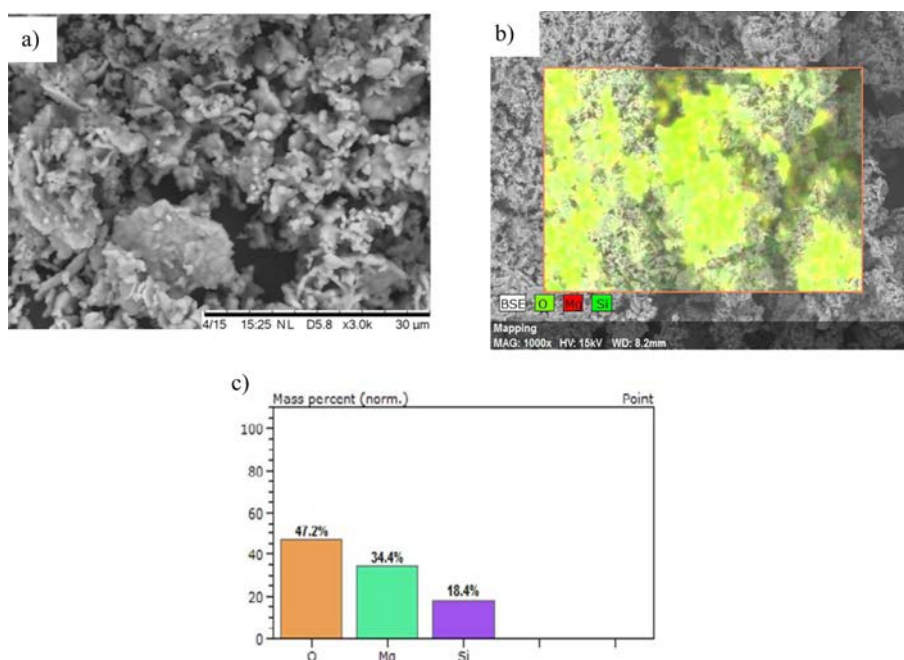**Fig. 3.** XRD patterns of CS samples sintered at different temperature.

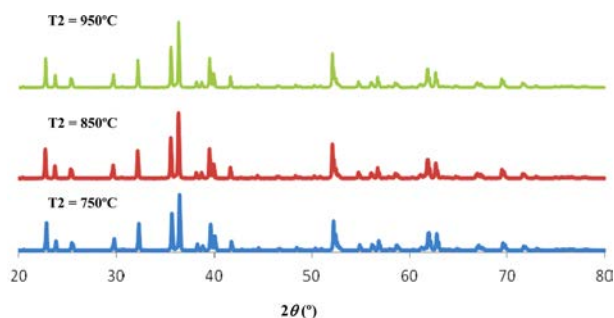**Fig. 4.** The morphology of forsterite powder heat treated at 1400 °C.

Fig. 5. XRD results of TSS profile compacts sintered at T1 = 1400ºC and different T2 temperatures showing the presents of forsterite phase only.

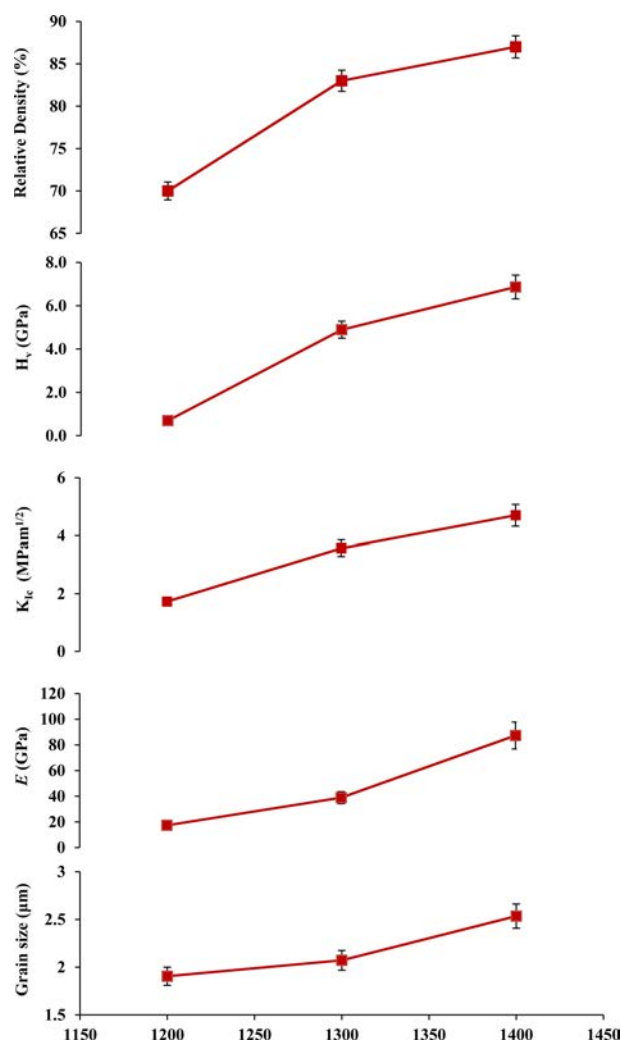**Fig. 6.** The effect of sintering temperatures on the mechanical properties and grain size of CS profile samples.
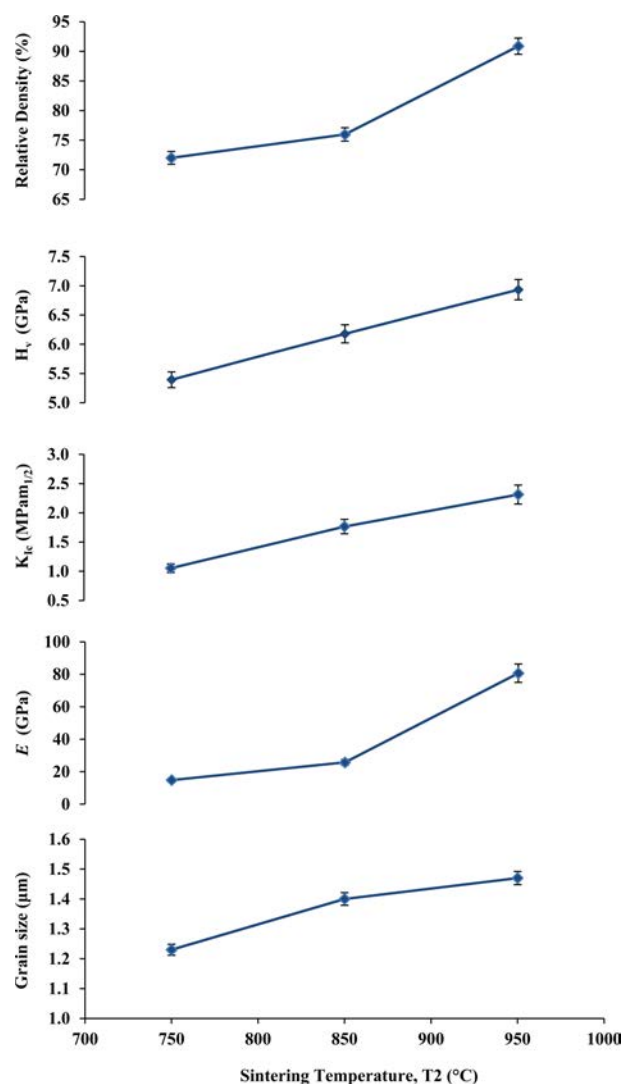

Fig. 7. The effect of sintering temperatures on the mechanical properties and grain size of TSS profile samples.

57 nm.

To study the effect of sintering temperature on the phases present in the forsterite sample, the 7 h ball milled powder was used to prepare samples and subjected to CS profile at temperatures ranging from 1200 ºC, 1300 ºC and 1400 ºC. The XRD results of the CS profile samples are shown in Fig. 3. The results indicated that sintering at 1200 ºC was not effective in preventing the formation of secondary phases such as enstatite and MgO. Sintering at 1300 ºC was also not effective as traces of MgO was present in the sintered body. However, sintering at 1400 ºC was effective in producing a phase-pure forsterite body. This result confirmed that the 7 h ball milling combined with sintering at 1400 ºC are needed to completely eliminate secondary phases within the sintered forsterite. This was also confirmed by EDX analysis performed on the forsterite powders which was sintered at 1400 ºC as shown in Fig. 4. The results indicated that only the

1400 ºC is shown Fig. 2. It was found that the minimum ball milling duration required to produce phase pure forsterite in the sintered body was 7 hours. In addition, the crystalline size of this powder taken at the most prominent XRD peak for the forsterite phase i.e. at $2\theta = 36.6º$ was about 15.5 nm. This value is small compared to that reported in the literatures [14, 15, 25, 26] which typically ranges between 30 nm and
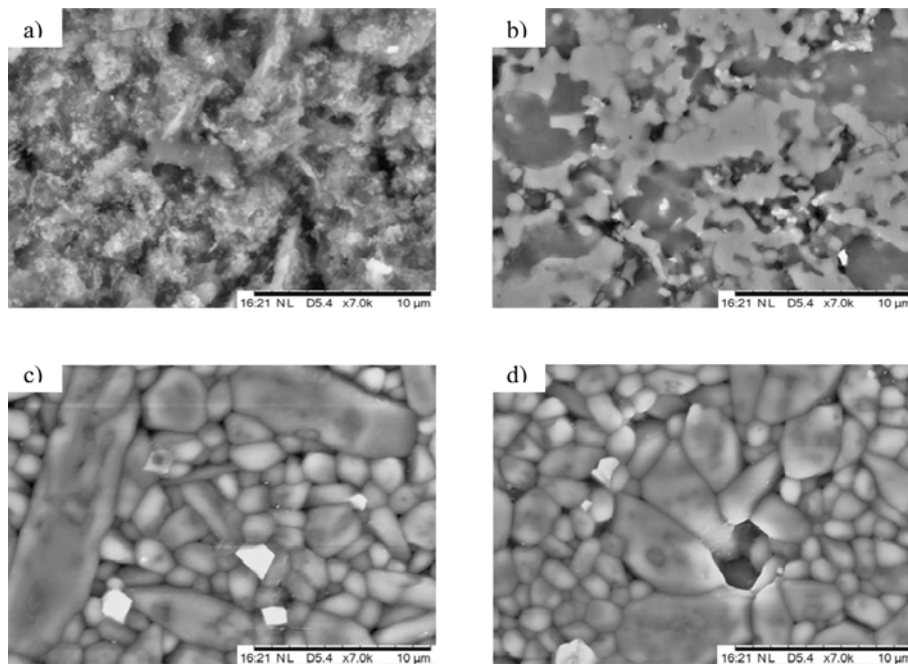
Fig. 8. Microstructural evolution of CS profile samples sintered at (a) 1200 °C, (b) 1300 °C, (c & d) 1400 °C.
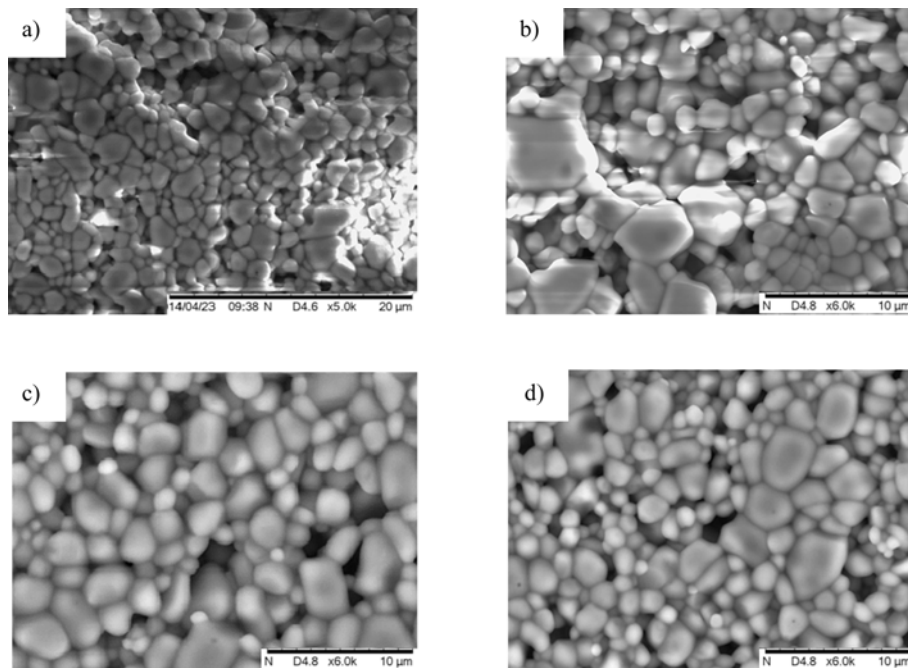

Fig. 9. Microstructural development of TSS profile samples sintered at T1 = 1400 °C and T2 (a) 750 °C, (b) 850 °C and (c & d) 950 °C.

main elements of forsterite i.e. Mg, Si and O were present in the powder.

In the TSS profile, the XRD traces of the sample sintered at T1 = 1400 °C and at various temperature T2 are shown in Fig. 5. The results indicated that a phase pure forsterite was retained in the samples in all the three TSS heating profiles.

The relative density, mechanical properties and grain sizes of the CS and TSS forsterite bodies are shown in Fig. 6 and in Fig. 7, respectively. It was found that for the CS samples (Fig. 6), the relative density of the forsterite increased with increasing sintering temperatures. As the sintering proceeded from 1200 °C to 1400 °C, the Vickers hardness increased sharply from 0.69 GPa to 6.86 GPa, whilst the Young's modulus increased from 17.8 GPa to 87.3 GPa. In addition, the highest fracture toughness of 4.88 MPam$^{1/2}$ was obtained for sample sintered at 1400 °C. This fracture toughness value was 30% greater than the fracture toughness values reported by Fathi and Kharaziha [10]. The grain size was also

found to increased with sintering temperature and reached a maximum value of 2.5 μm when sintered at 1400 °C.

In the case of TSS as shown in Fig. 7, the relative density increased with increasing temperature T2, from 71% at 750 °C to 91% at 950 °C. The 91% relative density obtained for the TSS is higher than that obtained for CS i.e. 87% when sintered at 1400 °C. In general, the mechanical properties of the samples increases with T2 with the highest value of $H_v = 7$ GPa, $E = 80.6$ GPa and $K_{Ic} = 2.3$ MPam$^{1/2}$ being attained at 950 °C. In comparison with the CS sample, the maximum fracture toughness of 2.3 MPam$^{1/2}$ obtained for the TSS sample when sintered at T1 = 1400 °C and T2 = 950 °C is about 52% lower than that recorded for the CS sample sintered at 1400 °C.

The microstructure development of CS compacts is shown in Fig. 8. A distinct forsterite grains were observed at 1400 °C. The grain morphology of the CS samples at 1200 °C and 1300 °C were not clearly visible and this could be associated with the formation of secondary phases as confirmed by XRD in Fig. 3. Although, densification improved with increasing temperature, prolong sintering at 1400°C as in the case of CS resulted in abnormal grain growth as depicted in Fig. 8(c, d). This, however was not the case for the TSS samples as shown in Fig. 9. A dense microstructure comprising of a homogeneous distribution of fine equiaxed grains were observed for the TSS samples sintered at the three T2 temperatures (750, 850 and 950°C). In general, the grain sizes of the TSS samples (ranges from 1.2 to 1.5 μm) are smaller than the CS sintered samples which are well above 2 μm. For example, the grain size obtained from TSS (T1 = 1400 °C and T2 = 950 °C) is 1.5 μm when compared to that obtained for the 1400 °C CS sample of 2.5 μm.

Conclusions

The present research revealed that phase pure forsterite could be produced through mechanical activation by ball milling the starting precursors at a minimum duration of 7 hours. The sintering behaviour of the green compacts prepared from this powder was investigated by using two different profiles i.e. the conventional sintering (CS) and a two-step sintering (TSS). The results showed that in the CS profile, sintering at 1400 °C was required to retain the forsterite phase and to enhance the fracture toughness of the sintered body. This was accompanied by grain coarsening and abnormal grain growth in the conventionally sintered samples. On the other hand, in the TSS profile, a denser body was attained accompanied by a homogenously distributed fine equiaxed forsterite grains was observed for samples subjected to a two step sintering at T1 = 1400 °C for 6 minutes and T2 = 950 °C for 15 hours. Hence, it was revealed that the two-step sintering was

effective in suppressing grain coarsening in forsterite ceramic. The study also showed that a high fracture toughness of 4.88 MPam$^{1/2}$ could be attained for the CS sample as compared to 2.3 MPam$^{1/2}$ in the TSS sample.

Acknowledgments

References

1. M. Sadat-Shojai, M. T. Khorasani, E. Dinpanah-Khoshdargi and A. Jamshidi, Acta Biomater. 9 (2013) 7591-7621.
2. K. S. Katti, Colloids Surf B Biointerfaces, 39 (2004) 133-142.
3. R. Murugan and S. Ramakrishna, Comp. Sci. and Tech., 65 (2005) 2385-2406.
4. C. Wolner, G. E. Nauer, J. Trummer, V. Putz and S. Tschegg, Mater. Sci. and Eng. C, 26 (2006) 34-40.
5. S.J. Kiss, E. Kostiæ, D. Djuroviæ and S. Boškoviæ, Powder Tech., 114 (2001) 84-88.
6. S. Yoshizawa, A. Brown, A. Barchowsky and C. Sfeir, Acta Biomaterialia, 10 (2014) 2834-2842.
7. F. Tavangarian and R. Emadi, Ceram. Inter. 37 (2011) 2275-2280.
8. S. Ramesh, A. Yaghoubi, K.Y. Sara Lee, K.M. Christopher Chin, J. Purbolaksono, M. Hamdi and M.A. Hassan, J. Mech. Behav. Biomed. Mater. 25 (2013) 63-69.
9. M. Kharaziha and M.H. Fathi, J. Mech. Behav. Biomed. Mater. 3 (2010) 530-537.
10. M.H. Fathi and M. Kharaziha, Mater. Letts. 63 (2009) 1455-1458.
11. T.J. Webster, C. Ergun, R.H. Doremus, R.W. Siegel and R. Bizios, Biomaterials 21 (2000) 1803-1810.
12. M.T. Tsai, J. Eur. Ceram. Soc. 22 (2002) 1085-1094.
13. A. Saberi, B. Alinejad, Z. Negahdari, F. Kazemi and A. Almasi, Mater. Res. Bull. 42 (2007) 666-673.
14. F. Tavangarian and R. Emadi, Mater. Res. Bull. 45 (2010) 388-391.
15. F. Tavangarian, R. Emadi and A. Shafyei, Powder Tech. 198 (2010) 412-416.
16. M.H. Fathi and M. Kharaziha, J. Alloys and Comp. 472 (2009) 540-545.
17. I.W. Chen and X.H. Wang, Nature 404 (2000) 168-171.
18. V. Pouchly, K. Maca and Z. Shen, J. Eur. Ceram. Soc. 33 (2013) 2275-2283.
19. K.L. Samuel Lai, C.Y. Tan, S. Ramesh, R. Tolouei, B.K. Yap and M. Amiriyan. The 5th Kuala Lumpur International Conference on Biomedical Engineering 2011 (BIOMED 2011). N.A. Abu Osman, W.A.B. Wan Abas, A.K. Abdul Wahab & H.-N. Ting (Eds.): The International Federation for Medical and Biological Engineering (IFMBE) Proceedings, vol. 35, pp. 102-104, 2011.
20. K.Y. Sara Lee, K.M. Christopher Chin, S. Ramesh, C.Y. Tan, W.D. Teng and I. Sopyan, Adv. Mater. Res. 576 (2012) 195-198.
21. U. Holzwarth and N. Gibson, Nature Nanotech. 6 (2011) 534.
22. K. Niihara, Ceram. Jap. 20 (1985) 12-18.
23. 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).

24. M. I. Mendelson, J. Am. Ceram. Soc. 52 (1969) 443-446.
25. F. Tavangarian and R. Emadi, Inter. J. Modern Phys. B 24 (2010) 343-350.
26. M.H. Fathi and M. Khraziha, Mater. Letts. 62 (2008) 4306-4309.