

Available online at www.sciencedirect.com**ScienceDirect**

Procedia Chemistry 19 (2016) 498 – 504

Procedia
Chemistry

5th International Conference on Recent Advances in Materials, Minerals and Environment (RAMM) & 2nd International Postgraduate Conference on Materials, Mineral and Polymer (MAMIP), 4-6 August 2015

The effect of microwave sintering on the microstructure and properties of calcium phosphate ceramic

Chuthathip Mangkonsu^a, Ishikawa Kunio^b, Lila Bunhan^c
Radzali Otman^{d*}, Ahmad-Fauzi Mohd Noor^{a**}

^aSchool of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang 14300, Malaysia

^bDepartment of Biomaterials, Faculty of Dental Science, Kyushu University, 3-1-1 Maidashi, Higashiku, Fukuoka 812-8582, Japan

^cDepartment of Industrial Engineering, Faculty of Engineering, Burapha University, Chonburi 20131, Thailand

^dFaculty of Manufacturing Engineering, Universiti Teknikal Malaysia Melaka, Malacca 76100, Malaysia

Abstract

Despite good ability to improved biological affinity and activity of calcium phosphate (CP) ceramic to the surrounding host tissue when implanted, CP ceramic is capable to encourage direct bond with bone as their chemical compositions are similar to the mineral phase of bone. However, the low mechanical property of CP ceramic restricts use in load-bearing applications. Therefore, the primary aim of this study was to fabricate dense CP ceramic via used of microwave sintering analyze the microstructure and mechanical properties comparison to conventional ceramic sintering. The sintered specimens were characterized by their surface microstructure, density measurement and hardness test. The result demonstrated that the density and hardness values of sintered CP ceramic specimens by microwave sintering were higher than conventional sintering. The microstructures of CP ceramic microwave sintered specimens show also better microstructures (analyzed by FESEM technique), with fines grain size and the present of apatite layer growth on the surface when examined with SBF solution. It can be concluded that the microwave sintering enhanced better microstructure and mechanical properties of CP ceramic.

© 2016 The Authors. Published by Elsevier B.V. This is an open access article under the CC BY-NC-ND license (<http://creativecommons.org/licenses/by-nc-nd/4.0/>).

Peer-review under responsibility of School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

Keywords: Bioceramics; calcium phosphate ceramic; microwave sintering

* Corresponding author. Tel.: +0-459-410-11; fax: 0-459-410-11.

** Correspondence to: M. N. Ahmad Fauzi, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia, Penang 14300, Malaysia *E-mail address:* radzali@utem.edu.my (R. Otman.), srafauzi@usm.my (M. N. Ahmad-Fauzi)

1. Introduction

The applications of calcium phosphate (CP) have been used in medical and dentistry for more than 20 years because of their excellent biocompatibility, bioactivity, and osteoconduction characteristics¹. Despite their biological properties being excellent, the disadvantage such as the low degradation rates (in the case of hydroxyapatite, HA), poor mechanical properties, and low osseointegration ability limit their clinical performance². Many attempts have been studied to overcome these disadvantages by used of various techniques to fabricate better property of CP ceramic. Sintering is necessary for all ceramic bodies to produce a microstructure with the required properties. Sintering greatly affect the final product properties since it enhance the optimal chemical composition and final microstructure design, which influence the mechanical performance and the biological behavior of calcium phosphate ceramics³. Generally, the purpose of sintering is to produce sintered part with reproducible and, if possible, designed microstructure through control of sintering variables. In general terms, microstructural control is defined as a control of grain size, sintered density and distribution of other phases including pores. Commonly, the final purpose of microstructural control is to prepare an entire sample with fine grain structure⁴.

During the last 15 years, several researchers have investigated the use of microwave energy to sinter ceramic materials⁵. Microwave sintering has attracted great attention due to its various advantages. Since the performance of microwave heating encourages the transfer of energy directly into the materials, thus more volumetric heating and thus permitting higher heating rate obtained⁶. Consequently, the advantages of microwave sintering in terms of energy consumption and processing cost are reduced, enhanced diffusion processes, very rapid heating rates and significantly reduced processing times as well as improved physical and mechanical properties⁷. The fundamental difference between microwave heating and conventional radiant heating is the volumetric heating. Conventional furnace heats sample using surface heating mechanism, and depending on the heating rate, creates a large thermal gradient from the surface to the center of the sample, particularly having poor thermal conductivity⁸. In contrast, microwave heating is a fast sintering process where energy can be deposited volumetrically throughout the material rather than relying on thermal conduction from the surface⁹. Herein, this study was carried out by using microwave and conventional sintering to fabricate dense CP ceramic. In order to demonstrate the effect of microwave sintering to the microstructure and mechanical properties of sintered CP ceramics, the same condition and parameters were used for both types of sintering.

1. Experimental procedure

1.1. Specimens preparation

The raw material used in this study was hydroxyapatite precursor powder as synthesized by a wet precipitation method in the Rekagraf Laboratory (USM). Calcium phosphate powder was pressed by uniaxially cold pressing into a cylindrical pellet form in a 12 mm diameter stainless steel die (with an applied pressure of 100 MPa) using a Specac manual hydraulic press machine.

1.2. Densification study

The specimens were sintered at different temperatures of 1200, 1250, 1300, 1350 and 1400 °C with 10 °C/min heating rate and 2 hours soaking time. For microwave sintering, the specimens were sintered in Syno Therm microwave furnace, while conventional sintering was sintered in Lenton muffle furnace. The apparent density was measured using Archimedeian principal on six specimens. In the microwave sintering, the sintered specimens at 1400 °C were cracked and surfaces were damaged specially on the edge area of the specimens. This defect resulted in the inability to measure the dimensions of specimens and could not be use for subsequent test. Therefore, for microwave sintering, the firing process was terminated at 1350 °C.

1.3. Phase analysis

X-ray diffraction was used to evaluate phase in the sintered specimens. Powdered samples were prepared by crushing the sintered specimens in a mortar. Phase analysis was done using a table-top Bruker D2 Phaser diffractometer with a copper anode ($\text{CuK}\alpha$, $\lambda=1.5406 \text{ \AA}$) target. Phase analysis was carried out over a 2θ range of 10° to 90° with a scan rate of $0.5^\circ/\text{min}$. Phases were compared between the microwave-sintered and the conventionally sintered specimens.

1.4. Mechanical property measurements

Microhardness of the sintered specimens was measured with Future Tech Vickers Hardness Tester FV-7.7, using 1 kilograms-force (Kg.f) load, and a dwelling time of 8 seconds. The tests were repeated on three different specimens of the same temperature. For each specimen, three indentations were made and recorded the results.

1.5. Microstructural analysis

The field emission scanning electron microscopy (FESEM) Supra 35VP Zeiss model was used to analyze microstructure of sintered CP specimens. Fractured surfaces of the sintered CP ceramic were also used for analysis after immersed in SBF solution for 7 days to assess the biocompatibility property of sintered CP ceramic. The simulated body fluid (SBF) preparation and immersion of specimens in SBF solution were followed by the Kokubo and his colleague's¹⁰.

2. Results and discussion

Fig. 1 shows the comparative XRD plots for microwave sintered (Fig. 1a) and conventional sintered (Fig. 1b) CP ceramic. It can be seen that the α -TCP phase were formed at high sintering temperature, while the β -TCP and HA can be found at the lower sintering temperatures¹¹. In this study, the transformation of β to α -TCP was found to be from the temperature of 1300°C until higher temperature in both microwave and conventional sintering. The quantitative analysis of the (crystalline) phases present was carried out using Rietveld analysis in the X-Pert High Score Plus software as shown the result in Table 1. It can be seen that with microwave sintering there were slightly higher of HA and β -TCP as compared to conventional sintering.

Fig. 2 shows the microstructure of the fracture surfaces of sintered specimens at temperature 1350°C by microwave sintering (Fig 2a) and conventional sintering (Fig 2b). It can be observed that, the average grain size of microwave sintered specimen was $3 \mu\text{m}$ which was smaller than the conventionally sintered specimen that has average grain size $5 \mu\text{m}$. Micro-cracks were observed even in the dense portions as well as both intergranular and transgranular crack (marked by the arrows) in Fig 2a and b. Since the formation of α -TCP caused the expansion of ceramic, consequently cracks were created and decreased the bulk density¹².

Fig. 3 presents bulk density for microwave and conventionally sintered specimens. It revealed that the density of sintered specimens by microwave was higher than that of conventional sintering. It can be observed that the densities decreased when the temperature increased in both sintering methods, perhaps due to the phase transformation and microcracks.

Fig. 4 shows the hardness of sintered the specimen. The general trend showed that the hardness of microwave sintered specimens is higher than conventional sintered specimens. However it can be observed that, the hardness rapidly decreased from the sintering temperature of 1250°C to 1300°C . This was significantly affected from the transformation of α -TCP phase as reported in Table 1. Moreover, the hardness is related to the density as can be seen between Fig. 3 and 4. The hardness values decreased with the decreasing of density in both conventional and microwave sintering.

To be concluded that CP ceramic is biocompatible, the bone bonding ability of CP ceramic is evaluated by examining the ability of apatite to form on its surface in a SBF with ion concentration similar to those of human blood plasma. From the Fig. 5 FESEM micrographs of the fracture surfaces of sintered CP ceramic after soaked in the SBF for 7 days. It can be seen that tiny agglomerated bone-like apatite particles were observed on the surfaces of

both sintered methods, although they were sintered differently. However, the morphology of the layer, which is supposed to be big agglomeration like as reported by others¹³⁻¹⁶, was not so visible from the FESEM analyses due to the small size of the agglomeration particles and the short immersion period.

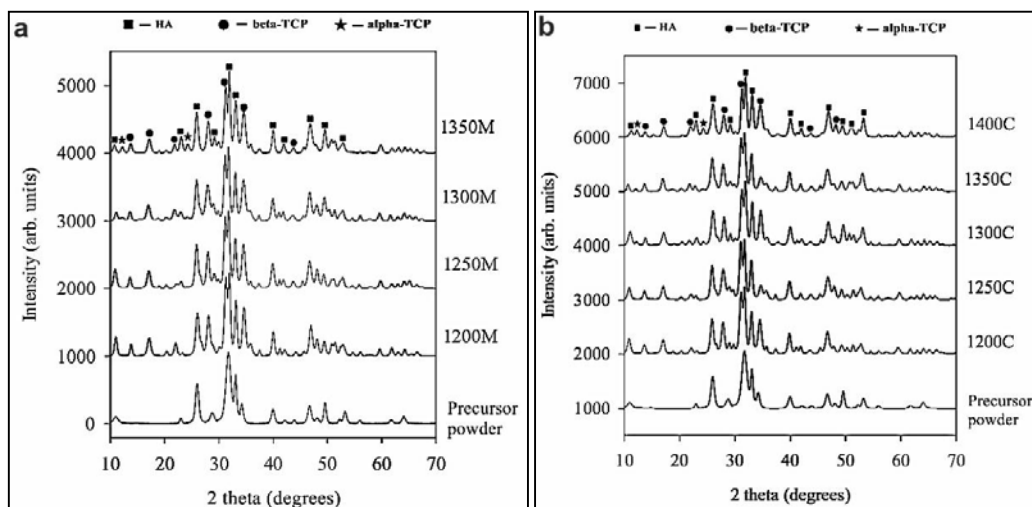


Fig. 1. XRD patterns of sintered CP by microwave (a) and conventional (b) sintering at different temperatures.

Table 1. A composition of sintered specimens by conventional and microwave sintering from Rietveld analysis.

| Sample code | Phase present (wt%) | | |
|------------------------|---------------------|--------------|---------------|
| | HA | β -TCP | α -TCP |
| Conventional sintering | 1200C | 48 | 52 |
| | 1250C | 48.6 | 51.4 |
| | 1300C | 44.7 | 45.7 |
| | 1350C | 42.4 | 44.9 |
| | 1400C | 44.9 | 33.5 |
| Microwave sintering | 1200M | 47 | 53 |
| | 1250M | 47.2 | 52.8 |
| | 1300M | 43.4 | 46.2 |
| | 1350M | 44.8 | 39 |

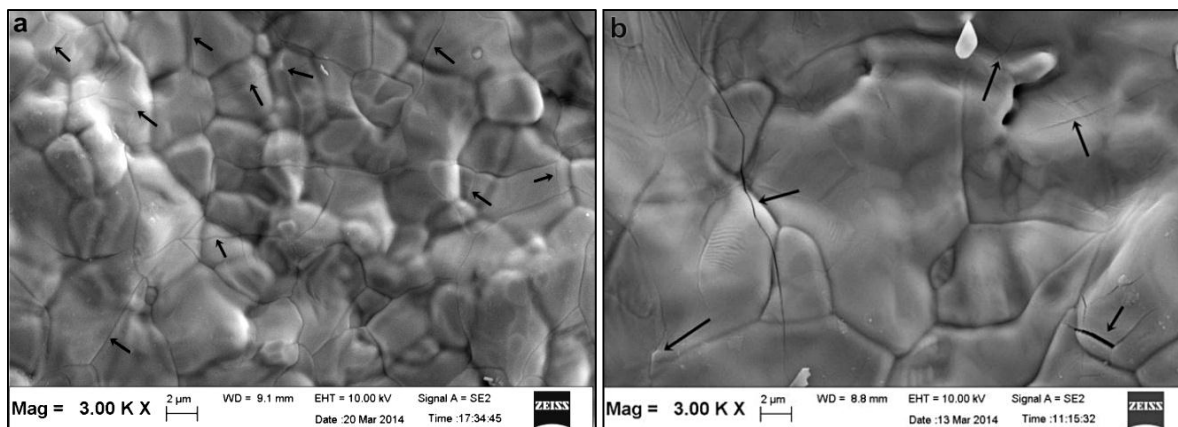


Fig. 2. Fracture surfaces of sintered specimens at 1350 °C by microwave (a) and conventional sintering (b)

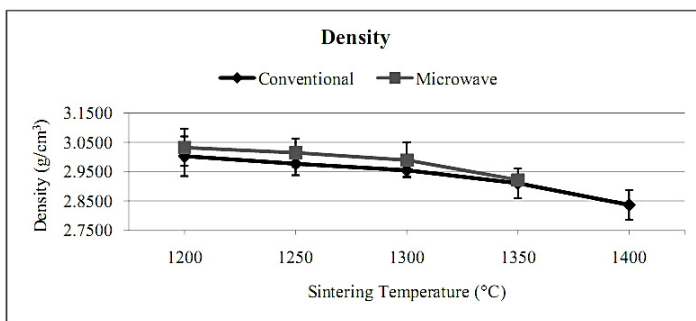


Fig. 3. Comparison of sintered CP ceramic bulk density by microwave and conventional sintering

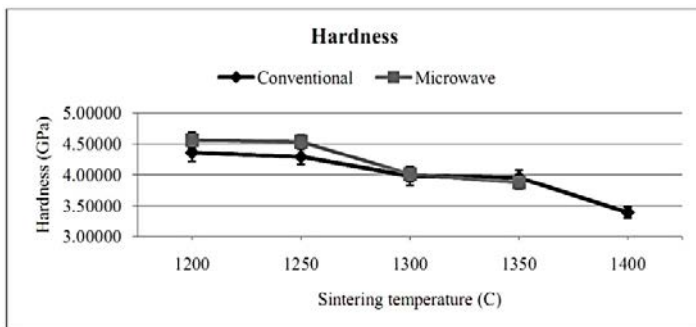


Fig. 4. Comparison of hardness of sintered CP ceramic by microwave and conventional sintering.

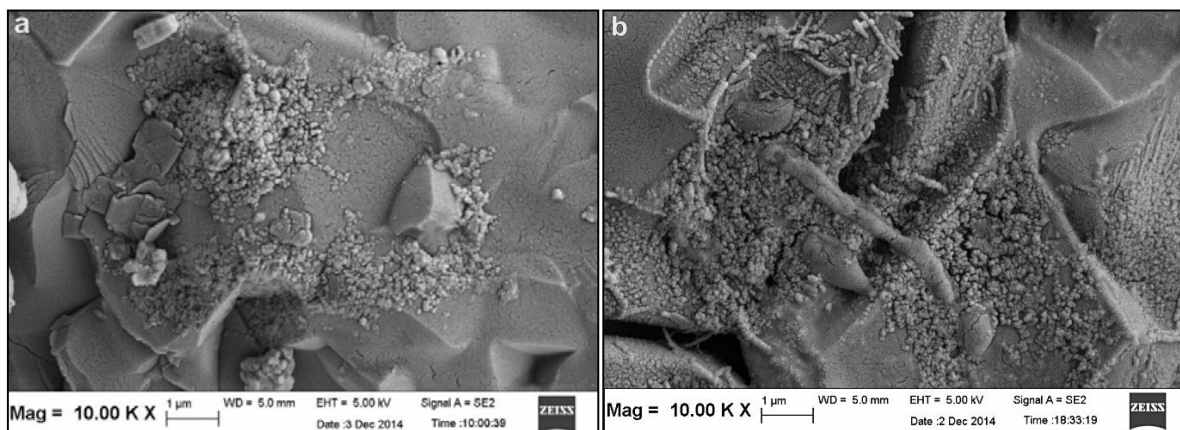


Fig. 5. FESEM micrograph of fracture surfaces sintered by microwave (a) and conventional sintering (b) after immersed in SBF solution

3. Conclusions

In the present study, dense CP ceramic was successfully fabricated with better mechanical property by using microwave sintering. These results indicated that the hardness, density and microstructure of sintered CP by microwave sintering were higher than conventionally sintered specimens. Moreover, the biocompatibility study of sintered CP by immersing in SBF solution exhibited the growth of apatite layer on the surfaces of sintered specimens in both microwave and conventional sintering. This suggests that dense CP ceramic is biocompatible.

Acknowledgments

The authors acknowledge the support from the School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia. This work is part of a research project funded by AUN/Seed –Net and JICA.

References

- Hesaraki S, Farhangdoust S, Ahmadi K, Nemati R and Khorami M. Phase evaluation and lattice parameters of strontium/magnesium incorporated beta-tricalcium phosphate bioceramics *Journal of the Australian Ceramic Society* 2012; 48: 166-72.
- Wolff DMB, Ramalho EG and Acchar W. Phase Transition behaviour of Tricalcium phosphate (TCP) doped with MgO and TiO₂ as additives *Materials Science Forum* 2006; 530-531: 581-6.
- Champion E. Sintering of calcium phosphate bioceramics. *Acta Biomaterialia*. 2013; 9.
- Kang SL. Basis of sintering science. *Sintering: Densification, Grain Growth, and Microstructure*. 2005, p. 16-20.
- Chockalingam S and Traver KH. Microwave sintering of b-SiAlON–ZrO₂ composites. *Materials and Design* 2010; 31: 3641–6.
- Menezes RR and Souto PM. Microwave Fast Sintering of Ceramic Materials. In: Lakshmanan A, (ed.). *Sintering of Ceramics - New Emerging Techniques*. Croatia: Intech, 2012, p. 13.
- Oghbaei M and Mirzaee O. Microwave versus conventional sintering: A review of fundamentals, advantages and applications. *Journal of Alloys and Compounds*. 2010; 494.
- Chanda A, Dasgupta S, Bose S and Bandyopadhyay A. Microwave sintering of calcium phosphate ceramics. *Materials Science and Engineering* 2009; 29: 1144–9.
- Wang X, Fan H, Xiao Y and Zhang X. Fabrication and characterization of porous hydroxyapatite/β-tricalcium phosphate ceramics by microwave sintering. *Materials Letters* 2006; 60: 455–8.
- Kokubo T and Takadama H. How useful is SBF in predicting in vivo bone bioactivity. *Biomaterials* 2006; 27.
- Perera FH, Martínez-Vázquez FJ, Miranda P, Ortiz AL and Pajares A. Clarifying the effect of sintering conditions on the microstructure and mechanical properties of β-tricalcium phosphate. *Ceramics International*. 2010; 36: 1929–35.
- Ryu HS, Youn HJ, Hong KS, Chang BS, Lee CK and Chung SS. An improvement in sintering property of β-tricalcium phosphate by addition of calcium pyrophosphate. *Biomaterials*. 2002 23 909–14.
- Xin R, Leng Y, Chen J and Zhang Q. A comparative study of calcium phosphate formation on bioceramics in vitro and in vivo. *Biomaterials*.

- 2005; 26: 6477–86.
14. Zhang Y, Ai J, Wang D, Hong Z, Li W and Yokogawa Y. Dissolution properties of different compositions of biphasic calcium phosphate bimodal porous ceramics following immersion in simulated body fluid solution. *Ceramics International* 2013; 39: 6751–62.
 15. Sadjadi MS, Ebrahimi HR, Meskinfam M and Zare K. Silica enhanced formation of hydroxyapatite nanocrystals in simulated body fluid (SBF) at 37 °C. *Materials Chemistry and Physics*. 2011; 130 67–71.
 16. Sun R, Li M, Lu Y and Wang A. Immersion behavior of hydroxyapatite (HA) powders before and after sintering. *Materials Characterization* 2006; 56 250–4.