

COMPARATIVE STUDIES ON PURE MIXING AND MILLING-MIXING OF Y_2O_3 - ZrO_2 /HAp BIOCOMPOSITE

Zaw Linn Htun¹, Nurazreena Ahmad², Aye Aye Thant³ & Ahmad-Fauzi⁴

Abstract

The milling-mixing Y_2O_3 - ZrO_2 /HAp biocomposites have been investigated compared to the pure mixing ones to distinguish the effects of those two methods. The milling method reduced appreciably the particles size of the powders and resulting to better homogeneity and enhanced sinterability. The better densification process of HAp with ZrO_2 favored to improve physical and mechanical properties of the biocomposite. The crystallized size of the milling-mixing samples was found to be 38.5 nm while pure mixing composite had a size of 46.2 nm. The former samples showed higher density than the latter ones in whole sintering temperature range (1050°C - 1250°C). Fine grains formation was also found in the milling-mixing samples. The highest flexural strength of 46.21 MPa and fracture toughness of 1.16 MPa.m^{1/2} were achieved by milling-mixing samples. The formation of apatite layer on the surfaces of Y_2O_3 - ZrO_2 /HAp biocomposite samples also indicated the biocompatibility and potential bone forming ability.

Keywords: biocomposite, flexural strength, fracture toughness, hydroxyapatite, zirconia.

Introduction

HAp is chemically similar to the inorganic mineral component of bone and teeth^{1,2} and possesses exceptional biocompatibility and unique bioactivity³. Although HAp offers high biocompatibility, relatively low density, high compressive strength and high hardness, application of HAp as a load bearing implant is limited because of its brittleness and relatively low mechanical properties. Hence, there is a necessity of reinforcement to HAp without hampering its biocompatibility⁴. For these reasons, the biocomposites of HAp and ZrO_2 was conducted in this work in order to combine the biocompatibility of HAp and the high strength and toughness of ZrO_2 using

¹. Assistant Lecturer, Department of Physics, University of Yangon

². Lecturer, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

³. Professor, Department of Physics, University of Yangon

⁴. Professor, School of Materials and Mineral Resources Engineering, Universiti Sains Malaysia

both pure mixing and milling mixing methods. The ZrO_2 has been found to retain high mechanical strength and toughness without degrading the biocompatibility of HAp when incorporated as a second phase^{5,6}. HAp- ZrO_2 biocomposites have shown the improved strength and toughness as compared to monolithic HAp itself⁷. However, the reaction between ZrO_2 and HAp will enhance the decomposition of HAp and leads to inhibit densification of the composite resulted in low mechanical properties. Again, the presence of ZrO_2 in the system decreases the decomposition temperature of HAp into tricalcium phosphate (TCP; α - or β -)⁸. Therefore, CaF_2 was added into the biocomposite to improve sinterability and to retain the HAp phase. Based on these backgrounds, the current study was performed to fabricate HAp and Y_2O_3 - ZrO_2 biocomposites through the incorporation of CaF_2 by air sintering at temperatures ranging from 1050 °C to 1250 °C. The effect of the added- CaF_2 on sintering behavior of Y_2O_3 - ZrO_2 /HAp was also investigated.

Materials and Methods

2.1. Materials fabrication

As starting materials, 95wt% of high-purity HAp (Fluka) and 5wt% of Y_2O_3 - ZrO_2 (Goodfellow) powders were used to fabricate (ZrO_2 /HAp) biocomposites with the addition of 1wt% CaF_2 (Merck KGaA, Germany) powders, designated as Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF respectively. The samples were produced by both pure mixing and milling-mixing with zirconia ball milling. In pure mixing, the composition of Y_2O_3 - ZrO_2 and HAp were added in ball milled with only 10 zirconia balls to aid mixing. For the case of milling-mixing system, the powders were wet mixed and milled with ball-to-powder weight ratio of 4:1 in ball milling for 24 hours in order to obtain a homogeneous and agglomerate-free powder mixture. Deionized water was used as a mixing media. After mixing, the mixture was dried in an oven at 100 °C for 24 h. Dry aggregates were lightly ground into fine powders using agate mortar and sieved through a 250 μ m screen. A 55 mm \times 10 mm die was used to form rectangular bar shape sample and a uniaxial pressure of 90 MPa was employed to compact. Sintering was conducted in air atmosphere at five different temperatures (1050, 1100, 1150,

1200 and 1250 °C) using *LENTON* muffle furnace. The schedule of sintering includes soaking time of 5 h with heating and cooling rate of 5 °C/min.

2.2. Characterization and Mechanical Test

Using Archimedes method, the density and apparent porosity of the sintered specimens were measured. The samples were subsequently ground using SiC paper, followed by polishing using 1 µm, 0.3 µm and 0.05 µm alumina powders. After etching at a temperature 100 °C below its sintering temperature for 2 h, their microstructures were analyzed by Zeiss Supra 35VP Field Emission Scanning Electron Microscope (FESEM). The specimens were also characterized by XRD Bruker DX 8 for the phase formed. The scan started from 20° to 80° 2θ, using copper (Kα Cu) with wavelength of 1.5406 nm as X-ray source.

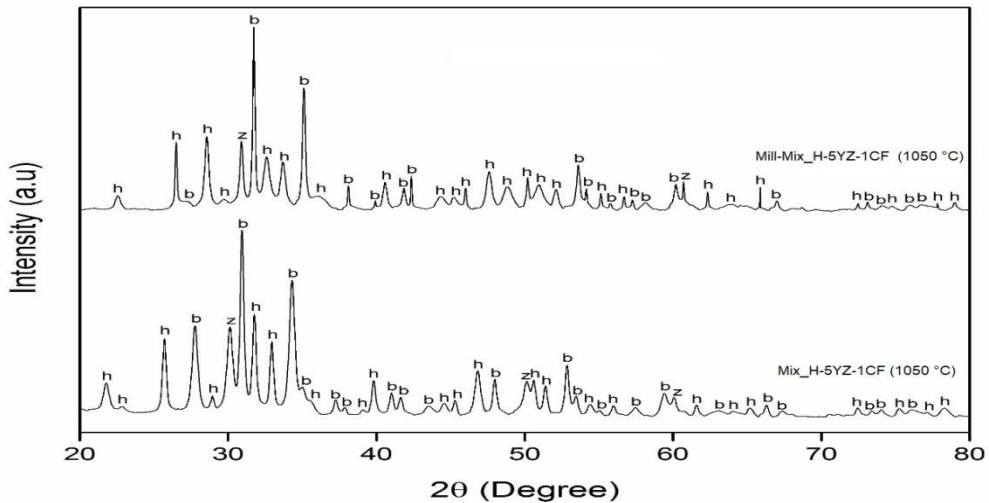
For the flexural strength, 3-point bending test was conducted using INSTRON 3366 universal testing machine with a crosshead speed of 0.5 mm/min, and outer span length of 40 mm. Microhardness of the specimens was measured by Vickers microhardness tester. A diamond indenter with 1 Kgf load was used to test the samples, and loading time of 12 seconds was applied. Indentation fracture in ceramic materials was suggested as a simple technique to determine fracture toughness value⁹. Based on this knowledge, fracture toughness measurement was determined by applying 3 Kgf load to make significant crack from the indent tips.

Results and Discussion

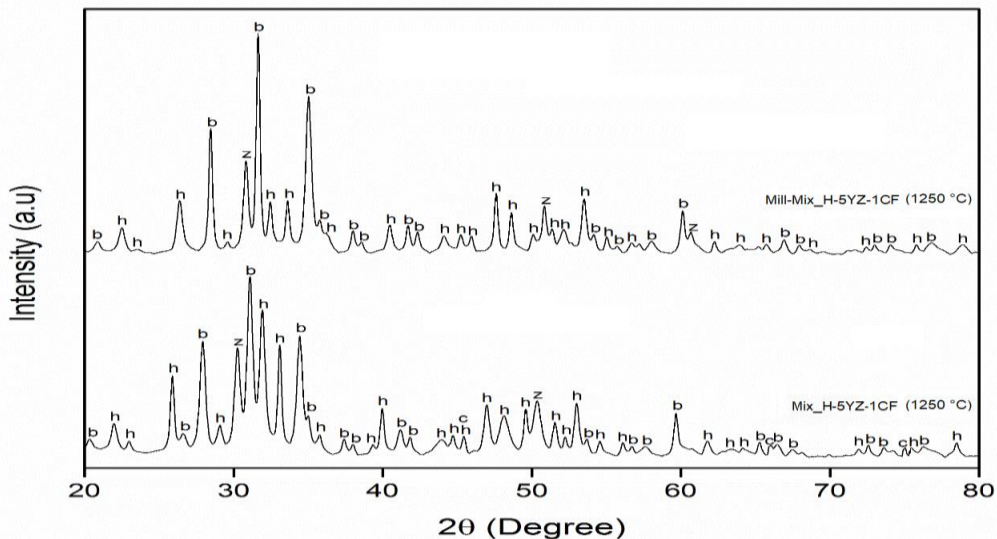
3.1. Phase Identification

From Fig: 1(a) and 1(b), the samples were found to contain β-TCP phase, which suggest that decomposition of HAp into β-TCP had occurred at both temperatures investigated in both pure mixing and milling-mixing of Y₂O₃-ZrO₂/HAp composites. The diffraction peaks of the samples sintered at different temperatures matches with the reference patterns of HAp at 25.87°, 31.97°, 32.28° and 33.16° (JCPDS card number 4-0506) and β-TCP at 27.78°, 31.01°, 31.05° and 34.35° (JCPDS card number 7-6561). Peaks at 30.17°, 50.17°, 50.58° and 60.04° matched with the peaks from tetragonal ZrO₂ (JCPDS card number 9-1974). When the temperature is higher, the transformation to β-TCP is increased and small amount of CaZrO₃ was also

found, especially in pure mixing samples (Fig: 1b). The peaks at 31.60° , 45.30° , 56.29° and 75.03° (JCPDS card number 6-2992) confirm the presence of CaZrO_3 . The formation of CaZrO_3 would indicate that HAp reacts with the $\text{Y}_2\text{O}_3\text{-ZrO}_2$ whilst the presence of 1wt% CaF_2 would not be able to prevent the reaction, as was suggested by Firmandika Harda¹⁰. Thus, 1wt% CaF_2 can be considered as being relatively low to prevent secondary reaction.



(a)



(b)

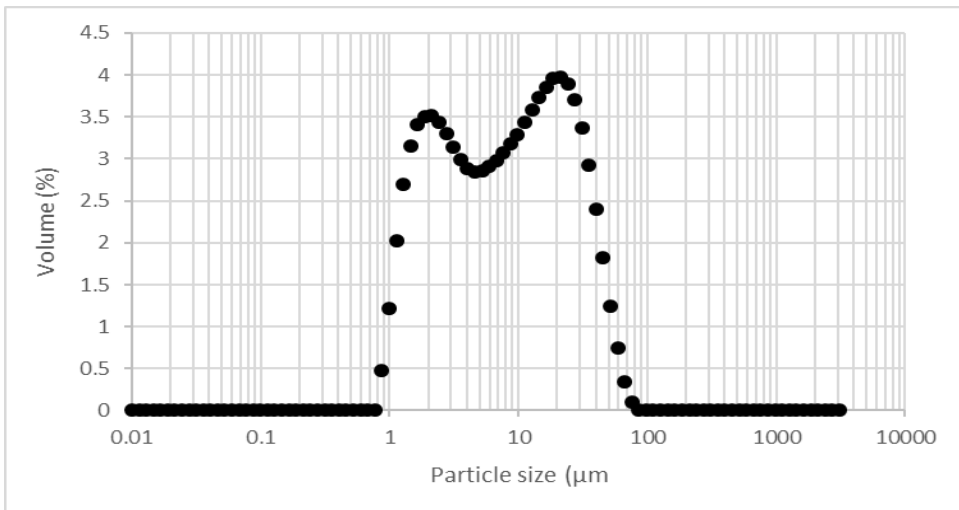
Figure 1: XRD patterns of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples at (a) 1050°C and (b) 1250°C Key: h = HAp, b = β -TCP, z = ZrO_2 (tetragonal), c = CaZrO_3

3.2. Crystallite Size Determination

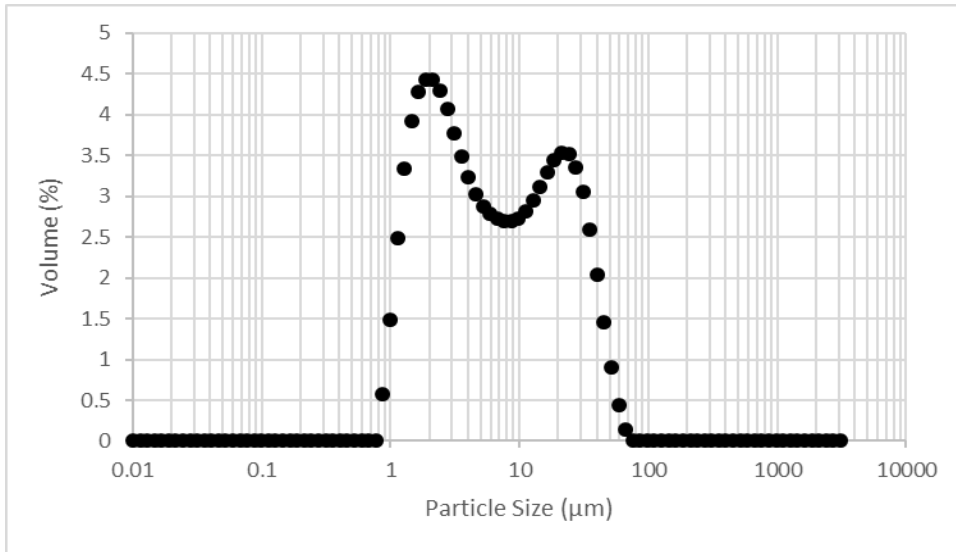
From Fig: 1(a), it reveals that the diffraction peaks of Mill-Mix_H-5YZ-1CF samples shifted to higher 2θ values and it can be known that the crystallite size of these samples becomes smaller than that of pure Mix_H-5YZ-1CF samples. For instance, the strongest peak shifts from the original 2θ position at 30.92° to 31.73° . Crystallite size calculated from the corresponded peak was found to be 38.5 nm for Mill-Mix_H-5YZ-1CF composite, while Mix_H-5YZ-1CF composite has a size of 46.2 nm. This could be resulted from the milling of the powders. The milling system reduces appreciably the particles size of the powders and resulting to better homogeneity and enhanced sinterability, and better densification process of HAp with ZrO_2 .

3.3. Particle Size Determination

The particle size distribution curves for Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples are shown in Fig: 2 and it was found that the average particle size of pure Mix_H-5YZ-1CF sample is about $8.51 \mu m$ (Fig: 2(a)) and that of Mill-Mix_H-5YZ-1C sample was about $5.36 \mu m$ (Fig: 2(b)). Based on this results, it could be realized that the particle size reduction was obtained by milling-mixing procedure.



(a)



(b)

Figure 2: Particle size distribution curves for (a) Mix_H-5YZ-1CF and (b) Mill-Mix_H-5YZ-1CF samples

3.4. Evaluation of Physical Properties

3.4.1 Bulk Densities

From the graph (Fig: 3), it can be observed that the increase in density values with consistency displayed at all temperatures for Mill-Mix_H-5YZ-1CF samples as compared to Mix_H-5YZ-1CF samples. The optimum density of 2.95 gcm^{-3} was reached at the temperature of 1250°C for these samples in the temperature range while the density at 1200°C was the highest for pure Mix_H-5YZ-1CF samples. At the highest temperature, 1250°C , it was unable to enhance the density of pure Mix_H-5YZ-1CF samples. In the whole sintering temperature range (1050°C - 1250°C), the densities of Mill-Mix_H-5YZ-1CF samples are noticeably higher than that of pure Mix_H-5YZ-1CF samples. This enhancement in density is because of better homogeneity as well as the particle size reduction by zirconia ball milling in 24 hours with ball-to-powder weight ratio of 4:1.

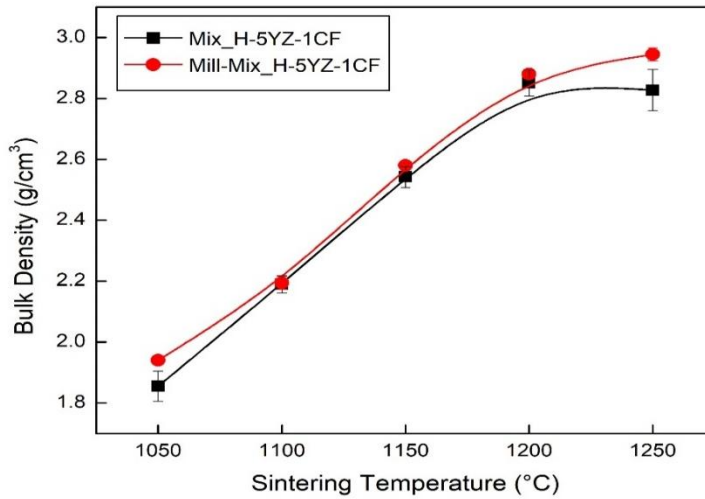


Figure 3: Bulk densities of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples as a function of sintering temperature

3.4.2 Apparent Porosities

Fig: 4 presents the apparent porosities of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples at various temperatures with soaking of 5 hours. It can be observed from the graph that the apparent porosities of Mill-Mix_H-5YZ-1CF samples are apparently lower than that of Mix_H-5YZ-1CF samples for all sintering temperatures. This result shows high consistency to the above density values, i.e., the higher the sintering temperature is, the lower the porosity and the greater the density will be. However, the minimum porosity in the firing range does slightly differ from the bulk density results.

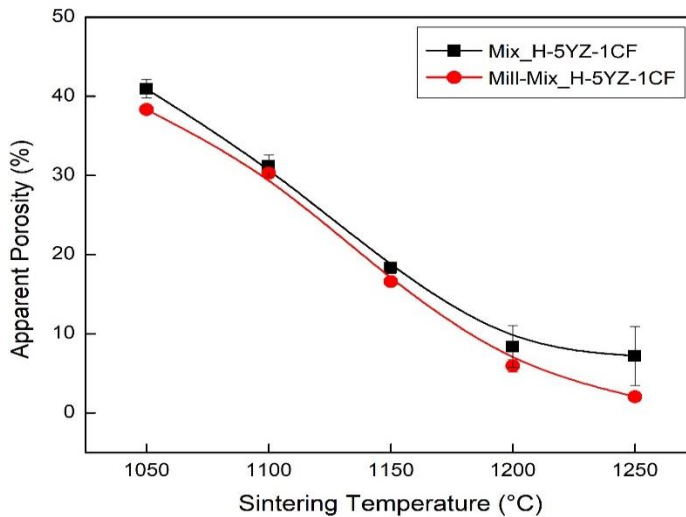


Figure 4: Apparent porosities of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples as a function of sintering temperature

3.5. Evaluation of Strength and Toughness

The flexural strength of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples after sintering at various temperatures for 5 hours are presented in Fig: 5. For the Mill-Mix_H-5YZ-1CF samples, the optimum strength of 46.21 MPa was achieved at the sintering temperature, 1150°C, and this value is apparently higher than that of pure Mix_H-5YZ-1CF samples which have the optimum value of 34.71 MPa at 1200°C. Therefore, a better strength was obtained by the milling-mixing method as expected.

The fracture toughness (K_{IC}) of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples are also presented in Fig: 6. From the graph, the optimum toughness values for Mill-Mix_H-5YZ-1CF samples occurred at 1250°C. The maximum K_{IC} values, in the range of ~ 0.54 to $1.16 \text{ MPa}\cdot\text{m}^{1/2}$, was obtained by the Mill-Mix_H-5YZ-1CF sample, while pure Mix_H-5YZ-1CF samples were giving values, in the range of ~ 0.47 to $1.08 \text{ MPa}\cdot\text{m}^{1/2}$. Although the toughness values of both biocomposites were not much different from each other's, better toughness was found in milling-mixing composites.

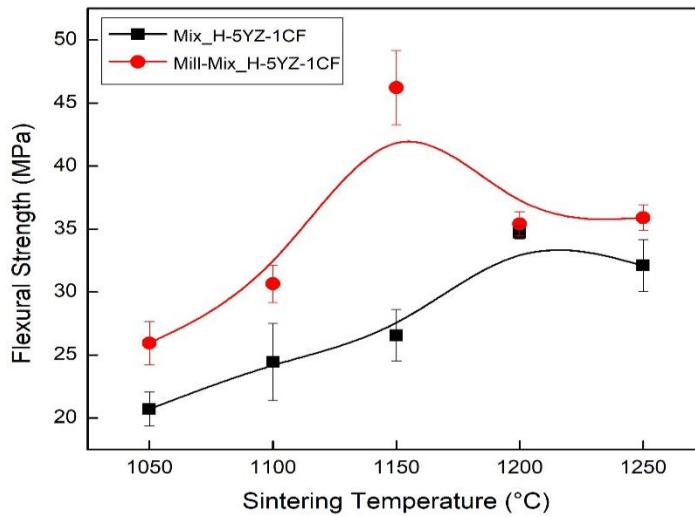


Figure 5: The flexural strength of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples after sintering at various temperatures for 5 hours

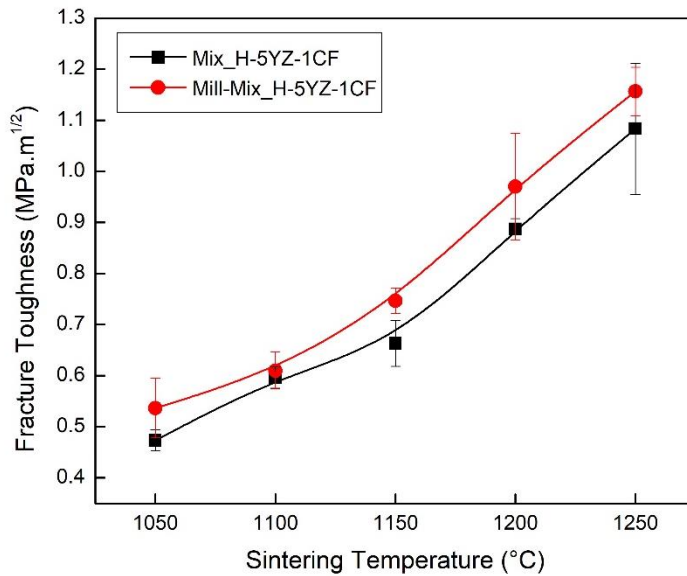


Figure 6: The fracture toughness of Mix_H-5YZ-1CF and Mill-Mix_H-5YZ-1CF samples after sintering at various temperatures for 5 hours

3.6. Microstructural observation

The SEM images of pure mixing and the milling-mixing samples are shown in Fig: 7 and Fig: 8. It can be observed from the images that excessive grain coarsening occurred at highest sintering temperature of 1250°C and also some large pores were observed in Fig: 7(b) for Mix_H-5YZ-1CF samples. It affected the densification process and thereafter results in the deterioration of mechanical properties of the biocomposite. Vasconcelos¹¹ reported similar effect on mechanical properties. On the contrary, uniformly distribution of ZrO₂ phase with uniform fine grains were observed in the SEM images of Mill-Mix_H-5YZ-1CF samples at 1250°C as shown in Fig: 8(b). Based on this observation, Mill-Mix_H-5YZ-1CF samples showed better densification and fine grains as compared to pure Mix_H-5YZ-1CF samples. This also confirmed the particle size reduction in milling-mixing procedure.

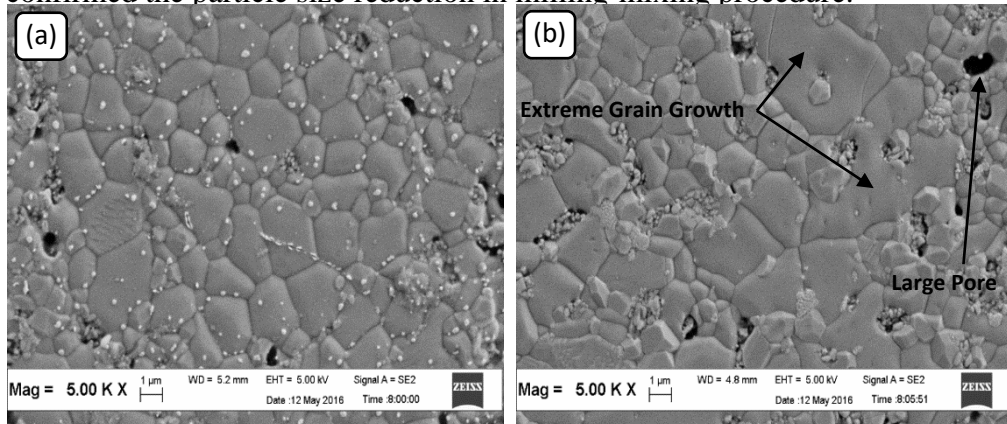


Figure 7: SEM images of Mix_H-5YZ-1CF samples sintered at (a) 1200°C and (b) 1250°C

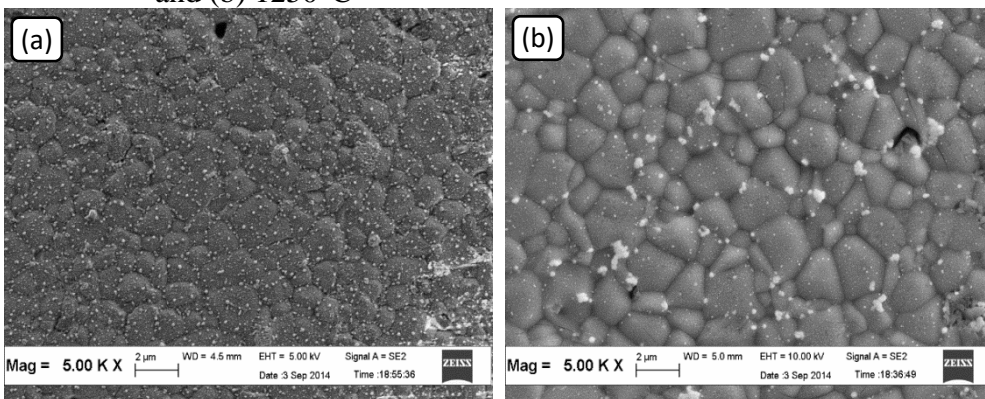


Figure 8: SEM images of Mill-Mix_H-5YZ-1CF samples sintered at (a) 1200°C and (b) 1250°C

3.7. Evaluation of Bioactivity in SBF

Fig: 9(a) and 9(b) shows 5000X and 20,000X magnifications SEM images of the Mill-Mix_H-5YZ-1CF samples sintered at 1250°C after soaking in SBF for 7 days. The magnified image shown in Fig: 9(b) clearly shows that spherical-like apatite particles has grown on the sample surface after 7 days. These apatite particles can be considered as the aggregates of small crystals as also reported by Yokogawa & Nagata (2005)¹². Therefore, it can be said from these findings that Y₂O₃-ZrO₂/HAP composites show the bone-bonding ability and can be considered to be useful as an implant.

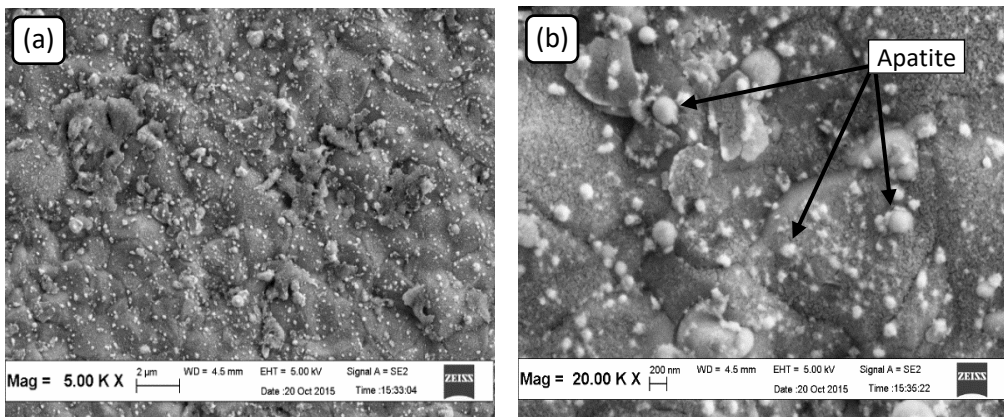


Figure 9: SEM images of the surfaces of Mill-Mix_H-5YZ-1CF sample sintered at 1250 °C at (a) 5000X and (b) 20,000X magnification after soaking in SBF for 7 days

Conclusion

Particles size reduction of the powders, better homogeneity and enhanced sinterability were achieved by the milling-mixing method. The better densification process of HAp with ZrO₂ was found to be improved physical and mechanical properties of the biocomposite. The smaller crystallized size of 38.5 nm was also observed in the milling-mixing samples, and fine grains formation as well. The highest flexural strength of 46.21 MPa and fracture toughness of 1.16 MPa.m^{1/2} were also achieved by milling-mixing samples. The apatite formation was also found on Y₂O₃-ZrO₂/HAP

biocomposite samples surface through bioactivity test, showing potential bone forming ability.

Acknowledgements

We are greatly indebted to Professor Dr. Khin Khin Win, Head of Department of Physics, University of Yangon for her kind permission.

The authors would like to thank AUN/SEED-Net for providing the research grant to conduct this project under Collaborative Research Program (CR) (304/PBAHAN/6050293/A119).

References

- Adolfsson E, Shen Z. Densification of Zirconia–Hydroxyapatite Ceramics Without Phase Changes. In: *Key Engineering Materials*. 2006. p. 1141–4.
- Balani K, Lahiri D, Keshri AK, Bakshi SR, Tercero JE, Agarwal A. The nano-scratch behavior of biocompatible hydroxyapatite reinforced with aluminum oxide and carbon nanotubes. *JOM J Miner Met Mater Soc*. 2009;61(9):63–6.
- EVans AG, Charles EA. Fracture toughness determinations by indentation. *J Am Ceram Soc*. 1976;59(7–8):371–2.
- Harda F. Zirconia Reinforced Hydroxyapatite Biocomposite for Strength and Toughness Improvement. *Universiti Sains Malaysia (USM)*; 2008.
- Hench LL, Wilson J. *An Introduction to Bioceramics*. Singapore: World Scientific; 1993. 386 p.
- Jarcho M, Kay JF, Gumaer KI, Doremus RH, Drobeck HP. Tissue, cellular and subcellular events at a bone-ceramic hydroxylapatite interface. *J Bioeng*. 1977 Jan;1(2): 79–92.
- Li J, Liao H, Hermansson L. Sintering of partially-stabilized zirconia and partially-stabilized zirconia—hydroxyapatite composites by hot isostatic pressing and pressureless sintering. *Biomaterials*. 1996 Sep;17(18):1787–90.
- Nayak AK. Hydroxyapatite synthesis methodologies: An overview. *Int J ChemTech Res*. 2010;2(2):903–7.
- Silva V V., Lameiras FS, Domingues RZ. Microstructural and mechanical study of zirconia-hydroxyapatite (ZH) composite ceramics for biomedical applications. *Compos Sci Technol*. 2001 Feb;61(2):301–10.
- Vasconcelos C. New Challenges in the Sintering of HA/ZrO₂ Composites. *Sinter Ceram - New Emerg Tech*. 2012 Mar 2;2:179–202.
- Yokogawa Y, Nagata F. Hydrothermal Synthesis of Hydroxyapatite – Polymer Composite Materials. In: *In Review in International Conference on the Properties of Water and Steam in Kyoto*. 2005. p. 373–6.
- Zhang J, Iwasa M, Kotobuki N, Tanaka T, Hirose M, Ohgushi H, et al. Fabrication of Hydroxyapatite/Zirconia Composites for Orthopedic Applications. *J Am Ceram Soc*. 2006 Nov;89(11):3348–55.