

Densification behavior of magnesium orthosilicate-hydroxyapatite composite

C.K.L. Jeffrey^{a,b}, S. Ramesh^{a,*}, C.Y. Tan^a and W.D. Teng^c

^aCenter for Advanced Manufacturing & Material Processing, Department of Mechanical Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia

^bSchool of Engineering, Taylor's University, 47500 Subang Jaya, Malaysia

^cCeramics Technology Group, SIRIM Berhad, 40911 Shah Alam, Malaysia

The purpose of this work is to evaluate the densification behaviour of magnesium orthosilicate-hydroxyapatite (MO-HA) composite. The composite was prepared in various compositions, by varying the magnesium orthosilicate content from 10 wt% to 50 wt% via mechanical ball milling and conventional pressureless sintering at 1000 °C to 1300 °C, using a ramp rate of 10 °C/minute for 2 hrs. The study revealed that a secondary phase formation was found in all the sintered. In general, the MO-HA composites exhibited lower mechanical properties across all the composition investigated. However, a high fracture toughness of 2.5 MPam^{1/2} was recorded for hydroxyapatite containing 20 wt% magnesium orthosilicate addition which indicated the potential of this composite to be used for load bearing biomedical applications.

Key words: Ceramic composite, Hydroxyapatite-Magnesium Orthosilicate Composite, Pressureless Sintering, Mechanical Properties.

Introduction

Hydroxyapatite (HA), Ca₁₀ (PO₄)₆ (OH)₂, is the primary mineral component of bone and is a calcium phosphate-based bioceramic which has been used in medicine and dentistry for more than 20 years due to its excellent osteoconduction, bioactivity, and biocompatibility with human tissues [1-3]. Thus, HA has been widely used in dental implants, alveolar bridge augmentation, orthopaedics, maxillofacial surgery etc. [4-6]. However, poor mechanical properties of hydroxyapatite such as inherent brittleness, poor fatigue resistance and strength, particularly its low fracture toughness (K_{Ic}) of < 1 MPa m^{1/2} are the major drawback for load bearing applications [7]. Some studies have been carried out previously to improve the low mechanical properties of HA by addition of dopants, however the findings showed no significant increase in fracture toughness [4]. Although some incorporation of large percentage of other intermetallic compounds provides vast improvements over pure HA, there are questions been posed over the biocompatibility of these composites [8]. Therefore, the need for improvement in the fracture toughness is thus required without sacrificing the biocompatibility nature of the modified ceramic with that of natural hard tissues.

Amongst the materials which play a crucial role in human include magnesium and silicon. Studies have shown that silicon is an essential element in skeletal development and is uniquely localized in the active

areas of young bone [9]. The findings from the literatures [9-12] showed that silicon (more than 5 wt.%) is localized in the active growth areas in the bones having a Ca/P ratio of 0.7 of young rats and involved in the early stage of bone calcification in physiological conditions. Schwarz and Milne [13, 14] also reported that the growth of the rats increased after the addition of silicon in their diet. The next important element in human body is magnesium and this element is closely associated with mineralization of calcined tissues and indirectly influences mineral metabolism [15, 16] which participates in the control of bone growth [17, 18].

To overcome the low mechanical properties of hydroxyapatite, there is a need to reinforced the HA with other ceramics having better mechanical properties. Magnesium orthosilicate (Mg₂SiO₄), also known as forsterite, could be a material of interest because of the higher fracture toughness and biocompatibility. The fracture toughness of magnesium orthosilicate ceramic has been reported to be about 2.4 MPam^{1/2} which is much higher than 1 MPam^{1/2} reported for bone implants and hydroxyapatite ceramic [19, 20]. Moreover, it is expected that addition of magnesium orthosilicate to form a composite with HA would have an effect in reducing the grain size which in turn may improve the mechanical properties of the ceramic composite, bioactivity and promote the stimulation for apatite formation which could be a suitable candidate for hard tissue engineering in load bearing applications [9, 21].

*Corresponding author:
Tel : +603-7967-5202
Fax: +603-7967-7621
E-mail: ramesh79@um.edu.my

Experimental Procedures

Synthesis of powders

In the present work a novel wet chemical method was employed to synthesis the HA powders [22]. The wet chemical method comprised of precipitation from aqueous medium by slow titration of orthophosphoric acid (85% purity, Merck) solution to a calcium hydroxide (98% purity, System) based on a molar ratio $\text{Ca/P} = 1.67$ and maintained at a pH of about 10-12 by the addition of small amounts of ammonium (NH_3) solution (25% concentration). Once the titration process has completed, the solution was stirred for an additional 6 hours. The precipitate was allowed to settle overnight before filtration. The filtered precipitate was rinsed three times using distilled water and dried in the oven at 60 °C overnight. Finally, the dried cake is crushed and sieved to obtain well-defined highly crystalline HA powder.

The magnesium orthosilicate (MO) powder was produced via combination of ultrasonification and mechanical ball milling method. A conventional ball milling method was employed for 3 hours to mix and refine the powder particles. After 24 hours drying in the oven at 60 °C, the dried cake of MO was sieved into powder form.

The MO powder in concentration varying from 10 wt% to 50 wt% was mixed with HA powder via ultrasonification and mechanical ball milling method. The samples were subsequently labelled as 10MO-HA, 20MO-HA, 30MO-HA, 40MO-HA and 50MO-HA. The final solutions were ball milled for 3 hours prior to the drying process and powder sieving.

Fabrication of samples

The HA-MO powders were compacted into disc and rectangular bar samples and subsequently cold isostatic pressed at 200 MPa (Riken Seiki, Japan) prior to sintering. The readily pressed green samples were consolidated by pressureless sintering in air using a box furnace (LT furnace), over the temperature of 1000 °C to 1300 °C, with ramp rate of 10 °C/min. (heating and cooling) and holding time of 2 hrs for each firing. The sintered samples were then polished to a 1 μm finish prior to testing.

Characterization of samples

Phase analysis by X-ray diffraction (XRD) (PANalytical Empyrean, Netherlands) of the sintered samples was carried out at room temperature using Cu-K α as the radiation source at a scan speed of 0.5 ° per minute and a step scan of 0.02 °. The crystalline phase compositions were identified with reference to the standard JCPDS card available in the system software. The microstructural evolution of the samples after sintering at varying temperatures was examined using a field emission scanning electron microscope (Phenom ProX, Netherlands).

Bulk density measurement of sintered samples was carried out based on the Archimedes' principle using distilled water as an immersion medium. The micro-hardness (H_V) of polished sintered samples was

determined using a Vickers hardness tester (Shimadzu, Japan). For this purpose, a load of 100-200 g with a dwell time of 10 seconds was applied on the polished sample to produce the indentation. Five measurements were taken at different locations on the sample, and the average value was obtained. The Young's modulus was determined for sintered rectangular bars (32136 mm) via the resonance frequency technique on a Grindosonic MK5 (Belgium) according to ASTM standards (E1876-97).

Results and Discussion

Phase Stability

The XRD patterns of the samples sintered at 1200 °C and 1300 °C are shown in Fig. 1 and Fig. 2, respectively. The XRD patterns of samples sintered below 1200 °C did not show any decomposition of the HA phase and therefore it is not shown here. The XRD patterns presented in Fig. 1 and Fig. 2 revealed the presence of hydroxyapatite and magnesium orthosilicate peaks in accordance with the JCPDS card No: 09-0342, and No: 34-0189. However, secondary phase of whitlockite (No: 96-900-0425) or better known as α -tricalcium phosphate (TCP), was detected in all the MO-HA composites after sintering above 1200 °C.

Similar findings were also reported by Emadi *et al.* [23] and Ebdani *et al.* [24]. This indicates that some of the hydroxyapatite phase used as the matrix has transformed into the TCP phase, due to the chemical reaction with magnesium orthosilicate during sintering.

Shrinkage and densification

The assessment on the shrinkage was taken as the average of the diameter and thickness of the disc samples. The resulting shrinkage of the sintered samples is shown in Fig. 3. In general, the monolithic HA samples attained higher shrinkage across the range of sintering temperatures investigated. A maximum shrinkage of 19.7% was attained from HA sintered at

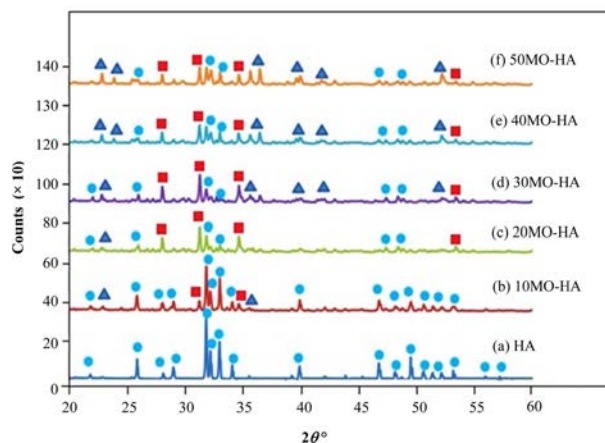


Fig. 1. XRD patterns of magnesium orthosilicate-hydroxyapatite (MO-HA) samples sintered at 1200 °C. For keys: ● = HA, ■ = β -TCP and ▲ = magnesium orthosilicate.

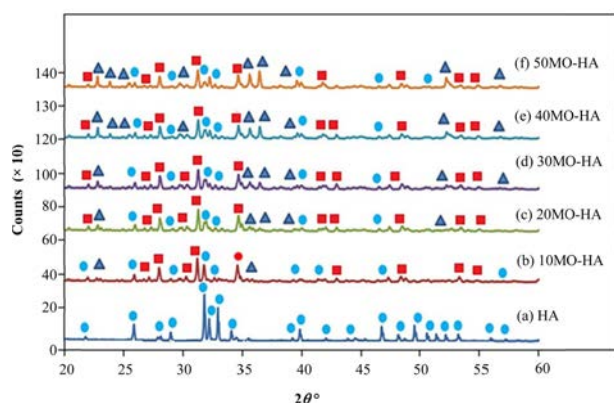


Fig. 2. XRD patterns of magnesium orthosilicate-hydroxyapatite (MO-HA) samples sintered at 1300 °C. For keys: ● = HA, ■ = β-TCP and ▲ = magnesium orthosilicate.

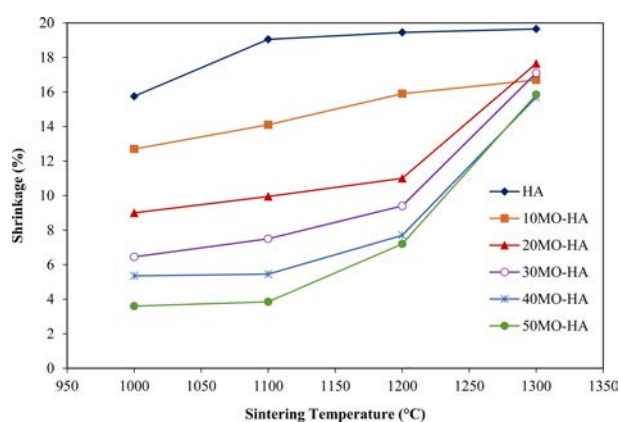


Fig. 3. The effect of sintering temperature on the shrinkage of HA and MO-HA composites.

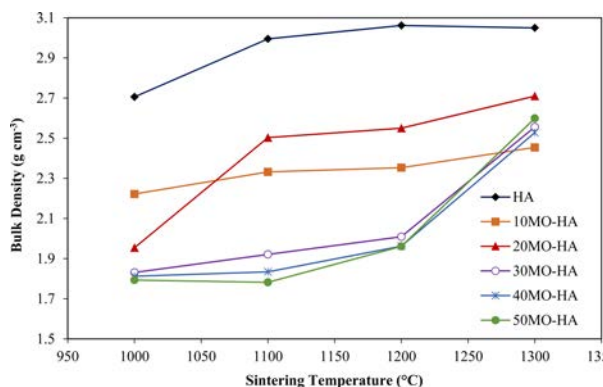


Fig. 4. Bulk density variation as a sintering temperature and magnesium orthosilicate content.

1300 °C while the composite (20MO-HA) managed to attain about 17.7% at the same temperature.

The effect of sintering on the bulk density of the HA and MO-HA composites is shown in Fig. 4. The results indicated that hydroxyapatite samples exhibited higher bulk density regardless of the sintering temperature employed when compared to the MO-HA composites. The bulk density of the HA sintered at 1000 °C was about 2.7 g/cm³ and attained a final density of above 3 g/cm³ when sintered and 1200–1300 °C. In contrast,

the 20MO-HA exhibited a bulk density of 1.9 g/cm³ at 1000 °C and 2.7 g/cm³ at 1300 °C. The densities of composites containing more than 20 wt% magnesium orthosilicate content were generally low when sintered below 1200 °C and progressively increased to reach a maximum at about 2.5 g/cm³ at 1300 °C as shown in Fig. 4. The lower bulk density recorded for these samples could be attributed to the decomposition of HA phase in the composite matrix.

Fracture toughness and Vickers hardness

The fracture toughness (K_{Ic}) of sintered samples with respect to sintering temperatures is shown in Fig. 5. Fracture toughness of HA and composites containing 10 to 50 wt% magnesium orthosilicate exhibited a similar trend with increasing temperature. The fracture toughness of the hydroxyapatite sample sintered at 1000 °C was 0.55 MPam^{1/2} and increases to about 1 MPam^{1/2} when sintered at 1300 °C. The beneficial effect of magnesium orthosilicate addition in enhancing the fracture toughness of the sintered ceramic has been revealed. In general, the addition of 10 to 20 wt% MO exhibited a much higher toughness than the undoped HA for sintering above 1200 °C. In particular, the 10MO-HA samples exhibited toughness of above 1.2 MPam^{1/2} when sintered above 1100 °C and attained a maximum of 2.4 0.1 MPam^{1/2} when sintered at 1300 °C. The highest fracture toughness of 2.5 0.1 MPam^{1/2} was measured at 1300 °C for hydroxyapatite containing 20 wt% magnesium orthosilicate composite (20MO-HA). This improvement in the fracture toughness in the composites could be associated with the presences of TCP in the composite matrix which could have interact with the propagating crack through a stress absorption mechanism although in general the presences of such secondary phase has been reported to be detrimental to properties of HA [1]. The fracture toughness values for most monolithic hydroxyapatite reported in the literature varied between 0.60 to about 1 MPam^{1/2}. The indentation fracture toughness of MO-HA composites obtained in this study was appreciably higher than those reported in many studies for dense hydroxyapatite ceramics [1, 25–28]. This finding is encouraging as it opens up opportunity for such HA composite to be used for biomedical load bearing implant.

The effect of sintering temperature on the Vickers hardness of composites is shown in Fig. 6. It is observed that the hydroxyapatite samples exhibited higher hardness than the composites throughout the sintering regime employed. An optimum hardness of 7.1 0.2 GPa was attained for hydroxyapatite when sintered at 1300 °C. In contrast, the highest hardness attainable for the composites containing 20 wt% magnesium orthosilicate was 2.9 0.1 GPa when sintered at 1300 °C. The lower hardness observed for the composites is associated with the lower bulk density of the sintered body as depicted in Fig. 4 and is in agreement with the

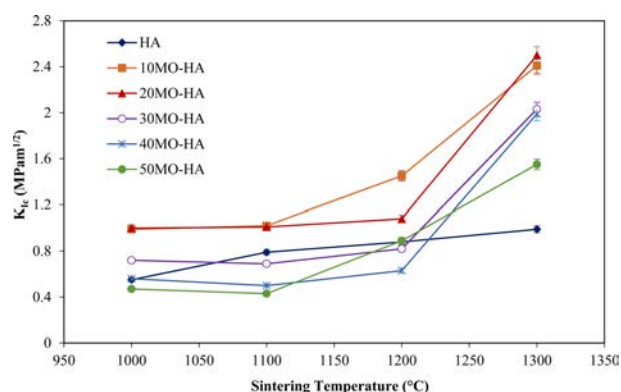


Fig. 5. Fracture toughness of sintered samples as a function of sintering temperature and magnesium orthosilicate addition.

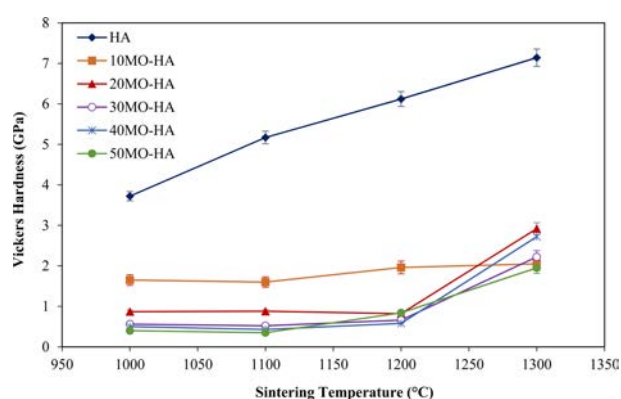


Fig. 6. Vickers hardness variation with magnesium orthosilicate addition as a function of sintering temperature.

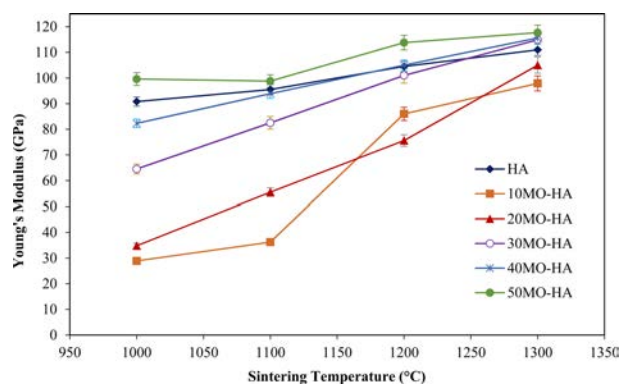


Fig. 7. Variation in the Young's modulus of sintered samples as a function of sintering temperatures.

literatures [7, 29-31].

The effect of sintering temperature on the Young's modulus of HA and MO-HA composites are shown in Fig. 7. It can be observed that the 50MO-HA composite exhibited high Young's modulus when compared to the monolithic HA regardless of sintering temperatures. The Young's modulus of the monolithic HA varied almost linearly from 90 GPa @ 1000 °C to about 111 GPa @ 1300 °C. In contrast, composites containing less than 50 wt% magnesium orthosilicate exhibited lower Young's modulus than the undoped HA when sintered at 1000 °C. Typical values recorded for the composites

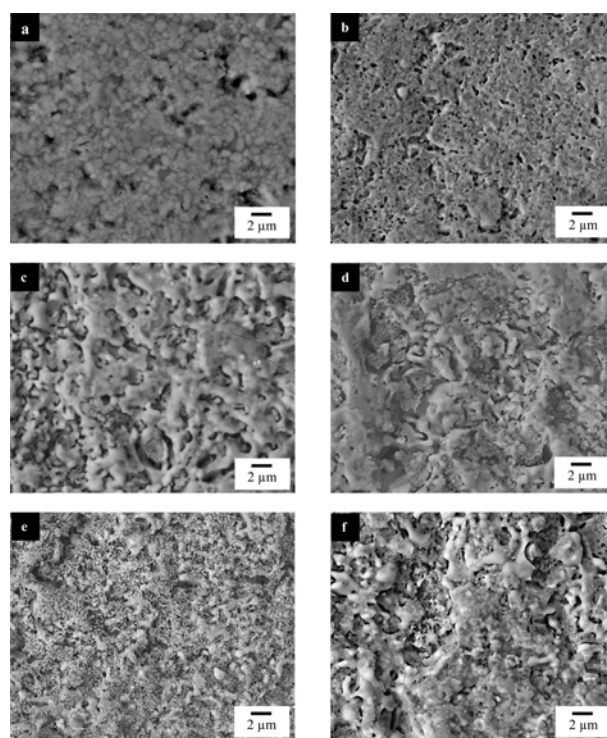


Fig. 8. SEM images of samples sintered at 1200 °C. (a) HA, (b) 10MO-HA, (c) 20MO-HA, (d) 30MO-HA, (e) 40MO-HA and (f) 50MO-HA.

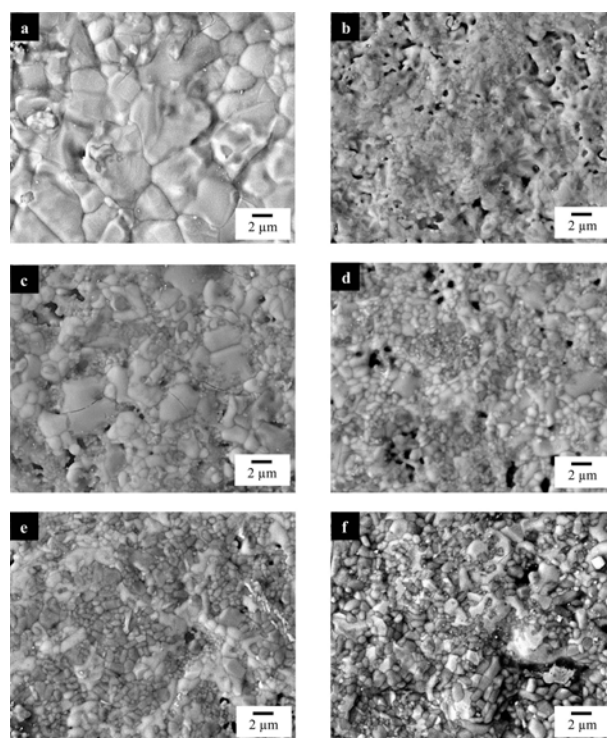


Fig. 9. SEM images of samples sintered at 1300 °C. (a) HA, (b) 10MO-HA, (c) 20MO-HA, (d) 30MO-HA, (e) 40MO-HA and (f) 50MO-HA.

are 29 GPa for 10MO-HA, 35 GPa for 20MO-HA, 64 GPa for 30MO-HA and 82 GPa for the 40MO-HA samples. It should be mentioned here that these low

Young's modulus exhibited by the composites can be beneficial when used as implant material due to the comparable value to that of human bones. However, the elastic modulus of the composites increased rapidly with increasing sintering temperature to attained values above 90 GPa. The maximum Young's modulus of 118 GPa was measured for the 50 wt% MO-HA composite when sintered at 1300 °C.

Microstructural development

Scanning electron micrographs (SEM) of the sintered samples at 1200 °C and 1300 °C are shown in Fig. 8 and Fig. 9. The SEM images of samples sintered at 1200 °C showed high amount of pores remaining in the structure after sintering, especially for the composites. These observations correspond well to the shrinkage and bulk density of the sintered composites discussed earlier. The monolithic hydroxyapatite sample sintered at 1200 °C shown in Fig. 8(a) exhibited a bimodal distribution of grains whereas a well-defined grains could not be visible for all the composites samples when sintered at 1200 °C and below. However, sintering at 1300 °C resulted in the formation of a denser microstructure, with well-formed grains being visible particularly for the composites. The beneficial effect of magnesium orthosilicate in suppressing the grain growth of hydroxyapatite has been revealed. The HA grains was observed to have grown rapidly, about ten times larger i.e. from an average of 0.55 µm at 1200 °C to about 5.5 µm at 1300 °C. On the other hand, the average grain sizes of the composites were much smaller than 0.55 µm as depicted in Fig. 9(b-f). The higher fracture toughnesses exhibited by the composites can be attributed to the fine grain size of the sintered body.

Conclusions

In the present work investigates the sintering behaviour of magnesium orthosilicate-hydroxyapatite (MO-HA) composites prepared via mechanical ball milling and conventional pressureless sintering method. It was found that regardless of sintering temperature, decomposition of hydroxyapatite to form β -TCP was inevitable in all the composites. Nevertheless, the composites exhibited higher fracture toughness than hydroxyapatite which could be associated with the presences of the secondary TCP phase in the ceramic matrix. A lower bulk density and Vickers hardness were observed for all the composites if compared to the monolithic HA. The beneficial effect of magnesium orthosilicate in suppressing the grain size of hydroxyapatite has been revealed. The composites exhibited a smaller grain size than 0.55 which explained the higher fracture toughnesses exhibited by the composites.

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