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Research paper

Sinterability of Magnesium Hydroxyapatite Bioceramic and Its Mechanical Properties

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Abstract

One of the most favoured material in bone tissue engineering field nowadays is hydroxyapatite (HA), which is also known to be bioactive and has a similar composition to human bone. However, developing an artificial bone or bone graft using biocompatible HA is a challenging task due to the lower strength of the main substance. To improve the mechanical properties of synthetic HA, introduction of metallic substance such as magnesium (Mg) into HA has been proposed. In this present study, 0, 10 15 wt% of magnesium hydroxyapatite (MgHA) nanopowders were prepared by a simple wet precipitation method. These nanopowders were then compacted using a 10-ton compression uniaxial press machine with 150 MPa pressure to form a disc shape of dense MgHA. After that, the MgHA discs were sintered at a temperature of 1000 °C and 1100 °C to remove the organic compounds and further densify the ceramics. XRD results showed that the crystallinity of MgHA increased when the sintering temperature increases. The compression test showed that the 10 wt% MgHA sample recorded the highest compressive strength (243.59 MPa) when sintered at 1100 °C, while pure HA has the lowest value with 49.37 MPa. This study also demonstrates that sintering temperature at 1100 °C gives significant improvement to the mechanical properties of the MgHA dense bodies compared to sintering at 1000 °C.

Keywords: *Compressive Strength; Hydroxyapatite; Magnesium; Mechanical Properties; Sintering*

1. Introduction

Sintering is necessary for all ceramic bodies to produce a microstructure with appropriate properties [1] to avoid detrimental effect on the mechanical properties of the final product. Generally, sintering will increase the mechanical strength of HA due to the increased densification. Biomaterial such as bioceramics HA has been largely use in biomedical engineering, including applications as bone and dental implants due to its similar chemical composition to the bone mineral phase [2]. However, one of the major concerns with synthetic HA is its low fracture toughness attribute. Numerous studies have been carried out to improve the mechanical properties of the sintered HA [1, 2]. One of the most promising approaches is by adding some metallic additives into HA. The use of metallic element such as magnesium (Mg) as a doping agent does not only improve the mechanical properties of synthetic HA, but it can also promote bone formation and bone growth, which is essential in developing artificial bone implants [3].
Continuous research was carried out to further improve HA as one of the best candidates to be used as a bone implant material [4]. The introduction of Mg as the doping agent was important in human metabolism and it is naturally present in bone tissue [5]. Previously, it was reported that the doping of Mg in HA helps in bone cell adhesion, proliferation and mineralization of the bone [6]. It is also well known that Mg is nearly conjoined with the mineralization of calcified tissues, exactly stimulating osteoblast proliferation [7]. A considerable number of studies have confirmed that that after heat treatment, the apatite structure of MgHA does not decompose or undergo any phase transformation at elevated temperatures [7, 8].
For sintering process of calcium phosphate ceramics, suitable temperatures were first identified to attain a good result. It has been proclaimed that ideal properties for calcium phosphates (including HA) could be gained by rising the sintering temperature to about 1300 °C. Another study done by Kamalanathan et al. [9] showed that the temperature for the sintering could be in the range of 800 °C to 1400 °C. On the contrary, the effect of sintering temperatures at lower than 1000 °C was not often assessed [10]. Nevertheless, the sintering temperature in this present study was varied at 1000 °C and 1100 °C, using a conventional furnace, to observe any difference on the physical characteristics of MgHA.

2. Methods

The preparation of pure HA and MgHA dense bodies started with the synthesis process (wet precipitation method) of pure HA through a mixture of calcium oxide, CaO, ammonium di-hydrogen phosphate, $(NH_4).H_2PO_4$ and distilled water. The synthesis of the 10 wt% MgHA and 15 wt% of MgHA was then carried out with an addition of magnesium nitrate, $Mg(NO_3)_2.6H_2O$ as the doping agent in HA.
After both pure HA and MgHA in a saturated solid form was completely dried, they were grounded using pestle and mortar to obtain fine powders. The powders were later calcined at 700 °C in the high temperature furnace (Thermolyne F 46110) to improve its crystallinity. Calcination temperature also usually causes growth in grain size due to the absorption of heat energy by the particles [11].

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Fig. 1: Crushed MgHA powder, using pestle and mortar

Finally, the powder was appropriately weighted at 3 grams per specimen and then a 150 MPa pressure was applied to compact the powder into a disc shape by using a uniaxial compression press machine. Too high pressure will cause the specimens to crack prematurely. The dimension of the product was approximately 22 mm (d) x 4 mm (h).

Sintering of the MgHA discs was carried out accordingly with a heating rate of 5 °C per minute, 2 hours of soaking time and then left to cool at room temperature. The slow heating rate was used to prevent cracking due to shrinkage. The sintering temperature was varied at 1000 °C and 1100 °C, with a total of 5 specimens for each temperature.



Fig. 2: Sintered bodies of dense MgHA

Phase analysis of the sintered MgHA was examined using X-ray diffraction (XRD, Rigaku, UltimaIV). The diffraction spectra were recorded in the range between 20° to 50° using monochromatic CuKα wavelength, 1.5406 Å, while the scan speed was set at 2 degree/min with step size of 0.01°. The identification of phase crystallographic was conducted by matching the samples with the standard data of HA (Card No. 9-432) obtained from the International Centre for Diffraction Data (ICDD) reference files.

Vickers hardness measurement was carried out at the room temperature using a standard microhardness tester (Mitutoyo MVK-H1, 281048) with a load of 1 Kg for 15 s. Each hardness value represents an average of three independent measurements from each specimen. Compression tests were carried out using a universal testing machine (Instron, 3382) with a constant compression speed of 0.1 mm s^{-1}.

3. Results and Discussions

Fig. 3 exhibits the powder morphology of pure HA, 10 wt% MgHA and 15 wt% MgHA prior to compaction procedure. These powders were first dried and calcined at 700 °C to remove excess water and part of the organic compounds. Besides contributing to the powder growth, calcination also served as a process to transform the synthesized powder from amorphous to crystalline phase. The figures clearly show that the particles are densely packed, globular in shape and increase in size as the Mg concentration in HA increases.

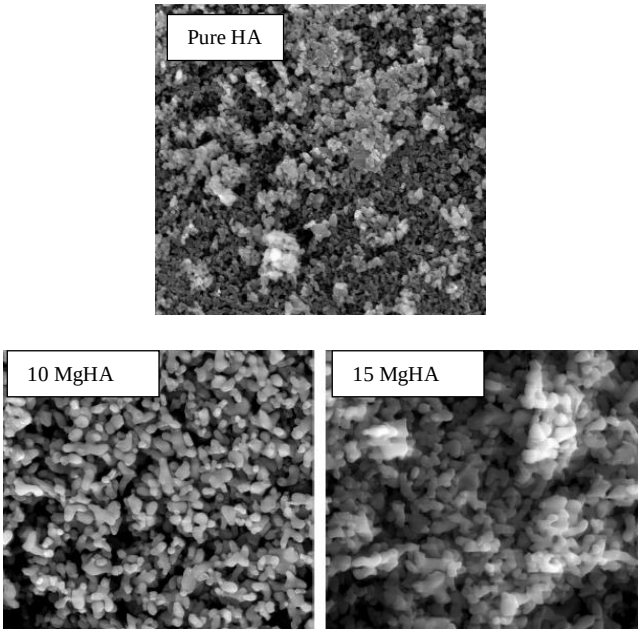


Fig. 3: Morphology of all MgHA powders after calcination at 700 °C, observed through FESEM

Table 1 and Fig. 4 display the hardness value of pure HA, 10 wt% MgHA and 15 wt% MgHA sintered at 1000 °C and 1100 °C recorded using Vicker's hardness tester. All samples show an increasing pattern in hardness values when the sintering temperature was increased to 1100 °C. It can also be noted that for both sintering temperatures, 10 wt% MgHA demonstrates a slight drop in its hardness and then rise dramatically for 15 wt% MgHA sample. This phenomenon was observed for both sintering cases. The maximum hardness was recorded for 15 wt% MgHA with 215.6 ± 18.7 HV compared to pure HA with 37.9 ± 3.7 HV, when both samples were sintered at 1100 °C. High hardness however, induced further brittleness of a ceramic biomaterial, resulting in low impact resistance property of a ceramic.

Table 1: Hardness values of pure HA, 10 wt% MgHA and 15 wt% MgHA sintered at 1000°C and 1100°C

	1000°C	1100°C
Sample	Hardness (HV)	Hardness (HV)
Pure HA	25.2 ± 4.5	37.9 ± 3.7
10 wt% MgHA	16.6 ± 2.1	27.1 ± 2.7
15 wt% MgHA	107 ± 8.7	215.6 ± 1.7

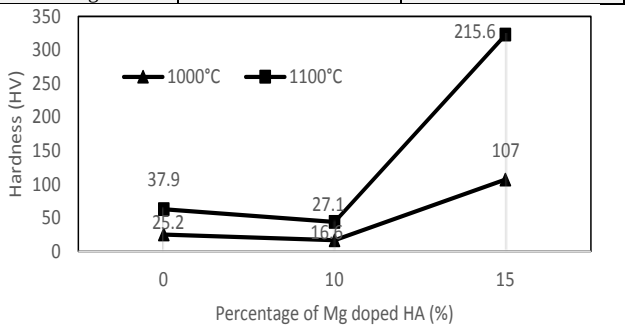


Fig. 4: The effect of sintering temperature on the hardness of all samples.

The X-ray diffractograms of pure HA, 10 wt% MgHA and 15 wt% MgHA sintered at 1000 °C are shown in Fig. 5. All samples displayed sharp and narrow peaks indicating that they were highly crystalline. The crystallinity increases when the sintering temperature was increased to 1100 °C, except for pure HA sample which shows a relatively low intensity for its three main HA peaks. This

can be seen in Fig. 6 where the diffraction patterns become broader and less intense for pure HA sample, but the other two samples' peaks remain sharp especially for 15 wt% MgHA. This result coincides with the study carried out by Thuault et al. [12], where he claimed that the addition of 15 wt% Mg into HA and then sintered at 1100 °C resulting in the peaks become narrower and sharper. On the other hand, a study by Adzila et al. [13] reported that an increase in Mg concentrations leads to the diminishing of HA phase and inducing the formation of secondary phase, such as beta tricalcium phosphate (β-TCP).

Based on this present study, it can be deduced that introducing Mg as a doping agent has not only increase the crystallinity of HA but also caused the phase to be stable at higher temperature (1100 °C) with no presence of other secondary phase.

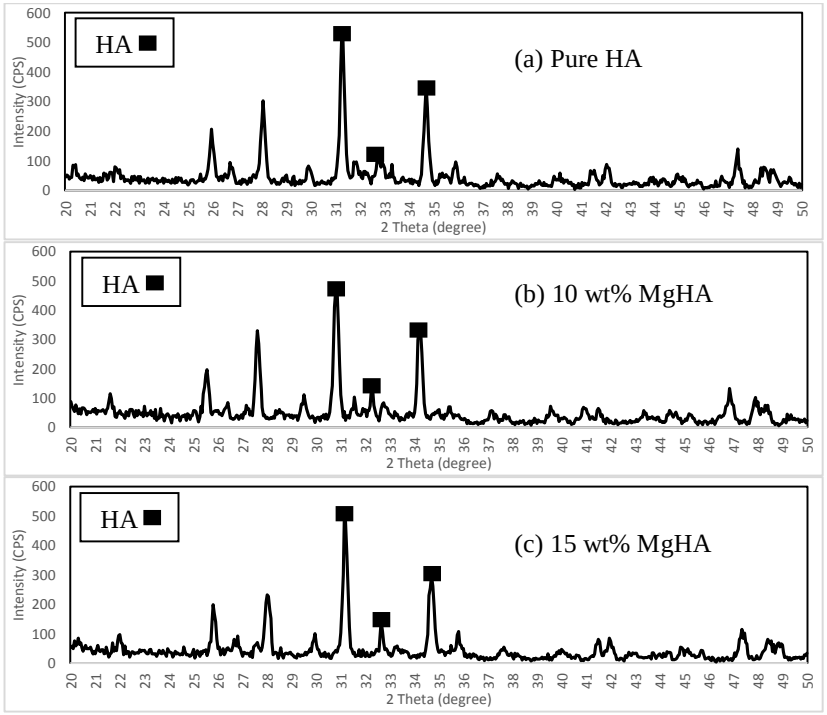


Fig. 5: XRD pattern for (a) Pure HA, (b) 10 wt% MgHA and (c) 15 wt% MgHA sintered at 1000 ºC

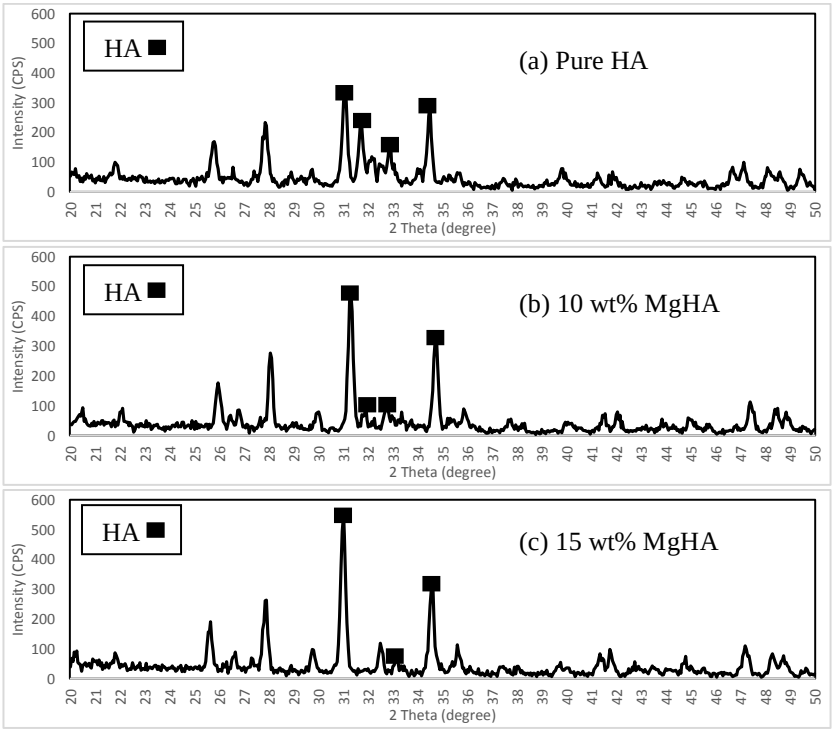


Fig. 6: XRD pattern for (a) Pure HA, (b) 10 wt% MgHA and (c) 15 wt% MgHA sintered at 1100 º

Wide ranges of compressive strength for all specimens sintered at 1100 °C are shown in Table 2 and Fig. 7. The results indicate that pure HA gives the lowest compressive strength value at 49.4 ± 5.2 MPa. This graph also implies that addition of 10 wt% Mg into HA has caused the strength to increase tremendously to 243.6 ± 3.5 MPa but when 15 wt% Mg was introduced, the effect subsided, reducing the compressive strength to 136.0 ± 2.8 MPa.

It is worthwhile to note that the compression resistance of a cortical human bone is around 130-180 MPa but the compressive strength of a ceramic biomaterial can reach up to 896 MPa [14] depending on its preparation method. Based on this data, it can be

concluded that both 10 wt% MgHA and 15 wt% MgHA dense bodies produced in this present work fall within the compression strength range of a human cortical (dense) bone. Hence, it can be assumed that these MgHA can be a suitable candidate for future biomaterials in the biomedical industry.

Table 2: Compressive strength of all samples sintered at 1100°C.

Sample	Compressive Strength (MPa)
Pure HA	49.4 ± 5.2
10 wt% MgHA	243.6 ± 3.5
15 wt% MgHA	136.0 ± 2.8

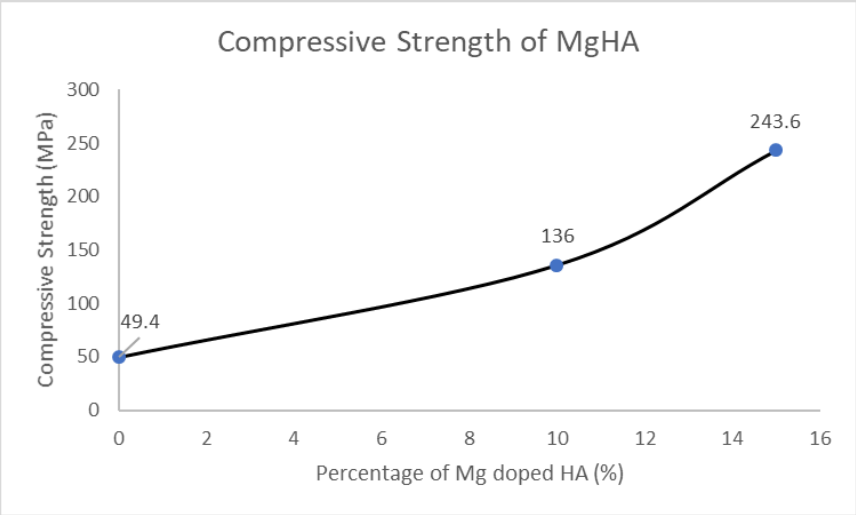


Fig. 7: Graph of the compressive strength for all specimens sintered at 1100°C.

4. Conclusion

HA dense bodies containing various concentration of Mg were successfully prepared via a simple uniaxial pressing technique, using powders derived from the wet precipitation method. XRD spectra confirmed that all samples (Pure HA, 10 wt% MgHA and 15 wt% MgHA) are highly crystalline, with no appearance of any secondary phase at both sintering temperatures (1000 °C and 1100 °C). Increasing the sintering temperature ultimately increase the hardness property of MgHA. On the other hand, pure HA was recorded as having the lowest compressive strength but then substantially progresses to almost 5 times higher, when 10 wt% Mg was substituted into it, specifically when sintered at 1100°C. This study proves that the role of doping agent, Mg as a sintering additive is very significant in improving the mechanical properties of HA, in terms of its hardness as well as compressive strength. However, too much amount of Mg in HA might deteriorate its physical stability which in return might reduce the mechanical performance of its dense bodies. In this present study, it was found out that addition of 15 wt% Mg had reduced the compressive strength by almost half compared to 10 wt% MgHA. Future *in-vitro* assessments shall be carried out to predict the biocompatibility of MgHA upon their exposure to the human body condition. This assessment will further ensure that MgHA capable to be used as a bone implant or other biomedical devices.

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