

SINTERING AND MECHANICAL PROPERTIES OF MgO-DOPED HYDROXYAPATITE BIOCERAMICS

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ABSTRACT

In the present research, nano hydroxyapatite (HA) powder doped with magnesia (MgO) was studied. The dopant was added to pure HA powder and ball milling was done for 1 hour. Green samples, in the form of discs and rectangular bars, were prepared and consolidated in air at temperatures ranging from 1000 °C to 1300 °C. The sintered samples were characterized to determine the phase stability, relative density, hardness, fracture toughness and Young's modulus. The phase analysis revealed that the HA phase was not disrupted regardless of dopant additions and sintering temperature. It has been revealed that all HA samples achieved > 98% relative density when sintered between 1100 °C - 1300 °C. However, the addition of 0.5 wt% MgO when sintered at 1100 °C was found to be most beneficial in aiding sintering with samples exhibiting the highest Young's modulus of 122.15 GPa and fracture toughness of 1.64 MPam^{1/2} as compared to 116.57 GPa and 1.18 MPam^{1/2} for the undoped HA.

Keywords: Hydroxyapatite; Sintering; Mechanical Properties;

INTRODUCTION

The development of advanced ceramics for biomedical applications is one of the fastest growing research areas. Due to the apatitic structure of human hard tissues, hydroxyapatite $\text{Ca}_{10}(\text{PO}_4)_6\text{OH}_2$ (HA) appear to be the best studied compounds among different forms of calcium phosphate ceramics [1]. Bone crystals are formed in a biological environment through the process of biomineralization [2]. The major inorganic component of bone mineral is a CaP-based apatite phase contains trace ions such as Na^+ , Mg^{2+} and K^+ , which are known to play a significant role in its overall performance [3]. Mg-deficiency could cause poor mechanical reliability of HA, thus, limiting its application to non-stressed loaded regions [4]. As a result, it is favorable to incorporate these ions that are found in human bone to improve the mechanical properties of synthetic HA without any decomposition. For instance, Li *et al.* [5] reported decomposition products such as TCP and TTCP were present in the structure when HA were doped with zirconia. Evis *et al.* [6] described the presence of TCP in HA when magnesium was added and samples sintered above 1000 °C. These secondary phases would have an adverse influence on the mechanical properties and biodegradability of the HA ceramics [7]. In this work, the primary objective is to study the phase stability and sinterability of synthesized HA ceramics by wet precipitation method when doped with up to 1 wt% magnesium oxide (MgO) via a new profile for

conventional pressureless sintering.

EXPERIMENTAL DETAILS

The HA powder used in the present work was prepared according to a novel wet chemical method comprising precipitation from aqueous medium involving calcium hydroxide and orthophosphoric acid [8]. The dopant used in this work was obtained from a commercial available MgO powder (99.99 % purity) and amount of dopant used were 0.1, 0.5 and 1.0 wt%. The synthesized HA and MgO powder were mixed in 150 ml of ethanol and followed by ball milling for 1 hour. After the mixing, the wet slurry was dried, crushed and sieved to obtain fine powder. The green samples were uniaxial compacted at about 1.3 MPa to 2.5 MPa into rectangular bar (4 × 13 × 32 mm) and circular discs (20 mm diameter) samples. The compacts were subsequently cold isostatically pressed at a pressure of 200 MPa (Riken Seiki, Japan). This was followed by consolidation of the particles by pressureless sintering performed in air using a rapid heating furnace (ModuTemp, Australia), over the temperature range of 1000 °C to 1300 °C, with ramp rate of 2 °C/min. (heating and cooling) and soaking time of one minute for each firing. All sintered samples were then polished to a 1 μm finish prior to testing. The phase stability studies of all samples were characterized by using X-ray diffraction (XRD-6000, Shimadzu, Japan). The bulk densities of the samples were determined by the water immersion technique (Mettler Toledo, Switzerland). The Young's modulus (E) by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic: MK5 "Industrial", Belgium). The modulus of elasticity or Young's modulus was calculated using the experimentally determined resonant frequency [9]. The fracture toughness (K_{Ic}) of the samples was determined using the Vickers indentation method (Matsuzawa, Japan). The indentation load (< 200 g) was applied and held in place for 10 seconds. Five indentations were made for each sample and the average value was taken. The K_{Ic} value was calculated using the equation derived by Niihara [10].

RESULTS AND DISCUSSION

The sinterability of the HA compacts were compared in terms of phase stability, relative density, Vickers hardness, fracture toughness and Young's modulus.

All the samples, regardless of sintering conditions and dopant addition have not shown any cracking or distortion after sintering. XRD phase analysis showed that through the sintering of MgO-doped and undoped HA samples, no secondary phases such as TCP, CaO and calcium hydroxide were verified as shown in Figure 1.

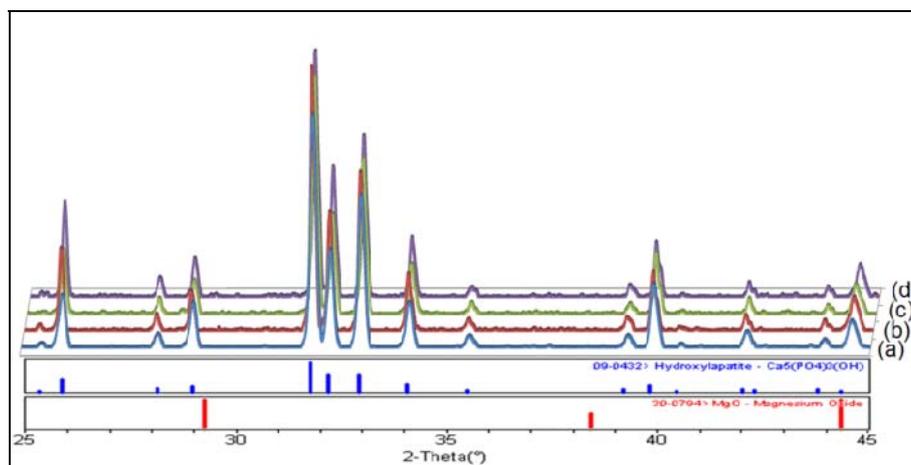


Figure 1: XRD patterns of (a) undoped HA and HA containing (b) 0.1 wt%, (c) 0.5 wt% and (d) 1 wt% MgO samples sintered at 1200 °C

The XRD results indicated that the phase stability of HA was not disrupted by the sintering schedule and temperature, pressing conditions prior to sintering as well as the dopant addition. This result is very encouraging as there are some findings showing that the addition of other materials into HA matrix may lead to decomposition of HA and formation of TCP and CaO [11, 12]. Sintering at high temperatures, above 1300 °C, has been reported in the literature to be detrimental as HA phase instability was observed. However, in the present work, decomposition of HA phase was not observed even when sintered at 1300 °C. This observation could be associated with the high local humid atmosphere that could have played a role in hindering dehydroxylation in the HA matrix during high temperature sintering.

The densification curves as a function of sintering temperatures is shown in Figure 2. In general, the bulk density variation of all the composition studied exhibited a similar trend with increasing sintering temperature. A general observation that can be made from Figure 2 is that the dopant incorporated has minor effect on the measured bulk density of HA samples. All the samples attained above 98 % of theoretical density when sintered above 1200 °C.

The relationship between the Young's modulus of the sintered body, sintering temperature and MgO additions are shown in Figure 3. The inclusion of MgO in HA lattice, particularly for the higher dopant concentration, was found to be beneficial in enhancing the stiffness of the sintered HA body. As shown in Figure 3, the highest value of 124.4 GPa is recorded for HA samples containing 0.5 wt% MgO when sintered at 1200 °C.

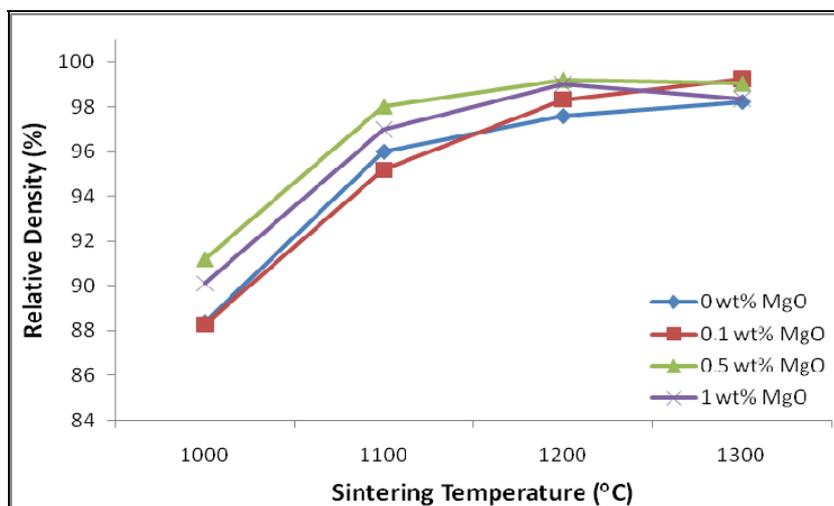


Figure 2: Relative density variation as a function of sintering temperatures for HA with different amount of MgO

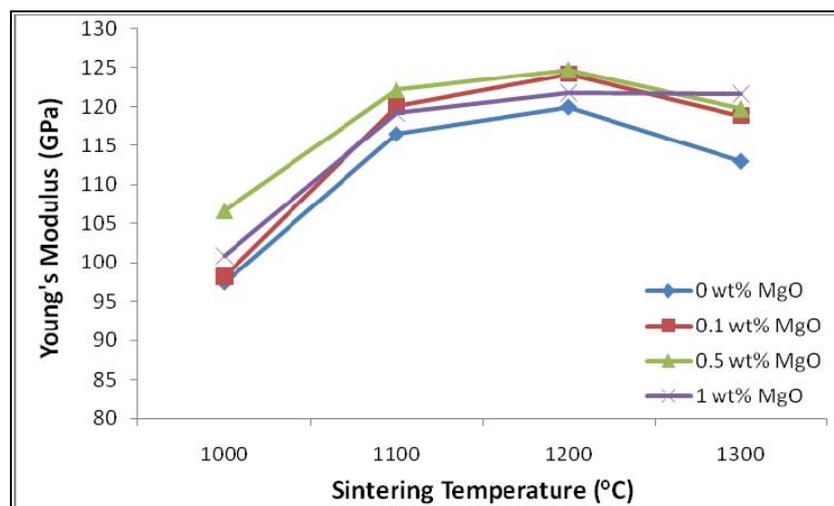


Figure 3: The effect of sintering temperatures and MgO addition on the Young's modulus of HA

The variation of the average Vickers hardness and fracture toughness of samples sintered at various temperatures is shown in Figure 4 and Figure 5, respectively. The beneficial effect of MgO especially for the 0.5 wt% addition in enhancing the hardness and toughness of HA has been revealed. Figure 4 shows that the measured hardness of all the samples revealed a similar trend, i.e. the hardness increased rapidly to a maximum value and then decreased slowly with increasing sintering temperatures. For example, the hardness of the undoped HA ceramic peaked at 1100 °C (8.1 GPa) and further increase in temperature > 1100 °C resulted in a decrease in the hardness.

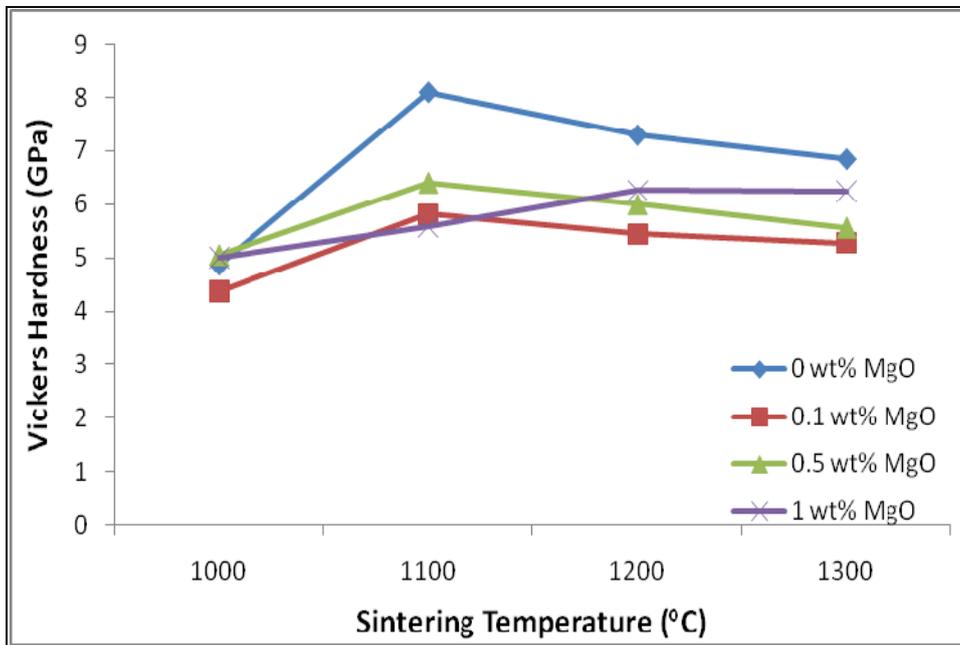


Figure 4: Effect of sintering temperature and MgO addition on the Vickers hardness of HA

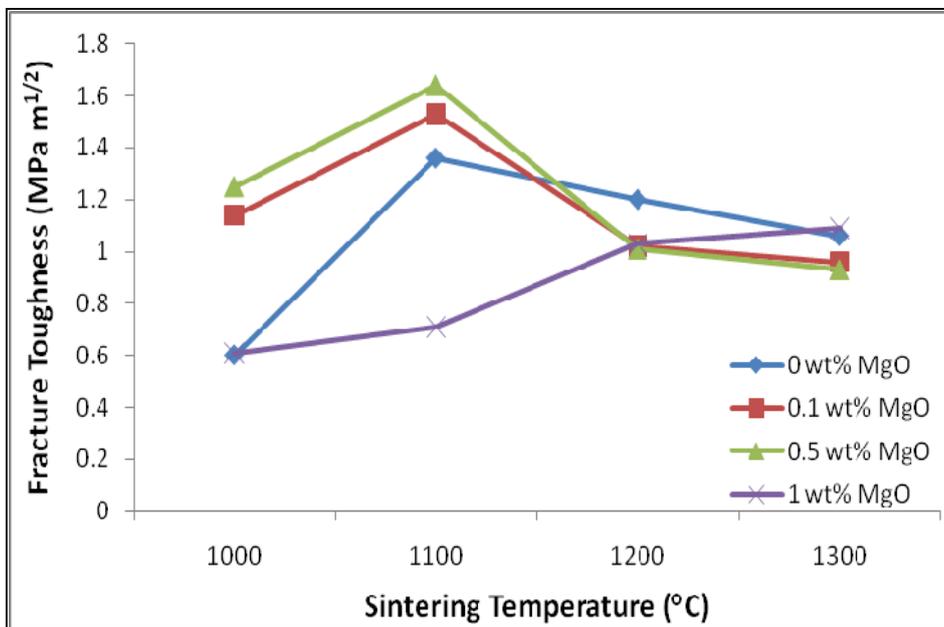


Figure 5: Effect of sintering temperature and MgO addition on the fracture toughness of HA

The fracture toughness of all compositions exhibited very similar trend as the sintering temperature increased (Figure 5). The results show that the addition of MgO was effective in enhancing the fracture toughness (K_{Ic}) of the synthesized HA, particularly when sintered at 1100 °C. The 0.5 wt% MgO-doped HA samples exhibited the highest fracture toughness of $1.64 \pm 0.17 \text{ MPam}^{1/2}$ as compared to $1.36 \pm 0.05 \text{ MPam}^{1/2}$ measured for the undoped HA. It should be highlighted here that the K_{Ic} value obtained for the MgO-doped HA is very encouraging, as most researchers had reported that the experimental K_{Ic} values for HA varied from $0.9 \text{ MPam}^{1/2}$ to about $1.2 \text{ MPam}^{1/2}$ [13-15]. Moreover, this improved in toughness in the presences of dopants reported by these researchers was accompanied by HA phase decomposition. From the results it can be concluded that MgO plays an important role in suppressing grain growth and this lead to higher fracture strength and hence higher fracture toughness.

CONCLUSION

This study has shown that the incorporation of small amount of magnesium oxide can be beneficial in enhancing the mechanical properties without affecting the HA phase stability even when sintered at 1300 °C. MgO doping, however was found to have a minor effect on the bulk density of sintered HA regardless of the sintering temperature employed. The addition of 0.5 wt% MgO and sintering temperature of 1100 °C was found to be most beneficial as the HA samples exhibited the highest Young's modulus of 122.15 GPa and fracture toughness of $1.64 \text{ MPam}^{1/2}$.

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