Sintering and Properties of Dense Manganese-Doped Calcium Phosphate Bioceramics Prepared Using Sol-Gel Derived Nanopowders

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Sintering and Properties of Dense Manganese-Doped Calcium Phosphate Bioceramics Prepared Using Sol-Gel Derived Nanopowders

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Dense manganese-doped biphasic calcium phosphate (Mn-BCP) ceramics were fabricated via uniaxial pressing using the sol-gel derived powders. The compacted discs were sintered in ambient atmosphere with temperatures ranging from 800°C to 1400°C. Manganese (Mn) level was varied in the range of 0.6, 1.9, 4.3, and 11.9 mol%, and its effect on physical and mechanical properties of the dense samples was investigated. All dense samples have been proved to show HA and β-TCP phases only. Mn doping has shifted the onset of the sintering temperature of the BCP, leading to the improved densification of BCP ceramics. The relative density also increased with sintering temperature. Considerable grain growth has been observed for Mn-doped BCP samples when compared to the undoped BCP. Furthermore, 11.9 mol% Mn-doped BCP dense samples showed the maximum hardness of 6.66 GPa compared to 2.89 GPa for the undoped BCP. The incorporation of Mn was also found to be beneficial in enhancing the fracture toughness of BCP throughout the temperature range employed. This study has shown that Mn doping was effective in improving the sintering properties of BCP without affecting the phase stability.

Keywords: Biomaterials; Ceramics; Characterization; Dopant; Manganese; Mechanical; Nanomaterials.

Introduction

Calcium phosphate bioceramics have widely been developed for biomedical applications due to excellent biocompatibility, bioactivity, and osteoconductivity characteristics. Among various phases of calcium phosphate, hydroxyapatite [Ca₁₀(PO₄)₆(OH)₂], HA and beta-tricalcium phosphate [Ca₃(PO₄)₂], β-TCP, with similar composition and crystal structure to natural bone, are the two most common calcium phosphate ceramics applied for medical purposes [1]. These materials have been fabricated in porous [2], coating [3], granular [4], paste [5], and dense forms [6].

Dense HA is described as HA that has porosity less than 5 vol% with micropores size diameter less than 1 μm and grain size bigger than 0.2 μm. The microporosity is unintentionally introduced and is dependent on compaction parameters as well as temperature and duration of sintering. It is important to note that dense HA has a compressive strength four times that of cortical bone, but yet it shows a significantly lower tensile strength and fracture toughness. Hence, multiple development efforts have been carried out in enhancing the mechanical properties of dense BCP including: a) varying the powder processing technique to manipulate powder properties such as particle size and shape, distribution, and morphology of the starting powders, b) control of sintering process, and c) incorporation of metal as sintering additive into the BCP.

Inclusion of trace metal elements has a significant role in improving the physical and biological properties of bioactive ceramics. Many trace metal elements like Mg, Sr, and Na have been incorporated into the CaP phase. However, the inclusion of Mn in BCP has not been studied extensively although numerous works have reported the significant role of manganese oxide in promoting densification in other ceramics systems [7]. The incorporation of manganese (Mn) as sintering additive into apatite structure has been of great interest as it improves its bone-like mechanical properties [7]. In addition, the influence of Mn on stability and particle growth of HA have also been recognized [8].

It is reported that Mn physically functioned as calcination additive of BCP powders without producing other secondary phases like α-TCP and CaO which possibly inducing microcracks [7, 9, 10]. Doping of Mn into BCP, hence, is expected to show better mechanical performance of the dense bodies. Biologically, it was found that divalent Mn²⁺ has influenced the activation of integrins, a family of receptors that mediate cellular interactions with extracellular matrix and cell surface ligands [8, 11]. The ligand affinity...
increases in the presence of Mn, resulting in the promotion of cell adhesion. Moreover, manganese in the bone was also found to cause a decrease in bone resorption [12].

Various research groups have attempted to dope calcium phosphate materials with manganese [7–10, 13, 14] through the solid-state reaction [8, 10] and precipitation method [8]. In this work, manganese has been doped into BCP powder via the sol-gel technique. No work on sol-gel derived Mn-doped BCP powders reported by other groups. Sol-gel synthesis allows the preparation of materials not easily accessible by other methods yet using mild and low energy conditions. The obtained sol-gel powders were then compacted and sintered to obtain dense BCP compacts with optimum mechanical properties. We have reported the synthesis of manganese doped BCP powder elsewhere [15, 16]. This report presents the effect of Mn content and sintering condition on phase behavior and mechanical properties of the BCP dense samples.

Experimental

Preparation of Dense Undoped BCP and Mn-Doped BCP Ceramics

Undoped (Mn-free) BCP and Mn-doped BCP powders used to produce dense compacts were synthesized via a sol-gel technique and have been reported elsewhere [15, 16]. The sol-gel undoped BCP and Mn-doped BCP powders with four different molar concentrations ranging from 0.6 mol%, 1.9 mol%, 4.3 mol%, and 11.9 mol% were synthesized. Manganese level in the BCP powder samples was determined on a Perkin Elmer atomic absorption spectrometer (AAS), model AAnalyst 400. The undoped BCP and Mn-doped BCP powders were uniaxially compacted at 2.5 MPa pressure into disc shapes (20 mm diameter × 5 mm thickness) using hardened steel mould and die set. For each powder concentration, seven samples were fabricated. Cleanliness of the mould and die set was strictly controlled to ensure that samples are not contaminated, and it was also cleansed with WD-40 to prevent powder lamination. The green bodies were sintered in air using a heating furnace (Protherm, PLF 160/5) at seven different temperatures ranging between 800–1400°C and held for 2 hours. The ramp-rate was fixed at 2°C/min for both heating and cooling process. Conventional pressureless sintering was used in all processes. It has been well established that, when the furnace ramp-rate exceeded 5°C/min, thermal and residual stresses would develop in the HA structure [17, 18]. The reason behind this phenomenon is due to the low heat conductivity and high shrinkage rate of HA which then led to the formation of microcracks and macrocracks in the samples [19].

Characterization of Dense Mn-BCP Ceramics

Prior to characterization, the sintered dense samples were ground and polished manually on one surface using Mecapol (Presi, P260). The samples were ground using silicon carbide (SiC) paper (600–1000 grit) in order to remove the roughness and refine the surface for characterization. The samples were then polished using diamond paste (3 μm–1 μm) slightly until an optically reflective surface was obtained. The presence of the crystalline phase in the sintered dense samples was analyzed by X-ray diffraction (XRD) (Shimadzu Diffractometer, XRD-6000), and the scans were performed on the surface of the polished dense samples. The change in color intensity of the produced dense samples was measured in the range of the visible light using UV-Vis Spectrometer (Perkin Elmer, Lambda 35) with a diffuse reflectance accessory (AS-00552-210). The bulk density of the sintered dense samples was measured by water immersion technique [20–22] based on the Archimedes principle using a standard densimeter (Alfa Mirage, MD-300S). The immersion medium used in the measurement was distilled water. Subsequently, the relative density was calculated by taking the theoretical density of HA as 3.156 g/cm³. For Vickers hardness determination, the indentations were made using a pyramidal diamond indenter (Mitutoyo, MHV H-2) with an applied load of 100 g. The load was applied smoothly, without impact, and held for 10 seconds. In the present work, three indentations were made for each sample, and the average value was taken. The fracture toughness (KIC) of the sintered dense samples was determined using Vickers indentation method and the KIC value was calculated using the equation reported by Niihara [23].

Results and Discussion

Detailed characterization of undoped BCP and Mn-doped BCP powders has been published elsewhere [15, 16]. The transmission electron microscopy (TEM) measurement of the undoped BCP powder calcined at 900°C shows spherical crystals with crystallite size distribution between 10 nm and 20 nm. The nanometric primary particles are globular in shape and tightly agglomerated into micrometric aggregates. Field emission scanning electron microscopy (FESEM) revealed that doping of Mn into BCP particles caused fusion of particles leading to larger individual particles. Figure 1 shows UV-vis absorption bands of the dense samples of undoped and Mn-doped BCP sintered at 1300°C. It was reported that intensity of the color increased with the increasing Mn content and calcination temperature [24]. In this study, the increase in Mn content has also increased the color intensity of dense BCP to darker shades, as verified by the increased light absorption for higher Mn content. This phenomenon was also probably influenced by the natural appearance of Mn itself as blackish or brown solid. The origin of the apatite blue color was due to the presence of Mn⁵⁺ or MnO⁴⁻ ions at the PO₄⁻ sites in the apatite crystal structure [24, 25]. Sintering at higher temperatures increases the intensity of oxidation in the oxidizing atmosphere and also provides enough energy for the oxidized manganese ion (Mn⁷⁺ to Mn⁵⁺) to migrate within the crystal lattice [24, 25]. Nevertheless, the change in color in the present work was found to have negligible effect on the phase stability for both Mn-doped BCP powder and dense samples. This is confirmed by the XRD phase analysis showing no presence of other phases other than HA and β-TCP up to the sintering temperature of 1200°C for the powder and 1400°C for dense samples [16].

XRD analysis on the dense bodies of undoped and 0.6 mol% and 4.3 mol% Mn-doped BCP are shown in Fig. 2. All dense compacts showed peaks of HA phase
that correspond to the standard International Centre for Diffraction Data (ICDD) card (no: 09-432 for HA) with no secondary phases such as α-TCP, TTCP, or CaO detected. Within the sintering regime employed, the phase transition of β-TCP to HA was observed where the presence of β-TCP peaks disappeared for Mn-doped BCP dense samples sintered at higher temperatures. For undoped BCP dense samples, β-TCP was still detected at the temperature of 900°C but disappeared at higher temperatures. For 4.3 mol% Mn-doped BCP, β-TCP phase started to disappear at a higher temperature, 1200°C. The phase transition occurred as free Ca, which was expelled from β-TCP by Mg substitution, which in turn reacts with β-TCP phase to form HA phase [26]. As a consequence, the HA peaks were observed with the increasing sintering temperatures. This result shows that at high sintering temperature >1200°C, β-TCP and Mn-doped β-TCP becomes unstable and contributes to a decrease in solubility limit of Mn in the β-TCP. Other possible factors that contributed to the disappearing of β-TCP during the sintering process is the presence of moisture [27] in the suspension and the fact that also during the thermal treatments which was carried out in air atmosphere [28]. Because of the characteristic of TCP as unstable phase at elevated temperature, it may react with the moisture present in the furnace atmosphere to form stable HA.

No peak of alpha-tricalcium phosphate (α-TCP), tetracalcium phosphate (TTCP), and calcium oxide (CaO) was detected in these dense samples throughout the sintering regime to 1400°C, which points out that the phase transition temperature from β-TCP to α-TCP probably happened above 1400°C. However, previous researches reported that HA ceramics started to decompose into secondary phases when sintered beyond 1350°C [29–31] and some even reported that it started at about 1300°C [32–37]. Hence, it could be deduced that in this research work, sol-gel derived HA phase stability was not disrupted by the fabrication of dense samples parameters such as the initial pressing conditions, sintering cycle, and temperature employed.

Wang et al. reported that sintering can lead to the partial thermal decomposition of HA into TCP and/or TTCP [38]. The decomposition is accompanied in two steps: dehydroxylation and decomposition. It was also stated that dehydroxylation to oxyhydroxyapatite proceeds at temperatures about 850–900°C by the fully reversible reaction in accordance to Eq. (1) [38]:

\[
\text{Ca}_{10}\left(\text{PO}_4\right)_{6}(\text{OH})_2 \rightarrow \text{Ca}_{10}\left(\text{PO}_4\right)_{6}(\text{OH})_{2-x}O_x + \text{H}_2\text{O}_{\text{gas}},
\]

The decomposition to TCP and TTCP occurs at a temperature greater than 900°C according to the reaction given in Eq. (2):

\[
\text{Ca}_{10}\left(\text{PO}_4\right)_{6}(\text{OH})_2 \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O}_{\text{gas}}.
\]

According to these equations, both the dehydroxylation and decomposition reactions include water vapor as a product. The rates at which these reactions proceed would depend on the partial pressure of H₂O in the sintering atmosphere [39]. Besides that, the high humidity content present in the sintering atmosphere has the tendency to slow down the decomposition rate by preventing the dehydration of the OH group from the HA matrix [16]. Thus, the secondary phases could be suppressed by controlling the moisture content in the sintering atmosphere.

In addition, it was observed from Fig. 2 that the HA crystallinity of the dense samples similar to the HA crystallinity of the corresponding powder [Fig. 2(d)] used for their fabrication. At 900°C, the crystallinity of undoped BCP dense samples was higher than the 4.3 mol% Mn dense sample due to higher crystallinity of its powder at that temperature.

The decomposition of β-TCP can be explained in details via the TG/DTA analysis performed on the as synthesized powder (Fig. 3). The presence of Mn caused a change in the sintering behavior of dense BCP. The results from the TG/DTA study suggest that the presence of Mn has shifted the onset of the sintering temperature of the BCP, indicating that the presence of manganese improves the densification of the β-TCP phase in the BCP mixture [9]. This analysis revealed that the Mn is an effective sintering additive for β-TCP, as it delayed the phase transformation of β-TCP to other phases, which are HA or α-TCP. This characteristic allows Mn-doped β-TCP to be sintered at higher temperatures which can produce denser materials with possibly better properties [9].

Densification behavior of the sintered samples can be affected by the difference in powder characteristics and morphologies. Moreover, in this study, the densifications are studied in terms of Mn content and sintering temperatures. From the effect of sintering temperature on the relative density, it was likely that the increase in relative density was irrespective of Mn content. For undoped BCP dense samples, the relative density also increased with the increasing sintering temperature, as Fig. 4 shows.
Moreover, it was observed that the density curve showed small increment before the onset of densification. This corresponds to the first stage of sintering in which necks are formed between powder particles [40]. Furthermore, the second stage of sintering would correspond to the onset of densification and the removal of the majority of porosity [17], as indicated by the dramatic increase in the sintered dense samples density between 1000°C and 1300°C.
Generally, all the compositions studied exhibited a similar trend in the bulk density variation as the sintering temperature increased. Figure 4 shows that all the samples showed relative density of above 82% of theoretical density at all temperatures. However, the undoped BCP achieved the highest value of only 91% after 1300°C sintering, which could be achieved by 4.3 mol% Mn-doped BCP at a lower temperature of 1200°C. For 0.6 mol% Mn and 1.9 mol% Mn, the maximum densification of 92% and 93%, respectively, was attained at 1300°C. Meanwhile, 11.9 mol% Mn only attained the highest of 98% relative density when sintered at 1400°C as compared to 4.3 mol% Mn which attained 99% densification at 1300°C and 1400°C.

Sintering at 1300°C resulted in a further increase in density to 99% for 4.3 mol% Mn compared to 91% and 92% relative densities for undoped and 1.9 mol% Mn-doped BCP compacts, respectively. This improvement in densification observed for the 4.3 mol% Mn-doped sample is believed to be influenced by the higher amount of stable β-TCP phase present in the starting powder as shown in Fig. 2(d). The stability of the β-TCP phase has been reported to have an influence on the densification of the material at higher temperatures [41]. In addition, it was found that the 4.3 mol% Mn-doped BCP has lower HA crystallinity and the smallest particle size among the synthesized powders [17]. It is well documented that smaller particle size would provide a higher heat transfer area and thus accelerate densification upon sintering [34, 42]. These features probably contributed to the highest densification achieved by the 4.3 mol% Mn-doped BCP in the present work.

The effects of sintering temperature on the Vickers hardness, $H_v$, of both the undoped BCP and Mn-doped BCP are shown in Fig. 5. It can be seen that the Mn doped samples exhibited superior hardness compared to those of undoped BCP throughout the sintering regime. For undoped BCP, the $H_v$ was $0.51 \pm 0.04$ GPa and $0.53 \pm 0.02$ GPa at 800°C and 900°C, respectively. These results were detrimental as the sample exhibited the lowest hardness throughout the sintering temperatures employed. The hardness continuously increased with sintering temperature and reached the maximum of 3.05 ± 0.02 GPa at 1300°C.

Further sintering at 1400°C, however, resulted in a decrease in hardness for all samples except for the 11.9 mol% Mn doped sample. The maximum values of $3.48 \pm 0.02$ GPa and $4.58 \pm 0.02$ GPa were obtained for the 0.6 mol% and 1.9 mol% doped BCP, respectively, at 1300°C. As Mn content increased to 4.3 mol% and 11.9 mol%, sharper increase in hardness with increasing sintering temperature between 900°C and 1200°C was observed, with values of $6.54 \pm 0.2$ GPa and $6.36 \pm 0.02$ GPa, respectively, being attained at 1300°C. For 4.3 mol% Mn this is the maximum value but for 11.9 mol% Mn sample, the hardness continuously increased to a maximum of $6.66 \pm 0.03$ GPa when sintered at 1400°C. In contrast, the undoped BCP could only be attained a maximum hardness of $2.89 \pm 0.01$ GPa when sintered at 1400°C. The maximum hardness achieved in the study is slightly lower than what we had reported previously, 7.58 GPa, for the precipitation method derived HA powder wet milled with MnO$_2$ [7].

The effects of sintering temperature and Mn doping on the fracture toughness of the BCP compacts are shown in Fig. 6. Similar trend of Vickers hardness was also observed for the fracture toughness ($K_I$) where the Mn doped BCP compacts exhibited better properties than the undoped BCP compacts throughout the sintering regime. For the undoped BCP sintered compacts, the $K_I$ was observed to increased from the lowest value of $0.31 \pm 0.01$ MPam$^{1/2}$ at 800°C to the maximum value of $0.72 \pm 0.01$ MPam$^{1/2}$ at 1300°C, followed by a decrement to $0.68$ MPam$^{1/2}$ at 1400°C. Likewise, the fracture toughness of the Mn doped sintered samples of 0.6 mol%, 1.9 mol%, and 4.3 mol% showed improvement with sintering temperature up to 1300°C, i.e., $0.73 \pm 0.01$ MPam$^{1/2}$, $0.75 \pm 0.01$ MPam$^{1/2}$, and $0.97 \pm 0.01$ MPam$^{1/2}$, respectively. Meanwhile, the $K_I$ for 11.9 mol% Mn continuously increased to $1.05 \pm 0.01$ MPam$^{1/2}$ at 1400°C, which was the maximum value of $K_I$ attained in this research work.
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relative density of 99% relative density was achieved at density, hardness, and fracture toughness. The maximum properties dense BCP ceramics as investigated in terms of mechanical properties dense BCP ceramics as investigated in terms of density, hardness, and fracture toughness. The maximum relative density of 99% relative density was achieved at 1300°C by the 4.3 mol% Mn doped BCP compact. The increased density of sintered BCP compact sintered at 1400°C sintering and Mn content and the maximum hardness of 6.66 GPa was obtained by the 11.9 mol% Mn doped compact sintered at 1400°C. Similarly, higher level of Mn doped and sintering temperature has enhanced the mechanical properties of BCP compacts, with the maximum value was obtained at 11.9 mol% Mn doping showing a fracture toughness of 1.05 ± 0.01 MPam$^{1/2}$ after 1400°C sintering. It can be concluded therefore that doping of Mn has greatly improved the mechanical properties of sintered BCP compacts.

CONCLUSION

Manganese doped biphasic calcium phosphate dense bodies with manganese concentrations of 0.6, 1.9, 4.3, and 11.9 mol% have been fabricated via uniaxial pressing followed by 800–1400°C sintering using the sol-gel derived powders. Manganese doping has improved the thermal stability of dense BCP in all sintering temperatures as no secondary phases other than HA and $\beta$-TCP peaks detected. The manganese doping also improved the mechanical properties dense BCP ceramics as investigated in terms of density, hardness, and fracture toughness. The maximum relative density of 99% relative density was achieved at 1300°C by the 4.3 mol% Mn doped BCP compact. The increased density of sintered BCP compacts with sintering temperature is attributed to the densification of $\beta$-TCP phase in the BCP structure. The hardness tended to increase with sintering temperature and Mn content and the maximum hardness of 6.66 GPa was obtained by the 11.9 mol% Mn doped compact sintered at 1400°C. Similarly, higher level of Mn doped and sintering temperature has enhanced the mechanical properties of BCP compacts, with the maximum value was obtained at 11.9 mol% Mn doping showing a fracture toughness of 1.05 ± 0.01 MPam$^{1/2}$ after 1400°C sintering. It can be concluded therefore that doping of Mn has greatly improved the mechanical properties of sintered BCP compacts.

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Figure 6.—Effect of sintering temperature and Mn doping on the fracture toughness of BCP (color figure available online).