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Investigations of the Effects of Initial Zn Concentration and Sintering Conditions on the Phase Behavior and Mechanical Properties of Zn-doped bcp.

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ABSTRACT

Sintering behaviour of zinc doped biphasic calcium phosphate was investigated over the temperature range of 1000–1300oC. The starting powders have been synthesized through Sol-Gel method. Zinc concentration was varied in the range of 0, 1, 2, 4, 5, 10 and 15mol%. After uniaxial pressing followed by isostatic pressing, the compacted samples were sintered via conventional pressureless sintering. The dense samples were studied in terms of phase stability, relative density, Vickers hardness, and fracture toughness. The results showed hydroxyapatite as the main phase and β-tricalcium phosphate as the secondary phase. However, parascholzite phase started to appear in 15mol%. Relative density results indicated that Zn-doped BCP dense samples showed the maximum relative density of 96.1% compared to 88.0% for Zn free-BCP fired at 1300oC. The maximum Vickers hardness and fracture toughness of 3.44 GPa and 1.43 MPa.m1/2 respectively, was achieved at 1200oC. This study showed that Zn doping improved the hardness and toughness of BCP.

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INTRODUCTION

Calcium phosphates (CaP) materials are of special importance to humans since they represent the inorganic part of human bones and teeth. They have been widely used for various bone and tooth implants due to their excellent biocompatibility and bioactivity. Among various phases of calcium phosphate, biphasic calcium phosphate (BCP) ceramic, an intimate mixture of hydroxyapatite (HA, $Ca_{10}(PO_4)_6(OH)_2$) and β-tricalcium phosphate (β-TCP, $Ca_3(PO_4)_2$), has been commonly used for biomedical applications for nearly three decades [1]. This mixture is considered to have better performance than its constituent phases i.e.; HA or β-TCP phase, due to its biocompatible, osteoconductive as well as osteoinductive characteristics to enhance growth of bone cells inside the implants [2, 3]. In recent studies clinical parameters have established that BCP can successfully support the osteoinductive process [4]. Therefore, BCP has received much attention in the field of biomaterials as an ideal bone graft substitute for human bone reconstructions.

It has been observed that chemical composition of apatite in human bone is complicated due to vacancies, foreign cations (Mg^{2+}, Mn^{2+}, Zn^{2+}, Na^{+}, Sr^{2+}) and anions (HPO_4^{2-}or CO_3^{2-}) which are absorbed from the surrounding body fluids during bone metabolism [5]. During recent years many researchers have tried to synthesize zinc doped calcium phosphate powder. This is due to the fact that Zn is known to be an essential trace element in bone mineral. It is involved in bone formation *in vitro* and *in vivo* and has potential of promoting tissue growth [6, 7]. The essential roles of zinc include prevention of bone loss and osteoporosis and stimulation of bone metabolism and growth [8]. Zinc also has antimicrobial property which increases with an increase in the amount of zinc. In addition, drug release from zinc-doped hydroxyapatite is higher than that from pure HA [9].

The applicability of HA as a biomaterial in medical purpose is, nonetheless, limited to non-load bearing bone application due to relatively low strength and susceptibility to brittle catastrophic fracture (fracture toughness about 0.8–1.2 $MPa.m^{1/2}$) [10]. To date various methods have been developed to enhance mechanical

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properties as well as bioactivity of HA [5, 11, 12].

A number of preparation techniques of zinc substituted hydroxyapatite have been tried so far. Some of them include chemical co-precipitation [13], hydrothermal mechanisms [14] and Sol-Gel [15]. Sol–Gel method has many advantages over these mechanisms as it involves mild and low energy conditions [16]. We have reported the synthesis of zinc-doped BCP powder elsewhere [17].

Zinc is well-known doping agent for hydroxyapatites employed in biomedical applications, because they improve the phosphate bioactivity in many ways. This is confirmed by the increased number of publications throughout the years investigating the role of Zn ions in hydroxyapatite. However, it seems that very few literature concerning mechanical properties description of Zn doped HA product. In this work, the effect of Zn concentration and sintering condition on phase behaviour and mechanical properties of Zn-doped BCP has been studied.

MATERIALS AND METHODS

Zn-free BCP and Zn-doped BCP powders used to produce dense compacts were synthesized via a sol-gel technique. Zinc concentration was varied in the range of 0, 1, 2, 4, 5, 10 and 15mol%. After uniaxial pressing the compacted samples were sintered via conventional pressureless sintering in the temperature range of 1000–1300^{o}C. The presence of the crystalline phase in the sintered dense samples was analysed by X-ray diffraction (XRD) (Shimadzu Diffractometer, XRD-6000). The bulk density of the sintered dense samples was measured by the Archimedes principle using a standard densimeter (Alfa Mirage, MD-300S). For Vickers hardness determination, the indentations were made using a pyramidal diamond indenter (Mitutoyo, MHV H-2) with an applied load of 200g. The fracture toughness (KIc) of the sintered dense samples was determined using Vickers indentation method and the KIc value was calculated using the Niihara equation. The morphology of the samples was investigated by FESEM (a JEOL JSM-6700F) and a FEI Technai T20 TEM operated at 200 kV, High Resolution.

RESULTS AND DISCUSSION

Figure 1 shows the TEM morphology image of Zn free-BCP and Zn-doped BCP powders. It can be seen the formation of nanocrystalline powder and the individual particles of Zn-doped BCP are globular in shape and tightly agglomerated into micrometric aggregates. The agglomeration of particle increases with an increase in Zn concentration. In addition, the powders show the agglomeration of the fine particles into microscale aggregates.

Figure 2 shows the XRD pattern of various mole percentages of dense Zn-doped BCP and Zn-free BCP sintered at 1300^{o}C. The figure presents peaks attributed to International Centre for Diffraction Data (ICDD), hydroxyapatite (HA, card no. 09-432) as the main phase and β-tricalcium phosphate (β-TCP, card no. 09-169) as the secondary phase. However, parascholzite phase ($CaZn_2(PO_4).2H_2O$)(card no 35-0495) starts to appear in 15mol%. No peak of alpha-tricalcium phosphate (α-TCP, card no 09-348), tetracalcium phosphate (TTCP, card no 11-0232), and calcium oxide (CaO, card no 37-1497) was detected in these dense samples throughout the sintering regime at 1300^{o}C, which infers that the phase transition from β -TCP to α -TCP probably happened above 1300^{o}C.

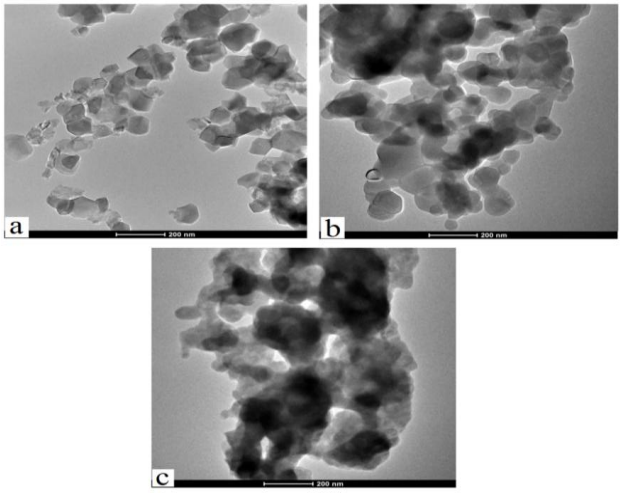

Fig. 1: TEM micrograph of Zn-doped BCP powders calcined at 900ºC: (a) Zn-free-BCP; (b) 5% Zn-BCP; and (c) 10% Zn-BCP

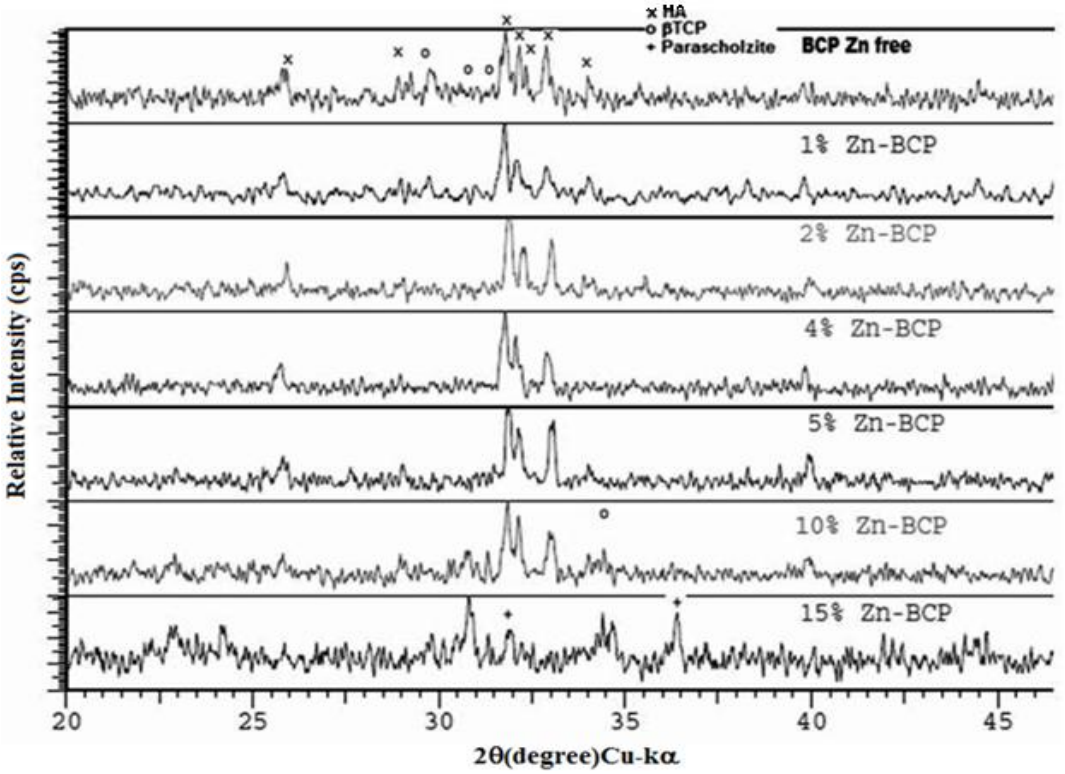

Fig. 2: XRD patterns of various concentrations of Zn-doped BCP dense samples sintered at 1300°C.

Figure 3 shows XRD pattern of 4mol% Zn-doped BCP dense sample sintered at various temperatures. Peak at 2θ = 31.5° that attributed to maximum peak of β-TCP, tends to increase at higher sintering temperature. In contrast, peak of HA at 2θ = 34° decreased when temperature of sintering increased and completely disappeared at 1300° C. The results show that HA decomposes into β-TCP when the sintering temperature is increased from 1000 °C to 1300 °C. It has been reported that when HA is sintered at 1100 °C -1350 °C for 4 h, it starts to decompose into β-TCP [18]. This result is in agreement with the report.

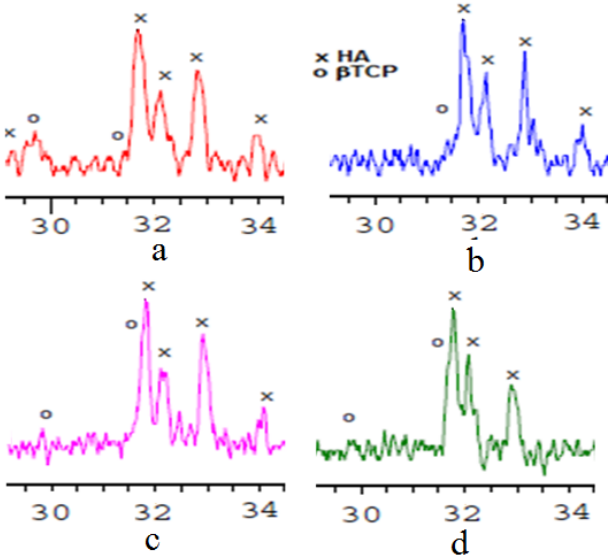

Fig. 3: XRD patterns of 4mol% Zn-doped BCP dense samples sintered at (a) 1000°C; (b) 1100°C; (c) 1200°C; and (d) 1300°C

Theoretically, the pores or the imperfections on the chemically attacked surfaces were as a result of three reasons: Firstly, due to the remaining microspores resulting from unfinished densification; secondly, the existence of *β*-TCP phase as the decomposition product which dissolved much faster than the pure HA phase; thirdly, the intrinsic chemical stability of the ceramics [19]. Different degrees of porosity on the surfaces of the

sintered 15mol% Zn-doped BCP was found to be lower than the sintered 4mol% Zn-doped BCP sample. From Fig. 4 and judging from the XRD peak ratios (Fig. 2), it can be seen that the β-TCP phase increased in amount from 4mol% Zn-doped BCP to 15mol% Zn-doped BCP samples. Thus, the β-TCP phase could be the dominant factor causing the porosity. However, the formation of β-TCP was directly related to the concentration of added Zn. These results were in accordance with the FESEM analysis, which showed the existence of intergranular pores for all samples sintered at 1200^{o}C as typically shown in Fig. 4.

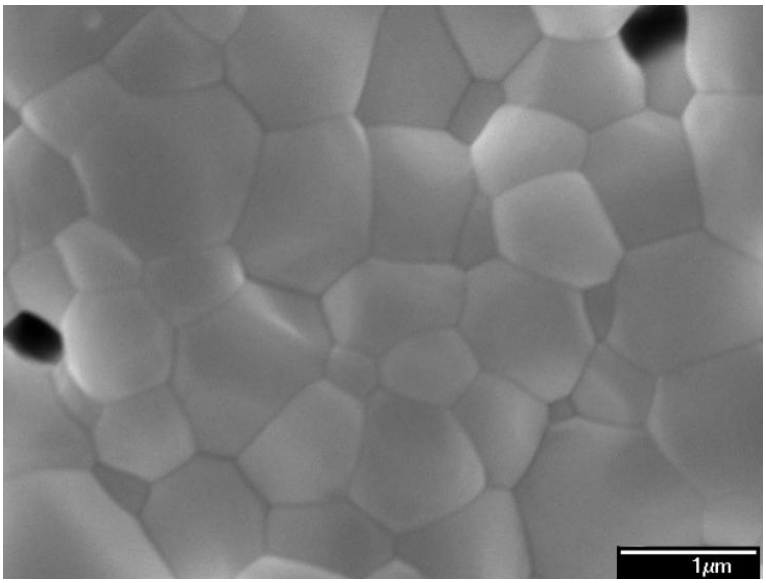

Fig. 4: Typical FESEM morphology of 4mol%Zn-doped BCP fired at 1200^{o}C.

Figure 5 shows the relative density of various percentage moles of dense Zn-doped BCP sintered at temperature range 1000-1300^{o}C. The maximum relative density of 96.1% was observed in the sample of 4mol% Zn-doped BCP sintered at 1300^{o}C as compared to 88.0% in Zn-free BCP sintered at same temperature.

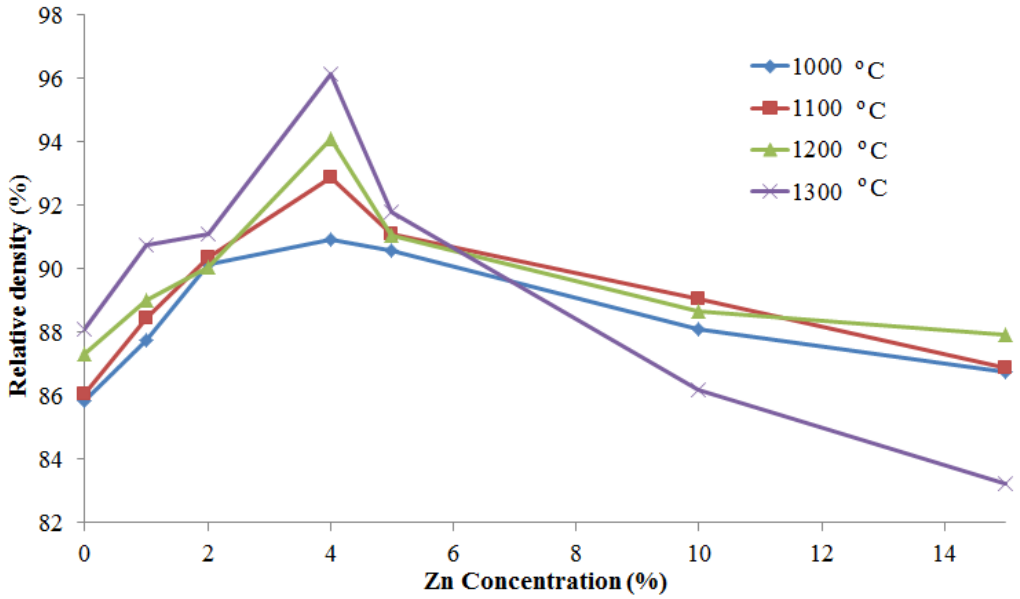

Fig. 5: The effect of Zn concentration and sintering temperature on relative density of BCP.

Figure 6 shows the Vickers hardness of various mole percentages of dense Zn-doped BCP. It can be seen that the Zn-doped BCP samples display superior Vickers hardness as compared to Zn free BCP. For Zn free BC Vickers hardness was 2.85 GPa and the maximum Vickers hardness of about 3.40 GPa was observed in the sample of 4mol% Zn-doped BCP. It can be seen that doping of Zn to BCP increased the hardness up to 4mol%

followed by a decrease at 5mol% when sintered at temperature range 1100 – 1300°C. However, the addition of Zn did not have a significant effect on the hardness value when sintered at low temperature.

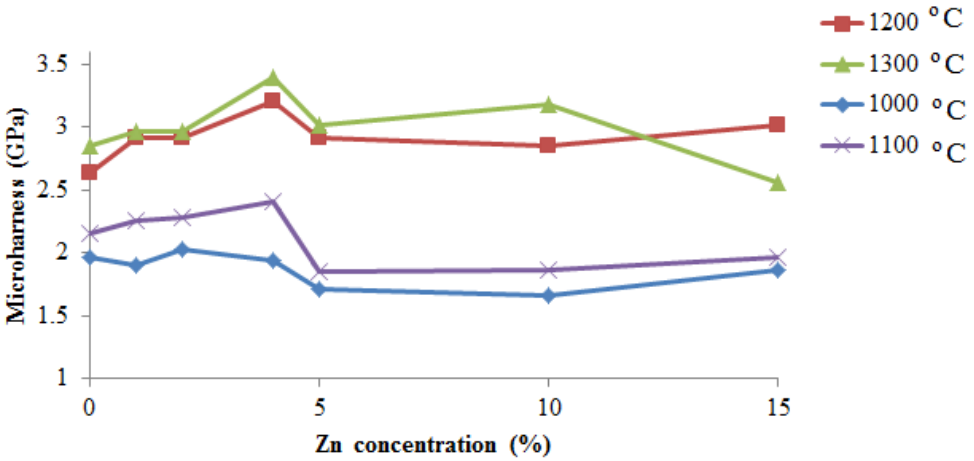

Fig. 6: The effect of Zn concentration and sintering temperature on Vickers hardness of BCP.

In general, the addition of Zn was effective in improving the fracture toughness (KIc) of the synthesized BCP, particularly when doped with 4%mole Zn sintered at 1200°C. The 4mol% Zn-doped BCP samples exhibited highest fracture toughness of 1.43 MPa.m$^{1/2}$ as compared to 1 MPa.m$^{1/2}$ measured for the Zn free BCP. One plausible explanation for the remarkable rise in KIc in the 4%mole Zn-doped BCP could be associated with the influence of grain size that acts to create a torturous path for crack propagation. As it can be seen from Fig. 4, average grain size is about 0.7 μm. It is clear that Zn doping up to 4%mole can effectively suppress grain growth BCP and thus enhance their mechanical properties significantly. It was reported that maximum fracture toughness of 0.7 MPa.m$^{1/2}$ was attained when 2.5 wt% of ZnO was doped in HA and sintered at 1250 °C [20]. However, in the present work, the advantage of using 4%mole Zn was achieved with the maximum fracture toughness of 1.43 MPa.m$^{1/2}$. It should be highlighted here that the KIc value obtained for the Zn-doped BCP is very promising, as most researchers have informed that the experimental KIc values for HA vary from 0.9 MPa.m$^{1/2}$to about 1.2 MPa.m$^{1/2}$ [21, 22].

Conclusion:

In this study, sintering behaviour of zinc doped was investigated. The phase of samples was hydroxyapatite and *β*-tricalcium phosphate. The presence of Zn caused a change in the sintering behaviour of dense BCP. 4mol% Zn-doped BCP had a improved value of relative density of about 8.1% as compared to Zn-free BCP fired at 1300°C. The *β*-TCP phase could be the dominant factor causing the porosity. The maximum fracture toughness of 1.43 MPa.m$^{1/2}$ and Vickers hardness of 3.44 GPa were achieved at 1200°C by 4 and 5mol% Zn-doped BCP respectively. This study showed that Zn doping was beneficial in producing high toughness of BCP.

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