Journal of Ceramic Processing Research. Vol. 18, No. 1, pp. 69~72 (2017)

J O U R N A L O F
Ceramic Processing Research

Thermal phase stability and properties of hydroxyapatite derived from bio-waste eggshells

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In the present work, hydroxyapatite (HA) derived from calcined eggshell via a wet chemical precipitation method was investigated. The as-received eggshells was calcined at 900 °C to produce crystalline calcium oxide which reacted with orthophosphoric acid under controlled conditions. The final solution was filtered, dried and sieved to obtain ready to press, phase pure hydroxyapatite powder as confirmed by X-ray diffraction (XRD) analysis. Green samples were prepared and sintered in air at various temperatures ranging from 900 °C to 1300 °C at a ramp rate of 10 °C per minute and 1 hr holding time. The sintered samples were evaluated in terms of HA phase stability, relative density, grain size, Vickers hardness and fracture toughness. The results showed that the HA phase remained stable even after sintering at 1300 °C. In addition, the relative density, Vickers hardness and fracture toughness were found to increase rapidly between 900 to 1100 °C and reached a plateau thereafter. A relatively density of 98.5%, high Vickers hardness of 5.9 GPa and fracture toughness of 1.09 MPam$^{1/2}$ was achieved at 1250 °C despite having a large grain size of 2.5 μm at this temperature.

Key words: Hydroxyapatite, Eggshell, Biowaste, Synthesis, High sintering temperature.

Introduction

Hydroxyapatite (HA) with chemical formula [$Ca_5(PO_4)_3(OH)$] is known as a bioactive material, which has wide range of applications in dentistry and orthopaedic as dental material and implants [1, 2]. One of the important purposes of using this material is the replacement of bone in human body, because of similarity to bone structure and its biocompatible nature, but on the other hands, its poor mechanical properties like fracture toughness which is lower than 1 MPam$^{1/2}$, limit usage of this material at load bearing applications including implant part adjacent and spinal merger [3-5].

There are many processes to synthesis hydroxyapatite such as sol-gel method, wet chemical method, mechano-chemical method, and hydrothermal method. Wet chemical route is one of the favourite method for researchers due to it simple setup and cost effectiveness [6-10]. Besides, different materials can be used for each process as calcium precursor including calcium oxide, calcium nitrate and calcium hydroxide [11]. Calcium oxide which is normally the main starting precursor used in sol gel, hydrothermal and wet chemical methods, can be extracted from bio-waste sources such as eggshell, seashell, plants and animal bones [12-15]. However, the final characteristics of the derived HA from bio-waste would very much dependent on the processing method and raw materials used [15]. For example, it has been reported that a calcination temperature of 1000 °C [6] coupled with sintering of HA at a heating rate of 2 °C per minute and 2 h hold time were necessary to produce a stable HA phase with desired mechanical properties [16].

In the present work, the objective was to produce high quality HA with higher thermal stability by using bio-waste chicken eggshells as the calcium source. This study investigates the HA phase stability, mechanical properties and microstructural evolution of the synthesized HA when sintered at various temperatures ranging from 900 °C-1300 °C.

Experimental Procedure

Clean and dry eggshells were crushed and calcined in an electrical box furnace at 900 °C for one hour with heating and cooling rate of 10 °C per minute to convert intrinsic carbonated calcium ($CaCO_3$) to calcium oxide

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(CaO). The derived calcium oxide powders were added to distilled water to produce calcium hydroxide solution. Orthophosphoric acid (85% purity-Merck) was subsequently added to the calcium hydroxide solution via a titration method. The amount of calcium oxide and phosphoric acid used was calculated based on 1.67 : 1 molar ratio. The reacted mixture was left to precipitate overnight, filtered and washed with distilled water. The hydroxyapatite cake was dried at 60 °C in an oven for 24 hrs prior to sieving to obtain ready-to-press HA powder.

Disc samples were then manufactured by uniaxial pressing at 10 MPa followed by cold isostatic pressing at 200 MPa. The compacted green samples were then sintered in air at various temperatures ranging from 900 to 1300 °C for 1 hr using a ramp rate of 10 °C/min (heating and cooling). Sintered samples were then ground using silicon carbide sand paper and polished to a 1 µm mirror finish using diamond paste prior to evaluation.

The as-synthesized and sintered samples were characterized by X-ray diffraction (XRD), (EMPYREAN, PANalytical, Netherlands) operated at 45 kV and 40 mA using a monochromatic Cu-Kα beam (λ = 1.5406 Å). The 2θ scanning range was performed from 20 °-60 ° at a step size of 0.02° and a scan speed of 0.5°/min.

The microstructures and elemental composition of the samples were characterized using a Carl Zeiss Auriga field emission scanning electron microscope (FESEM) with energy dispersive X-ray spectroscopy (EDX). The grain size of the sintered samples was determined from the FESEM images based on a line intercept method [17].

Bulk density measurement of sintered samples was carried out based on the Archimedes' principle using distilled water as an immersion medium. Relative densities of the sintered samples were calculated by taking the theoretical density of HA as 3.156 gcm^{-3}. The micro-hardness (H_V) and fracture toughness (K_{Ic}) values of polished sintered samples were determined via a Vickers hardness indenter (Shimadzu, Japan) using an applied load of 100-200 g with a dwell time of 10 s. Five indentations were made for each sample and an average value was taken. The indentation fracture toughness was calculated from Eq. (1) derived by Niihara et al. [18].

$$K_{IC} = 0.230 \times \left(\frac{c}{a}\right)^{-1.5} \times H_V \times (a)^{0.5} \quad (1)$$

Where c is the characteristic crack length and a represents the half diagonal of the indent.

Results and Discussion

The XRD analysis of the sintered HA are shown in Fig. 1. Regardless of sintering temperature, there were no secondary phase detected for all samples such as TCP or TTCP. The intensity of the highest peak, corresponding to the (211) lattice plane, at $2\theta = 31.8$ °, increases from 900 to 1300 °C revealing a highly crystalline HA structure has been formed. The high thermal stability of the HA observed at 1300 °C clearly indicated that the eggshell-derived HA are superior than the chemically produced HA as reported by many researchers. According to the literatures, most of the HA derived through the chemical route would be thermally unstable when sintered beyond 1250 °C, resulting in decomposition of the HA phase [19-28].

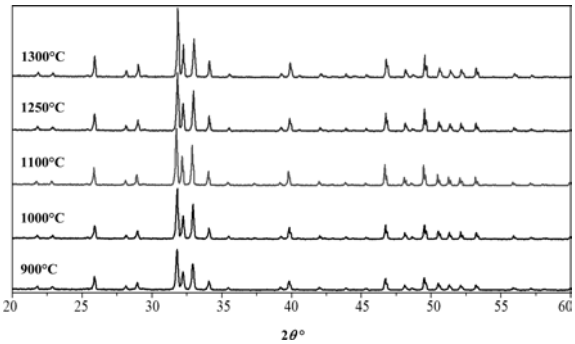

Fig. 1. XRD signatures of HA samples sintered at various temperatures.

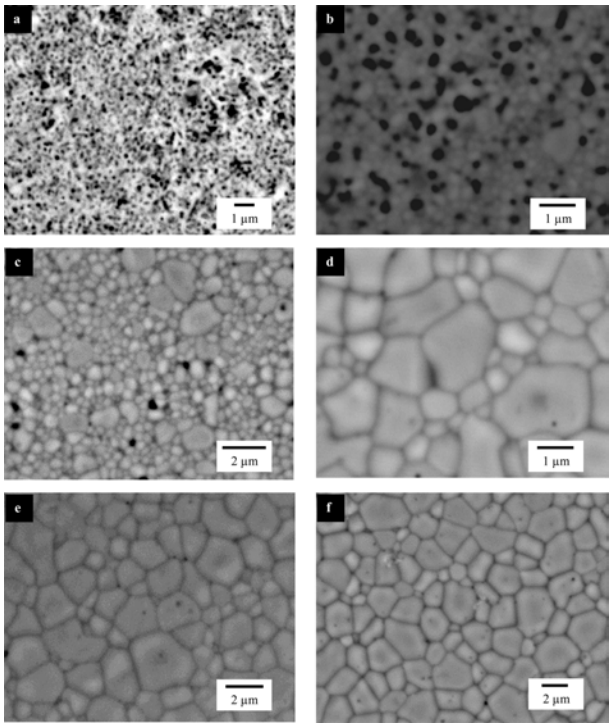

Fig. 2. FESEM micrographs of eggshell-derived HA sintered at (a) 900 °C, (b) 1000 °C, (c) 1100 °C, (d) 1200 °C, (e) 1250 °C and (f) 1300 °C.

The microstructure evolution of sintered samples at different temperatures are shown in Fig. 2. A porous structure can be observed for sample sintered at 900 °C when compared to sample sintered at 1000 °C. However, as the temperature increased to 1100 °C and beyond, this was accompanied by densification and elimination of porosity. It is obvious from Fig. 2 that the HA grains

started to grow as the sintering temperature increases from 1000 to 1300 °C, resulting in the formation of equiaxed grains having a bimodal grain size distribution.

The effect of sintering temperature on the average grain sizes of HA is shown in Fig. 3. The graph shows that an almost linear relationship exist between grain size and sintering temperature. The smallest grain size of 0.6 μm was measured at 1000 °C, whereas the largest grain size of 2.5 μm was obtained at 1250 and 1300 °C. Rapid grain growth was observed when sintered between 1100 and 1200 °C. However, the rate of grain growth noted in the present work is not as significant compared to that observed in the literature [16] where the HA grain size increased from approximately 2 to 8 μm when sintered from 1200 to 1250 °C. This suggests that the eggshell-derived HA in the present study is not susceptible to rapid grain growth, resulting in smaller grain sizes which would be beneficial for the mechanical properties [29, 30].

The variation in relative density of HA as a function of sintering temperature is shown in Fig. 4. Sintering at 900 °C resulted in low relative density of 80% and this is in agreement with the FESEM images which confirm the existence of a porous HA structure. However, the relative density increased rapidly to 97% when sintered at 1100 °C and thereafter fluctuated slightly and attained a maximum value of 98.5% for sintering at 1250 and 1300 °C. The results obtained in the present work is considered high when compare to those reported by other researchers [13, 16, 19]. For example, a maximum relative density of 97.4% was reported by Kamalanathan et al. [19] when sintered under similar conditions at 1250 °C.

The influence of sintering temperature on the Vickers hardness of eggshell-derived HA is shown Fig. 5. The graph shows that the Vickers hardness exhibited a similar trend as that observed for the relative density. A low hardness of 1.9 GPa was measured at 900 °C and this can be attributed to the low bulk density of the sintered sample. However, as the sintering temperature as increased this was accompanied by a steady increased in the Vickers hardness from 3.7 GPa at 1000 °C to reached a maximum of 5.9 GPa when sintered at 1250 and 1300 °C. This behavior is in good agreement with the increased in the relative density.

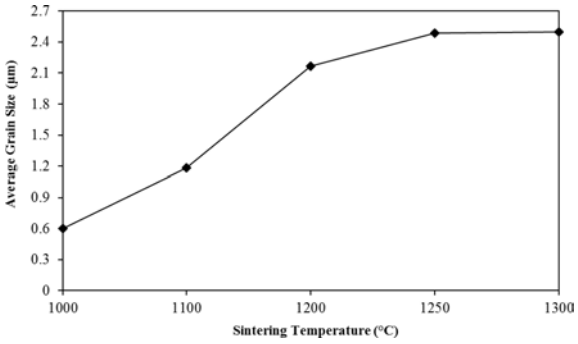

Fig. 3. The variation of grain size as a function of sintering temperature.

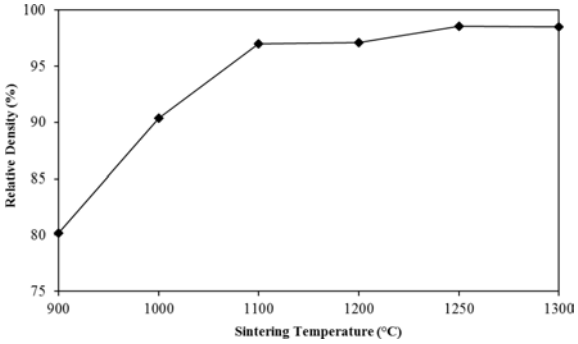

Fig. 4. Variation in relative density of eggshell-derived HA samples sintered at various temperatures.

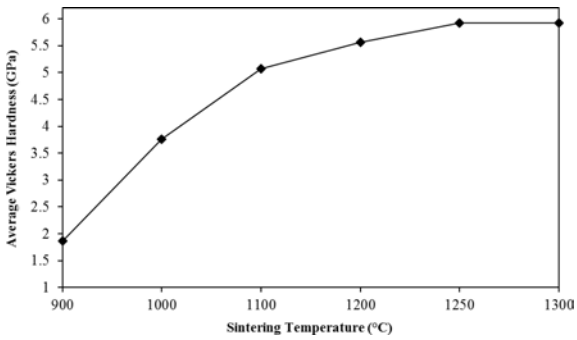

Fig. 5. The effect on sintering temperatures on the Vickers hardness of eggshell-derived HA.

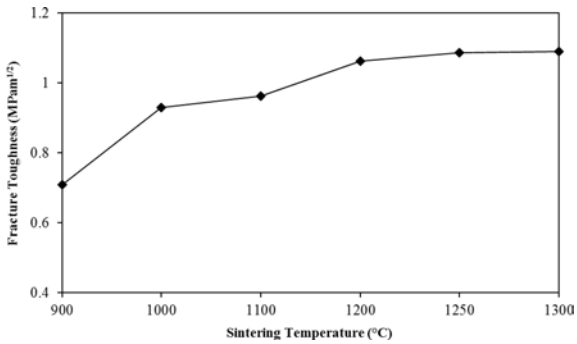

Fig. 6. Fracture toughness variation with sintering temperature for eggshell-derived HA.

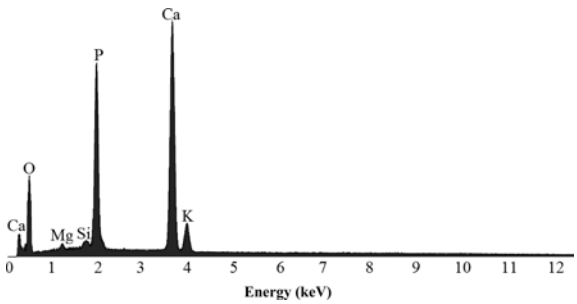

Fig. 7. Typical EDX analysis of eggshell-derived HA sintered at 1300 °C.

The fracture toughness variation with sintering temperature for the eggshell-derived HA is shown in Fig. 6. The graph shows that the fracture toughness increased sharply from 0.71 $MPam^{1/2}$ at 900 ºC to 0.93 $MPam^{1/2}$ at 1000 ºC. Thereafter, the fracture toughness fluctuated slightly between 1.06-1.09 $MPam^{1/2}$.

EDX analysis of all the sintered samples shows two major elements, Ca and P, were present along with other minor elements of Mg, Si and K as typically shown in Fig. 7. These elements present in the HA are believed to originate from the eggshells and are in good agreement with that commonly found in natural bones [24, 25]. The Ca/P ratio as calculated from the EDX data for the sintered HA was about 1.67 ± 0.03 regardless of the sintering temperature and this value correlates well with that of the stoichiometric molar ratio of pure HA. The Ca/P ratio has been reported to have an influence on the properties and reactivity of the HA powder. For instance, if there is less or excess of calcium or phosphate added during the reaction, this would result in a non-stoichiometric Ca/P ratio. Hence, during sintering, decomposition of the HA phase will take place and this in turn would have an adverse effect on the mechanical properties of the sintered body [26, 27].

Conclusions

The sintering behavior of hydroxyapatite derived from bio-waste eggshells was investigated. HA phase thermal stability was not disrupted even after sintering at high temperature of 1300 ºC. Sintering at 1250-1300 ºC was beneficial in producing a solid dense (relative density of 98.5%) HA body having high Vickers hardness of 5.9 GPa and high fracture toughness of 1.09 $MPam^{1/2}$ despite developing large grain size of 2.5 μm. This research has demonstrated the viability of producing highly crystalline, phase pure hydroxyapatite from bio-waste eggshells. The derived bioceramic fulfilled the stoichiometric Ca/P ratio of 1.67 without compromising on the thermal stability of the HA phase and the sintered eggshell-derived HA body exhibited excellent mechanical properties suitable for biomedical application.

Acknowledgments

This study was supported under the PPP Grant No. PG078-2015A.

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