Consolidation of nanocrystalline hydroxyapatite powder

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Abstract

The effect of sintering temperature on the sinterability of synthesized nanocrystalline hydroxyapatite (HA) was investigated. The starting powder was synthesized via a novel wet chemical route. HA green compacts were prepared and sintered in atmospheric condition at various temperatures ranging from 900–1300°C. The results revealed that the thermal stability of HA phase was not disrupted throughout the sintering regime employed. In general, the results showed that above 98% of theoretical density coupled with hardness of 7.21 GPa, fracture toughness of 1.17 MPa m^{1/2} and Young’s modulus of above 110 GPa were obtained for HA sintered at temperature as low as 1050°C. Although the Young’s modulus increased with increasing bulk density, the hardness and fracture toughness of the sintered material started to decline when the temperature was increased beyond 1000–1050°C despite exhibiting high densities >98% of theoretical value. The occurrence of this phenomenon is believed to be associated with a thermal-activated grain growth process.

1. Introduction

The use of hydroxyapatite (HA) as a potential bioactive calcium phosphate ceramics has gained popularity in recent years due to its close chemical resemblance with the mineral components of natural bone and teeth [1,2]. Several studies have been carried out and the results demonstrated that HA can accelerate initial biological response with host tissues at the implanted site in the body and improves the bone-implant adhesion [3,4]. Evidence of rapid bone formation and subsequently healing around damaged sites in the body were also observed [5,6]. Due to these excellent biocompatibility properties, HA ceramics have been widely used in many medical, orthopaedic and dental applications including the augmentation of the jaw, dental implants, spinal surgery, maxillofacial surgery and artificial middle ear implants [1,2].

However, one of the major setbacks of HA is the poor mechanical properties inherited by the sintered body [4]. Owing to the brittle nature and the low fracture toughness (<1 MPa m^{1/2}) of the sintered HA, such implants could only be utilized successfully in non-load bearing applications [7]. Therefore, the development of bioactive HA that has improved and ultimately bone-like mechanical properties are desirable. As a result, a great number of studies have been devoted to improve the mechanical properties of HA materials [4,5,8].

The success of HA ceramic in biomedical application is largely dependent on the availability of a high quality, sintered HA that is characterized having refined microstructure and improved mechanical properties [9]. Intensive research in HA involving a wide range of powder processing techniques, composition and experimental conditions have been investigated with the aim of determining the most effective synthesis method and conditions to produce well-defined particle morphology [10–12]. Among the available synthesis methods, wet precipitation technique, which involves aqueous solutions, is most widely used by many researchers [13]. The advantages of this process are that the by-product is almost water and the probability of contamination during processing is reported to be very
low [14]. Although numerous studies on HA synthesized via wet precipitation technique are carried out, nevertheless, reports on the sinterability of HA synthesized through this technique are rather scarce.

Therefore, in this work, a wet chemical technique was employed to manufacture nanocrystalline HA powder using high purity Ca\(^{2+}\) precursor. The sinterability and properties of the sintered product derived from these powders were evaluated.

2. Methods and materials

The HA powder used in the present work was synthesized using a novel wet chemical method [15]. The morphology of the synthesized HA particles were examined by using a transmission electron microscope (TEM). Prior to examination, the powder was suspended in 1–2 ml of spectroscopic grade acetone (or double distilled water), agitated by pipette and, after allowing the largest granules to settle, approximately 50\(\mu\)l of the smaller particles were transferred to a 200 mesh nickel grid coated with a silicon monoxide film. Microscopy was carried out in a Hitachi H7100FA TEM operating at accelerating voltages of 100–125 kV. Images were captured directly in the TEM using a Gatan 789 camera system.

The as-prepared, nanocrystalline HA powder was uniaxial compacted at about 1.3–2.5 MPa into rectangular and circular discs samples. The green compacts were subsequently cold isostatically pressed at 200 MPa. Consolidation of the particles by pressureless sintering was performed in air using a rapid heating furnace (Modu-Temp, Australia), at various temperatures ranging from 900 to 1300 °C, maintained at the soak temperature for 2 h before cooling to room temperature. All the sintered samples were subsequently polished to a 1 μm mirror finish prior to evaluation.

The nature of the crystalline phases in the powder and sintered body were examined by X-ray diffraction (XRD; Rigaku Geiger-Flex Japan) under ambient conditions using Cu-K\(\alpha\) as the radiation source. The peaks obtained were compared to standard reference JCPDS files available in the software for HA, tricalcium phosphates (TCP) and tetracalcium phosphate (TTCP).

The bulk density of the sintered samples was measured by Archimedes’ method, with distilled water as the immersion media. The relative density was calculated by taking the theoretical density of HA as 3.156 g cm\(^{-3}\). The Young's modulus (E) by sonic resonance was determined for rectangular samples using a commercial testing instrument (GrindoSonic: MK5 “Industrial”, Belgium). The instrument permits determination of the resonant frequency of a sample by monitoring and evaluating the vibrational harmonics of the sample by a transducer; the vibrations are physically induced in the sample by tapping. The modulus of elasticity or Young’s modulus was calculated using the experimentally determined resonant frequency [16].

The microstructural evolution of the HA under various sintering temperature was examined by using a Philips XL30 scanning electron microscope (SEM) and the grain size was determined from SEM micrographs using the line intercept analysis [17].

The microhardness (H\(_{v}\)) and fracture toughness (K\(_{lc}\)) of the polished samples were determined using the Vickers indentation method. Five indentations were made for each sample and the average value was taken. The indentation fracture toughness was determined from the equation derived by Niihara [18].

![Fig. 1. Room temperature XRD signatures of nanocrystalline HA powder. All peaks corresponded to stoichiometric HA phase.](image-url)
3. Results and discussion

The XRD analysis of the synthesized powder in this study as shown in Fig. 1 exhibited peaks that corresponded to stoichiometric HA. Thus, it is evident that the filtered crystals were mainly single-phase HA and is believed to be very small. Estimates of crystal size from peak broadening using the Scherrer’s formula [19] for the synthesized powder gives about 11 nm from the 211 reflection and about 30 nm from the 002 reflection. The nanocrystalline nature of the derived powder was also confirmed by TEM as shown in Fig. 2. This result correlates well with the XRD analysis, which revealed that the particles were very small i.e. in the nanometer size range.

In addition to that, the XRD analysis of all the sintered samples, regardless of sintering temperature ranging from 900 to 1300 °C, produced only peaks that corresponded to stoichiometric HA. This result indicates that HA did not decompose to secondary phases upon sintering even when consolidated at high temperature above 1200 °C. A similar result was also obtained in previous work even for sintering at high temperature of 1400 °C [20]. The fact that decomposition of HA phase was not observed in the present material even for the high temperature (i.e. 1200 °C) sintered samples is not in agreement with the findings of Royer et al. [21] and Wang et al. [22] who reported that decomposition of HA starts at about 1300 °C, accompanied by deterioration of mechanical properties of HA ceramics. In general, sintering of HA can lead to the partial thermal decomposition of HA into TCP and/or TTCP [23]. The thermal decomposition is accompanied in two steps i.e. dehydroxylation and decomposition. Dehydroxylation to oxyhydroxyapatite proceeds at temperatures about 850–900 °C by the fully reversible reaction in accordance to Eq. (1) [23]:

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow \text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_{2-2x}\text{O}_x + x\text{H}_2\text{O}_{\text{gas}}.
\] (1)

The decomposition to TCP and TTCP occurs at temperatures greater than 900 °C according to the reaction given in Eq. (2) [23]:

\[
\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2 \rightarrow 2\text{Ca}_3(\text{PO}_4)_2 + \text{Ca}_4\text{P}_2\text{O}_9 + \text{H}_2\text{O}_{\text{gas}}.
\] (2)

According to these equations, both the dehydroxylation and decomposition reactions include water vapour as a product. The rates at which these reactions proceed...
depend on the partial pressure of H$_2$O in the furnace atmosphere \[23\].

Therefore, the secondary phase formation during sintering could be suppressed by controlling the moisture content in the sintering atmosphere. The high moisture 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. The difference in result in the present work with Royer et al. and Wang et al. could in part be attributed to the difference in relatively humidity in the sintering atmosphere and also the nature of the starting synthesized powder.

The effect of sintering temperature on the relative density and Young’s modulus of sintered HA is shown in Fig. 3. The maximum relative density of 99% was attained for sample sintered at 1150 °C. In general, the relative density increases rapidly from 83% at 900 °C to 97% at 1000 °C and then increase monotonically to >98% for sintering >1050 °C. Thereafter, the bulk density did not change very much with increasing temperature up to 1300 °C. This could be associated with the final stages of sintering where small levels of porosity are removed.

The variation in Young’s modulus ($E$) for the HA with sintering temperature is in agreement with the bulk density trend as shown in Fig. 3. The HA attained $E$ values >100 GPa when sintered at a temperature as low as 1000 °C. In general, Fig. 3 shows that the Young’s modulus of sintered HA increase up to a maximum of >100 GPa with increasing bulk density up to >98% of theoretical value. This result is in agreement with the work of Liu [24] who observed that the Young's modulus of HA was controlled by the fraction of porosity in the sintered body.

The SEM investigation revealed that when HA sintered at low temperature below 1000 °C, a uniform microstructure and distribution of equiaxed fine grains were obtained. However, as the sintering temperature was increased >1000 °C, this was accompanied by grain coalescence with occasionally exaggerated grain growth observed, particularly for HA sintered >1150 °C as shown in Fig. 4. The dramatic change in the average grain size with sintering temperature is shown in Fig. 5. It was found that initially the grain size increased slowly from 0.12 μm at 900 °C to about 0.88 μm at 1150 °C and thereafter accelerated by a factor of more than seven, to 7.13 μm when sintered at 1300 °C.

The effect of sintering temperature on the fracture toughness and Vickers hardness of the synthesized HA is shown in Fig. 6. It has been found that the fracture toughness of the sintered body increased with sintering temperature up a maximum of 1.22 MPa m$^{1/2}$ at 1000 °C and thereafter deceased almost linearly with increasing sintering temperature up to 1300 °C. Further to that, it was found that the variation in Vickers hardness with sintering temperature (Fig. 6) is in good agreement with the fracture toughness trend. The hardness of the sintered HA increases rapidly from 2.8 GPa at 900 °C and reached a maximum of 7.21 GPa at 1050 °C before decreasing almost linearly to about 5.7–5.8 GPa at 1300 °C.

The change in Vickers hardness and fracture toughness with grain sizes for samples sintered at various temperatures are presented in Figs. 7 and 8, respectively. It was found that samples with an average grain size of 0.3–0.5 μm (i.e. sintered at 1000–1050 °C) exhibited the highest hardness and fracture toughness. The low fracture toughness and hardness obtained for HA sintered at ≤1000 °C and ≤1050 °C, respectively, are in agreement with the low measured bulk density (Fig. 3). In contrast, as the grain sizes increases beyond 0.5 μm resulting from sintering above 1050 °C, the ceramics exhibited a gradual decrease in both the $K_{IC}$ and $H_v$ even though they possessed high relative densities above 98% as shown in Fig. 3. This
decreased in mechanical properties could not be due to bulk density effect but rather can be interpreted as due to a grain size effect as depicted in Figs. 7 and 8. As can be noted from both figures, the $K_{IC}$ and $H_v$, increases with grain size and reached a maximum value at a certain grain size limit before decreasing further with increasing grain size resulting from sintering at higher temperatures. More work is in progress to evaluate the hardness/fracture toughness-grain size relationship in HA.

4. Conclusions

1. The sinterability of synthesized nanocrystalline HA particles was investigated. It was found that the sintering temperature plays an important role in determining the densification of the HA body.

2. The phase stability of the synthesized HA was not disrupted through the sintering regime employed even when sintered at 1300°C.

3. The relative density of >98% of theoretical value and a Young’s modulus of above 100 GPa were obtained for samples sintered above 1000°C. In addition, the Young’s modulus of synthesized HA was found to increased with bulk density, indicating that the matrix stiffness is governed by the density of the sintered ceramic.

4. The average HA grain size was found to increase by a factor of more than seven, from 0.88 μm at 1150°C to

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**Fig. 5.** The effect of sintering temperature on the average grain size of sintered HA.

**Fig. 6.** The effect of sintering temperature on the fracture toughness and Vickers hardness of sintered HA.
7.13 μm at 1300 °C. This in turn was found to have an adverse effect on the fracture toughness and Vickers hardness of the sintered material. The fracture toughness started to decrease above 0.3 μm grain size whereas the hardness started to decline above 0.5 μm despite exhibiting relative densities above 98% of theoretical value.

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