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Rapid densification of nanocrystalline hydroxyapatite for biomedical applications

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Abstract

The effect of rapid sintering by microwave heating on the properties of nanocrystalline hydroxyapatite (HA) bioceramic powder was studied. The starting high-purity nano HA crystals was synthesized using a wet chemical precipitation technique. The HA compacts were microwave-sintered over the temperature range 1000–1300 °C, using a rapid sintering schedule of 30 min for each temperature. Shrinkage of all compacts was uniform and the sintered material did not exhibit any cracks. XRD phase analysis indicated that the HA phase stability was not disrupted throughout the sintering regime employed. A relative density of 90–91% was attained for samples sintered at 1000 °C, whereas a higher relative density of above 96% and ~98% was measured for HA sintered at 1100 °C and 1300 °C, respectively. The present work revealed that microwave heating was beneficial in preventing grain growth, particularly when sintered at temperatures <1200 °C, and coupled with improved mechanical properties, i.e., high fracture toughness of 1.45 MPa $m^{1/2}$ and hardness of 6.38 GPa were measured for HA compacts sintered at 1050 °C and 1150 °C, respectively.

Keywords: C. Mechanical properties; Hydroxyapatite; Bioceramic; Microwave sintering

1. Introduction

Hydroxyapatite or commonly known as HA has received considerable attention as suitable bioceramic for the manufacture of endosseous implants, because of its excellent osteoconductive and bioactive properties which is due to its chemical similarity with the mineral portion of hard tissues [1]. However, the brittle nature and the low fracture toughness (<1 MPa $m^{1/2}$) of this ceramic have been the main drawback of the widespread use of this material in load-bearing clinical application [2,3]. Consequently, a great number of studies have been undertaken to improve the mechanical properties of sintered HA [1,4–6].

Many of these investigations concentrated on powder processing techniques, composition and experimental conditions, with the aim of obtaining the most effective synthesis method and conditions to produce well-defined particle morphology [5,7]. One of the most important controlling parameter that must be considered during the processing of hydroxyapatite is the selection of a suitable powder consolidation/sintering method to obtain a solid, high density HA body that is characterized by having fine microstructure. The most commonly used consolidation technique is the conventional pressureless sintering method. However, this technique often requires long sintering schedule, typically above 18–24 h which in turn result in coarse-grained microstructure and low mechanical properties [3,8,9].

As a result, a more rapid, yet effective consolidation technique such as microwave processing has been reported to produce a dense sintered HA body that possessed fine microstructure coupled with improved mechanical characteristics [10,11]. In microwave sintering (MS), since heat is generated within the material instead of being radiated from outside the body as in conventional sintering [12,13], a more rapid and uniform heating are achievable within minutes of exposure thus resulting in densification.

The objective of the present work was to study the effect of microwave sintering on the densification behaviour and mechanical properties of nanocrystalline hydroxyapatite powder prepared via a wet chemical technique.

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2. Materials and methods

The nanocrystalline hydroxyapatite (HA) powder used in the present work was prepared according to a wet chemical method comprising precipitation from aqueous medium involving calcium hydroxide and orthophosphoric acid [14]. The resulting precipitate was filtered, washed, dried and then ground to a fine powder of high purity. The morphology of the synthesized HA crystals was examined using TEM (Hitachi H7100FA) operating at accelerating voltages of 100–125 kV. The particles were 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 μl of the smaller particles were transferred to a 200 mesh nickel grid coated with a silicon monoxide film. Images were captured directly in the TEM using a Gatan 789 camera system.

The as prepared powder was uniaxial compacted into discs samples and were subsequently cold isostatically pressed at ~200 MPa. Sintering was performed in a microwave furnace (M.M.T., Knoxville, TN) provided with a variable power output magnetron source capable of operating from 0 to 3 kW at 2.45 GHz. The cavity is large and overmoded, thus ensuring mixing of the microwave modes and resulting in a homogeneous field distribution. The HA compacts were sandwiched between two SiC susceptors and surrounded with alumina fiber before sintering over the temperature range of 1000 °C to 1300 °C. The sintering schedule for all samples was kept constant at duration of 30 min. The temperature of the samples was measured via a pyrometer (Model M77, Mikron Corp.) and the power of the microwave system adjusted accordingly to maintain the required temperature.

Sintered pellets were ground and mirror polished to 1 μm surface finish using diamond paste. Phase analysis by X-ray diffraction (XRD) (Rigaku Geiger-Flex, Japan) of synthesized powder and polished samples were carried out at room temperature using Cu Kα as the radiation source at a scan speed of 0.5° per minute and a step scan of 0.02°. The different phases were identified with reference to standard JCPDS cards available in the system software. The microstructure evolution of the sintered samples was investigated by SEM (Philips XL30 scanning electron microscope) and the grain size of polycrystalline HA was determined from the SEM micrographs using the line intercept analysis [15]. Prior to SEM analysis, the polished HA samples were etched with 0.5% HF to delineate the grain boundaries.

The density of the sintered compacts was measured by water immersion technique and the relative density was calculated by taking the theoretical density of hydroxyapatite as 3.156 g cm^{-3}. The microhardness (H_v) and fracture toughness (K_{Ic}) of polished samples were determined using the Vickers indentation method. The indentation load (<200 g) was applied and held in place for 10 s. Five indentations were made for each sample and the average value was taken. The indentation K_{Ic} was determined from the equation proposed by Niihara [16]:

$$K_{Ic} = 0.203\left(\frac{c}{a}\right)^{-1.5}(H_v)(a)^{0.5} \quad (1)$$

where H_v is the Vickers hardness, a the half diagonal of the indentation, c the radial crack dimension measured from the centre of the indent impression, i.e., $c = L + a$ and L is the crack length.

3. Results and discussion

3.1. Morphology of the synthesized powder

The TEM micrograph of the synthesized nano powder, shown in Fig. 1, revealed elongated rod-like crystals of size distribution varying between 50 nm and 100 nm. The peak broadening of the diffraction pattern of the nanocrystalline powder shown in Fig. 2 is in agreement with the TEM observation. Agglomerates of the crystal are also visible from the micrograph. However, this is believed to be soft agglomerates as the HA powder was easily compacted to form green body.

X-ray diffraction analysis of the synthesized HA powder produced only peaks which corresponded to the standard JCPDS card no: 74-566 for stoichiometric HA. Secondary phase such as tricalcium phosphate (TCP), calcium oxide or calcium hydroxide was not detected in the synthesized nano powder. In addition, the XRD pattern of the synthesized powder is in good agreement with that of enamel of a human tooth as shown in Fig. 2.

3.2. HA phase stability and mechanical properties

The general observation was that all the samples did not show any sign of cracking after sintering despite the high heating and cooling rate (about 100 °C/min) that were employed during microwave sintering. The XRD phase analysis for compacts that were sintered between 1000 °C

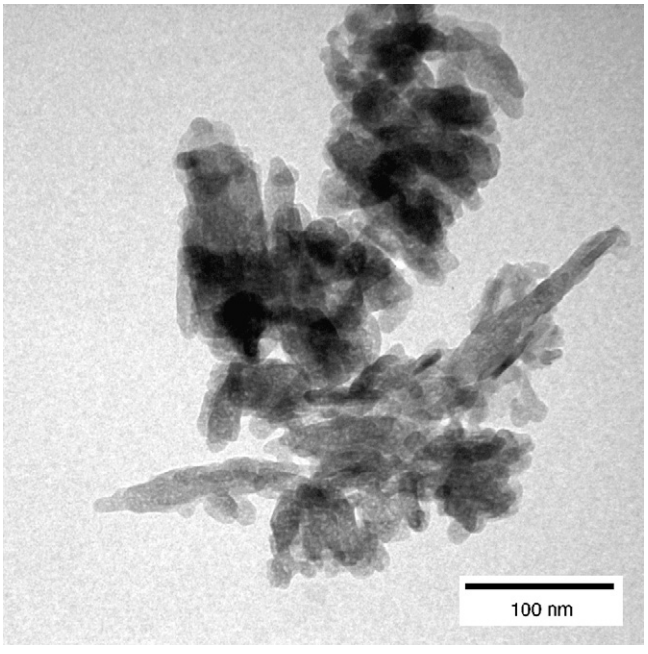

Fig. 1. TEM micrograph of as-synthesized nano HA crystals.

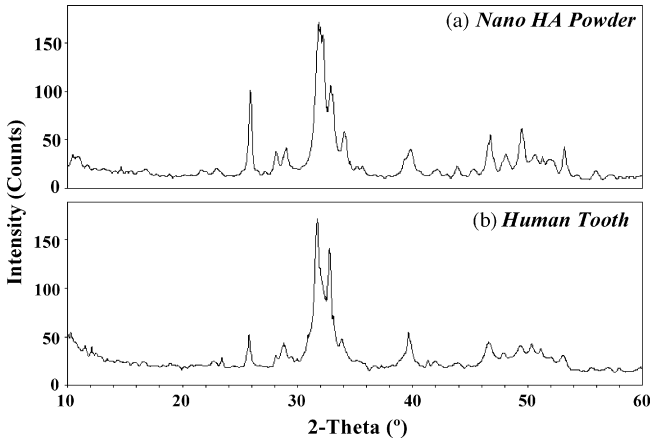

Fig. 2. Comparison of XRD patterns of synthesized nano HA powder with that of a human tooth (courtesy of Dr. S. Ramesh). All peaks corresponded to stoichiometric HA phase.

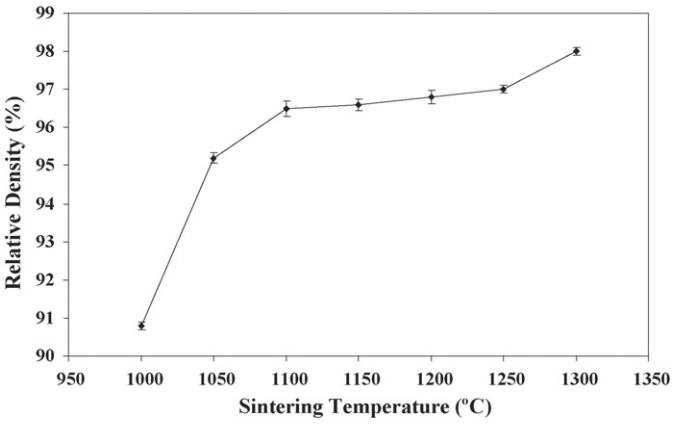

Fig. 4. The relative density of microwave-sintered HA as a function of sintering temperature.

and 1300 °C are shown in Fig. 3. The XRD traces of the sintered samples were in good agreement with each other and correlated well with that reported by Kutty et al. [17]. In general, there was no secondary phases present in the HA lattice and the XRD signatures of all the samples, regardless of sintering temperature as shown in Fig. 3, belong to that of stoichiometric HA. These results indicate that the phase stability of HA was not disrupted by microwave heating.

The effect of MS on the densification of HA compacts are shown in Fig. 4. In general, the bulk density variation of the HA samples sintered by microwave method was found to increase with increasing sintering temperature. The microwave-sintered ceramics exhibited 90–91% of theoretical density (T.D.) when sintered at 1000 °C and achieved above 96% T.D. when sintered at 1100 °C. A maximum of 98% T.D. was attained for compacts sintered at 1300 °C. These results are in good agreement with that reported in the literature for microwave-sintered HA [10,17–19].

Taking into consideration of the attained densities based on the total time of sintering (i.e., about 0.5 h), the beneficial effect of microwave energy in promoting densification of HA can be realized. For instance, by using the conventional pressureless sintering method, a density of 96% T.D. was attained for HA when sintered at 1000 °C for more than 18 h using a heating/cooling rate of 2 °C/min, with 2 h holding time [3,8,9]. Although, a higher temperature of 1100 °C is needed by microwave sintering to achieve a similar density, this effect is offset by the very short sintering time taken for densification, i.e., microwave sintering took a fraction of less than 3% of the total time taken by the conventional pressureless sintering to achieve the same density.

The efficacy of microwave heating in suppressing grain coarsening of HA compacts when sintered below 1200 °C is shown in Fig. 5. It was found that the mean grain size of HA increased slowly with sintering temperature up to 1150 °C and thereafter, the rate of grain growth increased rapidly for samples sintered ≥1200 °C. The grain size of HA increased by a factor of about 2.4 from 0.86 μm to 2.08 μm when the temperature increased by 100 °C from 1200 °C. Nevertheless, these values are relatively small if compared to the mean grain

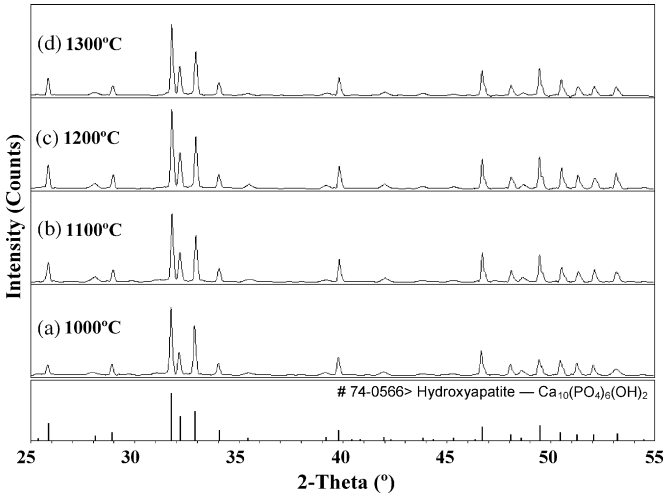

Fig. 3. XRD patterns of HA compacts consolidated at different temperature. All the phases corresponded to that of stoichiometric HA.

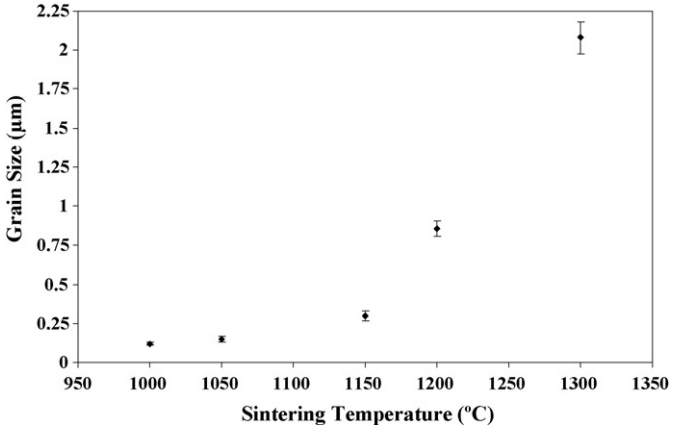

Fig. 5. Grain size variation with sintering temperature for HA consolidated by microwave heating.

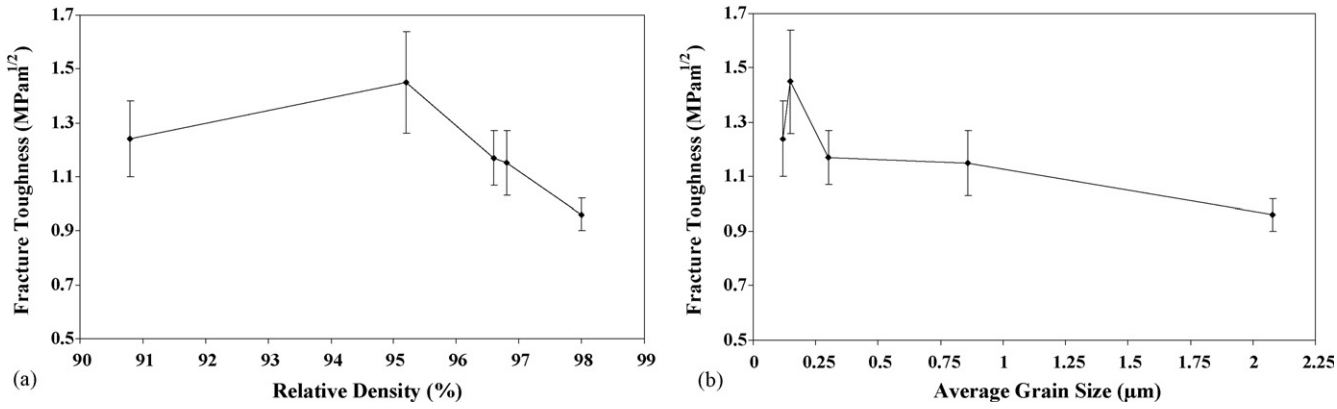

Fig. 6. (a) The indentation fracture toughness versus relative density of HA and (b) fracture toughness dependence on the grain size of microwave-sintered hydroxyapatite.

sizes obtained via the conventional pressureless sintering method. For instance, grain sizes as large as 5 μm was reported for HA conventionally sintered at 1300 °C [3,8] as compared to about 2.1 μm measured in the present work for microwave-sintered HA.

The effect of relative density and grain size on the fracture toughness (K_{Ic}) of synthesized HA are shown in Fig. 6(a) and (b), respectively. The average toughness was found initially to increase with density and grain size from 1.24 MPa $m^{1/2}$ (∼91% T.D. and 0.12 μm) to 1.45 MPa $m^{1/2}$ (∼95% T.D. and 0.15 μm) and thereafter decrease almost linearly with further increase in grain size, i.e., down to 0.96–1 MPa $m^{1/2}$ when sintered at 1300 °C despite having high density of 98% of theoretical value.

In general, the fracture toughness of the HA was found to vary between 0.96 ± 0.06 MPa $m^{1/2}$ and 1.45 ± 0.19 MPa $m^{1/2}$. The latter value is the maximum K_{Ic} attained for the HA sintered at 1050 °C. The minimum value of fracture toughness obtained for the microwave-sintered HA was in agreement with values reported in the literature for synthetic HA sintered up to 1300 °C [3,19–21]. In general, the maximum K_{Ic} for most HA reported in the literature varied between 0.96 and 1 MPa $m^{1/2}$. Thus, the high value of 1.45 MPa $m^{1/2}$ attained in the present work for microwave-sintered HA was encouraging. It is believed that the improvement in fracture toughness could be attributed to both the improved characteristics of the synthesized HA crystals as well as the improved sinterability of the powders with very limited grain growth during microwave sintering.

The influence of sintering temperature as reflected by the relative density on the Vickers hardness of HA sintered by microwave technique is shown in Fig. 7. In agreement with the fracture toughness trend, the hardness of HA was also found to increase with relative density (sintering temperature) and peaked at 6.38 ± 0.30 GPa when sintered at 1150 °C (∼96.6% dense) and then decreased with further increase in density resulting from increasing temperature up to 1300 °C.

In comparison with the data obtained for the effect of sintering temperature on the sintered densities (Fig. 4), the relative density of HA increased from 90.8% at 1000 °C to 95.2% at 1050 °C and 96.7% at 1150 °C. This increase in density is clearly reflected in the improved toughness and hardness as shown in Figs. 6(a) and 7, respectively.

However, sintering beyond 1150 °C, the hardness started to decrease although the densities of these compacts above this temperature range was still high, i.e., above 96% of theoretical density (Fig. 7). This decrease in toughness and hardness is believed to be associated with a grain size effect as depicted in Figs. 6(b) and 8, respectively. The graphs suggest that the properties increased with grain size and reached a maximum

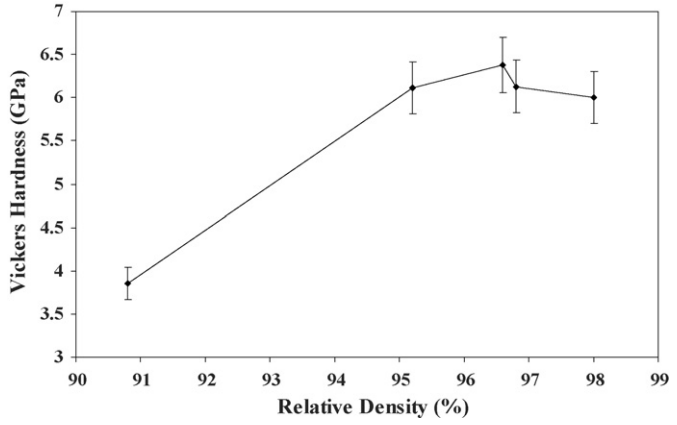

Fig. 7. The effect of relative density on the Vickers hardness of sintered HA.

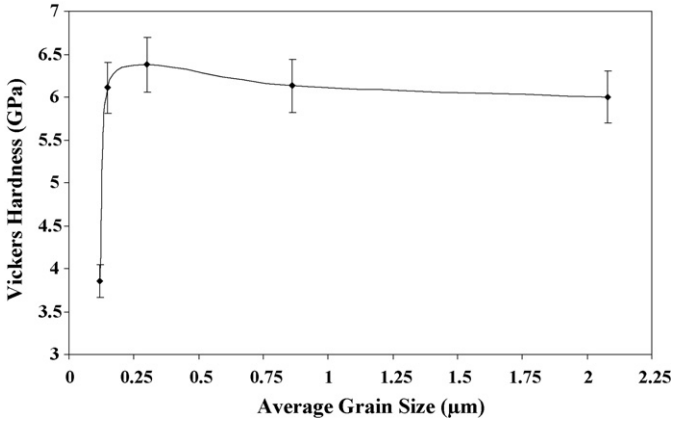

Fig. 8. Vickers hardness dependence on the grain size of microwave-sintered HA.

value at a certain grain size limit (d_c). Thereafter, both the toughness and hardness started to decrease with increasing grain size resulting from sintering at higher temperature.

Based on these results, it is hypothesized that below some grain size limit (d_c) the toughness as well as hardness is governed by bulk density (or porosity). In contrast, above d_c the bulk density is not the controlling parameter but grain coarsening. This was evident from Fig. 8, where the d_c for the microwave-sintered HA in the present work was in the range of 0.15–0.3 μm, above which resulted in a decreased in mechanical properties. However, further testing is to be carried out and also TEM investigation in order to examine the temperature dependence of grain growth as well as the grain size effect on the mechanical properties of hydroxyapatite.

4. Conclusions

The consolidation of nanocrystalline HA by microwave sintering was found to be beneficial in terms of densification and mechanical properties. Rapid sintering of nano HA via microwave achieved densities of above 96% T.D. with a temperature of 1100 °C and sintering time of 30 min, while maintaining fine-grained microstructure. In general, the HA phase was not disrupted by microwave heating and the relative density of the compacts varied between 90% and 98% with high values of 96% and 98% dense being attained in samples consolidated at 1100 °C and 1300 °C, respectively.

The beneficial effects of microwave heating in suppressing grain coarsening that normally is unavoidable via conventional pressureless sintering have been revealed. Fine grain size of 0.12 μm was achieved when sintered at 1000 °C for 30 min. In terms of mechanical properties, a maximum fracture toughness of 1.45 MPa $m^{1/2}$ and Vickers hardness of 6.38 GPa was attained for compacts microwave-sintered at 1050 °C and 1150 °C, respectively.

The effect of sintering temperature on the sintered densities of HA was reflected in the toughness and hardness values up to the point where the material attained 95–96% T.D. However, further sintering the mechanical properties were not governed by density effect but are believed to be associated with a grain size effect.

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