I O U R N A L O F

Ceramic Processing Research

Effects of two-step sintering on the properties of hydroxyapatite bioceramic

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In the present study, the sintering behaviour of hydroxyapatite (HA) was investigated by employing the two-step and conventional sintering methods. Comparisons were made between different combinations of sintering temperatures to examine their influence on the sinterability of the samples. The sintered samples were examined in terms of phase stability, relative density, grain size, Vickers hardness, and fracture toughness. The results revealed that the two-step sintering cycle was effective in suppressing grain coarsening when compared to conventional sintering. The study also found that while employing the two-step sintering, the selected temperature (T_1) at which densification occurs plays a major role in determining the mechanical properties of HA samples.

Key words: Bioceramic, Two-Step Sintering, Densification, Sinterability.

Introduction

Fracture and damage of bones often caused by injuries and age-related degenerative diseases [1, 2] threaten their sufferers with excruciating long-term and debilitating pain. While bones are known to have remodelling and regeneration abilities [3, 4], there have been many instances when natural healing and conventional surgical intervention are unable to alleviate pain and restore function as effective as bioceramic implants [2, 5].

Various kinds of bioceramics such as alumina, zirconia, tricalcium phosphate, hydroxyapatite, bioactive glasses, and glass-ceramics have been explored as implant materials in the past [1, 2]. Nevertheless, HA, $Ca_{10}(PO_4)_6(OH)_2$, a type of calcium phosphate phase [1, 6], remains as one of the most widely used bioceramic for various clinical applications. HA has attracted tremendous research interests in regard to improvements in the mechanical properties through chemical and microstructure manipulations [7, 8]. This is because of the need for the material to sustain load while at the same time to integrate well with the human body and form resilient bonds to bones [9, 10], owing to its excellent osteoconductive [11, 12] and biocompatibility

[13, 14] characteristics.

Since the first declared successful HA implant in 1988 [9], a great deal of different methodologies to sinter HA has been developed in order to improve its mechanical properties through powder consolidation. Some examples include the conventional pressureless sintering (CS) [15, 16] and non-conventional techniques such as the two-step sintering (TSS) [17, 18], liquid phase sintering [19, 20], hot pressing [21, 22], hot isostatic pressing [23, 24], ultrahigh pressure [25], microwave [26, 27], and spark plasma sintering [12, 28].

The TSS method is one of many interesting methods found to successfully control the undesirable grain coarsening during densification [29-31] that primarily occurs with CS [15, 32]. Generally, the deterioration of mechanical properties such as fracture toughness have been associated with grain growth [33-36]. TSS involves heating the sample at a high temperature, T_1 for a short time (i.e. 1 min) followed by rapid cooling for densification at a lower temperature, T₂ for an extended duration (i.e. 20 h). In order to succeed in TSS, it is important to first attain an adequately high intermediate relative density (~75%) by elimination of the pores at sintering temperature, T_1 . Only then, by using a lower temperature, T₂, densification will continue to occur without abnormal grain growth [17, 18, 37].

HA compacts are typically sintered between

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temperatures, T_1 of 900 °C-1400 °C [35, 38]. It is known that the highest relative densities of HA are not attainable at lower temperatures (i.e. < 1200 °C) while higher sintering temperatures (i.e. > 1300 °C) tend to promote grain growth and cause thermal decomposition of the HA phase [32, 39-41]. On the other hand, soaking temperatures, T_2 in the range of 800 °C-1150 °C have been used in previous studies [17, 18, 29, 30]. However, the actual effect of the different soaking temperatures on HA are not well understood.

While previous publications have already outlined the basic guidelines to succeed in TSS, the consequence of employing different combinations of temperatures T_1 and T_2 on the properties of HA has yet to be investigated and hence form the main aim of the present research.

Experimental Procedures

In the present study, HA with a molar ratio of Ca/P = 1.67 was synthesised using the wet precipitation method according to the procedure developed by Ramesh [42] following the chemical reaction:

$$10Ca(OH)_2 + 6H_3PO_4 \rightarrow Ca_{10}(PO_4)_6(OH)_2 + 18H_2O$$
(1)

According to this method, 0.6 M orthophosphoric acid solution, H_3PO_4 (85% purity, Merck) was added at a rate of 6 to 11 drops/s to 1 M calcium hydroxide solution, Ca(OH)₂ (R&M Chemicals) under magnetic stirring (~ 600 rpm) at room temperature. Ammonia solution (25% concentration, Merck) was added to maintain a pH value of above 10.5. At the end of the reaction, the slurry was allowed to continuously stir for an additional 6 h. It was then aged overnight. The resulting precipitate was rinsed with distilled water, filtered and subsequently dried in an oven at 60 °C for 12 h. Finally, the dried cake was crushed and sieved through a 212 µm mesh to obtain a well defined pure HA powder.

HA disc samples (diameter 20 mm) were prepared by compacting the HA powder through uniaxial pressing at 2 MPa. The samples were then sintered using CS and TSS methods at various temperatures (T_1 and T_2). The ramp rate was set at 2 °C/min to avoid unnecessary thermal stresses that could result in micro- and macrocracking occurring on the surface of the HA sample [43]. The different sintering profiles used in the present study are summarised in Fig. 1 and Table 1.

The phase stability of the sintered samples was analysed using X-ray diffraction (XRD) (PANalytical Empyrean, Netherlands) at voltage and current of 45 kV and 40 mA, respectively. The XRD patterns were recorded in the range 20 ° $\leq 2\theta \leq 50$ at a scan speed of 1/min and time step size of 0.017 ° with Cu-K α as the radiation source. The recorded XRD patterns were compared to standard reference JCPDS-ICDD (Joint



Fig. 1. Conventional sintering (CS) and two-step sintering (TSS) profiles employed in present study.

Table 1. Sintering profiles employed in the present study.

Sample	Sintering Method	Sintering Profile
C1	^a Conventional Sintering (CS)	$T_1 = 1200C (2 h)$
C2		$T_1 = 1250C (2 h)$
C3		$T_1 = 1300C (2 h)$
TS1	^b Two-Step Sintering (TSS)	$T_1 = 1200 ^{\circ}C (1 \text{ min}),$ $T_2 = 950 (20 \text{ h})$
TS2		$T_1 = 1200 \text{ °C} (1 \text{ min}),$ $T_2 = 1050 (20 \text{ h})$
TS3		$T_1 = 1300 \text{ °C} (1 \text{ min}),$ $T_2 = 950 (20 \text{ h})$

^aSintering temperatures for conventional sintering of HA were based on previous studies where high densification are achieved without thermal decomposition [32, 39-41].

^bSintering parameters for two-step sintering of HA were developed according to previous studies [17, 18, 29, 30].

Committee of Powder Diffraction Standard-International Centre for Diffraction Data) files. The average crystallite size (D_{002}) of the sintered samples was calculated by using the Scherrer's equation [44]. The morphology and microstructure development of the sintered samples were examined using a scanning electron microscope (SEM) (Hitachi Benchtop SEM TM3030, Japan). The grain size of the samples was determined from the SEM micrographs via the line intercept method [45].

The bulk densities of the samples were measured by the Archimedes' principle using the distilled water as immersion medium and an electronic balance (Shimadzu AY220, Japan). Relative density was calculated by taking the theoretical density of HA, as 3.156 g/cm³.

The mechanical properties of the sintered samples were evaluated through Vickers and fracture toughness measurements. The samples were ground (SiC paper at 800 grit and 1200 grit) and polished to a 1 μ m finish prior to properties evaluation. The microhardness of sintered HA was measured with a Vickers hardness tester (Shimadzu HMV Series Micro Hardness Tester, Japan). Three indentations were performed on each

sample where an average value was taken. The fracture toughness (K_{Ic}) value was obtained by using the Niihara's equation [46].

Results and Discussion

The XRD pattern obtained for the synthesised powder is illustrated in Fig. 2. The pattern conforms to the JCPDS-ICDD standard for phase pure HA. There were no intermediate apatite phases or secondary phases of α - or β - TCP (tricalcium phosphate) detected. The XRD peaks have a broad appearance indicating a low crystallinity. This is typically observed with HA powders prepared by the wet precipitation method [47, 48]. The crystallite size calculated by using the Scherrer approximation taken at (0 0 2) peak was found to be about 36.5 nm which is smaller than the 60 to 100 nm as reported by other researchers [15, 43]. It has been documented that HA powders having small crystallite size was beneficial in enhancing the bioactivity and osseointegration with hard tissues in the body when compared to coarser particles [49, 50].

The XRD patterns of the HA compacts after sintering at different temperatures are shown in Fig. 3. In general, all the samples exhibited the HA phase only. It can be observed that the patterns vary with different sintering methods and sintering temperatures. HA samples sintered using CS (C1, C2, C3) exhibited sharper peaks as compared to samples sintered with TSS (TS1, TS2, TS3), which are generally broader, indicating lower crystallinity than the former. Narrower peaks for the CS method are observed at higher sintering temperatures which is consistent with the literature [50]. However, this was not the case for the TSS samples where the XRD peaks was observed to broaden with increasing temperature, T₁.

The effect of CS and TSS on the relative density of HA is presented in Fig. 4. It can be observed that



Fig. 2. XRD pattern of as-synthesised HA powder prepared by wet precipitation method.



Fig. 3. XRD patterns of HA samples sintered using CS (a) C1, (b) C2, (c) C3 and TSS (d) TS1, (e) TS2, (f) TS3.



Fig. 4. Effect of sintering temperature, T_1 on relative density of both CS and TSS samples.

relative density improves with increasing sintering temperature of T_1 . This generally leads to better mechanical properties such as Vickers hardness and fracture toughness. Nevertheless, it should be noted that selecting a very high sintering temperature could reverse this effect due to the detrimental effect of grain growth [33-36] and dissociation of HA into TCP and TTCP (tetracalcium phosphate) that could occur at 1300 °C [51] and 1400 °C [15].

Furthermore, no significant differences in the final



Fig. 5. SEM micrographs comparing the difference in grain sizes between CS (a) C3 and TSS (b) TS3 at the final sintering stage ($T_1 = 1300$ °C).



Fig. 6. Comparison of grain size according to increasing relative density between CS and TSS samples.

bulk density between sintering methods (i.e. CS and TSS) are found with respect to the sintering temperature, T_1 . This indicates that while the temperature, T_1 plays a pivotal role in densification, soaking temperature, T_2 does not. This observation is supported by the similar recorded relative density values between samples TS1 ($RD \sim 70\%$) and TS2 ($RD \sim 72\%$). Both samples employed identical sintering profiles except for holding temperatures, $T_2 = 950$ °C for TS1 and 1050 °C for TS2 (see Table 1).

The SEM micrographs for HA samples sintered at temperature, $T_1 = 1300$ C using CS and TSS are shown in Fig. 5. A relatively dense microstructure with small amount of pores can be observed for both sintering methods. While both samples (C3 and TS3) exhibited a bimodal grain distribution, the TSS method appears to produce finer grains compared to CS.

The variations of final grain sizes of sintered HA samples according to relative density are shown in Fig. 6. It can be observed that grain size increases with relative density. Improvements for CS in relative density between samples C1 ($RD \sim 70\%$) and C2 ($RD \sim 81\%$) resulted in a moderate grain growth of ~45%

when the sintering temperature increase from $T_1 = 1200 \text{ °C}$ (C1) to 1250 °C (C2). Further densification recorded between samples C2 ($RD \sim 81\%$) and C3 ($RD \sim 92\%$) resulted in a dramatic grain growth of ~ 156% at sintering temperatures $T_1 = 1250 \text{ °C}$ (C2) and 1300 °C (C3), respectively. It is expected that beyond this temperature regime, the grains of the sample would continue to rapidly grow with little or no increase in relative density [15, 32].

In comparison, TSS exhibited a near-linear grain growth trend which is in good agreement with the variation in relative density. No evidence of abnormal grain growth normally found with CS is observed. As a consequence, significant reductions (i.e. $\sim 56\%$) in final grain sizes without compromising on final relative densities is obtained between samples C3 ($RD \sim 92\%$) and TS3 ($RD \sim 91\%$) using the CS and TSS methods, respectively at sintering temperature, $T_1 = 1300$ °C. This can be qualitatively confirmed from the SEM micrographs in Fig. 5 where the TSS method is shown to produce finer grains (~ $2.87 \mu m$) as compared to the CS method (~ $6.46 \,\mu$ m). These values are smaller than the reported 9-10 µm of grain sizes for HA consolidated with CS at 1300 °C [32, 35].

This demonstrates the effectiveness of TSS in suppressing the rapid increase in grain growth at the final sintering stage. The observed grain growth impediment is largely attributed by the reduction in grain junction mobility through the occurrence of the triple-point drag due to the lower holding temperature (T_2) (i.e. 950 °C). Therefore by allowing grain boundary diffusion to remain active while suppressing the grain junction mobility, densification can occur without the occurrence of significant grain growth [18, 37].

The behaviour of Vickers hardness with relative density and grain size are presented in Fig. 7 and 8, respectively. It is observed with CS that an improvement relative density (from $RD \sim 70\%$ to $RD \sim 81\%$) contributes to a gradual increase of Vickers hardness between samples C1 (~ 1.02 GPa) and C2 (~ 1.21 GPa) sintered at temperatures, T₁ = 1200 °C (C1) and 1250 °C



Fig. 7. Comparison of Vickers hardness behaviour according to increasing relative density between CS and TSS samples.



Fig. 8. Comparison of the effect of grain size on Vickers hardness between CS and TSS samples.

(C2), respectively. Similarly, this can be observed with TSS where an improvement in relative density (from $RD \sim 70\%$ to $RD \sim 72\%$) coincides with a small variation in Vickers hardness between samples TS1 (~ 1.19 GPa) and TS2 (~ 1.08 GPa), respectively with increasing soaking temperature, T₂ from 950 °C (TS1) to 1050 °C (TS2).

However, at the highest point of densification for both sintering methods (RD > 91%) using sintering temperature, T₁ = 1300C, a dramatic improvement of Vickers hardness is recorded with CS (from ~ 1.21 GPa (C2) to ~ 3.22 GPa (C3)) and TSS (from ~ 1.08 GPa (TS2) to ~ 2.15 GPa (TS3)). This occurrence is indicative of the influence of grain size on Vickers hardness (see Fig. 8). In this figure, the exceptional improvements in Vickers hardness coincide with the final grain growth occurring in both CS and TSS.

The variations of fracture toughness for the sintered HA samples according to relative density and grain size are shown in Fig. 9 and 10, respectively. In



Fig. 9. Comparison of fracture toughness behaviour according to increasing relative density between CS and TSS samples.



Fig. 10. Comparison of the effect of grain size on fracture toughness between CS and TSS samples.

agreement with the Vickers hardness trend, the fracture toughness of sintered HA was found to be highest when sintered at 1300 °C.

For CS, there were no significant differences in fracture toughness between samples C1 (~ 0.55 MPa.m^{1/2}) and C2 (~ 0.51 MPa.m^{1/2}) when employing sintering temperatures 1200 °C (C1) and 1250 °C (C2), respectively. However when increasing the sintering temperature to 1300 °C, a remarkable (~ 123%) improvement in fracture toughness of C3 (~ 1.1 MPa.m^{1/2}) is observed.

For TSS, sample TS1 (~ 0.66 MPa.m^{1/2}) appears to obtain better fracture toughness as compared to sample TS2 (~ 0.50 MPa.m^{1/2}) when using different soaking temperature, $T_2 = 950$ °C (TS1) and 1050 °C (TS2), respectively. This result indicates that higher fracture toughness could be obtained when using a lower soaking temperature, T_2 (i.e. 950 °C). Further improvement (i.e. ~ 17%) to fracture toughness between samples TS1 (~ 0.66 MPa.m^{1/2}) and TS3 (~ 0.78 MPa.m^{1/2}) was observed for the same soaking temperature, $T_2 = 950$ °C when increasing the sintering temperature, T_1 from 1200 °C (TS1) to 1300 °C (TS3).

Despite obtaining similar final relative densities between the both methods (i.e. CS and TSS) at temperature, $T_1 = 1300$ °C, fracture toughness obtained with CS (~1.1 MPa.m^{1/2}) was superior to TSS (~ 0.78 MPa.m^{1/2}). The sintering of HA could be carried out at temperatures above 1300 °C (e.g. 1350 °C -1400 °C). However, the fracture toughness values for CS are expected to rapidly deteriorate due to extreme grain growth as reported previously [15, 32, 43, 52]. In contrast, due to the absence of abnormal grain growth in TSS, fracture toughness values are predicted to steadily improve with relative density and eventually surpassed that of CS as demonstrated in the literatures [17, 18, 35].

Conclusions

The phase stability, microstructure and mechanical effects of HA prepared using wet precipitation method and sintered using CS and TSS were investigated. All samples were found to exhibit XRD signatures of pure HA. The beneficial effect of two-step sintering on the densification and properties of HA has been revealed. It was found that samples sintered using TSS consistently produced finer grains if compared to samples sintered via the conventional sintering method. The study also shown for TSS that temperature, T_1 significantly influence the densification behaviour of HA and resulted in better mechanical properties as well as finer grain microstructure was produced when a lower soaking temperature, T_2 (i.e. 950C) was employed.

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