Calcining influence on the powder properties of hydroxyapatite

N. PATEL, I. R. GIBSON, S. KE, S. M. BEST, W. BONFIELD*
IRC in Biomedical Materials, Queen Mary and Westfield College, Mile End Road, London, E1 4NS, UK
E-mail: I.R.Gibson@qmw.ac.uk

The effect of different calcination temperatures on the powder characteristics and the sintered density of synthetic hydroxyapatite (HA) powders, produced using two different processing routes, was examined. Powders were produced by either drying, milling and sieving an as-precipitated HA or by spray-drying a slurry of precipitated HA. Calcining the two powders at temperatures between 400 and 1000 °C did not significantly affect the powder particle size. The specific surface areas of the two powders, however, were reduced from 70–80 m^2/g for a calcination temperature of 400 °C to approximately 5–7 m^2/g for 1000 °C. Analysis of the surfaces of the HA powders using scanning electron microscopy (SEM) illustrated the coarsening and subsequent sintering of the sub-micron crystallites that constitute a powder particle as the calcination temperature increased, corresponding to the decrease in surface area of the powders. The sintered densities of the final ceramics were not significantly affected by calcining the powders. Microhardness measurements of ceramics prepared from powders calcined at different temperatures showed no significant variations with calcination temperature or powder processing method. The results of this study have illustrated that for applications where HA may be used in powder form, for example in plasma-spraying and for the production of HA-polymer composites, calcining the HA will significantly affect the powder properties, namely the surface area and morphology of the powders. For applications requiring HA in a dense ceramic form, for example as granules or blocks, calcining the powders does not significantly affect the properties of the final ceramic.
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1. Introduction

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is used for a number of biomedical applications in the form of granules, blocks or porous implants to fill bone defects [1], as a deposited coating, such as a bioactive coating on a bioinert implant to allow biological fixation of the implant to the surrounding tissue [2], or as a filler phase of a polymer-ceramic composite material, such as hydroxyapatite-polyethylene, HAPEX™, implants for bone augmentation and as middle-ear implants [3].

The properties of these implants are highly dependent upon the powder properties of the HA used. For example, for the production of HAPEX™ composites, small changes in particle size and morphology of the HA powders used were shown to have significant effects on the mechanical properties of the final composite [4]. In producing HA powder for biomedical applications, it is essential to have complete control of the powder properties of the final powder. This will ensure that the powder properties, such as particle size, surface area, morphology and crystallinity, can be tailored for each specific application in order to maximize the properties of the final biomedical implant.

A common method for the preparation of synthetic HA is the aqueous precipitation of a calcium salt solution and a phosphate solution at high pH [5,6]. A number of studies have shown the effects of powder properties on the sinterability of the HA powders [7–15]. The effects of calcining HA powders prior to sintering have received less attention; Fanovich and Porto Lopez studied the effects of calcining synthetic and commercial powders on the sintered densities and mechanical properties [14]. As a result of only using two calcination temperatures and the HA used being non-stoichiometric, the results are not very clear, but a decrease in properties was observed when a high calcination temperature, 1000 °C, was used.

Gibson *et al.* [15] reported the effects of the powder properties of an HA powder, produced by the aqueous precipitation of $Ca(OH)_2$ and H_3PO_4, on its sinterability; the HA produced by this method sintered to high densities at much lower temperatures than a commercial HA. The improved sinterability of this synthetic HA was believed to be due to a combination of the powder having a high surface area and a high level of chemical purity compared to the commercial HA.

The aim of this study was to examine the effect of

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*Now at Department of Materials Science and Metallurgy, University of Cambridge, Pembroke Street, Cambridge, CB2 3QZ, UK.

calcining two HA powders, synthesized by the same chemical route but processed to a powder by two very different methods, on their powder properties and sinterabilities. The results would reveal how the powder properties of the two HA powders may be varied and controlled. Additionally, the results would illustrate if the sinterability of the powders was affected by changing the powder properties through calcining, or if the excellent sinterability previously observed with this HA powder was independent of powder properties.

2. Materials and methods
2.1. Sample preparation
A stoichiometric hydroxyapatite (Lab HA) was prepared using the precipitation reaction between calcium hydroxide, $Ca(OH)_2$ and orthophosphoric acid, H_3PO_4, based on the method described elsewhere [5, 15]. The stoichiometric HA used in this study had a Ca/P molar ratio of 1.67 and, after sintering/calcining at temperatures between 800 and 1300 °C, did not decompose to form secondary phases such as TCP or CaO. The precipitation reaction was carried out at room temperature and the pH was maintained at 10.5 by the addition of ammonium hydroxide solution. After complete mixing of the reactants, the suspension was aged overnight.

The resulting precipitate was processed to produce a powder by two different methods; this would ensure that the HA powders in this study were chemically identical, with the only differences between them being the physical properties of the powders caused by the processing method. The first method, termed Direct Method, involved the precipitate being filtered, dried at 80 °C overnight and then ground to a powder in a mortar and pestle. The powder was then dry ball milled, using a porcelain mill pot with alumina milling balls, for 1 h and then passed through a series of sieves; as a result of this process, the particle size of the final powder that was used in this study was < 75 μm in size. The second method, termed Spray-Dried Method, involved removing the supernatant from the aged precipitate and then spray-drying the HA slurry using a LabPlant SP-05 spray-drier. The conditions used were an inlet speed of 220 °C, a pump speed of 600 ml/h and an exhaust temperature of 110 °C. The powder was used as-spray-dried, with no further processing.

Portions of the two different powders were calcined in a Carbolite RHF 1600 Furnace at temperatures between 400 and 1000 °C; the heating rate was 2.5 °C/min, the dwell time was 30 min and the cooling rate to room temperature was 10 °C/min.

Powder compacts of the calcined powders were prepared by pressing uniaxially 1 g of HA powder into a 16 mm diameter steel die. The compacts were sintered in a Carbolite RHF 1600 Furnace at 1200 °C for 2 h, with a heating rate of 2.5 °C/min and a cooling rate to room temperature of 10 °C/min [15].

2.2. Characterization techniques
The phase composition and crystallinity of the HA powders calcined at different temperatures were analyzed by X-ray diffraction (XRD) using a Siemens D5000 diffractometer. Data were collected over the 2θ range 25–40° with a step size of 0.02° and a count time of 2.5 s. Identification of phases was achieved by comparing the diffraction patterns of HA with ICDD (JCPDS) standards [16].

The particle size distribution and mean particle size were measured using a Malvern Mastersizer X. The specific surface area of the powders was determined by the Brunauer-Emmett-Teller (BET) method using a Micromeretics Gemini II 2370 Surface Area analyzer. Scanning electron microscopy (SEM) of the powders was performed using a Field Emission JEOL F6300 SEM, which provided information about the morphology of the individual powder particles and also confirmed the particle size distribution results obtained from PSA.

The green and sintered densities of compacts were obtained from the measurement of geometric dimensions and sample mass for low density samples (< 95% of the theoretical density) and by the water immersion method for high density samples (> 95%); for low density samples, the water immersion method allows water to enter the pores, resulting in false values of the sample density. All densities were quoted as a percentage of the theoretical density of HA, 3.156 gcm^{-3} [16].

The Vickers hardness, H_v, of sintered specimens was determined using a Shimadzu microhardness indenter. A 1 kg load was applied for 10 s to produce an indent. The average diagonal length of the indent was measured and this was repeated five times for each sample. The Vickers hardness, H_v, was calculated from the method described in the ASTM E384 [17].

3. Results
3.1. Powder characterization
The effect of calcination temperature on the phase composition/crystallinity of the HA powders produced by the Direct Method and the Spray-Dried Method is illustrated in Fig. 1a and b respectively. For calcination temperatures between 400 and 700 °C, broad diffraction peaks were obtained that were similar to the diffraction patterns obtained for the non-calcined powders. For both powders there was a clear change in the diffraction peaks obtained at 700 and 800 °C; at and above the latter temperature, the diffraction pattern was composed of sharp, narrow diffraction peaks. All powders, for all calcination temperatures used in this study, resulted in diffraction peaks that only corresponded to the standard for hydroxyapatite [16] and no secondary phases, indicative of decomposition of the HA, were observed.

Particle size analysis of the as-processed, non-calcined powders produced particle size distributions as presented in Table I. The HA processed by the Direct Method had larger values of $d_{0.1}, d_{0.5}$ and $d_{0.9}$ than the Spray-Dried powder and the former produced a much wider distribution of sizes; approximately 3–67 μm compared to 2–17 μm. The effect of calcination temperature on the mean particle size, $d_{0.5}$, of the two HA powders is illustrated in Figs 2 and 3. The value of $d_{0.5}$ for the HA processed by the Direct Method showed only a small decrease of approximately 5–10% as the calcination temperature increased above 700 °C. The Spray-Dried HA powder, however, produced a sudden increase in $d_{0.5}$
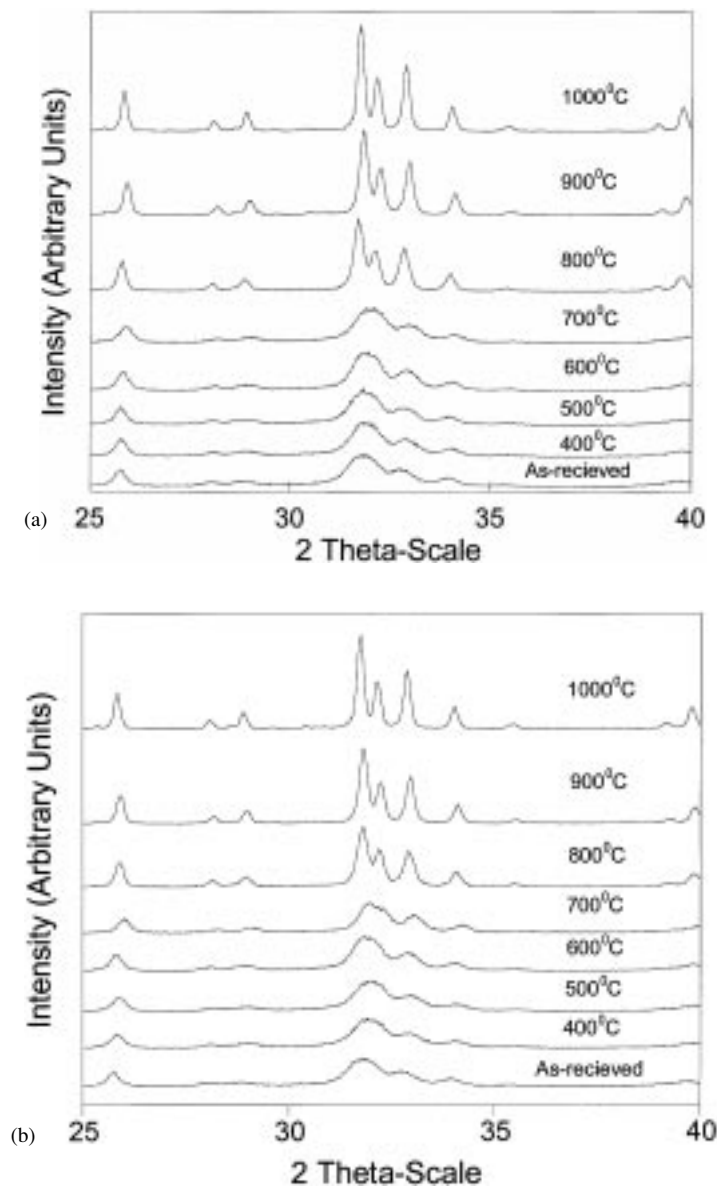
Figure 1 XRD patterns of HA powders processed by (a) Direct Method and (b) Spray-Dried Method, calcined between 400 and 1000 °C.

of almost 50% as the calcination temperature increased from 900 to 1000 °C. This was also reflected by an increase in the corresponding $d_{0.9}$ from approximately 16 μm at 900 °C to 63 μm at 1000 °C.

The specific surface areas (SSA) of the two different powders calcined at different temperatures are also shown in Figs 2 and 3. Both as-processed, non-calcined powders had large SSA, with the HA powder processed by the Direct Method having a slightly larger value than the Spray-Dried powder. Increasing calcination temperature from 400 to 1000 °C produced a steady decrease in the SSA and between 800 and 1000 °C the two powders had very comparable values.

The morphologies of the as-processed, non-calcined HA powder particles processed by a Direct Method and a Spray-Dried Method are shown in Fig. 4a and b respectively. The powder processed by the former method was composed of angular particles with a broad range of particle sizes, as was reflected in the results from particle size analysis (Table I). The powder processed by a Spray-Dried Method was composed, in contrast, of highly spherical particles that were smaller and of a narrower size distribution than the powders processed by the Direct Method.

The effect of calcination temperature on the particle size of the HA powders, using the powder processed by

TABLE I Particle size distributions of HA powders processed by Direct Method and Spray-Dried Method ($d_{0.1}$, $d_{0.5}$ and $d_{0.9}$ refer to the measured particle size, or diameter, of 10, 50 and 90% of the powder particles)

HA processing method	$d_{0.1}$ (μm)	Particle size $d_{0.5}$ (μm)	$d_{0.9}$ (μm)
Direct Method	3.2	26.8	66.9
Spray-Dried Method	2.4	7.1	16.7

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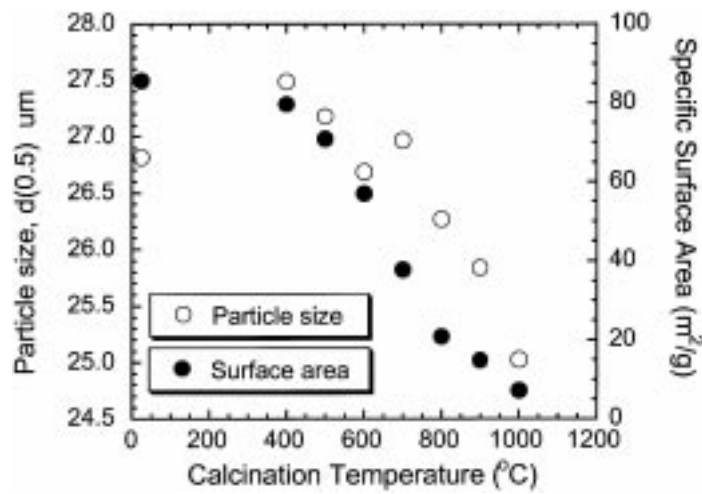*Figure 2* The effect of calcination temperature on the mean particle size $d_{0.5}$ (μm) and the SSA (m^2/g) of an HA powder processed by Direct Method.

the Spray-Dried Method as an example, is illustrated in Fig. 5a–d. The observed particle sizes did not change significantly as the calcination temperature was increased, in agreement with the results presented in Fig. 2 from PSA. A change in the surface microstructures of the powders could be observed as the calcination temperature was increased. For low temperatures the surface appeared to be composed of very small crystallites which gave the appearance of a rough surface of the powder particle. At higher calcination temperatures, for example Fig. 5d, the powder particles appeared to have a fused surface, which gave the appearance of a smooth surface of the powder particle. By examining an individual powder particle at high magnification, these microstructure changes could be observed more clearly, (Fig. 6a–d). As the calcination temperature increased from 700 to 800 °C these needle-shaped crystals began to sinter together, with subsequent coarsening of the microstructure; neck formation between the crystallites could be observed at these temperatures. The microstructure of the surface of the powder particle calcined at 900 °C, Fig. 6d, was markedly different to that observed

in the non-calcined powder, Fig. 4b. The surface was now composed of a framework of sub-micron sintered particles with a high level of porosity.

3.2. Sinterability of HA powders–sintered densities and vickers hardness

The sintered densities of compacts of HA powder processed by the Direct Method, calcined between 400 and 1000 °C prior to compaction, were unchanged from the value obtained for a compact of non-calcined powder; values were, within the experimental deviation of 0.5%, 97.3% of the theoretical density, or 3.07 gcm^{-3}. For HA processed by the Spray-Dried Method, powder compacts were unstable and could not be formed for powder that was non-calcined or calcined at 400 °C. For calcination temperatures between 500 and 1000 °C, the sintered densities of compacts showed small variations between 95.6 and 97.3% of the theoretical density, but no trend was apparent for the calcination temperatures used.

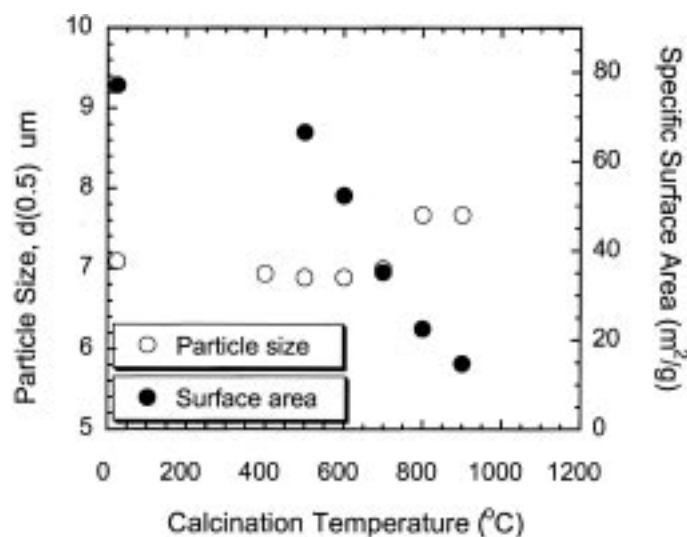Although the sintered densities of the samples prepared from the two different HA processing methods

Figure 3 The effect of calcination temperature on the mean particle size $d_{0.5}$ (μm) and the SSA (m^2/g) of an HA powder processed by Spray-Dried Method.
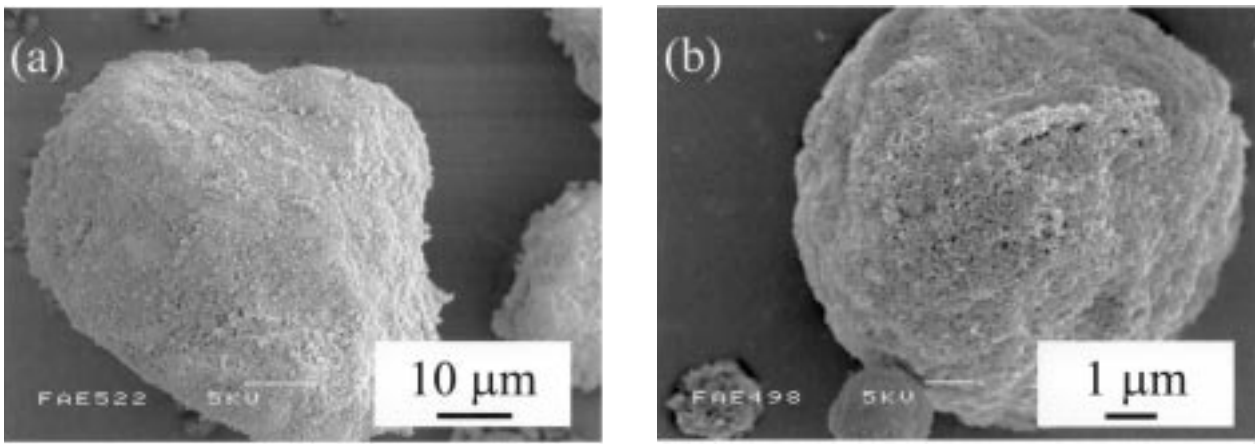
Figure 4 SEM micrographs of as-processed, non-calcined HA powders processed by (a) Direct Method and (b) Spray-Dried Method.

were very similar and no direct effect of calcination temperature on the sintered density was observed, a clear decrease in the linear shrinkages of the sintered samples was observed, Fig. 7. This decrease corresponded to a concomitant decrease in the weight loss on sintering of the ceramic specimen.

The microhardness values obtained for sintered disks of the two different HA powders showed no dependence on calcination temperature, with the Vickers hardness numbers (VHN) ranging from 237–344. The values showed considerable scatter and no trend could be detected, as observed for the sintered densities.

4. Discussion

XRD and SEM analysis showed that the HA powders processed by the two different methods undergo a clear change in morphology with increasing calcination temperature. Powders that are as-processed and have been calcined at temperatures between 400 and 700 °C are composed of nanometer-sized needle-shaped crystallites; this microstructure is comparable to that observed when apatite precipitates on the surface of a bioactive material immersed in simulated body fluid (SBF) [18, 19]. Increasing the calcination temperature to between 800 and 1000 °C, however, results in powders
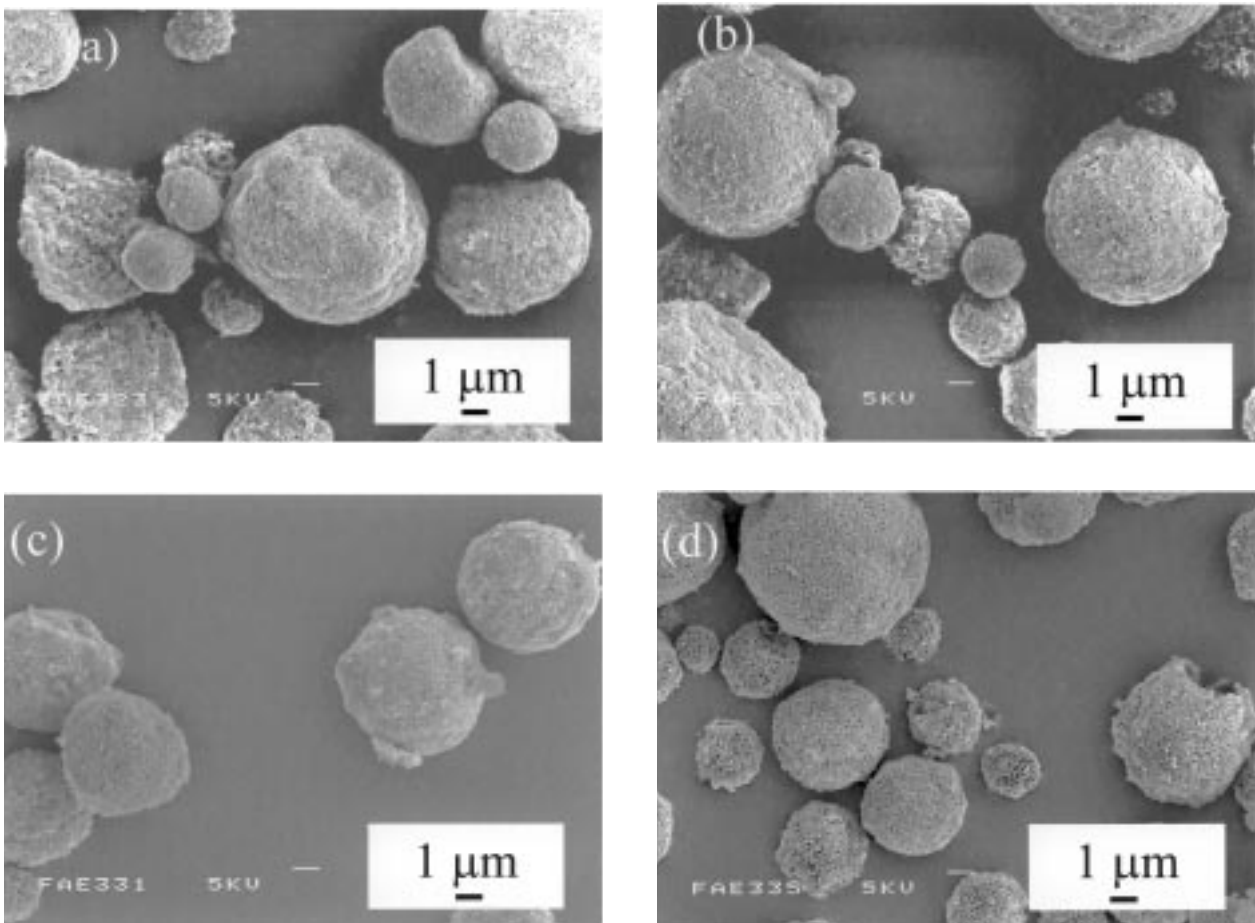

Figure 5 Low magnification SEM micrographs of HA powder processed by Spray-Dried Method, calcined at (a) 600 °C (b) 700 °C, (c) 800 °C and (d) 900 °C.
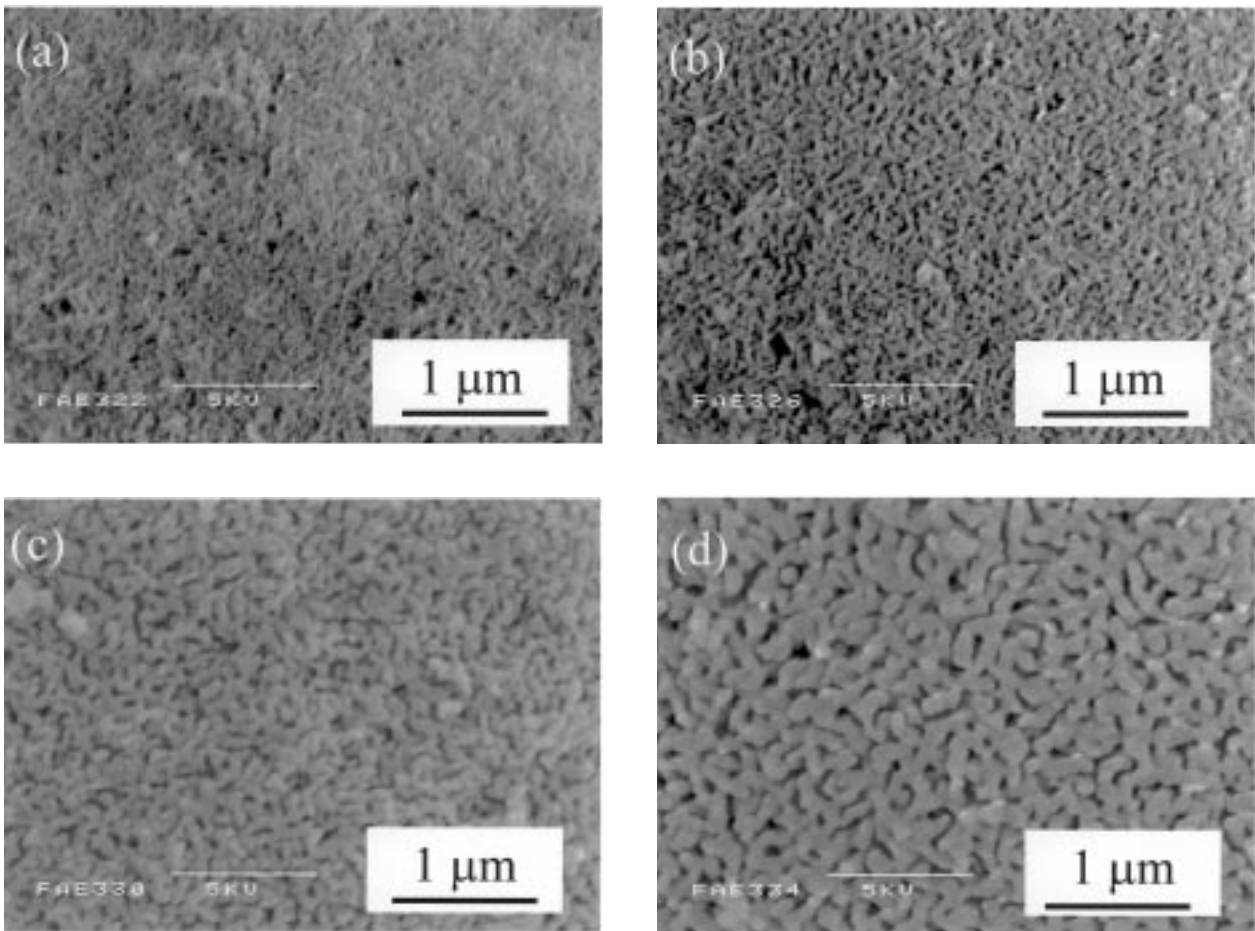
Figure 6 High magnification SEM micrographs of HA powder processed by Spray-Dried Method, calcined at (a) 600 °C (b) 700 °C, (c) 800 °C and (d) 900 °C.

that are made up of highly crystalline, fused, sub-micron particles. A previous study by Gibson *et al.* [15] showed that a non-calcined HA, similar to the HA powder processed by the Direct Method in this study, started to sinter at 800 °C and by 1000 °C it had achieved 80% of the theoretical density of HA. The important implication of this change in morphology is that it may affect the physical properties of the powder and have a concomitant effect on the sinterability of the powders.

The two different processing routes used in this study resulted in non-calcined HA powders with very different particle size distributions and powder morphologies, but with comparable specific surface areas. Spray-drying of ceramic powders allows a large degree of control over the particle size distribution and enables highly spherical powder particles to be achieved; this was demonstrated for hydroxyapatite by Luo and Nieh [20, 21]. Mechanical particle size reduction of a filter-cake using ball-milling
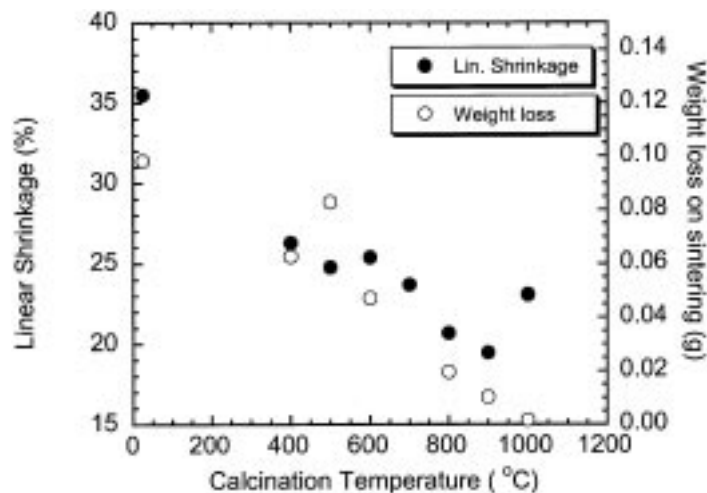

Figure 7 Effect of calcination temperature on the linear shrinkage of compacts of HA powder processed by two different routes, using a sintering temperature of 1200 °C.

and sieving can result in non-spherical particles and wide particle size distributions and high impact milling equipment and long milling and sieving times are required to achieve narrow size distributions.

Calcining the HA powders between 400 and 1000 °C did not significantly affect the particle sizes, although the powder processed by the Spray-Dried Method did show a sudden increase for a calcination temperature of 1000 °C, with powder particles beginning to sinter together. The SSA were, however, significantly affected by calcination temperature, with an almost linear decrease in SSA observed between 400 and 1000 °C, Fig. 3. This decrease in SSA could be related to the coarsening of the crystallites of HA that constitute an individual powder particle, as observed by high-magnification SEM of the particle surface, Fig. 6a–d. For applications where the SSA and surface morphology of HA powder particles is important, for example in the production of polymer-hydroxyapatite composites [4], controlled calcination of these HA powders can be carried out to obtain the optimum powder properties.

As a number of biomedical applications of HA involve the sintering of HA powder to form a ceramic body, the effect of the changes that were observed in the HA powder properties with increasing calcination temperature on the sintered density and microhardness values of sintered powder compacts of the two different HA powders was determined. The sintered densities and microhardness values of ceramics produced from HA powders processed by the Direct Method and the Spray-Dried Method were similar and showed no effect from calcining the powders. The only difference that was observed was a decrease in the linear shrinkage of the sintered samples with increased calcination temperature, which could be related to a loss of weight on sintering. As a result of the aqueous precipitation route that was used to produce these HA powders and the relatively low temperatures used to dry/spray-dry the powders, considerable levels of adsorbed water will remain in the powders; additional species such as carbonate and ammonia will also be adsorbed to the synthetic HA. This is why the largest linear shrinkage and weight loss on sintering was associated with the non-calcined powder, where the shrinkage is associated with both the densification process and the loss of water etc. When the powders were calcined at temperatures above 800 °C the linear shrinkage was due purely to the densification on sintering and not to the loss of volatile species.

Gibson *et al.* [15] showed that a non-calcined HA powder, comparable to the powder used in this study, exhibited excellent sinterability and began to sinter at a temperature approximately 150–200 °C lower than a calcined, commercial HA. Reducing the SSA and changing the surface morphology through calcining between 400 and 1000 °C did not have an adverse effect on either the sintered density or the microhardness values, so the excellent sinterability of these synthetic hydroxyapatites is not compromised by calcination. A study by Fanovich and Porto Lopez [14] showed that the density of sintered compacts of synthetic HA powder calcined at 1000 °C was less than for the same powder calcined at 500 °C. The authors stated that this was due to a decrease in the SSA with increasing calcination

temperature, although they did not report any surface area values in their study. The synthetic HA that they used had a Ca/P ratio of 1.77, so it is possible that calcination at 1000 °C resulted in more CaO being present in the calcined powder which is known to affect the sinterability of HA [22].

5. Conclusions

HA powders with a narrow size distribution and spherical particle morphology can be produced by spray-drying. The conventional mechanical particle size reduction method of ball-milling and sieving resulted in HA powders that had angular morphology and had a wide particle size distribution. Although the physical powder properties obtained by these two different ceramic processing routes were very different, the sintered densities and microhardness values of sintered ceramics were comparable.

The physical powder properties of the two HA powders can be altered by calcining the powders at temperatures between 400 and 1000 °C. The most significant changes were a decrease in the specific surface area and increased coarsening of the microstructure of the powder surface as calcination temperature was increased. These changes are very important for biomedical applications where HA is used in powder form, such as in the production of polymer-hydroxyapatite composites, as calcining allows the powder properties to be controlled in order to optimize the properties of the final product.

When the HA powders were sintered to form ceramic specimens, no differences were observed in the sintered densities or microhardness values of ceramics produced from calcined powder compared to non-calcined powder. For this reason, for biomedical applications where HA is used to produce ceramic implants, such as granules or porous blocks, there appears to be no benefit in pre-calcining the powders prior to sintering.

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