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Densification and Decomposition Behavior of Isostatically Pressed and Sintered Hydroxyapatite Powders of Nano and Submicron Sizes

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Abstract

Nanosized and submicron sized hydroxyapatite (HA) powders were produced by using chemical precipitation method and by calcination of animal bone, respectively. The obtained powders, both separately and mixed at equal proportions, were isostatically pressed. The compacts were sintered at two different temperatures, 900 and 1200 °C, in order to investigate the effects on microstructure, densification and HA decomposition. Mechanical properties of obtained samples were compared by means of compressive strength and microhardness measurements.

Keywords: Hydroxyapatite, calcium phosphate, sintering, mechanical properties, microstructure, isostatic pressing.

Introduction

Hydroxyapatite (HA), $Ca_{10}(PO_4)_6(OH)_2$, is widely used in medical and dental applications such as implants, maxillofacial surgery and drug delivery systems due to its similarity in chemical composition and high biocompatibility with natural bone tissue [1].

Although a number of ceramic and chemistry based processing routes have been developed for synthesizing and sintering of nanosized HA powders, it is difficult to produce high purity HA because calcium phosphates have many derivatives and the synthesis of calcium phosphates strongly depends on the reaction conditions [2]. Most commonly used techniques for HA formation are precipitation, solid state reaction, sol-gel methods, hydrothermal route, emulsion and microemulsion techniques, mechanochemical reaction and ultrasonically assisted reaction [2,3]. The most convenient and commonly used one among those is the wet chemical process, which is based on precipitation route [2,3]. Among the precipitation methods the acid-base method which is suitable for industrial production of HA has the widest usage since the reaction involves no foreign elements and the only by-product is water [2,4].

Alternatively to the synthetic processing routes HA can also be produced directly from HA containing natural sources, such as bone and teeth. For this purpose bone or teeth is deprotenized by several methods leaving HA for further use [5,6]. The most direct way to deprotenize HA containing materials is direct calcination method which is based on burning off the organic fraction found in bone and teeth at elevated temperatures [7,8]. The so obtained HA can further be ground or milled to regulate the particle size and used the same way as its synthetically produced counterpart [9].

Understanding the sintering behavior of HA powders is important, because this allows designing ceramics with controlled grain growth, microstructure and mechanical properties [10]. Sintering of HA is complicated by the fact that HA is hydrated phase which decomposes to anhydrous calcium phosphates such as tricalcium phosphate (TCP) at ~1200-1450 ºC. At temperatures higher than 1350 ºC, β-$Ca_3(PO_4)_2$ irreversibly transform to α–$Ca_3(PO_4)_2$. The degradation occurs at varying degrees in the order of α-TCP > β-TCP > HA. Decomposition of HAP must be avoided since it results in enhanced in vitro dissolution and the formation of other calcium phosphate phases [11].

The aim of this study is to compare the densification, sintering behavior and mechanical properties of naturally produced and chemically synthesized HA powders.

Experimental

Acid-base method was used to synthesize HA powders chemically and the procedure described by Wei [12] was followed. 5.0 g of $Ca(OH)_2$ (~99%, Merck, Germany) was dissolved in 200 ml of deionized water using a magnetic stirrer. 4.669 g of liquid H_3PO_4 (85%, Merck, Germany) was added slowly (to maintain pH>9.5-10) to the $Ca(OH)_2$ solution while the solution was continuously stirred by the magnetic stirrer. The pH value of the solution was continuously monitored using a pH meter (Orion 4 Star, Thermo, USA). Stirring was continued for 24 hours at constant temperature of 40 °C after H_3PO_4 addition [12]. Then centrifugation, supernatant decantation and resuspension in deionized water were applied 5 times. Obtained precipitates were oven-dried at 100 °C for 12 hours. Half of the obtained powders were calcinated [13] in air atmosphere at 850 °C for 4 hours (heating rate of 300 °C/hour), followed by light grinding by hand with an agate mortal and pestle for 10 minutes.

Naturally derived HA powders were obtained from calf femoral bones. Both ends of the bones were cut and the bones were boiled. Afterwards, bone marrow was removed and bones were cleaned from all soft tissues attached to them. Middle part of the femur was taken and cut into four circular pieces and each of these

circular pieces were further cut into quarters [5,8,9]. These pieces were calcined at 850 °C for 4 hours for complete removal of organic phase. The calcined parts were first ground by using a mortar and pestle and further ground in a planetary ball mill to decrease the particle size.

Three batches of powders have been prepared. The first containing only synthetically produced HA and the second one containing only HA naturally obtained from calf femoral bone. The third batch is a mixture of both powders in equal proportions.

Powders from the three different batches have first been compacted using a uniaxial press into cylindrical specimen in a steel die with a pressure of 80 MPa. The pressed cylindrical specimens have further been compacted in a cold isostatic press at 400 MPa.

The prepared specimens were sintered at 900 °C and 1200 °C for 2 hours with a heating and cooling rate of 100 °C/hour in air atmosphere.

The phase purity and constitution of the produced powders and sintered batches were investigated to check any possible decomposition of HA by powder X-ray diffractometry (XRD) (Model D/Max-Ultima+PC, Rigaku, Japan). The XRD data were collected at a room temperature over the 2θ range of 10° - 70° at a step size of 0.02° and a count time of 0.6 sec.

The morphology and particle size of the produced HA powders and densification behavior during sintering were observed by using SEM (Model Supra 35VP, Leo, Germany) at an accelerating voltage of 2 kV. Prior to SEM examination, all the samples were dried at 80 °C overnight, and sputter coated by carbon to minimize any possible surface charging effects. The images were obtained before and after sintering stage.

Compression and Vickers microhardness tests were conducted on the sintered samples. The samples from the three different batches were compared based on their SEM pictures.

Results and Discussion

XRD spectra of both powders produced naturally and synthetically clearly show that the only existing phase is HA in both powders, as visualized in Figure 1. Codes “N” and “S” are used for naturally produced and chemically synthesized powders, respectively.

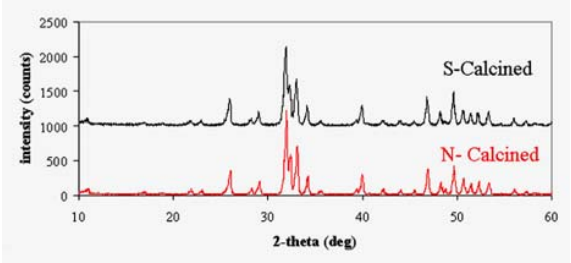


Fig. 1. XRD spectra of naturally and synthetically produced powders after calcination.

The specimen prepared from both of the powders and their mixture are isostatically pressed. In order to gain deeper insight into the compaction behavior of the powders the SEM images are taken, as seen in Figure 2. Figures 2a and 2b show that all of the three different batches of powders are compacted satisfactorily. However, the mixed batch, as shown in Figure 2c, shows an inhomogeneous distribution of the relatively bigger particles of natural HA in the smaller particles of synthetic HA. This can be a result of improper mixing prior to compaction as well as a result of agglomeration of particles of similar sizes.

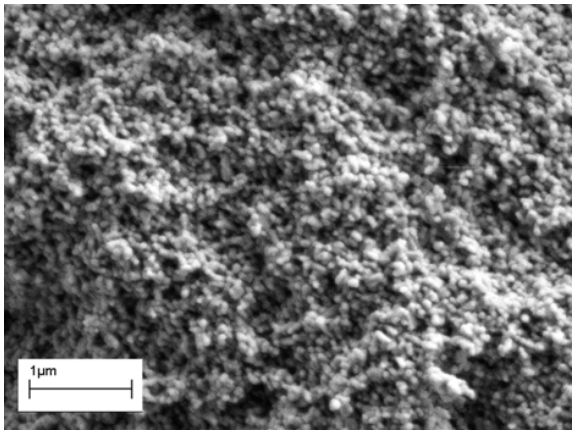
Regarding the morphology of the powders it can be stated that both kind of powders have nearly nodular shapes and an even particle size distribution within themselves. The particle size of the synthetic powder is in the range of 50 to 100 nm whereas the particle size of the natural HA is of the order of 1 µm.

The isostatically pressed specimen are sintered to improve the mechanical characteristics of HA. Although higher sintering temperatures enhance mechanical properties of HA, at excessive temperatures HA decomposes into TCP. To determine the phase purity of HA at the selected sintering temperatures XRD data are taken for all the three batches at both of the temperatures after sintering. XRD spectra and results of phase identification for sintered batches are presented in Figure 3. The code “NS” refers to the mixture of naturally produced and chemically synthesized HA in equal proportions. The observed phases in all the samples were determined by powder XRD to be completely HA (International Centre of Diffraction Data (ICDD), Powder Diffraction File (PDF) No: 00-009-0432).

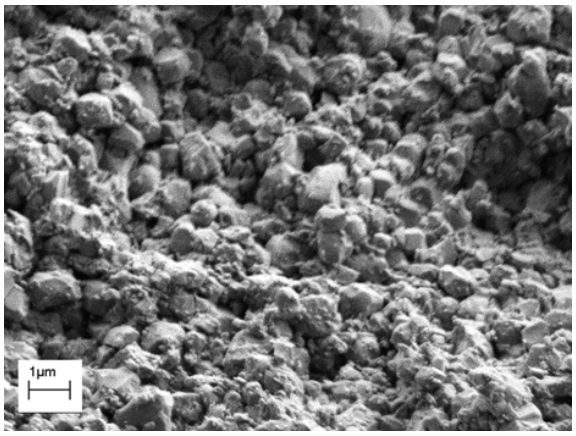
The spectra obviously show that both kinds of powders are pure HA both at 900 and 1200 °C as shown in Figure 3. There is no decomposition of HA into TCP even at 1200 °C for none of the samples. Therefore, it can be stated that a sintering temperature as high as 1200 °C can safely be chosen for HA without any risk of decomposition. This result is consistent with the data found in literature [14].

Effects of the different sintering temperatures were determined by the observation of the SEM images of the samples sintered at 900 and 1200 °C. The SEM images of the sintered samples indicate that sintering is not fully achieved at 900 °C, seen in Figure 4. However, at 1200 °C both the pure samples as well as the mixture are completely sintered (Figure 5).

There is a significant difference in the SEM images of the natural and synthetic powders. The synthetic powders produce a smooth fracture surface without obvious grain boundaries as opposed to the natural powders. This is due to the fact that the densification level depends predominantly on the surface area of the HA powder. Since smaller sized powders have greater surface area the synthetically produced HA powders exhibit better sintering characteristics. This is based on the assumption that the surface roughness is similar for both powders which can be justified by the observation of the SEM images.



(a)



(b)

(c)

Fig. 2. SEM images of the HA samples after cold isostatic pressing: (a) synthetically produced, (b) naturally produced, (c) mixture of the naturally and synthetically produced.

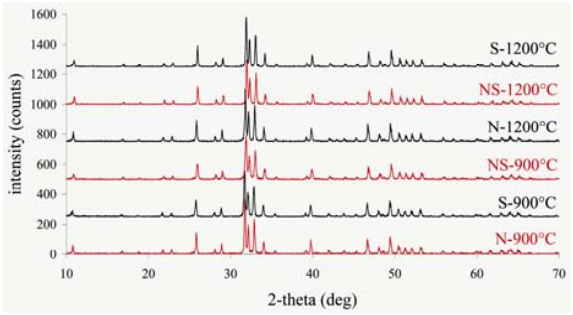


Fig. 3. XRD spectra of the three different samples sintered at two different temperatures.

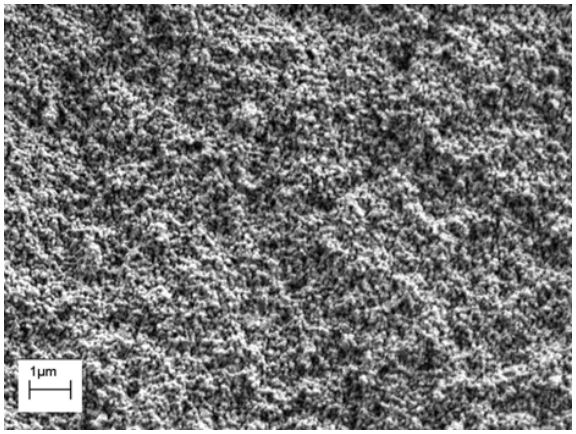
The compaction behavior of the sintered bodies as observed on the SEM images mainly depends on the homogeneity and the particle size distribution of the precursor powders, which is clear on Figures 5a and 5b. Since the samples on Figures 5a and 5b are produced of pure powders they show a good densification behavior. However, there is an obvious porosity in Figure 5c which shows the sintered body produced from two different powders of significantly different particle sizes. Therefore, it can be stated that an improved packing homogeneity leads to an improved sinterability in the form of a higher densification after sintering at a given sintering temperature.

The results of the compression measurements to obtain the mechanical properties of the batches prepared from different powders seem to be consistent with the above observation based on the SEM images in Figure 5. Table 1 shows the compressive strengths of the samples of different compositions after sintering at different temperatures. An increase in the sintering temperature clearly enhances the compressive strength for both batches prepared using pure powders. However, the mixed batches have a very low compressive strength as compared to the other two samples.

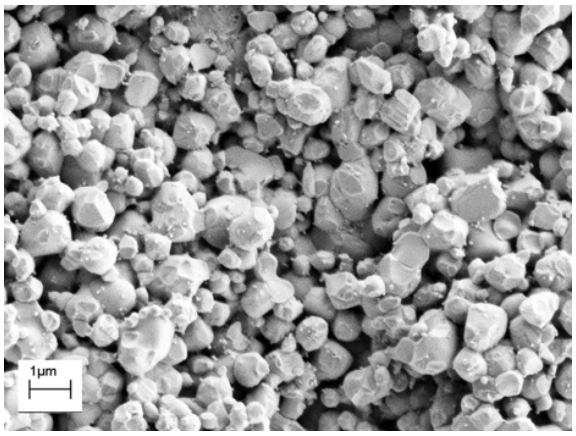
Table 1. Compression strengths of the samples.

Specimen	Compression Strength (MPa)
S-900	119
N-900	117
NS-900	54
S-1200	297
N-1200	268
NS-1200	112

The microhardness measurements are summarized in Figure 6. Increasing the sintering temperature increases the hardness for all set of powder compact samples. However, increase in the hardness of the synthetically produced HA is more pronounced than the others.



(a)



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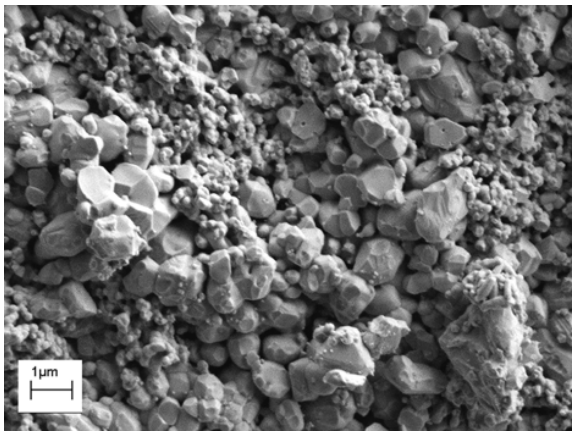
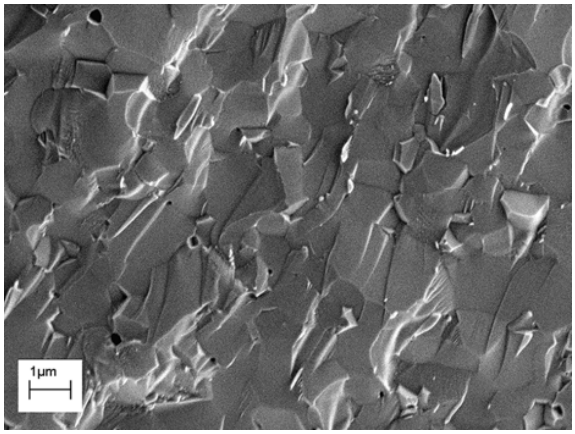
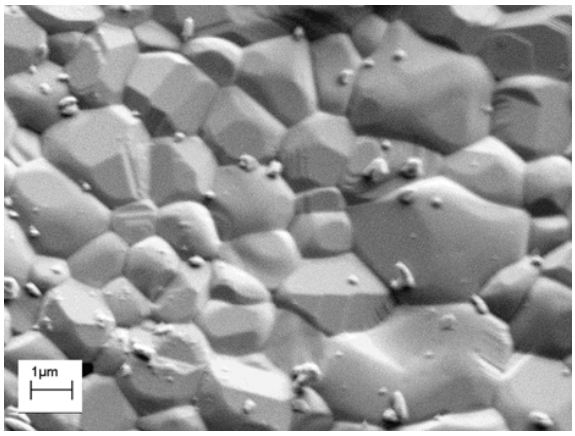


(c)

Fig. 4. SEM images of the HA samples sintered at 900 °C: (a) synthetically produced, (b) naturally produced, (c) mixture of the naturally and synthetically produced.



(a)



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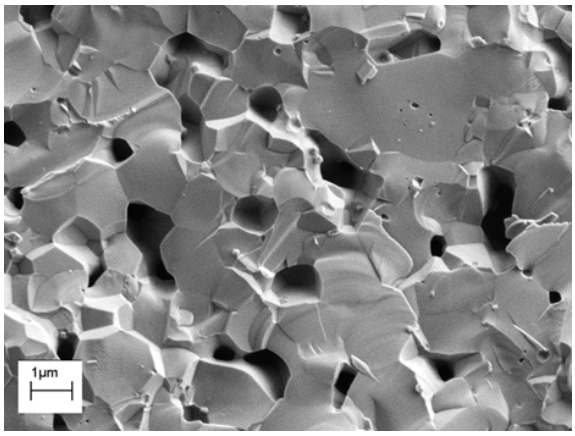

(c)

Fig. 5. SEM images of the HA samples sintered at 1200 °C: (a) synthetically produced, (b) naturally produced, (c) mixture of the naturally and synthetically produced.

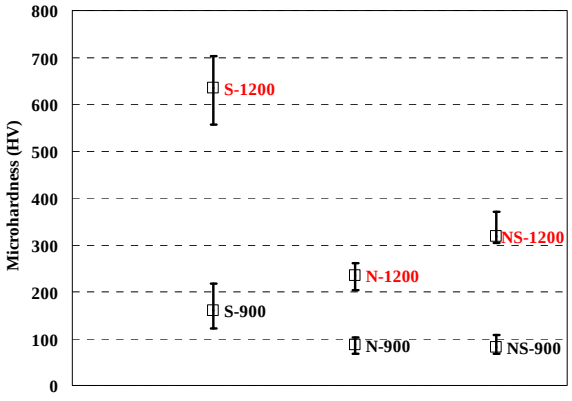

Fig. 6. Microhardness measurements of the samples.

Conclusions

Naturally produced HA (~1μm) obtained from animal bone, chemically synthesized HA (50-100 nm) and an equal weight mixture of both powders were isostatically pressed, sintered and compared with respect to densification and mechanical properties. For the set of both powder compacts (N-1200, S-1200) sintering was found to be accomplished at 1200 °C with good densification. However, significant porosity was observed in the set of mixture powder compacts (NS-1200). The comparison of the SEM images after pressing and sintering shows that the homogeneity of the powders in size may have increased the sinterability of HA compacts.

Mechanical properties of HA is known to be affected by the decomposition at high temperatures during sintering. XRD analysis revealed that both the natural and synthetic powders are completely HA and do not show any decomposition behavior even at 1200 °C.

Sintering temperature has a significant effect on the microhardness values and compression strengths of N, S and NS coded samples. Hardness increased with temperature for all the samples (significantly for the S coded ones). Compression strength values for all samples increased approximately 2 fold when the temperature was increased from 900 to 1200 °C. While the strength values of the N and S coded samples were approximately same, NS coded ones were much lower. The reason of this may be induced by improper mixing (NS-900) and pores (NS-1200) as observed in SEM micrographs.

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