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Processing and properties of transparent hydroxyapatite and β tricalcium phosphate obtained by HIP process

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Abstract

Stoichiometric *β*-tricalcium phosphate (β-TCP) and hydroxyapatite (HA) powders were synthesized by chemical precipitation of aqueous solutions of diammonium phosphate and calcium nitrate. After a calcination treatment and a milling step, the powders were shaped by slip casting. The sintering temperature effect on the relative density and the average grain size was investigated. By natural sintering at 1200 and 1120 °C, densities of 98% and 99% were obtained for HA and TCP, respectively. After determination of minimum temperatures to obtain only closed porosity and a pre-sintering at these temperatures, hot isostatic pressing (HIP) treatment was carried out. Transparent or translucent samples were obtained, indicating a relative density very close to the theoretical value ($>99.9\%$). Mechanical properties (three-point bending strength, fracture toughness, Young's modulus and Vickers hardness) were measured on both materials with similar grain size ($\sim 1\ \mu m$). Bending strengths of 181 and 105 MPa were measured for TCP and HA, respectively.

Keywords: Sintering; Hydroxyapatite; β-Tricalcium phosphate; Mechanical properties

1. Introduction

Hydroxyapatite (HA) and tricalcium phosphate (TCP) are the materials commonly used for clinical applications and, in particular, to repair and reconstruct damaged parts of the human skeleton [1–4]. Their Ca/P ratios close to that of bone provide excellent biocompatibility. This property, associated with an adapted porous architecture, allows optimal bone rehabilitation in the implant site [5,6]. However, the poor mechanical properties of HA and TCP limit their use in load bearing application which requires the use of a fixation device.

A possible way to improve the mechanical properties of these bioceramics is the manufacturing of a material with full density and fine grain microstructure. Among the most effective ceramic densification processes, hot isostatic pressing allows such full densification with a minimum grain growth. Moreover, this technique, applied on pre-sintered samples permits the densification of parts with very complex shapes.

The aim of this work is to improve the densification level of hydroxyapatite and tricalcium phosphate bioceramics by a hot isostatic pressing post-treatment and to evaluate mechanical properties of the ceramics.

In a first-step, HA and TCP stoichiometric powders were prepared by the aqueous precipitation technique, slip-casted and pre-sintered by pressureless sintering, up to a complete open porosity elimination. Hot isostatic pressing was then used in order to complete the densification with limited grain growth. The mechanical properties such as bending strength, E modulus, fracture toughness and hardness of the as-obtained fully dense materials were determined and compared with data of stoichiometric HA and TCP ceramics presenting similar grain size.

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2. Experimental procedure

HA and TCP stoichiometric powders were prepared by the aqueous precipitation technique using diammonium phosphate solution $(NH_4)_2HPO_4$ (Carlo Erba, France) and calcium nitrate solution $Ca(NO_3)_2 \bullet 4H_2O$ (Brenntag, France). For HA synthesis, the solution pH was adjusted at a constant value of 8.0, by continuous addition of ammonium hydroxide at a constant temperature of 50 °C. For TCP, the pH was adjusted to 6.5 and temperature to 30 °C. After 24 h ripening, solutions were filtered and the precipitates were dried at 70 °C.

The initial Ca/P ratio was adapted to obtain stoichiometric HA and β-TCP powders following a process previously discussed [7]. The phase compositions of powders were characterized by X-ray powder diffraction [8] (Panalytical Xpert Pro). The presence of pyrophosphate groups (in $Ca_2P_2O_7$ or CPP) in TCP phase was determined from infrared spectra of powders recorded on a Fourier transform spectrometer (Jasco-FT/IR-460 Plus). The absence of calcium oxide in HA was checked by the phenolphthalein test [9].

The as-synthesized powders exhibit a very high specific surface area ($> 60\ m^2/g$), that does not permit to obtain stable slurry for the slip casting process. The average primary particle size of TCP and HA precipitates was increased by a thermal treatment at 750 and 800 °C, respectively (the specific surface area of HA powder calcined at 750 °C was too high to enable the manufacturing of HA ceramics by slip casting). After this step, powders were ground to break up agglomerates formed during calcination and to reduce the powder to its ultimate particle size. This grinding step was carried out by ball milling using a HDPE milling jar and Y-PSZ grinding media. The grinding times were fixed to 48 and 3 h for HA and TCP, respectively. After this treatment, the specific surface areas of ground powders were recorded by the BET method (Micromeritics, Flow Sorb 3). HA and TCP powders were then shaped by the slip casting process, aqueous slurries being prepared with a powder concentration equal to 65 wt% and the dispersion powders being obtained by adding a commercial organic agent (Darvan C, R.t. Vanderbilt Co.) in amounts equal to 1.5 wt% of powder content.

The sample densification was carried out in two steps: first, HA and TCP green compacts (cylinders $\Phi = 10$ mm, $h = 20$ mm) were pressureless sintered at temperatures ranging from 1000 to 1250 °C for 5 h in air atmosphere. Heating and cooling rates were fixed to 300 °C/h. Secondly, to complete the sample densification and to reach a density close to the theoretical value, pre-sintered samples undergo a hot isostatic pressing (HIP). Trials were performed in GPS VITEK HIP equipped with a platinum furnace, under Ar/O_2 atmosphere (80/20 vol%). Temperatures of 1050 and 1100 °C at a heating rate of 5 °C/min and an isostatic pressure of 160 MPa for 1 h were used.

The open porosity and relative density of pre-sintered and hipped samples were determined by the Archimedes' method. Microstructures of these samples were observed by scanning electron microscopy (Hitachi S-3500N) after mirror polishing and thermal etching were carried out in air at 30 °C below the sintering temperature. The average size of HA and TCP grains was determined by the linear intercept method.

Three-point bending tests were performed with a mechanical testing machine ZWICK Z100 for a specimen geometry of $3 \times 4 \times 25\ mm^3$ with a span length of 15 mm and a crosshead speed equal to 0.5 mm/min. Six samples were tested for each condition. Samples with the same geometry were used to measure the fracture toughness by the SEVNB method (Single-Edge-V-Notched Beam) [10].

The hardness was measured by the Vickers indentation technique (Future-Tech Corp). HV measurements were carried out on polished surfaces of hipped materials with a load of 5 N held for 15 s. The average hardness number was determined from 30 indents for each sample. Young's modulus was determined by a non-destructive technique using ultrasonic waves according to NF EN 843-2 standard [11]. Longitudinal and transverse wave velocities were measured by the reflection method (pulse echo method) at 5 MHz, which needs the use of only a single transducer.

3. Results and discussion

3.1. Characterization of HA and TCP powders

X-ray diffraction patterns of HA and TCP show the mineralogical purity of the powders (Fig. 1). No trace of TCP and HA appears on the patterns of HA and TCP, respectively.

Except the peaks at 3460 and 1650 cm^{-1} (that can be assigned to adsorbed H_2O and CO_2), all the bands in the FTIR spectrum (Fig. 2) correspond to PO_4^{3-} groups (stretching modes between 900 and 1130 cm^{-1} and bending modes between 550 and 600 cm^{-1}). The characteristic lines of calcium pyrophosphate (due to a possible defect of calcium) at 723, 1185 and 1210 cm^{-1} are not observed,

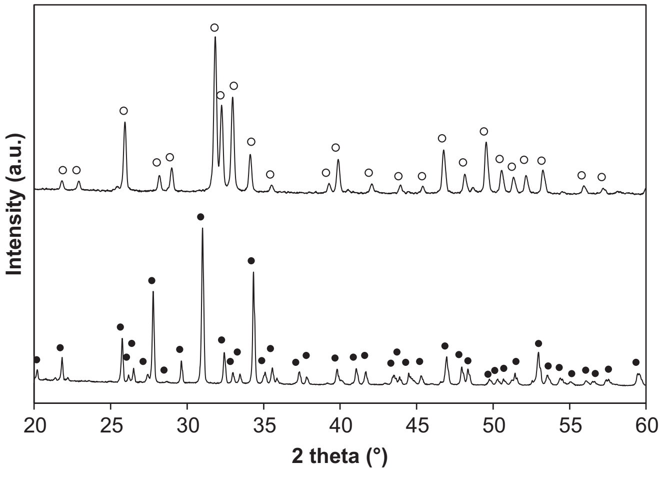

Fig. 1. XRD patterns of HA (○) and β-TCP (*).

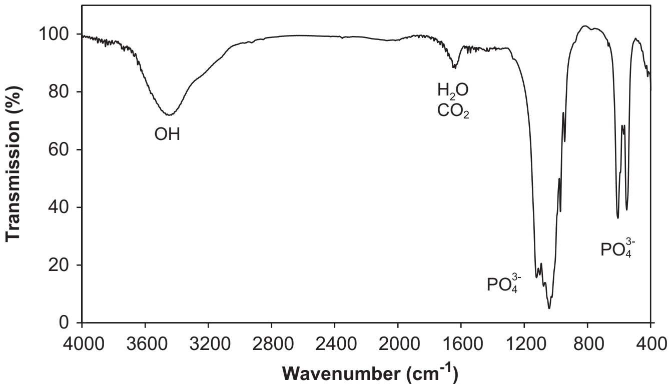

Fig. 2. IR spectrum of β-TCP.

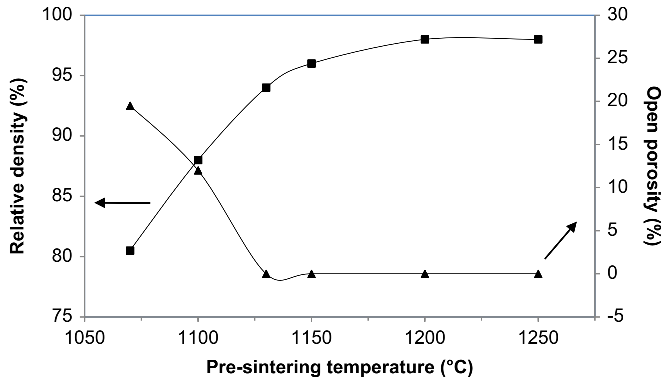

Fig. 3. Relative density and open porosity of HA at different pre-sintering temperatures.

proving that the TCP powder is free of $Ca_2P_2O_7$. Finally, the colorless phenolphthalein solution containing the HA indicates the absence of calcium oxide. Specific surface areas of HA and TCP precipitates after calcination and ball milling treatments are equal to 23 and 8 m^2/g, respectively.

3.2. *Pre-sintering of HA and TCP samples.*

The densification by HIP of non-encapsulated samples requires the closing of the porosities by a prior thermal treatment. The minimum temperatures to obtain only closed porosity were determined by various pressureless sintering trials carried out at different temperatures. Figs. 3 and 4 show the evolution of relative density and open porosity of HA and TCP samples, respectively, according to the temperature used for material densification. For HA cylinders, the relative density reaches a maximum of around 98.0% at 1200 °C and then stabilizes for higher temperatures. Pores are completely closed from a temperature of 1130 °C corresponding to a relative density of 94%. For TCP, the β→α phase transformation occurring around 1140 °C does not allow to perform sintering tests at higher temperatures. Indeed, this phase transformation induces crackings in the sample due to the material expansion generated by the density mismatch between β and α phases (3.07 and 2.86 respectively) [12,13]. The relative density reaches a maximum of 98.8% at 1120 °C and then decreases for temperatures higher than 1140 °C due to the β→α transformation mentioned before. Pores are completely closed from a temperature of 1050 °C corresponding to a relative density of 92%.

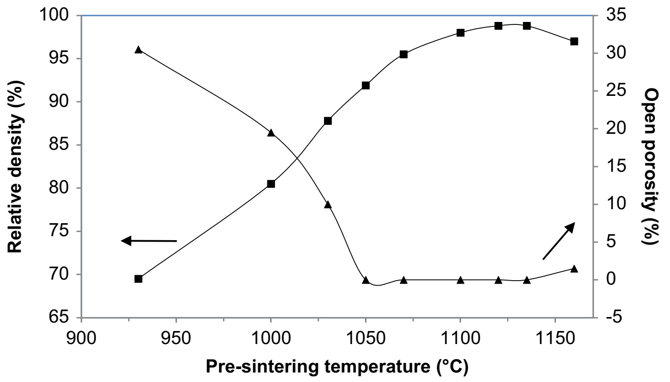

Fig. 4. Relative density and open porosity of β-TCP at different pre-sintering temperatures.

It is striking to notice that a density close to 99% of the theoretical density can be obtained on the TCP samples at 1120 °C, from micro-size powders, shaped by slip casting. The literature describes the difficulty in densifying the β-TCP [7,12–17], leading the authors to use nano-size powders, dopants or even specific sintering processes to improve the ceramic densification. Our work shows that such a result can be obtained with the optimization of the following parameters:

- the use of a highly reactive powder obtained after both a carefully chosen calcination temperature and an optimized milling process;
- a perfect control of the powder stoichiometry and particularly the absence of CPP;
- a controlled thermal cycle carried out at a temperature lower than the β→α phase transition temperature.

HA and TCP grain size versus sintering temperature are presented in Fig. 5. For HA samples, the grain size increases from 0.5 to 2.6 μm for sintering temperatures increasing from 1050 °C to 1250 °C. The average grain size is 1.3 μm for the sample with the maximum densification level (1200 °C). The complete closure of open pores, a necessary condition for further densification by HIP (obtained for a sintering temperature equal to 1130°) corresponds to a mean grain size of 800 nm. For TCP, grain sizes are equal, respectively, to 0.6 and 2 μm for the lowest (900 °C) and the highest sintering temperatures (1135 °C), which correspond to the maximum densification. A closed porosity, obtained at 1050 °C, shows a grain size close to 1 μm.

In order to compare the mechanical properties of HA and TCP with similar grain size (~1 μm), HA ceramics were therefore pre-sintered at a higher temperature, i.e. 1160 °C.

SEM micrographs of these pre-sintered samples are presented in Fig. 6. These micrographs show grains with irregular size and shape, and the presence of residual intergranular porosity.

The relation between the average grain size and the relative density for HA and TCP specimens is presented in Fig. 7. These curves show two distinct regions: the first stage is characterized by a limited grain growth; for HA, the grain size increases from 550 to 670 nm when the temperature increases from 1050 to 1100 °C. For higher sintering temperatures, a significant grain growth occurs and the grain size reaches 2.6 μm at 1250 °C. For TCP, similar phenomena are observed, and the grain size increases slightly from 600 nm to 1 μm with temperature increase from 900 to 1050 °C. Then in a second stage, the grain growth becomes more significant and the grain size reaches 2 μm at 1135 °C. For both materials, the transition between these two regions corresponds to relative densities around 92–94% which coincides with the complete closure of open pores (Figs. 3 and 4).This behavior can be explained by a pinning of grain boundaries by the connected network of open porosity which hinders grain boundary migration when the relative density is less than 92–94%. When the relative density is higher than these values, porosity closes and the isolated pores are less effective in pinning the grain boundaries, leading to an accelerated grain growth [18,19].

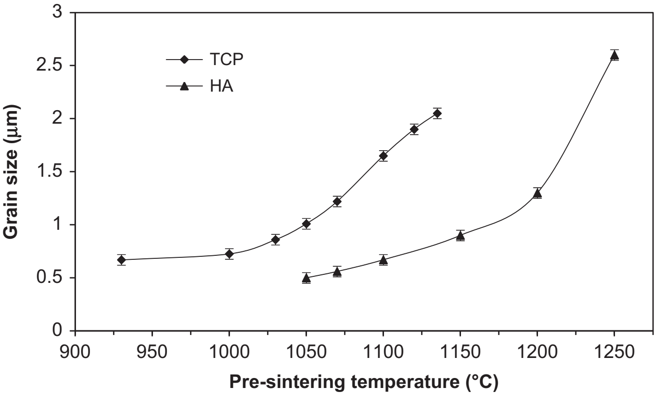

Fig. 5. HA and TCP grain size versus. pre-sintering temperature.

3.3. HIP of HA and TCP samples.

HIP treatments were carried out on closed porosity TCP and HA samples. Hipping was performed at 1050 and 1100 °C for TCP and HA pre-sintered compacts, respectively. Samples obtained after this treatment are completely densified with relative densities greater than 99.9%. Moreover, these samples exhibit (after polishing) a translucent or even transparent appearance (Fig. 8).

The purpose of this study was not to obtain transparent materials, however, the translucency or transparency of ceramics indicates that the densities of these materials are

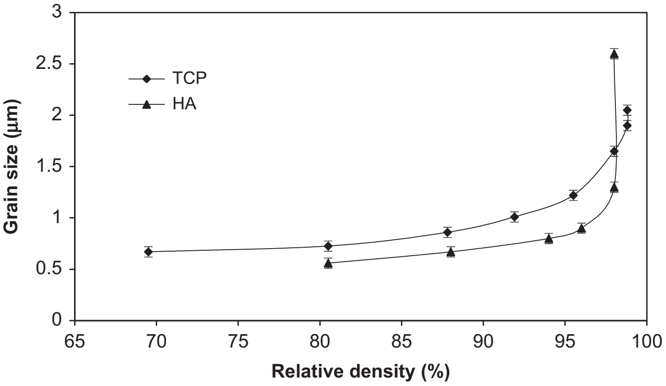

Fig. 7. Relation between grain size and relative density for HA and TCP.

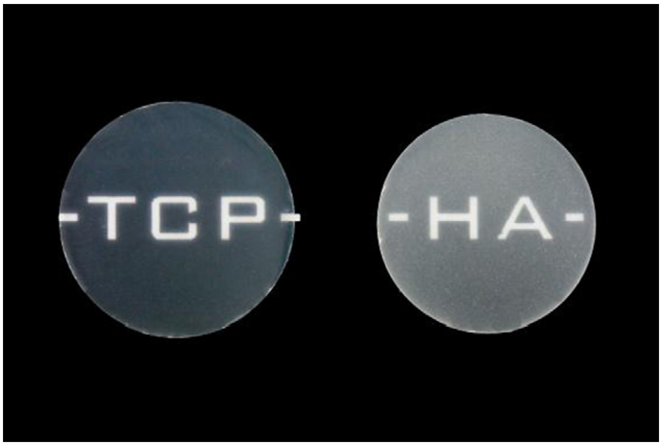

Fig. 8. HA and TCP samples after HIP treatment ($\Phi \sim 0.9$ mm).

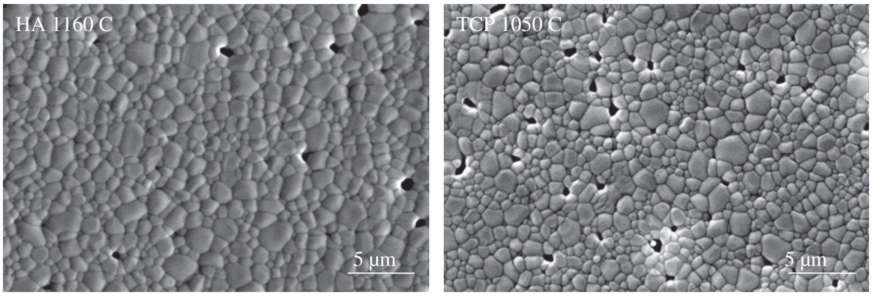

Fig. 6. HA and TCP SEM micrographs.

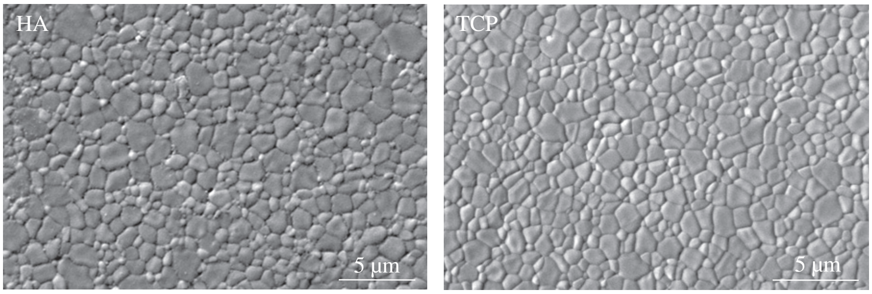

Fig. 9. HA (pre-sintered at 1160 °C) and TCP (pre-sintered at 1050 °C) SEM micrographs after HIP treatment.

Table 1
Mechanical properties of fully densified HA and β-TCP materials.

	Three-point bending strength (MPa)	Fracture toughness (MPa $m^{1/2}$)	E modulus (GPa)	Hardness (GPa)
TCP(Φ grain = 1 μm)	181 ± 12	1.03 ± 0.09	105	4.9
HA(Φ grain = 1 μm)	106 ± 11	0.92 ± 0.02	122	6.1

very close to the theoretical value. Indeed, possible causes of transmission losses are absorption and light scattering at grain boundaries, at pores, at second phase or inclusions and rough surfaces [20,21]; furthermore, in non-cubic ceramics (e.g. HA and TCP) birefringence phenomena cause an additional light scattering due to optical anisotropy at crystal grain boundaries. The major factor which is detrimental to the transparency of the material is the residual porosity: it has been shown that a residual porosity lower than 0.1% is necessary to obtain an initial transparency and that the last hundredths of percent of porosity are needed to obtain a clear transparency [21].

The grain size of HA and TCP measured in the hipped samples are identical to the grain size of the pre-sintered samples, i.e. 1 μm (Fig. 9). X-ray diffraction patterns and IR spectra of hipped specimens show no changes compared to those of the pre-sintered materials.

3.4. Mechanical characterizations.

It is well known that the mechanical strength of a ceramic is related to the presence of many defects among which are pores, grain size and grain boundaries. The general request is to reach the highest density value with the lowest grain size possible. As a consequence, the values found in the literature are highly variable and difficult to compare, because these mechanical properties are assessed on samples with different physical and chemical properties [22–29]. In our study, we have controlled most of these parameters, particularly:

- the stoichiometry of two calcium phosphates with HA phase, free of TCP and CaO, and TCP phase, free of CPP and HA;
- the chemical purity of the products (free of any dopants or foreign phases);
- the densities of these materials, very close to their theoretical densities, therefore free from open or closed porosity (as shown by the translucent or transparent appearance);
- a similar grain size, necessary for the comparison of the mechanical properties of HA and TCP, and notably the flexural strength, that is generally strongly influenced by this characteristic.

Thus the measured values (Table 1) correspond to the intrinsic values of our materials (for 1 μm grain size), materials very homogeneous in terms of defects in stoichiometry or density. The bending strength of TCP is clearly higher than that of HA; conversely, the hardness value of TCP is lower than for HA. The HA results are consistent with the literature data measured on high density HA ceramics, within this grain size range. Regarding TCP, only few comparable results are available: in fact, few authors have obtained high densities with micro-size powders without adding doping agents. Similarly, some literature results are questionable as they were obtained on materials sintered at temperatures above 1140 °C, i.e. above the phase transformation $\beta \rightarrow \alpha$ temperature. Except the results from Lin et al. [16], who measured a bending strength of 199 ± 5 MPa with a median grain size around 0.3 μm, the materials prepared by the method described in this paper show a better bending strength and higher Young's modulus values. Such good mechanical performances can be explained by the highest density of our samples and their low grain size.

4. Conclusion

The densification of β-tricalcium phosphate and hydroxyapatite has been studied. By natural sintering, relative densities of 99% and 98% were obtained for β-TCP and HA, respectively. These excellent densities are due to a perfect control of all the processing parameters, such as stoichiometry and purity of the powders, optimization of their thermal reactivity and optimized sintering cycle. However, high temperature treatments are necessary to obtain such high densities, leading to an increase of the average grain size of the ceramics. To improve the mechanical properties without grain growth, sintering at lower temperature, followed by hot isostatic pressing has been applied. After this treatment, dense, transparent or translucent, β-TCP and HA samples ($>99.9\%$ dense) have been obtained. Mechanical properties of these two fully densified materials with identical microstructure (mean grain size ~ 1 μm) have been measured. Results for HA are consistent with the literature data; however, properties measured on TCP ceramics are promising because both bending strength and Young's modulus values are higher than those generally reported for micro-size powders. This study allowed determining the intrinsic mechanical properties values of these two calcium phosphates, data of which could be used as reference values in future works.

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