

Processing and properties of calcium phosphates bioceramics by hot isostatic pressing

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Abstract. Stoichiometric β -tricalcium phosphate (β -TCP), hydroxyapatite (HA) and biphasic calcium phosphate (TCP/HA 60/40 %wt, BCP40) powders were synthesized by chemical precipitation of aqueous solutions of diammonium phosphate and calcium nitrate. After a calcination treatment and a milling step, powders were shaped by slip-casting. The sintering temperature effect on the density and the average grain size was investigated. By natural sintering, densities between 98 and 99.8% were obtained. Hot Isostatic Pressing (HIP) treatment was carried out after a pre-sintering of these materials. 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 hipped materials with similar grain size ($\sim 0.7\mu\text{m}$).

INTRODUCTION

Calcium phosphates are materials commonly used for clinical applications and, in particular, to repair and reconstruct damaged parts of the human skeleton [1]. However, the poor mechanical properties of these materials limited their use in load bearing applications. 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.

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

EXPERIMENTAL PROCEDURE

Powders were prepared by aqueous precipitation technique using diammonium phosphate solution $(\text{NH}_4)_2\text{HPO}_4$ and calcium nitrate solution $\text{Ca}(\text{NO}_3)_2 \cdot 4\text{H}_2\text{O}$. For HA synthesis, the solution pH was adjusted at a constant value to 8.0, by continuous addition of ammonium hydroxide at a constant temperature of 50 °C. For TCP and BCP40, the pH was adjusted to 6.5 and temperature to 30 °C. For all synthesis, the initial Ca/P ratio was adjusted to obtain the desired composition [2]. After 24 hours ripening, solutions were filtered and the precipitates were dried at 70 °C.

The average primary particle size of precipitates was increased by a thermal treatment at 750 (TCP and BCP) and 800 °C (HA). After this step, powders were ground to break up agglomerates formed during calcination and

to reduce the powder to its ultimate particle size. Powders were then shaped by slip casting process.

The sample densification was carried out within two steps: first, green compacts were pressureless sintered at temperatures ranging from 1000 to 1200 °C for 5 h in air atmosphere. 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/O₂ atmosphere (80/20 vol.%). Temperatures between 1000 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.

Three-point bending tests were performed with a mechanical testing machine ZWICK Z100. Fracture toughness was measured by the SEVNB method (Single-Edge-V-Notched Beam).

The hardness was measured by Vickers indentation technique (Future-Tech Corp) and the Young's modulus was determined by a non-destructive technique using ultrasonic waves according to NF EN 843-2 standard.

EXPERIMENTAL RESULTS

Figure 1 shows the evolution of relative density of HA, BCP40 and TCP samples according to the temperature used for material densification and leads to the following remarks:

- β -TCP shows excellent sintering behavior with maximum density at 1130 °C equal to 99.8%. Even at lower

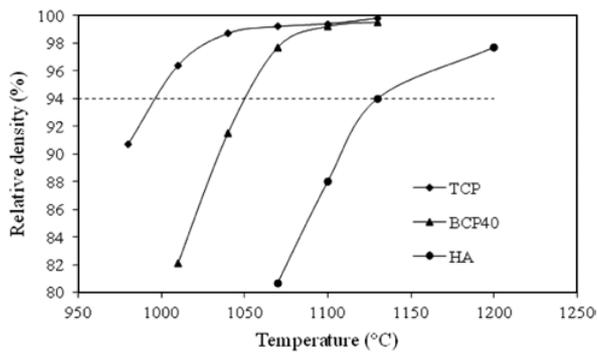


Figure 1. Relative densities as a function of sintering temperature.

Table 1. Relative density and grain size of hiped samples, grain size of samples pressureless sintered at higher temperatures (1130 °C for TCP and BCP40, 1200 °C for HA).

	TCP	BCP40	HA
Relative density (%)	≥ 99.9	≥ 99.9	≥ 99.9
Grain size (μm) hiped material	0.77	0.73	0.75
Grain size (μm) pressureless sintering	1.83	1.51	0.79



Figure 2. Picture of hiped samples.

sintering temperature, high densities are obtained (close to 99% at 1040 °C);

- For BCP40, very high densities are measured at 1130 °C (99.5%) and densification value remains excellent after sintering at 1070 °C (98%);
- A sintering at 1200 °C allows obtaining hydroxyapatite samples with density close to 98%.

The HIP treatment is performed on parts pre-densified in order to close the porosity. The pre-densification temperature is chosen as low as possible to limit the grain growth. The literature indicates that relative densities of 92–94% are requested to obtain materials free of open porosity³. In this study, a rate of 94% is retained and temperatures corresponding to this densification value are graphically determined using Fig. 1 and experimentally verified.

Table 1 shows the relative densities obtained after HIP treatment and compares grain sizes values measured for pressureless-sintered and hiped materials.

After these HIP treatments, transparent materials are obtained for all compositions (Fig. 2).

Table 2 summarizes mechanical properties measured on all hiped materials.

Table 2. Mechanical properties of hiped samples.

	TCP	BCP40	HA
Vickers hardness (GPa)	4.9 ± 0.1	5.3 ± 0.1	6.1 ± 0.1
Young's modulus (GPa)	105 ± 4	112 ± 4	122 ± 4
Flexural strength (MPa)	180 ± 11	189 ± 10	106 ± 12
Fracture toughness (MPa.m ^{1/2})	1.05 ± 0.1	0.98 ± 0.1	0.92 ± 0.1

An increase of the elastic modulus and Vickers hardness values is observed with increasing Ca/P ratio of materials.

No real evolution of fracture toughness values is observed between all compositions.

A maximum value of the flexural strength is obtained for the biphasic composition, value close to pure TCP.

CONCLUSIONS

The densification of calcium phosphates has been studied. By natural sintering, relative densities higher than 98% were obtained. These excellent densities are due to a perfect control of all the processing parameters, as stoichiometry and purity of the powders, optimization of their thermal reactivity and optimized sintering cycle. However, high temperatures 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 samples (density ≥ 99.9%) have been obtained. Mechanical properties of these fully densified materials with identical microstructure (mean grain size ~0.7 μm) have been measured. Results for HA are consistent with the literature data. Experimental data on fully dense and stoichiometric TCP are interesting due to the lack of results in the literature. A maximum of the flexural strength is obtained for the BCP40 composition.

References

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