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# Manufacturing and mechanical properties of calcium phosphate biomaterials

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ABSTRACT

In this study, the influence of powder manufacturing and sintering temperature on densification, microstructure and mechanical properties of dense $\beta$-tricalcium phosphate ($\beta$-TCP) bioceramic has been studied. Densification results show that the $\beta$-TCP can be sintered at 1160 °C for 3 hours to have good density and high performance mechanic properties (Vickers hardness, toughness and Young's modulus). X-ray diffraction and SEM microscopy are used to check the microstructure changes during the sintering temperature. The used processing of $\beta$-TCP ceramic improved its densification, microstructure homogeneity and mechanical properties.



## 1. Introduction

Calcium phosphate biomaterials are defined as synthetic materials that are used directly or replacing the functions of living tissues of human body. Two important criteria which biomaterial must fulfill are biocompatibility and biofunctionality [1–3]. Tricalcium phosphate $Ca_3(PO_4)_2$ is frequently used as bone graft substitutes in many surgical fields like the orthopedic [4], dental [5], plastic surgeries [6], exhibiting an excellent biocompatibility and osteointegration properties since its chemical composition is close to bone [7]. Moreover, it shows a high resorbability in the human biological environment allowing a significant recolonization of the operational site by advancing bone growth during the progressive degradation of this material. In early works on bioceramics development, several calcium phosphates such as hydroxyapatite and tricalcium phosphate powders derived bone, dentine or commercial have been tested for biomedical applications [7,8]. Dense $\beta$-tricalcium phosphates are well known for their interesting mechanical properties and characterized by the Young modulus near to those of alloys with an evidenced increase in strength and ductility through grain refinement [9,10]. They show that mechanical properties vary with their chemical composition, porosity and particles morphology [9,11]. Thus, the structure and mechanical properties of synthetic $\beta$-TCP can be improved by varying the processing manner and the optimization of the synthesis process [12,13]. Consequently, to understand some parameters influencing the development of mechanical properties of stoichiometric $\beta$-TCP bioceramic, it is necessary to perform the mechanical tests on sintered samples, which determine the optimal sintering temperature. The preparation method of stoichiometric $\beta$-TCP using adequate calcium and phosphorus precursors seems to affect mainly the textural properties and therefore the mechanical behaviors. $\beta$-TCP ceramic is generally obtained by sintering process at high temperature. This can lead to crystal alterations (grain growth, loss in surface area, dehydration, and stoichiometry change) [9,10]. Thus, the conservation of $\beta$-TCP structure and chemical

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composition before and after sintering process appears as an interesting factor to obtain a dense biomaterial. In this regard, each manufacturing stage involving powder production, green body production, stoichiometry and sintering is crucial for bioceramics densification.

In this study, stoichiometric dense $\beta$-TCP is elaborated by an aqueous precipitation method and sintered at various temperatures determining the structural, textural and mechanic properties. The current results constitute a first step to improve the strength and toughness of $\beta$-TCP biomaterials in relationship with their microstructure and sintering temperature.

## 2. Experimental

### 2.1. Synthesis and densification process

The $\beta$-tricalcium phosphate powder ($\beta$-TCP) has been elaborated by chemical wet method using $(NH_4)_2HPO_4$ and $Ca(NO_3)_2{\cdot}4H_2O$ precursors in appropriate stoichiometric molar ratio $Ca/P = 1.5$. The pH has been adjusted at pH 10 by adding $NH_3$ (aq) (25%). The precipitated powder has been matured for 24 h, filtered with a Buchner funnel and the precipitate was re-suspended in deionized water and magnetically stirred for several hours. Then it was washed with bidistilled water as well as ethanol and dried at 120 °C overnight. The as-dried, calcined and processed powders have been compacted and sintered at various temperatures from 900 to 1350 °C for 3 h.

The $\beta$-TCP pellets have been obtained according to the protocol given by Laasri et al. [14]. They have been subsequently ground on 800, 1200 and 2400 grit SiC paper before polishing with a 1 mm diamond suspension as the final polishing step. This operation removed a 1 mm layer from the 4 mm thick pellet and thus avoided any surface features that eventually have formed on the outside of the sample during the sintering operation. The highly polished surface provided a suitable surface reproducible for the indentation. After drying and sieving, parallelepipedic bars with the dimensions of 40 mm × 20 mm × 3 mm are produced by pressing uniaxially at 60 MPa and isostatic pressing at 300 MPa. For mechanic experiments, the sintering process is performed at various temperatures from 1100 to 1250 °C for 3 h in air (5 °C min$^{-1}$ as heating rate).

### 2.2. Techniques

The resulting solid has been characterized using X-ray diffraction (X'Pert Pro MPD PANalytical diffractometer operating at Cu K$\alpha$ radiation) and infrared spectroscopy (Perkin-Elmer FT-IR1600 spectrophotometer). Dynamic light scattering (DLS) analyzed the particle size of the powders is recorded on a Zetaplus (Brookhaven Instruments) apparatus by suspending the powder in water by sonication. Nitrogen adsorption–desorption isotherms have been recorded at 77 K using a Micromeritics ASAP 2010 instrument. The specific surface areas ($S_{BET}$) have been estimated according to the Brunauer–Emmett–Teller (BET) method. Chemical analyses for calcium and phosphorus have been performed by AES-ICP technique. Scanning electronic microscopy SEM was performed on goldcoated samples using a PHILIPS XL20 instrument at an accelerating voltage of 10 kV.

The bulk density of samples has been determined by hydrostatic weighing and the relative density has been calculated by taking the theoretical density of $\beta$-TCP as 3070 kg/m$^3$. The Vickers indentation method has been used to determine both the microhardness ($H_v$) and the fracture toughness ($K_{1c}$) of the samples, using a Vickers hardness tester (microindenter WOLPERT) such as used for mechanical properties studies. The indentation load ($< 200$ g) has been applied and held in place for 10 s. Ten (10) indentations have been made for each sample and the average value has been taken. The indentation $K_{1c}$ has been determined from the equation proposed by Ramesh and Tan [15] and Niihara [16]:

$$K_{1c} = 0.203\left(\frac{c}{a}\right)^{-3/2}(H_v)(a)^{1/2}$$

where $H_v$ is the Vickers hardness, $\boldsymbol{a}$ is the half diagonal of the indentation, $c$ is the radial crack dimension measured from the center of the indent impression, i.e., $c = L + a$ and $L$ is the crack length. The strength measurements have been carried on INSTRON 8512.

## 3. Results and discussions

### 3.1. Structural and textural characterization

The X-ray diffraction pattern of as-received powder exhibits a poorly crystalline apatite phase. However, calcined at temperature beyond 900 °C it has a single phase attributable to $\beta$-$Ca_3(PO_4)$ with a standard JCPDS card no. 9-169 (Fig. 1), where the stability of the $\beta$-TCP phase has been not disrupted during the sintering regime employed in this study. The production process was followed by a heat treatment at 1160 °C for all variations to produce phase pure $\beta$-TCP ($Ca/P = 1.5$). Contrary to few works reported in the literature [17], alternative phases such as $\alpha$-$Ca_3(PO_4)_2$ are present and can affect the mechanical and biological properties of $\beta$-TCP biomaterials. Infrared spectra of elaborated $\beta$-TCP and their calcined samples display the vibration mode of $PO_4^{3-}$ groups at 1150 cm$^{-1}$, 975 cm$^{-1}$, 600 cm$^{-1}$, 550 cm$^{-1}$. These results are in good agreement with those cited in the literature [18,19]. From chemical analysis of calcium and phosphorus, the molar ratio Ca/P

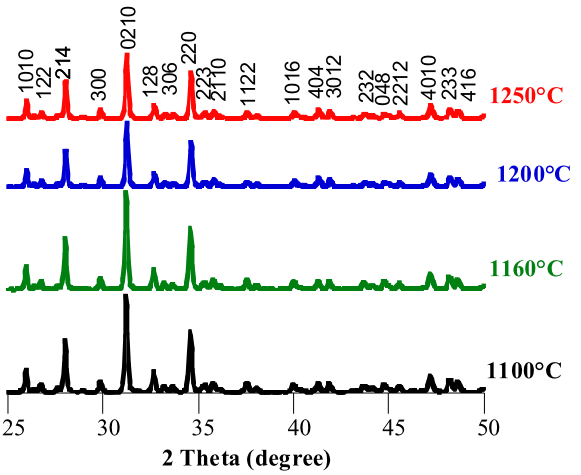


**Fig. 1.** XRD patterns of synthesized $\beta$-TCP calcined at various temperatures.

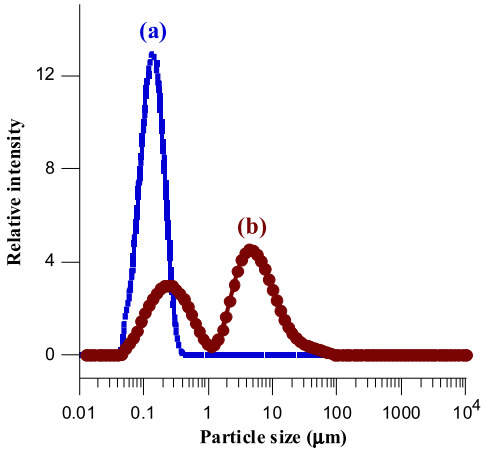


**Fig. 2.** Particle size distribution of $\beta$-TCP as monitored by DLS with (a), without (b) grinding process.

is close to stoichiometric value of 1.50, which remains invariant during the sintering process. DSL analysis determined the distribution of particles in $\beta$-TCP powders with and without attrition milling (Fig. 2). It revealed single size distribution using grinding method, whereas two particles populations are found for other manufacturing. The presence of two-grain sizes in powder ceramic can affect the densification and mechanical behaviors. The morphological results from SEM micrographs of $\beta$-TCP ceramics sintered at 1100, 1160 and 1250 °C are shown in Fig. 3, which consist of hard agglomerates of fine crystallites. The mean size of individual particles increases from 2.3 µm to 11.6 µm at 1050 °C and 1300 °C, respectively. Therefore, the sintering process favors the homogeneity of ceramic resulting thus an increase in grain size. Fig. 4 shows the effect of sintering temperature on the densification of $\beta$-TCP powders, where the final sintering temperature at 1160 °C is necessary to reach the maximum density (i.e. 98 wt%). Above 1160 °C, both curves of the density and grain size vary in opposite way. Therefore, the densities of the sintered bodies clearly depend on the crystalline growth of $\beta$-TCP particles and the removal of the most specimen porosity. Nevertheless, the irregularity of the high-temperature density is due only to the pores generation after the heat treatment. The decrease in density of 15% can be recognized to the presence of micro-cracks. One might argue micro-cracks onset could also be related to the increase in density of the material at longer sintering times, as porosity helps to relax residual stresses in the material. This suggestion agrees with those reported in the literature, where the final density limiting the densification level depends largely on the chemical composition and the surface area of $\beta$-TCP powders [10,20]. Consequently, the simple route for the elaboration of $\beta$-TCP by aqueous precipitation method in appropriate operatory conditions gives a stoichiometric and dense $\beta$-TCP with a considerable specific surface area (86 $m^2\,g^{-1}$) compared to that of hydroxyapatite $Ca_{10}(PO_4)_6(OH)_2$ [21] and there is stable up to 1160 °C. Thus, the poorly crystalline of as-elaborated sample exhibits a preliminary high green compact (56 wt%) and high relative density for sintered $\beta$-TCP pellets ($d = 98$ wt% at 1160 °C).

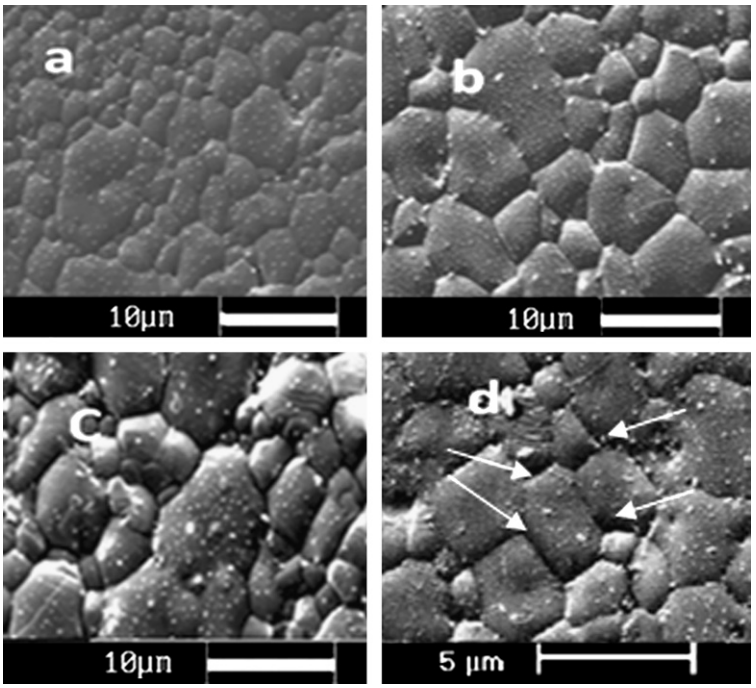


**Fig. 3.** SEM micrographs of $\beta$-TCP powders sintered at 1100 °C (a), 1160 °C (b), 1200 °C ((c) and (d)) (scale bars = 5 µm), arrows in (d) mark the presence of micro-cracks.

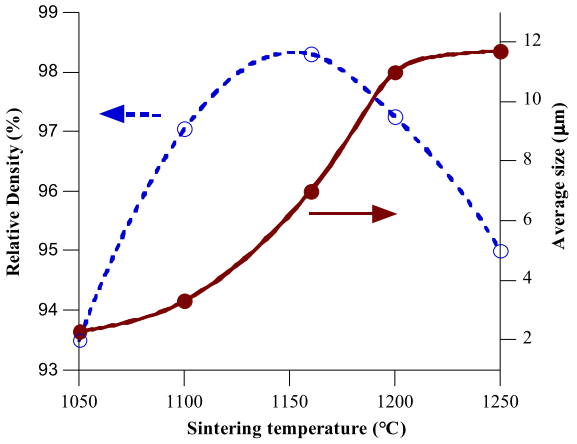


**Fig. 4.** Relative density and average grain size of $\beta$-TCP at various final sintering temperatures.

### 3.2. Mechanical properties

The resulting sintered $\beta$-TCP materials were then characterized with respect to their mechanical and physical properties. The mechanical characteristics (flexural strength, Young's modulus, Vickers hardness and toughness) are studied as a function of the sintering temperature (Figs. 4–6). All curves reveal a significant loss in mechanical properties for sintering temperatures up to 1160 °C, induced by an apparent density change affecting by sintering process. The decrease in density up 1160 °C attributed to the presence of micro-cracks and pore generation. We note that the micro-cracks are not developed at sintered temperature of 1200 °C (Fig. 3). The strength and hardness displayed a similar temperature-dependent behavior (Fig. 7). In Young's modulus, the immediate decrease occurred from 1160 °C (Fig. 5). The Vickers hardness and toughness increase and reach high values for $\beta$-TCP ceramics in 1100–1200 °C range temperature (Fig. 6). The maximum $K_{1c}$ and flexion toughness values obtained in this study are close to those reported for other calcium phosphate biomaterials using a classical process for the ceramic development, but with high relative density. Above 1160 °C as final sintering temperature, all mechanical data declined and related to the pore generation and to the presence of micro-cracks without major structure change such as demonstrated by X-ray diffraction and SEM analyses.

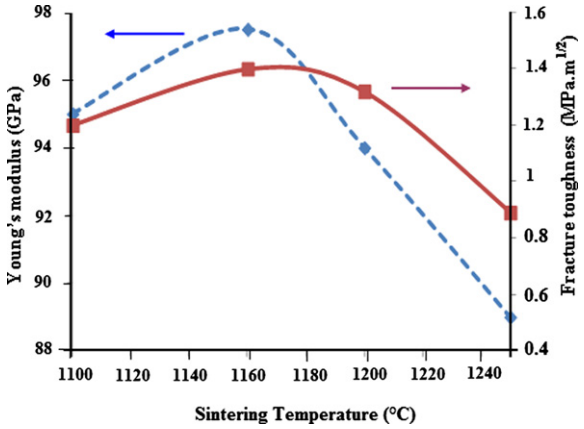


**Fig. 5.** Evolution of Young's modulus and fracture toughness versus sintering temperature.

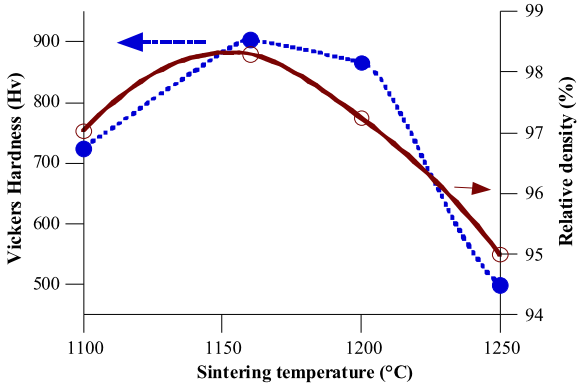


**Fig. 6.** Variation of the Vickers hardness and relative density of $\beta$-TCP with final sintering temperature.

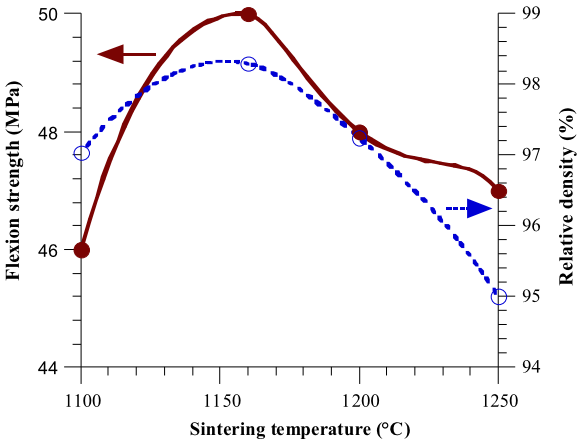


**Fig. 7.** The dependence of the flexion strength and relative density with final sintering temperature.

## 4. Conclusion

As described in the current study, the mechanical properties of $\beta$-TCP ceramic are very sensitive to the densification process. The results show that above 98% of theoretical density coupled with a higher hardness, fracture toughness and Young's modulus until 1160 °C as a critical temperature. The hardness and flexion toughness of the sintered material started to decrease when the temperature increases up 1160 °C, despite exhibiting high densities $>$ 97% of theoretical value. The occurrence of this phenomenon seems to be related to the thermal-activated grain growth and to the presence of micro-cracks affecting the density and the existence of pores helps to relax residual stresses in material.

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