

Effect of calcination conditions on phase formation of calcium phosphates ceramics synthesized by homogeneous precipitation

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Abstract: Phase composition of calcium phosphate ceramics is a characteristic directly related to the biological response of implants due to the differences in mechanical and biochemical properties of these compounds. In this sense, it was evaluated in this work the crystalline phase evolution of calcium phosphates samples synthesized by wet precipitation route. Fixing Ca/P atomic ratio as 1.67, precipitation was carried out from heated aqueous solutions of calcium chloride and ammonium hydrogen phosphate, in ammonium medium (pH = 10). After washing and drying steps, calcination was performed at 600 to 1100 °C for 1 and 3 hours. Milled and pressed powders were sintered at 1250 °C for 1 hour. Samples were characterized by X-ray diffraction, chemical analysis, scanning electron microscopy, gaseous adsorption, laser diffraction and apparent density measurements. Results indicate the formation of a biphasic calcium phosphate ceramic containing hydroxyapatite as a major phase and β - tricalcium phosphate, the later obtained by heat treatment above 600 °C.

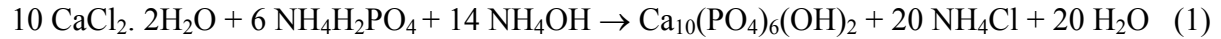
Introduction

Calcium phosphate based ceramics have great interest in medical and dentistry field due to their excellent biocompatibility and structural and composition similarity to mineral phase of human hard tissues (bones and teeth). Among these materials, particularly attention has been given to hydroxyapatite (HAp) - $\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$, owing to its bioactivity, and to β -tricalcium phosphate (β -TCP) - $\text{Ca}_3(\text{PO}_4)_2$, due to its resorbability in physiological medium. In order to combine the benefits of these properties, a biphasic calcium phosphate ceramic (BCP) has been developed. Therefore, the porosity generation in a dense BCP upon contact with by body fluids will induce in situ formation of biological apatite, improving bone reconstruction and regeneration [1-3]. Various methods have been developed to synthesize HAp, β -TCP and BCP ceramics, including solid-state reactions and wet chemical routes, such as precipitation, sol-gel methods and hydrothermal treatment [2-3]. Precipitation techniques from calcium and phosphate aqueous solutions, besides their low cost, allow a better control of composition and physical characteristics of powders. Some reports have shown the effect of reaction parameters (pH, temperature, Ca/P ratio and reagent concentration) and heat treatment conditions on bioceramic properties [4-14]. For quantitative analysis and structure characterization of crystalline phases, Rietveld refinement of XRD patterns has been widely used [15-17].

In this work the influence of calcination conditions on the formation of calcium phosphates was investigated. Powders, synthesized by precipitation route were pressed and sintered at 1250 °C for 1 hour. XRD analysis were performed for calcined powders and sintered ceramics and data were refined by the Rietveld method.

Experimental Procedure

Calcium chloride ($\text{CaCl}_2 \cdot 2\text{H}_2\text{O}$ PA, CAAL, Brazil), ammonium hydrogen phosphate ($\text{NH}_4\text{H}_2\text{PO}_4$ PA, CAAL, Brazil) and ammonium hydroxide (UqB, Brazil) were the starting materials used to synthesize hydroxyapatite ($\text{Ca}/\text{P} = 1.67$) according to the chemical reaction:



Chemical precipitation was conducted by dropping $\text{NH}_4\text{H}_2\text{PO}_4$ 0.2 molar aqueous solution into a reactor containing CaCl_2 0.5 molar solution. NH_4OH 5.5 molar was used to adjust at 10 the pH of the mixture. Temperature was maintained at 70°C for 1 hour to promote the reaction. The precipitation yield of calcium and phosphorus was determined by inductively coupled plasma with atomic emission spectrometry (ICP-AES – Spectro Flame M120 E, Spectro Analytical) analyzing the mother liquor.

The gel suspension was filtered and washed with water until no indication of residual Cl^- . To avoid the formation of hard agglomerates the precipitate was washed with ethanol and treated by azeotropic distillation with butanol. The distilled powder was oven-dried at 80°C for 24 hours and calcination experiments were carried out at a temperature range between 600 and 1100°C for 1 and 3 hours. Ball milling in ethanol for 16 hours, using zirconia balls as milling media, was employed to destroy large agglomerates. Sample codes include calcination temperature and holding time (example: 600-1). Powders were characterized by gas adsorption (BET Nova 1200, Quantachrome), laser diffraction (granulometer 1064, Cilas), scanning electron microscopy (SEM) (XL30, Phillips) and X-ray diffraction (XRD) using $\text{Cu K}\alpha$ radiation (D8 Advance, Bruker-AXS). Green pellets were prepared by uniaxial pressing at 100 MPa and sintering was performed in air at 1250°C for 1 hour. The characterization of as-sintered samples was carried out by apparent density measurements (Archimedes method), SEM and XRD. Quantitative phase analysis and determination of theoretical density of some powders and sintered samples were performed by Rietveld refinement of X-ray diffraction patterns. Data were collected from 5 to $80^\circ 2\theta$ with step of 0.02° and counting time 12 s. The DBWS-9807 program was used to refine the structures. Peaks shapes were modeled using a pseudo-Voigt distribution.

Results and discussion

Precipitation yield values show that phosphorus is completely precipitated, although calcium recovery is 94 wt%, leading to the formation of a calcium-deficient hydroxyapatite ($\text{Ca}_{10-x}(\text{HPO}_4)_x(\text{PO}_4)_{6-x}(\text{OH})_{2-x} \cdot n\text{H}_2\text{O}$, $0 < x < 1$), as reported in the literature [2, 6-8, 11,12].

Agglomerate mean size of calcined and milled powders is in the range of 1 and 3 μm (Fig.1). For powders calcined at temperatures lower than 1000°C , similar agglomerate/particle size and morphology were observed by SEM (Fig. 2). It was also observed that particle sizes are in the nanoscale. On the other hand, at 1000°C increasing of particle size starts. As a consequence of such behavior specific surface area values decrease drastically from 47 to 2 $\text{m}^2 \cdot \text{g}^{-1}$ as calcination temperature increases from 600 to 1100°C (Table 1). XRD results (Fig. 2 and Tables 2 and 3) indicate that the major phase after calcination is HAp, which belongs to hexagonal symmetry and space group $\text{P6}_3/\text{m}$. As calcination temperature increases, the formation of β -TCP with rhombohedral ($\text{R}\bar{3}\text{c}$) symmetry is enhanced. α -TCP having monoclinic ($\text{P}2_1/\text{a}$) symmetry was observed in ceramic sample prepared from powders calcined at lower temperature (600°C), indicating that the use of powders higher specific surface area promotes β -TCP \rightarrow α phase transformation during sintering process. According to the literature α -TCP is normally obtained by heating β -TCP above 1125°C and has a greater resorbability in physiological medium, compared to β -TCP [2].

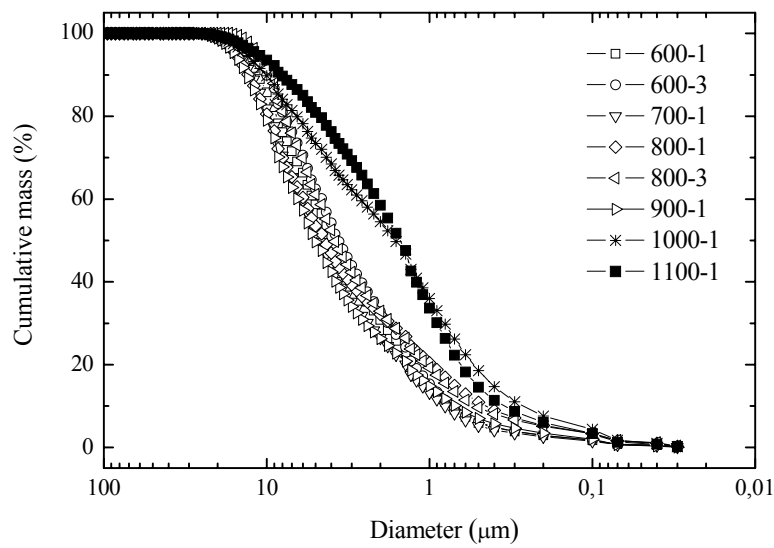


Table 1
Specific surface area of calcium phosphate powders.

Powder code	Specific Surface Area ($\text{m}^2 \cdot \text{g}^{-1}$)
600-1	45.6
600-3	45.5
700-1	27.8
800-1	12.1
800-3	16.6
900-1	19.7
1000-1	5.3
1100-1	1.9

Fig. 1: Cumulative size distributions of calcium phosphate powders, as a function of calcination conditions.

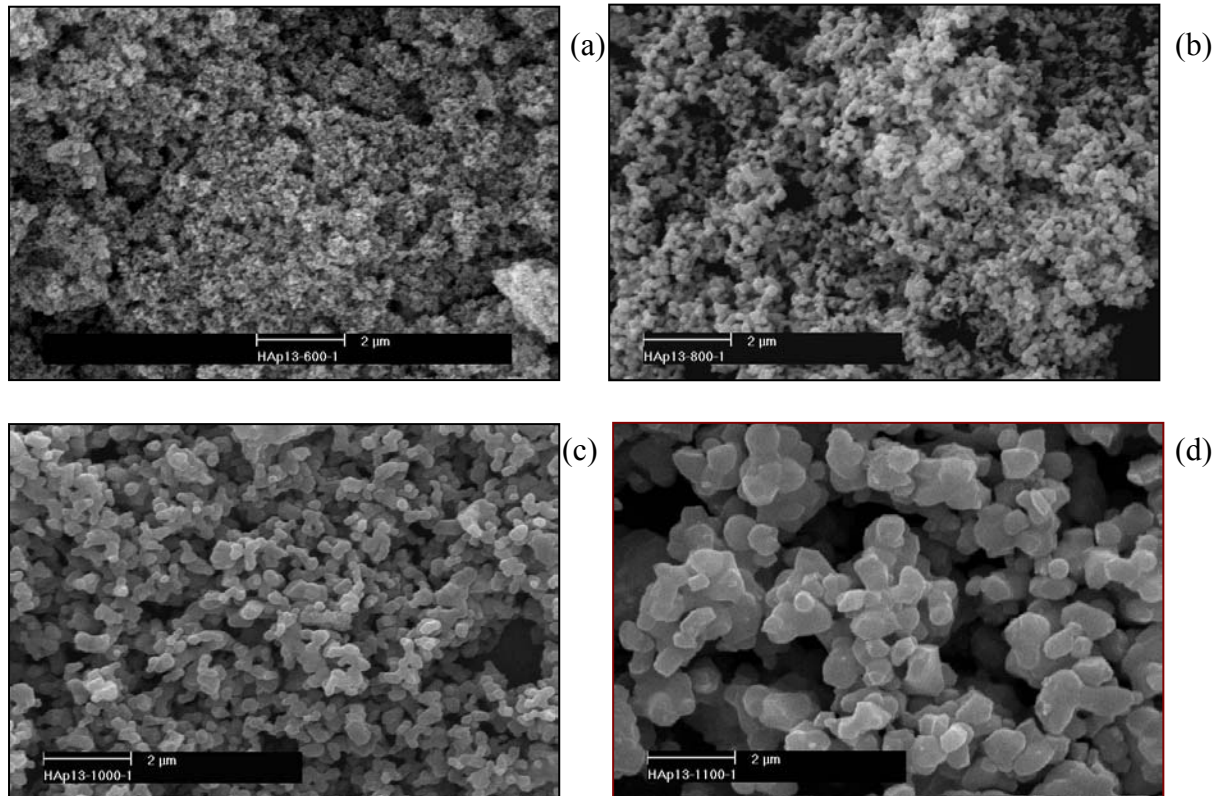


Fig. 2: SEM micrographs of calcium phosphate powders, as a function of calcination conditions: (a) 600 °C/ 1h, (b) 800 °C/ 1h, (c) 1000 °C/ 1h and (d) 1100 °C/ 1h.

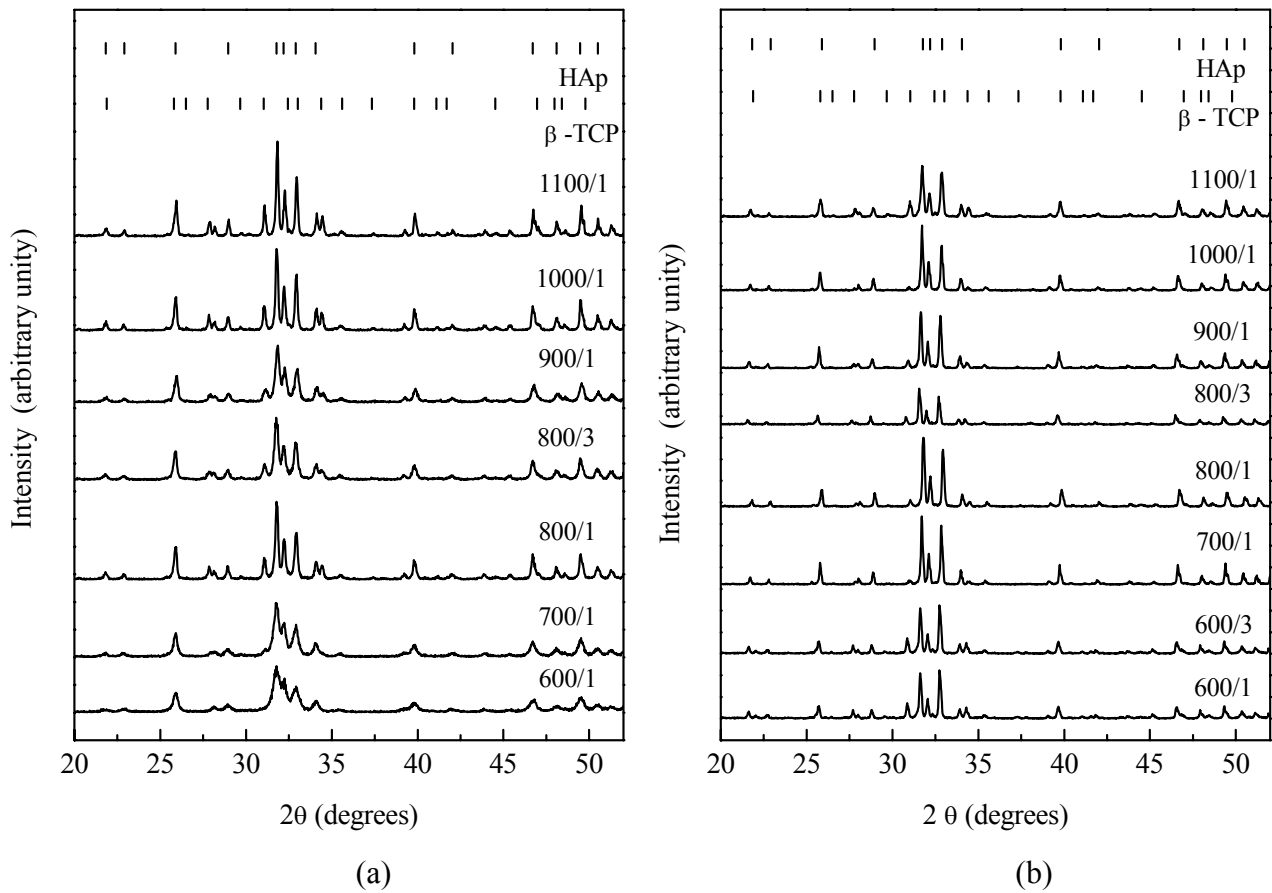


Fig. 3: XRD patterns of calcium phosphates powders (a) and sintered ceramics (b)

Table 2: Phase composition and theoretical density of calcium phosphates powders.

Powder code	Phase composition (wt%)		Theoretical density ($\text{g}\cdot\text{cm}^{-3}$)		
	HAp	β -TCP	HAp	β -TCP	BCP *
600-1	92.3 ± 0.8	7.7 ± 1.8	3.15	3.43	3.17
600-3	92.6 ± 0.8	7.3 ± 2.0	3.15	3.43	3.17
800-1	81.0 ± 0.5	19.1 ± 1.3	3.16	3.16	3.16
900-1	70.9 ± 0.8	29.2 ± 1.3	3.15	3.14	3.14
1000-1	70.6 ± 0.9	29.3 ± 2.1	3.15	3.14	3.15
1100-1	67.5 ± 1.9	32.5 ± 2.3	3.17	3.14	3.16

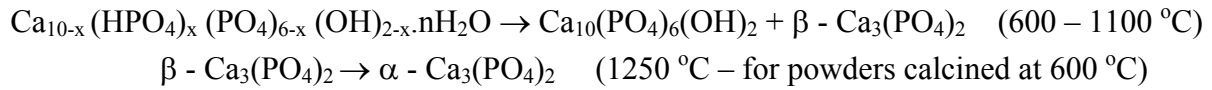
* Calculated considering phase composition and HAp and β -TCP theoretical densities.

Table 3: Phase composition and theoretical density of calcium phosphates ceramics.

Ceramic code	Phase composition (wt%)			Theoretical density ($\text{g}\cdot\text{cm}^{-3}$)			
	HAp	β -TCP	α -TCP	HAp	β -TCP	α -TCP	BCP *
600-1	79.8 ± 1.4	4.2 ± 1.7	16.0 ± 2.9	3.15	3.16	2.56	3.06
800-1	83.1 ± 0.6	16.9 ± 1.2	–	3.17	3.14	–	3.16
1000-1	79.0 ± 0.8	21.0 ± 1.6	–	3.16	3.13	–	3.15

* Calculated considering phase composition and HAp, α and β -TCP theoretical densities.

Considering XRD results, the following reactions summarize the overall process of calcium phosphate phase transformation, observed in experimental conditions adopted in the present work:



Fracture surface of the as-sintered calcium phosphate pellets are shown in Fig. 4. For samples prepared from powders calcined at lower temperature (600 °C) fracture is intergranular and grain size smaller than 5 μm. On the other hand, intragranular fracture is observed when powders are calcined above 800 °C.

Apparent density results of calcium phosphates ceramics (Table 4) indicate that density as high as 99% of the theoretical value can be achieved. The lowest density value was obtained for pellets prepared from powders calcined at 1100 °C. This result is in accordance with SEM observation (Fig. 4c).

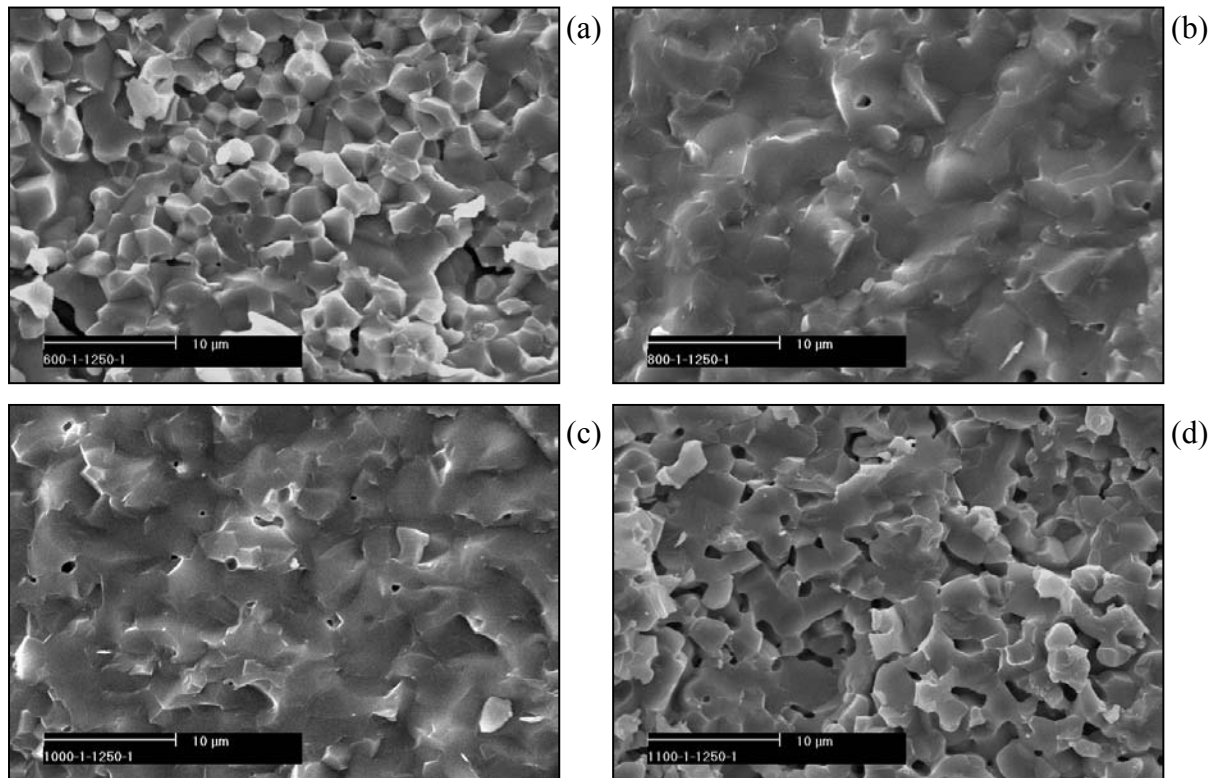


Fig.4: SEM fracture surface micrographs of calcium phosphate ceramics sintered at 1250°C/ 1h, as a function of calcination conditions: (a) 600 °C/ 1h, (b) 800 °C/ 1h, (c) 1000°C/ 1h and (d) 1100 °C/ 1h.

Table 4 – Apparent density of calcium phosphates ceramics.

Sample code	Apparent Density (g.cm ⁻³)	Sample code	Apparent Density (g.cm ⁻³)
600-1	3.03 ± 0.07	800-3	3.09 ± 0.01
600-3	2.92 ± 0.04	900-1	2.97 ± 0.03
700-1	2.98 ± 0.02	1000-1	3.09 ± 0.01
800-1	3.09± 0.02	1100-1	2.08 ± 0.01

Conclusions

Coprecipitation demonstrated to be a promising route for production of nanosized calcium phosphate powders. Starting from calcium and phosphorus aqueous solutions (Ca/P = 1.67), heated at 70 °C for 1 hour, deficient hydroxyapatite is precipitated in ammonium medium (pH=10). After washing steps, buthanol azeotropic distillation treatment, calcination and milling a biphasic hydroxyapatite / β -tricalcium phosphate composite is obtained. The concentration of each phase and powders physical characteristics are defined by the calcination conditions. HAp is the major phase and β -TCP content increases with temperature (8 – 33 wt%). Sintering behavior of biphasic calcium phosphate materials is greatly influenced by the properties of calcined powders. Dense ceramics can be obtained from powders calcined in the range of 600 – 1000 °C. However, it is important to notice that calcination at 600 °C promotes the formation of α -TCP in sintered ceramics, probably owing to the great powder reactivity. Taking into account the important role of phase composition and microstructure characteristics on mechanical and biological behavior of BCP ceramics, further investigations are under progress in order to correlate these aspects. An important feature that has to be evaluated is the mechanical reliability of ceramics submitted to volume variation due to phase transformations, such as $\alpha \rightarrow \beta$ -TCP, that occurs during cooling to room temperature after sintering.

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