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Crystallite size study of nanocrystalline hydroxyapatite and ceramic system with titanium oxide obtained by dry ball milling

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Abstract High energy dry ball milling has been used to produce nanocrystallite powders of Hydroxyapatite (HAP) using the starting materials $Ca(H_2PO_4)_2$ and $Ca(OH)_2$. The calcium phosphate system with titanium (CaP-Ti) were prepared with the raw materials $Ca(H_2PO_4)_2$ and TiO_2. The HAP was obtained after a couple of hours of milling (5, 10 and 15 h) and in the reaction with CaP-Ti was obtained after 5 h of milling. The HAP and the ceramic calcium phosphate with titanium (CaP-Ti) were studied by X-Ray powder Diffraction and Scanning Electron Microscopy (SEM). The grain size analysis through XRD shows that the particle size of HAP increase of the milling time and the size of $CaTi_4P_6O_{24}$ decrease with the increase of the milling time.

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Introduction

Ball milling has been used for almost two decades to produce many unique materials [1]. For ball milling we mean a process in which a metallic and/or non-metallic powder mixture is actively deformed in a controlled atmosphere, under a highly energetic ball charge [2]. Nowadays the technique is used in a large range of commercial products; moreover, most of these applications are on metallic domain. Ball milling has several intrinsic advantages, such as low-temperature processing, easy control of composition, relatively inexpensive equipment, and the possibility of scaling up. Although the ball milling technique is relatively simple, the physical mechanisms involved are not yet fully understood [3].

Synthetic hydroxyapatite [HAP, $Ca_{10}(PO_4)_6\,(OH)_2$) is widely used in reconstructive orthopedic and dental surgery of bone gaps and as a surface coating [4–11] due to its chemical similarities with the inorganic phase of the bone.

The synthesis of HAP and ceramic system with titanium (CaP-Ti) was developed because alloys with titanium have been used, with some success, in several bioimplant applications. Since TiO_2 coating are also known to be effective as chemical barriers against the in vivo of metals ions from the implants, a double layer HAP-TiO_2 coating in titanium alloys with HAP as the top layer and a dense TiO_2 film as the inner layer should possess a very good combination of bioactivity chemical stability and mechanical integrity [12].

In this work, we show that the HAP and calcium titanium phosphate can be usually produced at room temperature by ball milling technique from calcium oxide, calcium phosphate and titanium oxide compounds.

It was been obtained HAP and a ceramic system with calcium titanium with different degrees of crystallinity function of the time of milling. The XRD patterns indicate that the crystallite size is within the range of 17.6 nm for HAPA_5H and 81.1 nm for CaPTi_5H (Figs. 3 and 4).

The advantages of this procedure remains on the fact that melting is not necessary and the powders are nanocrystalline [13].

Experimental procedure

Ball milling has been used successfully to produce nanocrystalline powders of hydroxyapatite (HAP) using due experimental procedure [14]:

$$3\mathrm{Ca(H_2PO_4)_2} + 7\mathrm{Ca(OH)_2} \xrightarrow{\mathrm{IMPACTS}} \mathrm{Ca_{10}(PO_4)_6(OH)_2} + 12\mathrm{H_2O} \text{ Reaction 1 (HAPA)}$$

Commercial oxides ($Ca(H_2PO_4)_2$ (Aldrich, 85%) and $Ca(OH)_2$ (Vetec, 97% with 3% of $CaCO_3$) were used in the HAP preparation. To compare the efficiency of the milling process we also use Commercial Hydroxyapatite (HACOM, Vetec, 98%).

To produce nanocrystalline powders of ceramic calcium phosphate with titanium (CaP-Ti) it was used [14]:

$$\mathrm{Ca(H_2PO_4)_2} + \mathrm{TiO_2} \xrightarrow{\mathrm{IMPACTS}} \text{CaP-Ti} + \mathrm{H_2O} \text{ Reaction 2 (Cap-Ti)}$$

Commercial oxide TiO_2 (BDH, 98%) was used in the CaP-Ti preparation.

For all the reactions the material was ground on a Fritsch Pulverisette 6 planetary mill with the stechiometric proportionality between the oxides given in Eq. 1 for HAP and Eq. 2 for ceramic system with titanium. Milling was performed in sealed stainless steel vials and balls under air, with 370 rpm as rotation speed. The powder mass to the ball mass ratio used in all the experiments was near 1/6. To avoid excessive heating the milling was performed in 60 min milling steps with 10 min pauses. Ball milling was performed during 5, 10 and 15 h of milling for the two reactions.

The X-ray diffraction (XRD) patterns data were obtained on an X'Pert MPD Philips difractometer (CuK_α X radiation) with a curved graphite monochromator, a automatic divergence slit (irradiated length 20.00 mm), a progressive receiving slit (height 0.05 mm) and a flat plane sample holder in a Bragg-Brentano para-focusing optics configuration. Intensity dates were collected by the step counting method (step 0.05° in 4 s) in the range 2θ (20–60°).

The output data extracted from Rietveld refinement [15] is used to calculate the particle size. The analysis of the crystallite size (L_c) of the HAP and ceramics calcium phosphate phases has been done for all samples using the Scherrer's equation [16]:

$$L_c = \frac{k\lambda}{\beta \cos\theta} \tag{1}$$

where k is the shape coefficient (value between 0.9 and 1.0), λ is the wave length, β is the full width at half maximum (FWHM) of each phase and θ is the diffraction angle. For this purpose, we chose the single peak near 25.8° within the pattern and according to $P6_3/m$ space group of HAP and the single peak near 27.4° for the CaP-Ti, this peak correspond to hkl = 002, along to the **c** crystallographic axis. We have used the LaB_6 (SRM 660 -National Institute of Standard Technology) powder standard pattern to determine the instrumental width ($w_{inst} = 0.087°$) and afterward to calculate the crystallite size via Eq. 1. The β parameter has to be correct using the following equation:

$$\beta = \sqrt{w_{exp}^2 - w_{inst}^2} \tag{2}$$

where w_{exp} and w_{inst} are the experimental and instrumental width, respectively. w_{inst} is obtained from LaB_6 powder standard pattern using the following expression:

$$w_{inst} = \sqrt{Utg^2\theta + Vtg\theta + W} \tag{3}$$

where U, V and W were obtained from output file extracted from Rietveld refinement parameters of LaB_6 samples [16, 17].

The crystallite size and the error for all samples, assuming coefficient $k = 1$.

Microstructure was performed in a HITACHI S4100-1 system, on the surface of all samples covered with carbon before microscopic observation.

Results and discussion

Figures 1 to 2 presents the XRD pattern of reactions 1 and 2 respectively for hydroxyapatite (HAPA) powder and the ceramic calcium phosphate with titanium (CaP-Ti) (Fig. 2) for the reactions with 5, 10 and 15 h of milling.

After 5 h of milling the product of reaction 1 is HAP, with good identification of this phase. In Fig. 2 it

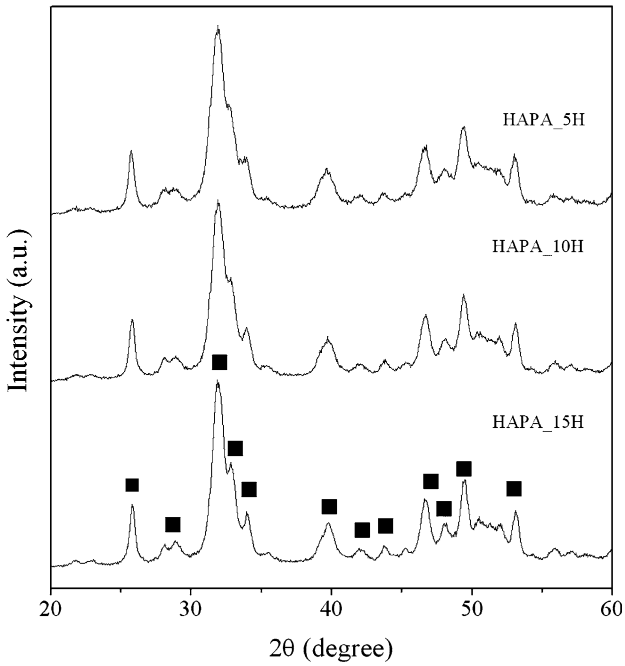

Fig. 1 XRD patterns of reaction HAPA milled for 15 h. HAP (■) [18]

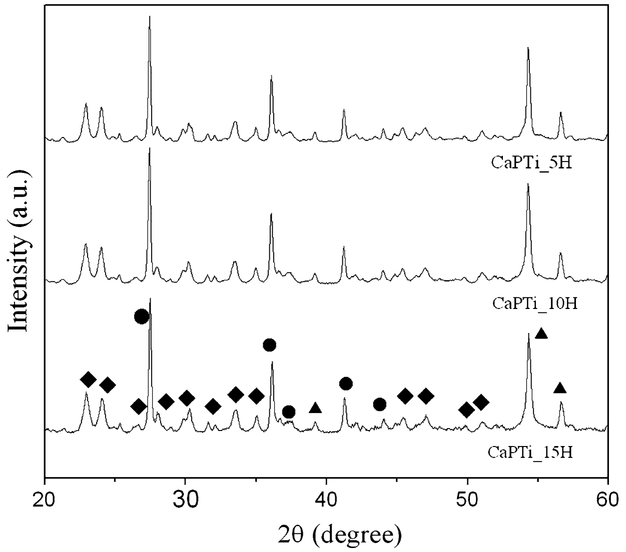

Fig. 2 XRD patterns of reaction CaP-Ti milled for 15 h. $CaTi_4P_6O_{24}$ (●) [18], $Ca(H_2PO_4)_2 \cdot H_2O$ (◆) [18] and TiO_2 (▲) [18]

was verified the existence of $CaTi_4P_6O_{24}$, $Ca(H_2PO_4)_2 \cdot H_2O$ and TiO_2 after 5 h of milling. The verified hydration of $Ca(H_2PO_4)_2$ can be due to the liberation of water during the formation of $CaTi_4P_6O_{24}$. The phases $Ca(H_2PO_4)_2 \cdot H_2O$ and TiO_2 were observed, even after 15 h, indicating that only a part of the initial materials have been transformed in $CaTi_4P_6O_{24}$.

The crystallite size (nm) obtained from X-Ray of the samples HAPA and CaP-Ti were shown in Figs. 3 and 4 with average dimensions 20.6 and 59.7 nm corresponding to 15 h of reaction respectively, with their associated errors after 15 h milling of time.

The Figs. 5, 6, 7 shows the SEM micrographs of the samples HAPA_15H (Fig. 5) and CaP-Ti_5H and CaP-Ti_15H (Figs. 6, 7).

In the reaction 1 it was observed an increase of the crystallite size with the increase of milling time. The increase of the size of grains can be explained by the formation of agglomerates in the moment of the milling. The error in this reaction was of ±0.39% at 5 h of milling and ±0.54% at 15 h.

In Fig. 4 it is observed a decrease of the $CaTi_4P_6O_{24}$ particle size with the increasing of the milling time in

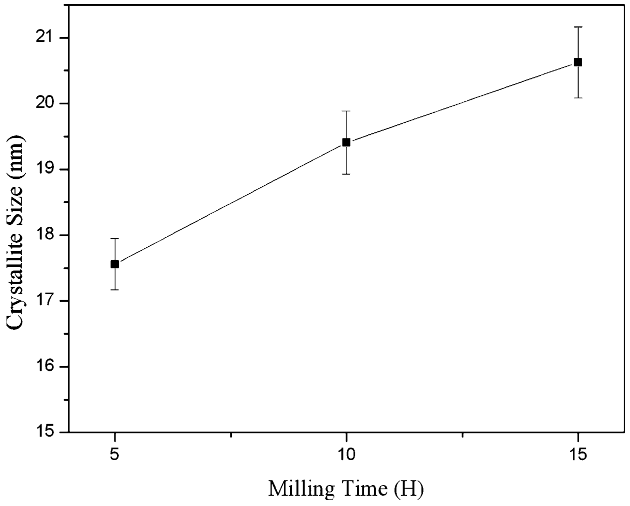

Fig. 3 Crystallite Size of the HAPA (■)

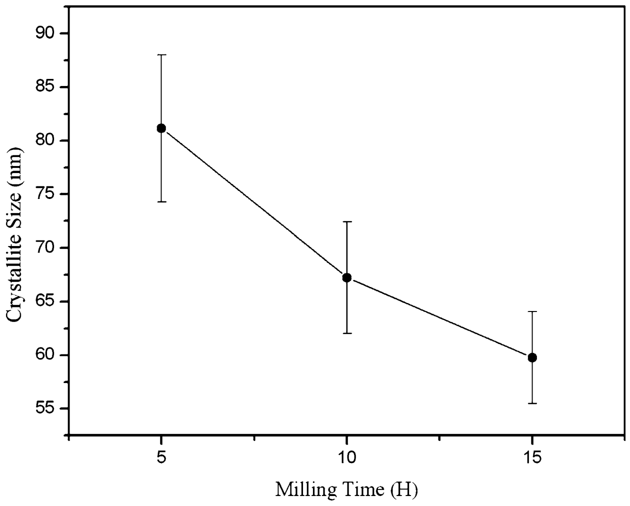

Fig. 4 Crystallite Size of the CaP-Ti (●)

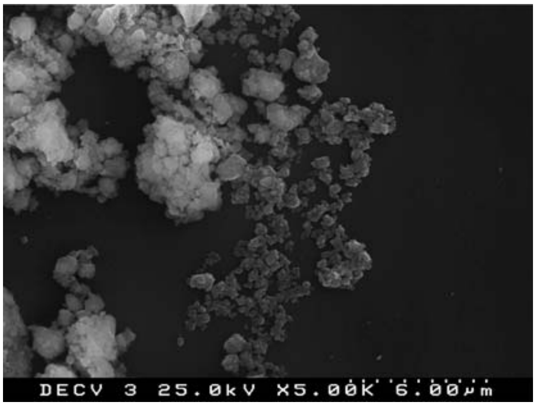

Fig. 5 SEM of the sample HAPA_15H with 5,000×

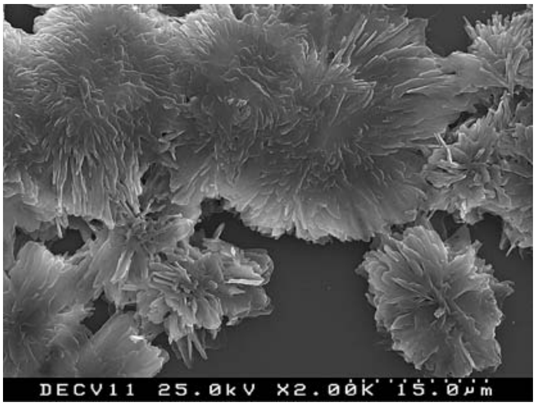

Fig. 6 SEM of the sample CaP-Ti_5H with 2,000×

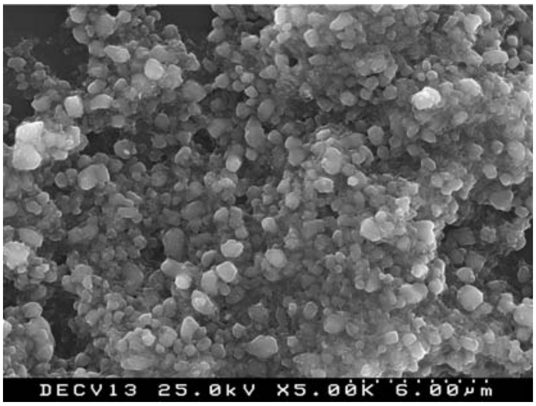

Fig. 7 SEM of the sample CaP-Ti_15H with 5,000×

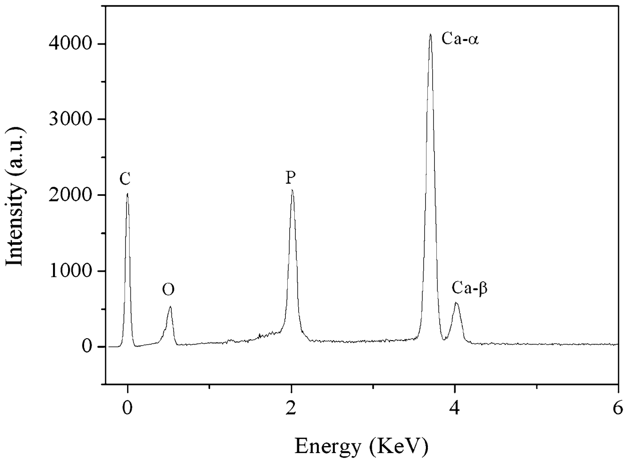

Fig. 8 EDS graphic of the sample HAPA_15H

the reaction 2. At 5 h formation of plates can be observed (Fig. 6) and with the increase of the time of grinding it was observed a break of these plates and the formation of spherical grains (Fig. 7). The error found in this reaction varies between ±6.87% as 5 h and ±4.30% as 15 h of milling time. The high values of those errors can by linked to the fact that diffraction intensity at $2\theta = 27.46^{\circ}$ is associated with a shoulder at $2\theta = 27.975^{\circ}$ attributed the formation of $Ca(H_2PO_4)_2 \cdot H_2O$ [19].

The microstructure of the samples is composed of sintered grain size in the range of 300 nm (HAPA_15H) and 800 nm (CaP-Ti_15H) measures in SEM. The grains observed in Figs. 5 and 6 are formed by smaller subunits of crystals [18]. The EDS of particles of the HAPA_15H ceramic (Fig. 8), showed a mass ratio of Ca/P = 2.17. These results suggest that the HAPA nanocrystalline ceramic is close to the expected value for the atomic ratio Ca/P for hydroxyapatite in 1.67 (Fig. 8).

Conclusions

It has been used $Ca(H_2PO_4)_2 + Ca(OH)_2)$ as raw material in the HAP preparation and $Ca(H_2PO_4)_2 + TiO_2$ as starting materials was preparing calcium phosphate with titanium. It has been obtained HAP with three times of milling (5, 10 and 15 h) and $CaTi_4P_6O_{24}$. This milling process presents the advantage that melting is not necessary and the powder obtained is nanocrystalline. In the reaction 1, $Ca(H_2PO_4)_2 + 7\ Ca(OH)_2$, it was obtained only the hydroxyapatite phase and in the reaction with titanium it was obtained the following phases: $CaTi_4P_6O_{24}$, $Ca(H_2PO_4)_2 \cdot H_2O$ and TiO_2. It was observed increase of the size of grains in reaction HAPA with the formation of agglomerates with the increase of the time of milling, while in the reaction with titanium (CaP-Ti) the inverse behaviour has been observed.

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