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Mechanochemical transformation of mixtures of $Ca(OH)_2$ and $(NH_4)_2HPO_4$ or P_2O_5

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Abstract

A detailed comparative study of the mechanochemical transformation of two mixtures: $Ca(OH)_2$–$(NH_4)_2HPO_4$ and $Ca(OH)_2$–P_2O_5, milled in a mortar dry grinder for different periods of time was carried out. The phase transformations obtained at each milling stage were studied by X-ray diffraction, infrared spectroscopy, transmission electron microscopy, differential scanning calorimetry and thermogravimetric analysis.

The transformations taking place during the first periods of milling are very different for both mixtures. However, prolonged milling, over nearly the same period, causes amorphization of both mixtures. DSC analysis of the milled powders showed the temperature of crystallization of hydroxyapatite and tricalcium phosphate (β-TCP). Calcinations of all the different milled powders at 800 °C for 2 h, results in the formation of hydroxyapatite and β-TCP.

Keywords: A. Inorganic compounds; C. Differential scanning calorimetry; C. X-ray diffraction

1. Introduction

The need for obtaining suitable biomaterials that fulfill the requirements for human bone replacement has always been an important issue. Synthetic calcium phosphates and hydroxyapatite (HAp) are chemically and crystallographically similar but not identical to the mineral constituent of human bones, presenting very good mechanical and biocompatibility properties depending on the fabrication route. Therefore, synthetic HAp materials look very promising as osseous substitutes. Many different chemical methods of synthesis have been tried out: precipitation, sol–gel and hydrothermal methods [1–9], each one has its own advantages and disadvantages. The search for new methods of synthesis has directed the attention to solid-state reactions. Among these, mechanical activation looks as a very promising alternative method due its apparent simplicity and versatility. The method consists on the perturbation of solid bonded species by pressure to enhance thermodynamic and kinetic reactions between solids.

Mechanochemistry transformation can be induced by mechanical milling due to the fracture of particles that continuously creates new fresh surfaces. This is assisted by the high local heat generated during the process inducing

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phase transformations at room temperature. Several works have been reported on the synthesis of biomaterials by mechanochemical methods [10–19]. These works show the importance of the precursors, nature and type of milling tools, and the environmental conditions, on the final products obtained.

In the present work a detailed comparative study of the mechanochemical transformation of two mixtures: $Ca(OH)_2$–$(NH_4)_2HPO_4$ and $Ca(OH)_2$–P_2O_5, milled in a mortar dry grinder for different periods of time was carried out, with the aim of evaluating the reactions taking place at each stage of milling. The thermal transformations of the milled powders were also studied.

2. Experimental procedure

Dry milling was carried in a Fisher, automatic open alumina mortar grinder (135 mm o.d. × 100 mm i.d.) mod. 155, operating at 60 rpm. The mechanism consist on back and forth motion of pestle and rotation of mortar applying grinding pressure over entire bottom of mortar. Stoichiometric mixtures of $Ca(OH)_2$ –$(NH_4)_2HPO_4$ and $Ca(OH)_2$–P_2O_5, with molar ratio Ca/P = 1.67 were employed. These mixtures (30.52 and 23.53 g, respectively) were previously homogenized for 2 h in a turbula and further milled for periods from 0.5 to 100 h in batches of 2.5 g/ea. The powders from each milling stage were calcined in air at 800 °C for 2 h. X-ray diffraction (XRD), IR spectroscopy, transmission electron microscopy (TEM), differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) were

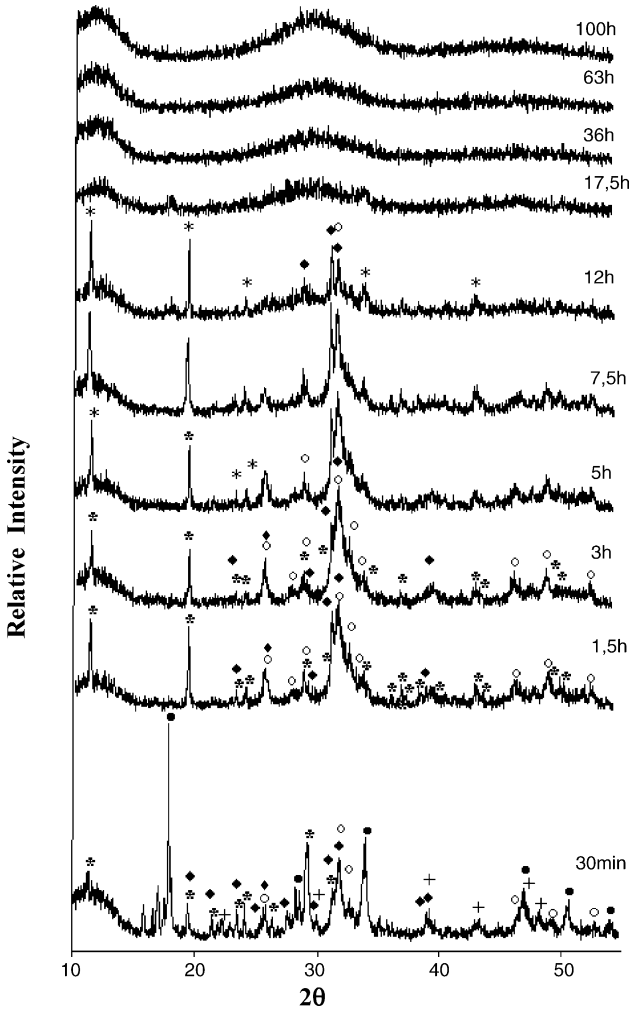

Fig. 1. XRD pattern of milled samples of $Ca(OH)_2$–$(NH_4)_2HPO_4$ mixture: (*) $NH_4CaPO_4{\cdot}H_2O$; (●) $Ca(OH)_2 + CaCO_3$; (○) $Ca_{10-x+y}(PO_4)_{6-x}(CO_3)_x(OH)_{2-x+2y}$; (◆) $Ca_{10}(PO_4)_6CO_3$.