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Optimization of milling parameters for the mechanosynthesis of nanocrystalline hydroxyapatite

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ABSTRACT

Here we report synthesis of nanocrystalline hydroxyapatite (HAP), a bone substitute, through dry mechano-chemical method using phosphorous pentoxide and calcium hydroxide powders as starting materials, in a specially designed high-energy dual-drive planetary mill which is able to generate a strong gravitational (around 100 g) field inside the planetary mill thereby reducing the synthesis time significantly. Effects of various milling parameters such as milling time, ball to powder weight ratio, ball size and critical speed of the mill were investigated to understand their effect on the milling process and formation of nanocrystalline HAP. The study shows that the optimum conditions for the synthesis of nanocrystalline HAP is achieved when grinding is performed at a critical speed of 60% using a 4 mm diameter ball at a charge ratio of 20:1 for 15 h. X-ray diffraction and Fourier transform infra red (FT-IR) analysis confirmed phase purity of the nanocrystalline HAP powders. Electron microscopy of the milled HAP powder shows that powder particles are spherical and around 100 nm in size.

1. Introduction

Hydroxyapatite is one of those few ceramic materials which are bioactive [1,2] as well as biocompatible [3–6] in nature. It is a form of calcium phosphate that has a large number of applications in biomedical field. This is one of the most promising materials for artificial bone replacement because of its crystallographic and chemical similarity to human hard tissues. Because of its bioactive nature, it also promotes bone growth when implanted [7]. Hydroxyapatite is also used for separation and purification of proteins [8–13] and in drug delivery systems [14].

Mechanochemistry has been used during the last decades as a powerful tool for the preparation of metastable crystalline and amorphous phases and nanostructured materials which cannot be prepared through conventional methods [15–17]. This is due to three fundamental reasons: shortening of reaction times, reduction of the high temperatures usually required for developing solid-state reactions and the possibility of obtaining materials with special properties. The high concentration of lattice defects introduced by the mechanical treatment often produces phases with distorted crystalline structures far from the thermodynamic equilibrium.

While there are different methods used to synthesize hydroxyapatite, it is often difficult to prepare pure hydroxyapatite. Only solid state reactions at high temperature (>900 °C) and hydrothermal reactions at moderately high temperature (>350 °C) can produce pure hydroxyapatite. Besides these methods, several other methods have been exploited to obtain hydroxyapatite, such as solution method [18,19] and sol–gel route [20]. However, hydroxyapatite obtained from these processes is microcrystalline in nature and is not suitable for hard tissue replacement due to its poor mechanical properties. Furthermore it shows relatively lower bioactivity in microcrystalline form [21]. To address this problem, the new concept of nanocrystalline hydroxyapatite has evolved. As nanocrystalline HAP powder exhibits greater surface area [22], it could provide improved sinterability and enhanced densification to reduce sintering temperature, which could improve the fracture toughness of HAP ceramic. Besides high fracture toughness, hydroxyapatite shows improved bioactivity [23–25] and better osseointegrative properties in nanocrystalline form [26]. Silva et al. [27] prepared nanocrystalline hydroxyapatite powder by mechanical alloying after 60 h of milling in planetary mill. Fathi et al. [28] also prepared nanocrystalline hydroxyapatite powder by mechanical alloying after 15 h of milling in planetary mill. Similarly, Yeong et al. [29] prepared nanocrystalline HAP from CaO and $CaHPO_4$ powder by mechanical activation for 25 h in a shaker mill. Tabrizi et al. [30] studied the effect of milling parameters (time and atmosphere) on the mechano-chemical synthesis of nanocrystalline. Recently, Lala et al. synthesized [31] nanocrystalline hydroxyapatite after 10 h of milling in a planetary mill (P5, M/S Fritsch, GmbH, Germany).

However, most of these reports show that synthesis of HAP by mechano-chemical technique takes very long time and hence bulk production of nanocrystalline hydroxyapatite powder remains a challenge.

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Another factor is that it takes long milling time to prepare nanocrystalline HAP. Faced with all these challenges we have reported a new and efficient method for synthesizing nanocrystalline hydroxyapatite powder at ambient temperature. For this purpose a very high energy dual drive planetary mill has been fabricated. This special mill can generate a force field which is 100 times the gravitational force [32]. Here, in this paper, the effect of important milling parameters like process time, ball diameter, ball to powder weight ratio and critical speed were extensively investigated to understand the mechanochemical process. Finally the HAP powder was characterized by different characterized techniques.

2. Experimental procedure

2.1. Mill design

The dual drive planetary mill developed specifically for the synthesis of nanocarbides has a rotating shaft that sweeps a circle of diameter 600 mm. The two steel jars of 105 mm diameter rotate about their own axes around the common axis of the main shaft. The planetary mill is powered by two motors. A 5 HP motor works on the main rotating shaft and 3 HP motor drives the jars. The rotating speed of both motors can be varied independently and continuously by a frequency controller. Details of mill design and mechanics are available elsewhere [33–35].

If we study mill mechanics, we get an expression for critical speed of mill K_c.

$$K_c = \frac{\varpi_2}{\varpi_1} = -1 \pm \sqrt{L/_{2R}} \tag{1}$$

Where ω_2 and ω_1 are jar speed and mill speed respectively. L and R are gyratory arm length (600 mm) and jar radius respectively.

The percent critical speed is

$$\%CS = \frac{n_2}{K_c \times n_1} \times 100 \tag{2}$$

Where n_1 and n_2 are the gyrating and jar speed respectively. In our case the mill was operated at three different critical speeds (60%, 75% and 90%). This was arrived by doing the following calculation:

$$K_c = -1 \pm \sqrt{\frac{600}{105}} = -1 \pm 2.39 \tag{3}$$

Conventionally minus sign is taken for opposite direction of motion between the jar and the main shaft.

Hence critical speed constant comes to be

$$K_c = -3.39 \tag{4}$$

The percent critical speed is calculated by varying only the mill speed keeping the main shaft speed constant.

$$\text{For 60\% critical speed}: \quad \%CS = \frac{510}{3.39 \times 250} \times 100 = 60 \tag{5}$$

$$\text{For 75\% critical speed}: \quad \%CS = \frac{635}{3.39 \times 250} \times 100 = 75 \tag{6}$$

$$\text{For 90\% critical speed}: \quad \%CS = \frac{760}{3.39 \times 250} \times 100 = 90 \tag{7}$$

2.2. Materials and methods

Stoichiometric amount of calcium hydroxide [$Ca(OH)_2$] (Loba Chemie Pvt. Ltd., India, 96% purity) and phosphorous pentoxide [P_2O_5] (Merck, India, 97% purity) powders were milled in the high energy dual drive planetary mill to synthesize hydroxyapatite.

The governing equation is given below.

$$10Ca(OH)_2 + 3P_2O_5 = Ca_{10}(PO_4)_6(OH)_2 + 9H_2O \tag{8}$$

The milling was carried out in dry condition and at a fixed vial filling (35%). A detailed investigation was carried out to see the effect of important milling parameters like milling time, ball diameter, ball to powder weight ratio and critical speed. Small amount of powder samples was collected at a regular interval to carry out X-ray diffraction study and particle size analysis. These results helped to investigate the progress of reaction and grinding kinetics. Finally, a combination of different milling parameters was chosen in such a way that the reaction can occur at a very fast rate and the particles of hydroxyapatite become very fine. X-ray diffraction of the as milled powder samples were performed using the diffractometer (model: ISO Debyeflex-2002, supplier: Rich Seifert& Co., Germany). The target (radiation) was CuK_α (wavelength, $\lambda = 1.542A^\circ$). X-ray diffraction was carried out with a scan speed of 3°/min. The crystal system and its corresponding lattice parameters were compared with the standard data file of International centre for diffraction data (ICDD), JCPDS. The particle size of the milled powder was measured in laser particle size analyzer (model: Malvern, Mastersizer 2000, UK). Chemical analysis was carried out through wet chemical method. The SEM micrograph of milled powder with optimized milling parameters was taken in scanning electron microscope (FEI QUANTA 200). The operating voltage was 20 KV. The powder sample was gold coated to make the sample conducting, before SEM operation. The TEM micrographs of the final milled powders were taken in a transmission telectron microscope (Model JEM-2000 FX II-JEOL). The operating voltage was 120 KV. Fourier transform infra red (FT-IR) spectroscopy was performed by using Bruker Vertex 70 spectrometer. Differential thermal and thermo-gravimetric analysis of the final sample was carried out by using NETZSCH STA 409C.

3. Experimental results

3.1. Optimization of milling parameters

Optimization of milling parameters is very important to get efficient milling. Here effect of four important milling parameters (milling time, ball size, ball to powder weight ratio and critical speed) were studied in detail.

3.1.1. Effect of ball diameter

3.1.1.1. X-ray diffraction. To observe the effect of ball size on mechanochemistry, milling was carried out using balls of different diameter (4, 6, 8 and 10 mm). Fig. 1 shows the XRD patterns of milled powders for different ball diameters at 60% critical speed and 20:1 ball to powder weight ratio after 15 h of milling. X-ray diffraction peaks of powders at different milling times are compared with diffraction peaks of initial powder mixture and standard hydroxyapatite [JCPDS File No: 9-432]. The entire process of reaction milling consists of three distinct stages. In the initial stage amorphization of precursor materials take place. Intermediate stage is characterized by the formation of new crystalline phase of hydroxyapatite. Finally new phase which is formed due to the mechanochemical reaction becomes amorphous. If peak intensity and broadening for different ball sizes are considered then it can be seen that reactions are complete after 15 h in all cases. But maximum amorphization takes place where smallest size balls (4 mm) are used.

3.1.1.2. Particle size measurements. The variation of particle size with ball diameter and milling time at 60% critical speed and 20:1 ball to powder weight ratio is shown in Fig. 2. It is clear from the figure that the trend of change of particle size with milling time is the same for different ball