Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 41 (2015) 13100–13104

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

The effect of heat-treatment on the structural characteristics of nanocrystalline chlorapatite particles synthesized via an in situ wet-chemical route

M. Ganjali*, S. Pourhashem, M. Mozafari

Bioengineering Research Group, Nanotechnology and Advanced Materials Department, Materials and Energy Research Center (MERC), P.O. Box 14155-4777, Tehran, Iran

Received 27 May 2015; received in revised form 15 June 2015; accepted 3 July 2015
Available online 11 July 2015

Abstract

In this research, nanocrystalline chlorapatite particles were synthesized via an in situ wet-chemical precipitation method at room temperature, and then various heat-treatment temperatures were examined to consider the effect of the heat-treatment process on the structure and morphology of the samples. According to the XRD results, by increasing the heat-treatment temperature, no phase transformation occurred, and all the samples were made of chlorapatite. However, the morphology of the nanoparticles changed from spherical to polygonal and grain growth occurred slowly. In addition, the Williamson–hall plot showed that the crystallite size before and after calcination at 500, 900, and 1200 °C was 13, 11, 20, and 34 nm, respectively, and a gradual increase in the crystallite size of chlorapatite was observed with increasing in the heat-treatment temperature.

Keywords: D. Apatite; Chlorapatite; Wet-chemical method; Heat-treatment

1. Introduction

Hydroxyapatite is the mineral component of natural bone [1]. Synthetic hydroxyapatite can be used in dental and orthopedic applications due to its chemical and structural similarities to biological apatite [2,3], in order to form chemical bonds with the bone [4]. As an innovative approach, the incorporation of other chemical species (such as Mg^{2+}, Na^{+}, K^{+}, F^{-}, Cl^{-} and CO_3^{-2}) found in natural bone into the hydroxyapatite structure is a way to introduce selective physical, chemical and biological features [5,6]. Meanwhile, chloride ions exist as a trace element in the mineral phase of bone and teeth [7], and they are able to provide an environment on the surface of the bone that activates osteoclasts in the bone resorption process [5]. However, no significant emphasis has been laid on the incorporation of chloride into the structure of hydroxyapatite. It is known that chloride can be incorporated into the lattice structure of hydroxyapatite replacing its hydroxyl group. It is expected that the total replacement of chloride in the structure of hydroxyapatite enhances the local environment acidity which is not favor for tissue engineering applications. Therefore, an understanding on the use of an optimum amount of chloride in the lattice structure of hydroxyapatite is vital.

The properties of apatite nanocrystals can be improved by controlling parameters such as size, distribution and structural morphology [8]. Synthetic apatite nanoparticles can be produced by a number of techniques categorized as dry methods (like mechanochemical methods), wet methods (like precipitation methods), high-temperature process (like pyrolysis), and combination procedures [9,10]. Among various methods, precipitation from solution is the most common synthesis route. Since the temperature does not usually exceed 100 °C in the precipitation method, nanometric-size crystals with different morphologies can

---

*Corresponding author.
Tel.: +98 936 0905246; fax: +98 263 6280033x417.
E-mail addresses: mozafari.masoud@gmail.com, monireh.gan@gmail.com (M. Ganjali).

http://dx.doi.org/10.1016/j.ceramint.2015.07.020
0272-8842/

be prepared. The crystallinity and calcium to phosphorus ratio of the synthesized nanoparticles with this technique strongly depend upon the preparation conditions. It has been frequently reported that this technique can produces nanoparticles lower than those for well-crystallized stoichiometric hydroxyapatite [11,12]. To this end, the present study aimed to use a simple chemical precipitation method for the synthesis of chlorapatite nanopowders. In addition, phase structure, particles morphology and functional groups were investigated by x-ray diffraction technique (XRD), scanning electron microscopy (SEM), and Fourier transform infrared spectroscopy (FTIR) techniques, respectively.

2. Experimental

Chlorapatite nanoparticles were synthesized by precipitation method. For this purpose, 1 l of a 1 M aqueous solution of calcium chloride (Merck Co.) was added into 1 l of a 0.6 M aqueous solution of potassium hydrophosphate (Merck Co.) at 60 °C [13]. The pH of the solution was adjusted to 7 by using potassium hydroxide (KOH), and aged for 30 min in the mother media at room temperature. The precipitated nanoparticles were collected from the bottom of the container. The powders were dried at 100 °C, and then heat-treated at 500, 900, and 1200 °C in order to investigate the effects of heat-treatment process on the structural characteristics of nanocrystalline chlorapatite particles. The samples were characterized by XRD (Philips PW 3710, 30 KV, 35 mA, Cu Kα), SEM (VEGA, TESCAN), and FTIR, before and after calcinations.

3. Results and discussion

3.1. Structural analysis

Fig. 1 shows the XRD spectra of the synthesized samples, prepared by precipitation method, before and after heat-treatment at 500, 900 and 1200 °C. As can be seen in Fig. 1, the samples dried at 100 °C and the samples heat-treated at 500 °C, are both composed of chlorapatite (JCPDS 01-70-1454) and potassium chloride (KCl) (JCPDS 00-041-1476). However, after calcination at 900 and 1200 °C, the KCl peaks disappeared and chlorapatite peaks became clear, and no other crystalline phases were detected. Moreover, the intensity of chlorapatite peaks increased by increasing the heat-treatment temperature indicating that the particles are highly crystalline. Therefore, high temperature treatment caused KCl component to burn out, and the mineral component became re-crystallize [13].

A gradual increase in the crystallite size is expected with increasing in the heat-treatment temperature. The crystallite size and structural strain were calculated using Williamson–Hall formula (Eq. 1) [14]

$$\beta \cos \theta = K\lambda / d + 4\varepsilon \sin \theta \qquad (1)$$

where β is the full width at the half-maximum in radians, ε is the micro-strain and k is the shape factor (about 0.9) [15]. The Williamson–Hall plot has been drawn between $\beta\cos\theta$ vs. $4\sin\theta$, shown in Fig. 2. The average crystallite size was estimated from the intersection with the vertical axis and micro-strain ε from the slope of the line, presented in Table 1 [16]. The crystallite size and lattice strain are two main properties which could be extracted from the peak width analysis [17]. As it can be seen in Fig. 2 and Table 1, the mean crystallite size of the sample dried at 100 °C and the sample heat-treated at 500 °C, are approximately the same, but the sample heat-treated at 500 °C showed a higher micro-strain value. By increasing the heat-treatment temperature to 900–1200 °C, the crystallite size increased significantly. However, the sample treated at 900 °C, has lower micro-strain than the sample treated at 500 °C, which is probably due to the burning out of KCl from the structure, and therefore, the structure relieves from the strain. Moreover, by increasing the heat-treatment temperature to 1200 °C, the micro-strain increased [18].

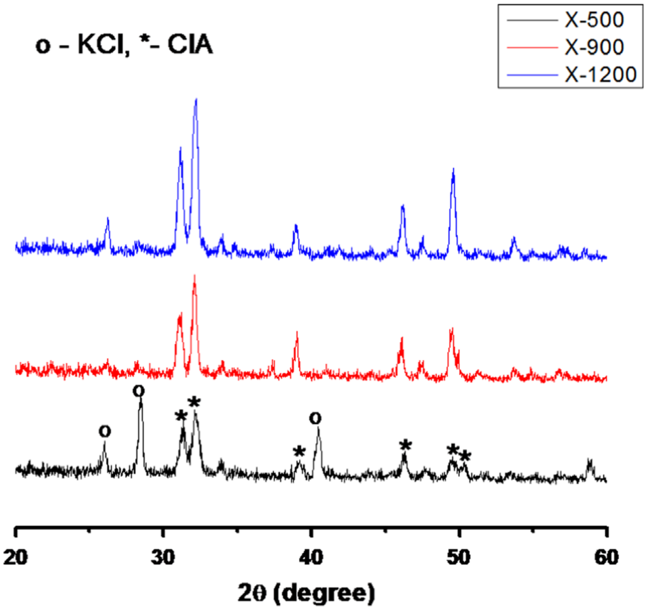

Fig. 1. XRD patterns of the synthesized powders after heat-treatment at 500 °C, 900 °C, and 1200 °C.

3.2. Microscopic observations

Fig. 3 shows SEM micrographs of the synthesized powders before and after heat-treatment at 500, 900 and 1200 °C. As it can be seen, the morphology of the as-received powder without heat-treatment was spherical and by heat-treatment at 500 and 900 °C, the morphology remained spherical but there were a tendency for growing the grains. When the heating temperature increased to 1200 °C, grain growth occurred due to a dramatic decrease in the residual elastic strain [15]. In this situation, the synthesized nanopowders usually show a high tendency to agglomerate, and therefore, the large particles are comprised of polygonal and sphere-like nanoparticles. Therefore, by increasing the heat-treatment temperature, a distribution of small particles and large agglomerates is observed, made from very fine particles [12]. Further, as heating temperature increased, the microstructure of chlorapatite nanopowders became denser with less pores.