Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 8341–8349

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Synthesis and dissolution behavior of nanosized silicon and magnesium co-doped fluorapatite obtained by high energy ball milling

T. Ahmadi[a,*], A. Monshi[a], V. Mortazavi[b], M.H. Fathi[a,b], S. Sharifi[c], B. Hashemi Beni[d], A. Moghare Abed[e], M. Kheradmandfard[a], A. Sharifnabi[f]

[a]*Biomaterials Research Group, Department of Materials Engineering, Isfahan University of Technology, Isfahan 8415683111, Iran*
[b]*Torabinejad Dental Research Center, Department of Operative Dentistry, School of Dentistry, Isfahan University of Medical Sciences, Isfahan 8174673461, Iran*
[c]*W.J. Kolff Institute, Department of Biomedical Engineering, University Medical Centre Groningen, University of Groningen, P.O. Box 196, 9700 AD Groningen, The Netherlands*
[d]*Department of Anatomical Sciences and Molecular Biology, School of Medicine, Isfahan University of Medical Sciences, Isfahan 81746-73461, Iran*
[e]*Dental Implant Research Center, Departments of Periodontics, School of Dentistry, Isfahan University of Medical Sciences, Isfahan 8174673461, Iran*
[f]*Biomaterials Group, Department of Metallurgy and Materials Engineering, Iran University of Science and Technology, Tehran 16844, Iran*

Received 22 December 2013; received in revised form 8 January 2014; accepted 10 January 2014
Available online 17 January 2014

Abstract

Nanosized hydroxyapatite (HA) powders exhibit a greater surface area than coarser crystals and are expected to show an improved bioactivity. In addition, properties of HA can be tailored over a wide range by incorporating different ions into HA lattice. The aim of this study was to prepare and characterize silicon and magnesium co-doped fluorapatite (Si–Mg–FA) with a chemical composition of $Ca_{9.5}Mg_{0.5}(PO_4)_{5.5}(SiO_4)_{0.5}F_2$ by the high-energy ball milling method. Characterization techniques such as X-ray diffraction analysis (XRD), Fourier transformed infrared spectroscopy (FTIR), energy dispersive X-ray spectroscopy (EDX) and transmission electron microscopy (TEM) were utilized to investigate the structural properties of the obtained powders. Dissolution behavior was evaluated in simulated body fluid (SBF) and physiological normal saline solution at 37 °C for up to 28 days. The results of XRD and FTIR showed that nanocrystalline single-phase Si–Mg–FA powders were synthesized after 12 h of milling. In addition, incorporation of magnesium and silicon into fluorapatite lattice decreased the crystallite size from 53 nm to 40 nm and increased the lattice strain from 0.220% to 0.296%. Dissolution studies revealed that Si–Mg–FA in comparison to fluorapatite (FA), releases more Ca, P and Mg ions into SBF during immersion. 175 ppm Ca, 33.5 ppm P and 48 ppm Mg were detected in the SBF containing Si–Mg–FA after 7days of immersion, while for FA, it was 75 ppm Ca, 21.5 ppm P and 29 ppm Mg. Release of these ions could improve the bioactivity of the obtained nanopowder. It could be concluded that the prepared nanopowders have structural properties such as crystallite size (~40 nm), crystallinity degree (~40%) and chemical composition similar to biological apatite. Therefore, prepared Si–Mg–FA nanopowders are expected to be appropriate candidates for bone substitution materials and also as a phase in polymer or ceramic-based composites for bone regeneration in tissue engineering applications.

Keywords: A: Milling; B: X-ray methods; E: Biomedical applications; Fluorapatite; Silicon

1. Introduction

Hydroxyapatite [$Ca_{10}(PO_4)_6OH_2$, HA], a bioactive ceramic, is widely applied in implanting or repairing bones due to its similarity in chemical composition with the inorganic matrix of bone [1]. On the other hand, existence of trace compounds and elements such as CO_3^{2-}, Na^+, K^+, Mg^{2+}, Cl^- and F^- in the structure of biological apatite causes the bioactivity of biological apatite to be superior to pure synthesized HA [2]. Moreover, HA properties, such as bioactivity, biocompatibility, solubility, osteoblastic adhesion and differentiation, can be altered using modification of the composition via ionic substitutions [3].

The role of fluoride in saliva and blood plasma has been shown, and its necessity in dental and skeletal development has

*Corresponding author. Tel.: +98 3113912750; fax: +98 3113912752.
E-mail address: tahmadi56@yahoo.com (T. Ahmadi).

0272-8842/$ - see front matter © 2014 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2014.01.040

also been proved. Fluoride has a great role in suppressing dental caries [4]. Osteoblastic response has been improved in terms of adhesion, differentiation, proliferation and mineralization processes by incorporating fluorine into HA as compared to pure HA [5]. Results have shown that the microhardness of the Mg^{2+}/F^{-} doped nanophase HA is increased by increasing the F^{-} content [6]. Moreover, there is a close relationship between magnesium and mineralization of calcified tissues [7]. Incorporation of Mg into HA modifies the dissolution rate and the biodegradation of related materials [8]. Increasing Mg^{2+} in the Mg^{2+}/F^{-} doped HA results in a decrease in microhardness values due to the formation of β-TCP phase [6]. Silicon (Si) is the essential element for the growth and development of the bone, teeth and some invertebrate skeletons. Silicon is localized in the osteoid. In the bioactive silicate glass ceramics, the silanol groups acts as catalysts for apatite nucleation [9]. Silicon substituted HA was reported by Gibson [10]. Si has a critical role in the bone calcification process. The incorporation of Si into the HA enhances the formation of a surface apatite layer in an artificial physiological solution [11].

With regard to the aforementioned points, achieving an ion doped HA with structural properties similar to biological apatite is of great importance since this would yield a bioactive ceramic with great biological properties. There are several methods such as precipitation method, hydrothermal synthesis, hydrolysis, mechanochemical activation or mechanical alloying, and sol–gel route to synthesize hydroxyapatite [12–15]. Mechanochemical activation by high energy ball milling is an effective method for preparing intermetallic compounds, composite materials, supersaturated solid solutions, nanocrystalline and amorphous materials. This method is a simple, powerful, and economical tool for the fabrication of several advanced materials [16]. Effective parameters in this method include high energy ball mill rotation speed, clash frequency, weight ratio of balls to powder, milling atmosphere, purity, size and shape of powder particles, milling time and temperature, and size and number of balls [17]. The aim of this work was to synthesize and characterize nanosized silicon and magnesium co-doped fluorapatite (Si–Mg–FA) powder via the mechanochemical activation method using high-energy ball milling. This attractive and innovative idea leads to the synthesis of a biomaterial via a simple method to enhance the bone tissue growth rate, and thereby improves bone fixation and enhances the lifetime of the implants. This nanopowder can also be used as one phase in polymer or ceramic-based scaffolds for bone regeneration in tissue engineering applications.

2. Materials and methods

2.1. Powder preparation

A mixture of phosphorous pentoxide (P_2O_5, Merck), calcium hydroxide ($Ca(OH)_2$, Merck), magnesium hydroxide ($Mg(OH)_2$, Merck), calcium fluoride (CaF_2, Merck) and silicon oxide (SiO_2, Sigma-Aldrich) powders was mechanochemically activated using a high energy planetary ball mill (Fretch Pulverisette 5) with a 125 ml zirconia vial and four 20 mm diameter zirconia balls at ambient temperature. Mechanochemical activation was performed using ball/powder mass ratio of 25:1 and rotation speed of 250 rpm. Ball milling was executed for 2, 5, 8, 12, 15 and 20 h. The designated degree of Ca^{2+} substitution by Mg^{2+} and PO_4^{3-} by SiO_4^{4-} in the mixture was indicated by the x value in the general formula of FA ($Ca_{10-x}Mg_x(PO_4)_{6-y}(SiO_4)_yF_2$), where x and y equal 0.5. The obtained powders with only Mg substitution were named Mg–FA, and the ones with both Si and Mg substitution were named Si–Mg–FA.

2.2. Powder characterization

Phase structure analysis of FA, Mg–FA and Si–Mg–FA was carried out by X-ray diffraction (XRD, Philips X'Pert-MPD) with Cu K_α radiation ($\lambda = 0.15418$ nm). The obtained experimental patterns were compared with the standards compiled by the Joint Committee on Powder Diffraction and Standards (JCDPS). The broadening of peaks in XRD can be used to estimate the crystallite size of the obtained powders based on the Scherrer equation [18],

$$t = \frac{0.9\lambda}{B\cos\theta} \tag{1}$$

where t is the crystallite size, λ is the wavelength of X-ray radiation (0.154 nm for Cu K_α), B is the full width at half maximum (FWHM) of diffraction peaks and θ is the diffraction angle. Moreover, the lattice strain of samples was calculated using the equation presented by Stokes and Wilson,

$$\varepsilon = \frac{B}{4\tan\theta} \tag{2}$$

where ε is the lattice strain, B is the FWHM of diffraction peaks and θ is the diffraction angle. For this purpose, three diffraction peaks, which had the advantage of being well-separated and high intensities, were chosen for the measurement. The crystallinity degree of samples (X_c) corresponding to the fraction of crystalline phase present in the examined volume was evaluated by the following equation [19]:

$$X_c = 1 - \left(\frac{V_{112/300}}{I_{300}}\right) \tag{3}$$

where I_{300} is the intensity of (300) reflection of HA and $V_{112/300}$ is the intensity of the hollow between (112) and (300) reflections. Lattice parameters (c and a) were calculated using XRD patterns and the cell parameters refinement software (Celref V.3). In addition, the unit cell volume of the obtained powder was calculated using Eq. (4) [18],

$$V = \frac{\sqrt{3}a^2c}{2} \tag{4}$$

The functional groups of prepared powders were analyzed by Fourier transformed infrared (FTIR, Bomem MB 100) spectroscopy. The spectra were recorded from 4000 to 400 cm^{-1} wavenumber with a resolution of 1 cm^{-1}.

Chemical composition of the samples and distribution of constitutive elements were studied and evaluated using energy