

Effects of manganese doping on properties of sol–gel derived biphasic calcium phosphate ceramics

I. Sopyan^{a,*}, S. Ramesh^b, N.A. Nawawi^a, A. Tampieri^c, S. Sprio^c

^a *Department of Manufacturing and Materials Engineering, Faculty of Engineering, International Islamic University Malaysia (IIUM), PO Box 10, 50728 Kuala Lumpur, Malaysia*

^b *Centre of Advanced Manufacturing and Materials Processing (AMMP), Department of Manufacture and Engineering Design, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia*

^c *Institute of Science and Technology for Ceramics (ISTEC), Via Granarolo 64, 48018 Faenza, Italy*

Received 13 May 2011; received in revised form 31 May 2011; accepted 15 June 2011

Available online 23 June 2011

Abstract

We have investigated the effect of manganese (Mn) doping on properties of nanosized biphasic calcium phosphate powders and their dense bodies. Manganese levels of 0.6, 1.3, 1.9, 4.3, 7.0 and 11.9 at.% were successfully incorporated into biphasic calcium phosphate via a sol–gel route. The prepared powders were calcined at temperatures of 500–1200 °C. The X-ray diffraction analysis revealed that a mix phase comprising of hydroxyapatite and β -tricalcium phosphate were present, however the content of each phases in the structure was affected by the Mn content. The studies found that the largest portion of β -tricalcium phosphate was detected at 4.3 at.% Mn doping. The incorporation of Mn has also greatly increased the crystallinity of the biphasic calcium phosphate powder due to progressive densification of particles. Characterization on their sintered dense bodies showed that manganese concentration affected the physical properties of the dense bodies. The highest density was found for 4.3 at.% Mn doped biphasic calcium phosphate sintered at 1300 °C.

© 2011 Elsevier Ltd and Techna Group S.r.l. All rights reserved.

Keywords: Mechanical properties; Biphasic calcium phosphate; Manganese doping; Sol–gel; Physical properties; Dense bodies

1. Introduction

Hydroxyapatite (HA), $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, whose chemical composition close to the mineral phase of bone is well known for its excellent biocompatibility with bone tissue. Representing ca. 69 vol.% of human bone, the mineral component of bones consists of poorly crystalline, Ca-deficient HA substituted partially with sodium, magnesium, citrate, carbonate and fluoride ions [1]. Together with β -tricalcium phosphate (β -TCP), $\text{Ca}_3(\text{PO}_4)_2$, HA has been for nearly three decades the most extensively used substitution materials for artificial bone grafts. Although many problems concerning infective risk, mechanical and biological stability, compatibility, storage and costs still remain, HA materials have been applied in orthopaedic as block implants, porous scaffolds, granules or coating materials [2].

Biphasic calcium phosphate (BCP) ceramics, a mixture of HA and β -TCP, on the other hand, have also received much attention in the field of biomaterials. These materials, regarded as suitable for synthetic bone applications, are considered superior when compared to either single phase HA or β -TCP components because of their unique dissolution characteristics which in turn promotes new bone formation at the implant site [3]. These two compounds have different resorbing capacities. β -TCP degrades about 20 times faster than HA, therefore for practical purposes, HA is considered as non-degradable while β -TCP is resorbable [4]. Although single phase HA is stable, it is not biodegradable and therefore the implant could not be replaced by hard tissues in the body. Moreover, its application is constrained to non-load bearing region in clinical orthopaedic and dental applications due to its brittleness and low fracture toughness [5]. In the case of β -TCP, it was found that its application as a biomaterial for alveolar ridge augmentation resulted in a very high rate of biodegradation [6] which makes it unfavourable too. In addition, a disadvantage of β -TCP as

* Corresponding author. Tel.: +60 361964592; fax: +60 361964477.

E-mail address: sopyan@iium.edu.my (I. Sopyan).

an implant material is its much lower low mechanical strength than HA. Therefore, it is envisaged that a mixture of HA and β -TCP would be appropriate as these two materials qualities off set each other's weaknesses. With a combination of enhanced bioactivity and mechanical stability difficult to achieve in single phase materials, characterization of BCP is of great importance and its characterization has consequently been well studied recently [7].

The inclusion of trace metal elements has a significant role in improving the physical and/or chemical properties of bioceramics. Many trace metal elements have been incorporated into the HA phase. In this work, manganese (Mn) was incorporated into the BCP as a sintering additive to improve the mechanical properties of dense BCP. Although numerous works have reported the significant role of manganese oxide in promoting densification in other ceramics systems, the inclusion of Mn in BCP has not been studied extensively [5]. The doping process were carried out chemically via an adapted sol–gel technique rather than by a physical method as reported by other researchers such as wet milling [5], mixing in an agate mortar [8] and ball milling [9].

The effect of Mn as a dopant on the stability and particle growth of HA has been investigated by some researchers. This dopant has been doped into calcium phosphate based materials by solid state reaction [10] and precipitation methods [10,11]. The motivation for the addition of Mn^{2+} ions to HA was due to the fact that divalent Mn^{2+} influences the activation of integrins, a family of receptors that mediate cellular interactions with the extracellular matrix and cell surface ligands [10,12]. The ligand affinity increases in the presence of Mn, resulting in the promotion of cell adhesion. In one study, manganese in the bone was found to cause a decrease in bone resorption [13]. It is also reported that Mn functioned as calcination and sintering additives of BCP powders without producing other secondary phases like α -TCP and CaO [5]. The formation of the α -TCP phase during the sintering process is not preferred as it induces micro-cracks, which eventually reduce the mechanical properties of the sintered specimens.

The doping of Mn into BCP is expected to show improvements in physico-chemical properties of BCP which will lead to improved biological performance in terms of bioactivity and bone mineralization. In a preliminary report, we have briefly described the synthesis of manganese doped BCP powder via a sol–gel technique [14]. Sol–gel method has been for the first time applied to synthesize hydroxyapatite powder by Sakka and co-workers using metal alkoxides as the monomers [15]. In this work, calcium nitrate tetrahydrate, manganese nitrate tetrahydrate, and di-ammonium hydrogen phosphate were used as the reactants. The calcined sol–gel powders were then subjected to uniaxial pressing to obtain the dense Mn-BCP bodies and then sintered at various temperatures. We present here the interesting effects of Mn content on phase behaviour, physico-chemical properties and the microstructure of the biphasic calcium phosphate (BCP) powder as well as of their dense bodies.

2. Experimental procedure

2.1. Preparation of powder

Calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$], di-ammonium hydrogen phosphate [$(NH_4)_2HPO_4$] and manganese (II) nitrate tetrahydrate [$Mn(NO_3)_2 \cdot 4H_2O$] were used as starting chemical precursors. Ethylenedinitrilotetraacetic (EDTA) acid (Titriplex II) (Merck kGaA, Germany) was added to 250 mL ammonium solution (11% solution, R&M Chemicals, UK) heated to 60 °C while stirring until it dissolved. In this technique, EDTA was used as chelating agent to prevent immediate precipitation of calcium compounds in the course of gel formation. A 100 mL aqueous solution of 65 g $Ca(NO_3)_2 \cdot 4H_2O$ (Merck kGaA, Germany) was then poured into the mixture followed by the dopant, 50 mL $Mn(NO_3)_2 \cdot 4H_2O$ (Merck kGaA, Germany). The addition of the $Mn(NO_3)_2 \cdot 4H_2O$ was based on the desired percentage (at.%) of manganese with regard to calcium to be doped into the BCP. The phosphorus precursor, 20 g di-ammonium hydrogen phosphate [$(NH_4)_2HPO_4$] (Merck kGaA, Germany) and 22.6 g urea (R&M Chemicals, UK), which acts as gelling agent and ammonium donor agent were subsequently added. The mixture was then refluxed at 100 °C for 4–5 h while stirring until a white gel of the Mn-BCP mixture was obtained. The urea in the solution was homogenised with regard to concentration and pH by stirring. The nitrate ion removal, which involved the white gel phase passing through a transparent sol phase, was done in only one reactor. The transparent sol obtained was not transferred to another reactor for the gelling process to avoid any possibility of contamination while transferring. The gel obtained was then dried at 340 °C in ambient air and subsequently subjected to heat treatment under flowing air. The synthesis of Mn-BCP was carried out at six different molar concentrations of Mn that is 0.6 at.%, 1.3 at.%, 1.9 at.%, 4.3 at.%, 7.0 at.% and 11.9 at.%.

2.2. Preparation of dense samples

The pure BCP calcined powder and four Mn doped BCP powders with Mn levels of 0.6 at.%, 1.9 at.%, 4.3 at.% and 11.9 at.% were chosen to be directly compacted into disks with diameter 20 mm, at 200 MPa using Uniaxial Press (Carver, 4350L). The green bodies were then sintered in a furnace (Protherm, PLF 160/5) at temperatures ranging from 900–1400 °C at a heating rate of 2 °C/min and with a 2 h holding time.

2.3. Analytical characterization

The synthesized powder was calcined at 900 °C to reach the optimum crystalline phase and ensure complete removal of organic and inorganic substance. The calcinations were carried out in the furnace (Protherm, PLF 160/5) with a heating rate of 10 °C/min to achieve the predetermined temperature followed by a holding time of 3 h before being cooled to room temperature in the furnace. In addition, the 4.3 at.% Mn-BCP black gel was calcined at different temperatures ranging from

Download English Version:

<https://daneshyari.com/en/article/1463063>

Download Persian Version:

<https://daneshyari.com/article/1463063>

[Daneshyari.com](https://daneshyari.com)