Powder Technology 257 (2014) 74–82

Contents lists available at ScienceDirect

Powder Technology

journal homepage: www.elsevier.com/locate/powtec

Phase transformation behavior of spherical tricalcium phosphate micro-granules prepared by a jet wheel impact atomization and calcination process

Dong-Hyun Kim [a], Seong Soo Park [b], Ju Dong Lee [c], Hong-Chae Park [a], Seog-Young Yoon [a,*]

[a] School of Materials Science and Engineering, Pusan National University, Busan 609-735, South Korea
[b] Division of Applied Chemical Engineering, Pukyong National University, Busan 608-739, South Korea
[c] Korea Institute of Industrial Technology, Busan 618-230, South Korea

ARTICLE INFO

Article history:
Received 17 October 2013
Received in revised form 6 February 2014
Accepted 20 February 2014
Available online 28 February 2014

Keywords:
Ceramics
Calcium phosphate
Spherical micro-granules
Phase transformation
Microporosity

ABSTRACT

Spherical tricalcium phosphate (TCP) micro-granules were prepared using a jet wheel impact atomization and calcination process. Spherical TCP granules were obtained which can exhibit phase transformation between the alpha and beta polymorphs as a function of the heating temperature. The progressive changes in the phosphate group of TCP granules were attributed to the phase transformation. Consequently, such structural changes in the TCP micro-granules can be used to control the dissolution and degradation of TCP through the controlled density and microporosity of the micro-granules.

1. Introduction

Calcium phosphate (CaP) materials have attracted considerable attention as a bone graft substitute in dental and orthopedic reconstructive medicine because of their excellent biocompatibility, bioactivity, and osteoconduction characteristics [1–3]. Different types of CaP ceramics, such as hydroxyapatite (HA), beta-tricalcium phosphate (β-TCP), biphasic calcium phosphate (BCP), amorphous calcium phosphate (ACP), and calcium-deficient HA (CDHA), have been studied as scaffolds, organic/inorganic biocomposites in hard and soft tissue engineering [4–8]. Among the different compositions of CaP materials, beta-tricalcium phosphate (β-TCP, β-$Ca_3(PO_4)_2$) is a bioceramic material that plays an important role in the biomineralization processes of bone formation because of its excellent biocompatibility, osteoconductivity and bioresorbability in the human biological environment [9–12].

Generally, TCP has three polymorphs: β-TCP, which is stable at temperatures less than ~1180 °C, and α-TCP and α′-TCP, which are stable at temperatures above ~1430 °C [13–15]. Despite having the same chemical composition, α-TCP and β-TCP show considerably different material properties, such as the crystallographic form, chemical stability, mechanical strength, and proper bioresorption rate. Such differences in TCP can be applied to the biomaterial properties, such as the different reactivity of α-TCP and β-TCP in biological aqueous systems, and the differences in biodegradability can affect the behavior of biomaterials when implanted into the animal body [16,17]. Therefore, both monophasic α-TCP and β-TCP are used in several clinical applications in dentistry and orthopedics because of their biological properties [18,19]. On the other hand, the phase transformation of TCP during the calcination process often hinders the densification of a sintered-bulk body and induces micro-cracking of the sample due to the difference in density generated by volumetric expansion of the crystal unit cell between the β- and α-phases [20–22]. For this reason, bioceramic applications of TCP might be effective in using powders or granules as bone cement materials than dense bulk typed products. In addition, β-TCP is applied as a component of several commercial biphasic bioceramic composites with a powder or granule type, and α-TCP is used as the major constituent of the powder component of various hydraulic bone cements [23–25]. Therefore, it is important to better understand the phase transitions of such materials to produce calcium phosphate materials with the required purity and control of the phase composition.

Spherical calcium phosphate micro-granules have attracted considerable interest for use as a bone grafting cement material in non-load-bearing situations, which allows better filling of irregular defects as well as high packing into damaged bone tissues [26,27], because the bio-resorption rate of porous granules is predicted to be faster than that of dense blocks. In addition, uniformly packed spheres with a homogenous pore distribution have been reported to increase the rate of bone ingrowth. Therefore, spherical calcium phosphate micro-granules can be used either as bone grafting materials or as carriers for

* Corresponding author. Tel.: +82 51 5102487; fax: +82 51 5120528.
E-mail address: syy3@pusan.ac.kr (S.-Y. Yoon).

http://dx.doi.org/10.1016/j.powtec.2014.02.055
0032-5910/

drugs or cells [28–31]. In addition, using a biphasic tuning system (α- and β-phases), the porosity of TCP can be controlled using a granulation and sintering process, which can cause ripple effects in the clinical bone graft efficacy in several applications in dentistry, maxillo-facial surgery and orthopedics. Porous CaP granules can be prepared using a vapor phase method, spray pyrolysis, chemical solution routes, etc. [32–36]. Among these methods, the spray drying atomization process is a promising approach for large-scale production and control of the structure and morphology of the particles [37]. In this process, a water or organic based slurry is transformed to a dry powder by atomization by spraying into a hot drying medium. On the other hand, many studies have attempted to control the microporosity of spherical granules in porous calcium phosphate materials prepared by a spray drying-wheel impact atomization process.

This paper reports the preparation, phase transformation behavior, and tailoring of the microporous properties of TCP spherical micro-granules obtained using a spray dryer based on a jet wheel impact atomization and calcination process. The difference of density and atomic ordering of TCP could be observed by the composition of relative crystal phase via phase transformation.

2. Experimental procedure

2.1. Preparation of TCP micro-granules

Calcium carbonate ($CaCO_3$, Junsei Chemical Co., CAS No. 471-34-1, purity 99.5%) and ammonium dihydrogen phosphate ($NH_4H_2PO_4$, Junsei Chemical Co., CAS No. 7722-76-1, purity 99%) were used as the starting materials to synthesize the precursors of TCP. The starting materials for β-TCP were co-mixed and adjusted to a 1.5 Ca/P molar ratio. After preparing the precursor powders, they were ground by attrition milling (RPM speed = 400) with deionized water and organic additives [5 wt.% binder (HS-BD 25, San Nopco Korea), a 1 wt.% dispersant (CERASPESE 5468CF, San Nopco Korea) and 1 wt.% defoamer (HS-ANTIFOAMER 551, San Nopco Korea)] for 4 h using zirconia balls. The as-prepared slurries were spray-dried using a jet wheel impact atomizer system (DJE-003R, Dong-Jin Spray Drying Technology, Korea) in co-current flow with a slurry feed rate of 40 ml/min. In the atomizer system, the inlet temperature ranged from 200 to 220 °C, and the temperature at the exit of the spray dryer was varied from 100 to 140 °C. The particle size distribution and yield (wt.%) of a typical product were determined using the sieving technique. To observe the effects of the granules by a sintering process, the spray-dried granules were sorted using sieves (mesh nos. 200 and 325) for selection at the appropriate size (45–75 μm). The as-sieved granules were calcined at temperatures ranging from 1000 to 1400 °C for 2 h to examine the phase transformation behavior of the TCP micro-granules.

2.2. Characterization of TCP micro-granules

The phases of the as-calcined granules were examined by X-ray diffraction (XRD, Philips X'Pert Pro) at 40 kV and 40 mA with a scanning speed of 1°/min. Standard Bragg–Brentano geometry was applied with a $K_{\alpha 1}$ monochromatic beam from the Cu anode. The phase identification,

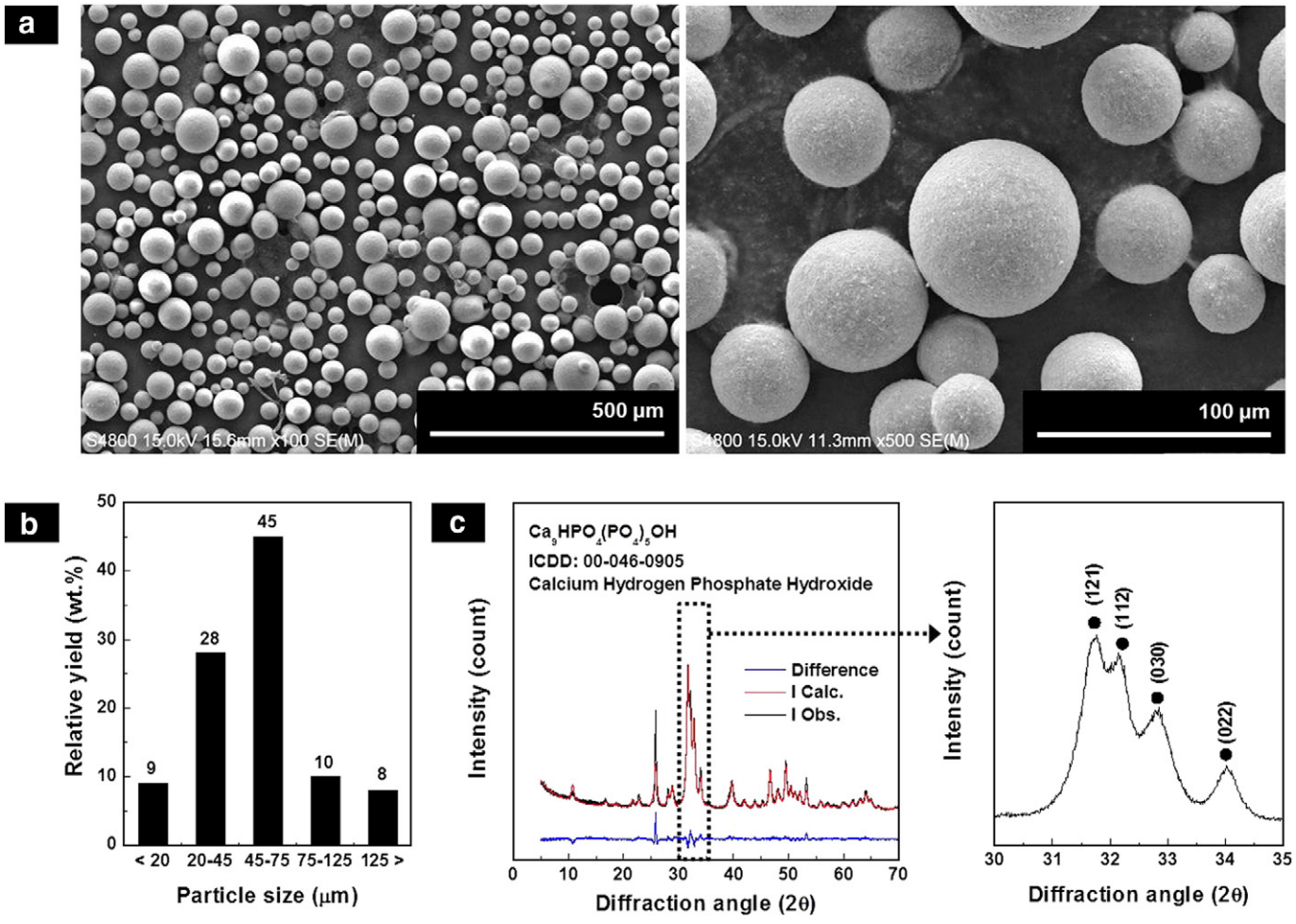

Fig. 1. Characterization of the spray dried precursor granules; (a) FE-SEM image, (b) particle size distribution, and (c) XRD pattern.