Materials Science and Engineering C 67 (2016) 345–352

Contents lists available at ScienceDirect

Materials Science and Engineering C

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

Synthesis and characterization of sintered beta-tricalcium phosphate: A comparative study on the effect of preparation route

Rupita Ghosh *, Ritwik Sarkar

Department of Ceramic Engineering, National Institute of Technology Rourkela, Odisha 769008, India

A R T I C L E I N F O

Article history:
Received 2 March 2016
Received in revised form 11 April 2016
Accepted 2 May 2016
Available online 07 May 2016

Keywords:
Beta-tricalcium phosphate
Calcination
Sintering

A B S T R A C T

Beta-tricalcium phosphate (β-TCP) was prepared by three different routes namely, wet chemical coprecipitation, sol-gel and solution combustion synthesis. The synthesized powders were calcined at different temperatures and characterized for phase evolution study, thermal analysis, Fourier transform infrared (FTIR) spectroscopy, microstructural study for comparative analysis. The optimal thermal treatment required to prepare pure β-TCP powders was determined and after calcination of the synthesize powders prepared by different routes, pure β-TCP was obtained. The sintering temperature required to prepare fully dense β-TCP completely free from α-form was identified. The powders were then used to make dense and compact bodies sintered at 1200 and 1250 °C. The sintering behaviour of the dense bodies was analysed using dilatometry, densification and microstructural study. It was found that the pellet prepared from powder synthesized via co-precipitation route attained maximum density compared to the pellets prepared from powders synthesized via sol-gel and solution combustion route.

1. Introduction

Calcium phosphate (CaP) bioceramics are widely used in surgical fields as orthopedic and dental implants due to its excellent osteoconductivity and ensuring colonisation of material by new bone, bioactivity and biocompatibility with surrounding living tissue [1,2]. These properties of CaPs are mainly because of its close resemblance to the inorganic component of bone and teeth. Among the CaPs, β-TCP has excellent bioresorbability in the human biological environment that allows progressive replacement of the natural host tissue with the gradual degradation of the implanted material making it ideal for bone reconstruction [3,4].

β-TCP can be synthesized by different chemical routes, among which solid state synthesis [5] and wet chemical precipitation are the conventional methods. The different routes have different advantages and disadvantages. Wet chemical coprecipitation is preferred because of its simplicity of experimental operations, low operating temperature and high yields of pure products at a reasonable cost but sometimes the incomplete reaction and precipitation results in the alteration of stoichiometry which results in undesirable impurities [6,7]. Sol-gel and solution combustion methods are also used to synthesize β-TCP but not reported much. Sol-gel synthesis is preferred due to its excellent homogenous molecular mixing and the ability to generate nano-sized particles compared to other alternatives. But the starting material is very costly and often the precursor formed is extremely moisture sensitive [8,9]. Solution combustion is a rapid exothermic and energy-saving technique involving a self-sustaining chemical reaction between an oxidant and a suitable organic fuel, in an aqueous solution. Exothermic reaction supplies the heat required to sustain the combustion and once initiated no external heat source is needed [10–12]. The various synthesis methods have a varying effect on the particle size, crystallite size, densification behaviour, shrinkage and morphology.

Literature provides much information on the synthesis and characterization of the β-TCP powder, the influence of processing parameters on the powder. But so far the study on the sintering behaviour of β-TCP ceramic, and the influence of synthesis route and the powder characteristics on the sintered body are few. β-TCP ceramics should be sintered at a lower temperature than that of phase transition to α-TCP, nearly 1200 °C. Fully densified β-TCP was not obtained at below 1200 °C in any report so far [13]. Studies have shown that to densify β-TCP up to 95% calcium pyrophosphate doping is done which also prevents transformation of pure β-TCP to α-TCP at 1200 °C making it denser [14]. However, the pyrophosphate phase has a harmful effect due to the enlargement of the grain of sintered material which is detrimental to mechanical properties and generates significant cracking. The presence of small quantity of hydroxyapatite phase inhibits the particle enlargement and thus, allows a better densification of about 99% or above [15]. Fully dense and translucent β-TCP totally free from α modification was successfully prepared by hot-pressing [16]. The sintering ability of the nano-size β-TCP powders was observed to be much higher than

---

* Corresponding author.
E-mail address: rupita.ghosh@gmail.com (R. Ghosh).

http://dx.doi.org/10.1016/j.msec.2016.05.029
0928-4931/

the micron size β-TCP powders. Using nano-size β-TCP powders as raw materials is an effective way to obtain dense ceramics [17]. For surgical β-TCP implants very high mechanical strength is desirable for which the ceramic must achieve high densification. Therefore, the main objective of the study is to produce dense β-TCP implant and the effect of synthesis route on densification.

The present study aimed to focus on the synthesis of pure phase β-TCP via different routes and calcination and fabrication of dense bodies from the synthesized calcined powders. The effects of different synthesis routes on the calcination, phase evolution, morphology of the calcined powders are studied. As well as, the various effects on the densification, shrinkage, microstructure of the dense sintered β-TCP pellets were characterized.

2. Experimental

β-TCP was prepared by three different routes. For all the synthesis routes the Ca/P ratio of the starting precursor powder was maintained at 1.5. All the reagents used for the synthesis were of analytical grade.

2.1. Wet chemical precipitation

In this method, calcium nitrate tetrahydrate [$Ca(NO_3)_2 \cdot 4H_2O$] (99% purity, Loba Chemie, India) and diammonium hydrogen phosphate [$(NH_4)_2HPO_4$] (>99% purity, Loba Chemie, India) solution was mixed and stirred. The solution turned turbid immediately which was made transparent by adding concentrated HNO_3 (69% concentration, Loba Chemie, India). The ammonium (NH_4OH) (25% concentration, Loba Chemie, India) solution was then added dropwise to maintain the pH above 10. Stirring was continued for 2 h, and the precipitate was allowed to settle for overnight. The precipitate was filtered, dried and finally calcined. The process is followed as carried out in the previous work [18].

2.2. Sol-gel

Calcium nitrate tetrahydrate, citric acid (>99.5% purity, Loba Chemie, India) and diammonium hydrogen phosphate were added one by one in distilled water. The citrate to nitrate ratio in the mixed solution was 1:1. Concentrated HNO_3 was added dropwise to maintain the pH between 2 and 3. The reaction was conducted in an acidic medium to prevent precipitation before gel formation or the combustion starts. The mixed solution was heated at 70–80 °C. Simultaneously vigorous stirring was also continued for 3–4 h until the reaction becomes dehydrated and transforms into a transparent viscous gel. On further heating, the gel was calcined to yield black ash which on calcination produced phase pure β-TCP.

2.3. Solution combustion synthesis

In this method, NH_4OH solution basic medium was used as the solvent. The solution was heated to 60 °C in which EDTA (>98% purity, Loba Chemie, India) powder was dissolved. Subsequently, $Ca(NO_3)_2 \cdot 4H_2O$ solution was added dropwise followed by $(NH_4)_2HPO_4$ and urea (>99% purity, Loba Chemie, India) powder. EDTA was used as a chelating agent to prevent precipitation in the course of gel formation and urea as a gelling and ammonium donor agent. The solution mixture was heated to 100 °C and stirred for 2 h. The solution gradually turned turbid and thicker resulting in the formation of a dehydrated gel. The gel was dried at 70 °C for 24 h and finally calcined.

2.4. Characterization of calcined powders and preparation of sintered bodies

The powders obtained after synthesis were calcined at different temperatures from 600 °C up to 1300 °C. The phase evolution of the calcined powders was studied using powder X-ray diffractometer (Rigaku, Ultima IV, Japan) with Cukα = 1.5418 Å radiation generated at a voltage of 40 kV and a current of 40 mA. The radiation scanned the diffraction angle (2θ) between 20° and 50° with a step size of 0.05° per second. Differential scanning calorimetry (DSC) and thermogravimetric (TG) analysis were done using a thermal analyser (Netzsch, 449C, Germany). The functional groups were identified from FTIR spectra taken in an FTIR spectrometer (PerkinElmer, Spectrum Two 95277) using potassium bromide (KBr) pellet. To make dense bodies, the powders were mixed with 6% PVA (4 wt.%) and given shapes by hydraulic pressing in tool-steel dyes of 15 mm diameter and sintering was done at 1200 °C and 1250 °C. The bulk density and apparent porosity of the sintered bodies were measured using Archimedes principle. Linear dimensional changes of the samples with increasing temperature were studied by using a horizontal dilatometer till 1250 °C (Netzsch 409C, Germany). Morphology of the calcined powders and dense bodies was observed under field emission scanning electron microscope (FESEM) (FEI Nova Nano 450, USA). Mechanical properties of the sintered samples of different preparation routes were evaluated by measuring the microhardness of the samples in a Vickers microhardness tester (LECO Corporation, USA) at a load of 50 g for 15 s. Any data represented in the paper is an average of 5 individual samples.

2.5. Bioactivity study

From the above study, the optimized batch was taken for bioactivity study in SBF (Simulated Body Fluid) to evaluate the bone-like apatite formation on the sintered samples. SBF is a solution in which the inorganic ion concentration and pH is almost equivalent to that of human blood plasma. SBF was prepared according to Tas et al. [19] formulation (pH of 7.4 at 37 °C). The sintered samples were immersed in SBF for 7, 14 and 21 days. The surface morphology of the immersed samples

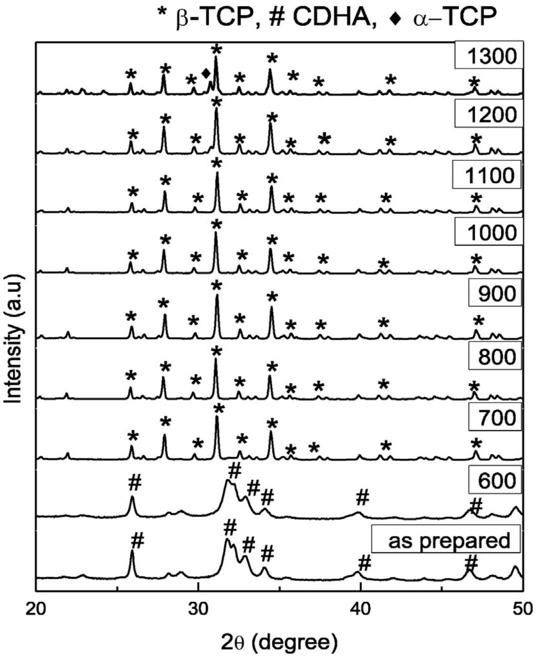

Fig. 1. XRD analysis of β-TCP powder synthesized by wet chemical precipitation method calcined at different temperatures.