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Dense fine-grained biphasic calcium phosphate (BCP) bioceramics designed by two-step sintering

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Abstract

In this study, dense, fine-grained biphasic calcium phosphate bioceramics were designed *via* the two-step sintering method. The starting powder was nanosized calcium-deficient hydroxyapatite, whose phase composition, average particle size and morphology were characterized by XRD, FTIR, Raman spectroscopy, laser diffraction and FE-SEM. The phase transformations of the initial powder during heating up to 1200 °C were examined using TG/DSC. At first, conventional sintering was performed and the recorded shrinkage/densification data were used to find out the appropriate experimental conditions for two-step sintering. The obtained results show that two-step sintering yields BCP ceramics, consisting of hydroxyapatite and β-TCP, with full dense, homogeneous structure with average grain size of 375 nm. Furthermore, BCP ceramics obtained by the two-step sintering method exhibit improved mechanical properties, compared to conventionally sintered BCP.

Keywords: Grain growth; Microstructure-final; Apatite; Two-step sintering

1. Introduction

Synthetic calcium phosphate ceramics (CaP) are widely studied as implant materials for bone tissue reconstruction because of their chemical similarity with natural bone tissue and excellent biocompatibility. There are different kinds of CaP bioceramics, with different composition and physical properties. Hydroxyapatite ($Ca_{10}(PO_4)_6(OH)_2$, HAp), represents the stable phase, with very slow bioresorbility rate. Dense HAp is surface-reactive and can be directly attached to the bone through chemical bonding called bioactive fixation. On the contrary, beta tricalcium phosphate, (β-$Ca_3(PO_4)_2$, β-TCP), is a bioresorbable ceramic, on which place, natural bone can ingrow after the implantation. Which type of CaP bioceramics will be used for the implantation depends on whether bioactive or bioresorbable ceramic is needed.[1,2] The concept of biphasic calcium phosphates (BCP), consisting of HAp and β-TCP ceramics, was developed by Daculsi et al.[3] The aim of their approach was to provide an optimal ratio of bioactive/bioresorbable ceramics within the implant that would allow natural bone ingrowth (osteogenesis) in the place of the implanted material while making chemical bonds between the implant material and the bone. The contribution of β-TCP is to dissolve faster than HAp in a biological environment, followed by the precipitation of carbonated hydroxyapatite similar to the biological bone mineral at the implant/tissue interface. The events that occur at the bioceramic/bone interface are dynamic physico-chemical processes, including crystal–protein interactions and cell and tissue colonization.[3–6] The presence of β-TCP could be beneficial due to its better protein adsorption capacity compared to pure HAp.[7] By tailoring the HAp/β-TCP ratio, it is possible to control the biodegradation rate, where a larger amount of β-TCP would increase the overall resorbility.[8] BCP ceramics can be prepared by mechanical mixing of HAp and β-TCP or through decomposition of calcium-deficient hydroxyapatite (CDHAp) by sintering above 700 °C.[9] The second procedure seems to be better because the mixture of phases on the atomic level leads

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to an increased purity, conserved bioactive and biodegradable properties and better mechanical characteristics,[10] as well as an improved sintering behaviour.[11] The extent of decomposition depends on the initial Ca/P ratio in the starting CDHAp powder and the sintering temperature.[4] Generally, CaP ceramics have poor mechanical properties that do not allow their use for load-bearing applications.[12] A few studies have shown that the mechanical properties of HAp-based ceramics, like hardness and fracture toughness, can be improved by decreasing the grain size to the nanometer level, while attaining a dense and uniform microstructure.[13,14]

Sintering is a complex process, involving the evolution of the microstructure through the action of several different transport mechanisms (surface diffusion, evaporation–condensation processes, volume diffusion, grain boundary diffusion, etc.).[15,16] An important processing goal is to obtain a uniform microstructure, with a high density and the desired grain size.[17] However, producing dense BCP ceramics with a fine uniform microstructure by pressureless sintering does not seem to be a routine process because BCP shows lower sinterability than pure HAp.[13,18] During the initial stage of sintering, the particle coalescence is significant, which difficults further densification process,[18] requiring higher sintering temperatures and leading to displacive β- to α-TCP transformation at temperatures above 1125 °C.[12] This could be detrimental for the further sintering of BCP ceramics because of both, grain growth and a slower densification process.[18,19]

Other pressureless sintering techniques, like microwave sintering, result in a decrease of the sintering temperature, but that is not enough to obtain a dense specimen with fine and uniform microstructure.[19] Hot pressing could be a promising method for obtaining highly dense, nanostructured BCP ceramics[20]; nevertheless the disadvantage of these sintering techniques is the sophisticated equipment, their high cost and a limited number of samples that can be simultaneously processed, still keeping these techniques away from industrial applications. One of the approaches enabling the control of the sintering process of BCP ceramics is the addition of another phase, like MgO, which is found to stabilize the β-TCP phase and improve densification; however, the obtained microstructure is not very uniform because of the bimodal grain size distribution.[21] The substitution of naturally occurring ions, like Na^+, $Mg^{2+}$and K^+, improved the stabilization of the β-TCP phase, too.[22] Also, it should be very careful in using additives because the addition of more amount of the other phase than critical could yield negative effects.[21]

Chen and Wang have proposed a novel pressureless two-step sintering (TSS) method which exploits the difference in kinetics between the grain boundary diffusion and grain boundary migration in the final sintering stage to suppress grain growth while promoting densification.[23] This method of sintering consists of two steps in the heating schedule. In the first step of TSS, samples should be heated to a higher temperature (T_1), which has to be sufficiently high to achieve critical density; particularly, the critical density represents the percentage of theoretical density (TD) at which pores become thermodynamically unstable against shrinkage. After short attaining at T_1, the temperature must be immediately lowered to the temperature of the second step of TSS (T_2) at which sintering yields high densities without grain growth.[23] Until now, this method has been used to fabricate nanostrustured ceramics from various nanopowders like Y_2O_3,[23,24] $BaTiO_3$,[25] Ni–Cu–Zn ferrites,[25] ZnO,[26] SiC,[27] YCSZ,[28] Al_2O_3,[29] YAG transparent ceramics,[30] 3Y-TZP,[31] corundum abrasives,[32] oxide ceramics with different crystal structurem,[33] forsterite[34] and as well as to suppress grain growth in some sub-micrometer powders.[35] Considering biomaterials, TSS method is successfully applied to prepare dense nanostructured HAp ceramics with enhanced mechanical properties.[36] To the best of our knowledge, until now, there are no published papers dealing with the synthesis of the CDHAp nanopowder and consequently two-step sintering.

Therefore, this study was focused on the preparation of dense fine-grained BCP ceramics with homogenous microstructure and improved mechanical properties, both hardness and fracture toughness, from the CDHAp nanopowder *via* two-step sintering. Previously, conventional sintering was applied on the CDHAp in aim to find appropriate conditions for TSS. Finally, the phase composition, microstructure and mechanical properties of BCP ceramics prepared by conventional and two-step sintering were compared.

2. Experimental

Hydroxyapatite nanopowder was prepared by a hydrothermal treatment of a precipitate. The precipitate was prepared by adding a filtered supersaturated alkaline solution of $Ca(NO_3)_2$ drop-wise in a mixture of H_3PO_4 and ammonia water at 50 °C, under constant stirring of 700 rpm. The starting Ca/P ratio of the precursors was 1.63; since the stoichiometric Ca/P ratio is 1.67, the obtained nanopowder is nominated as CDHAp. About 1 l of the as-obtained suspension was hydrothermally treated in 2 l *Parr* stainless steel stirred reactor on 200 °C under the pressure of 2 MPa, under constant stirring of 400 rpm. After the treatment, the autoclave was quenched down to room temperature. The precipitate was washed with distilled water to remove NH_4^+ ions, and then dried on 90 °C in air for 24 h.

The qualitative analysis of the synthesized powder and sintered ceramics were carried out by X-ray diffraction (XRD) using a Bruker D8 Advance automated diffractometer with primary Ge monochromator (Johanson type, CuKα = 1.54059 Å). The X-ray generator operated at 40 kV and 40 mA. The patterns were collected in the 2θ range 8–70° with a scanning step of 0.05°, at room temperature. The amounts of the phases present in the samples are determined according to DIFFRAC^{plus} Evaluation Package Release 2003-EVA V9.

The average crystallite size (D) of the powder was calculated from the half height width (β_m) of the XRD reflection of (0 0 2) plane (at 2θ = 25.8°), using the Scherer's equation (1),

$$D = \frac{K\lambda}{\beta_m \cos\theta} \quad (1)$$

where λ is the wavelength of X-ray radiation; K is the shape coefficient and is approximately equal to one; θ is the diffraction angle (°). The unite cell parameters (a and c) were determined