Designing of dense nanostructured calcium-phosphate-based bioceramics

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Introduction

Various calcium-phosphate-based (CP) bioceramics represent the most promising material for hard tissue reconstruction due to its excellent biocompatibility and bioactivity. The main disadvantage of CP bioceramics rests in their poor mechanical properties, which excludes its application in load-bearing implants. Recently, it has been shown that dense CP bioceramics with uniform nanostructure can improve both mechanical properties and biological response after implantation, because of the high volume fraction of energetically rich grain boundaries.

In this work, hydroxyapatite (HA) nanopowders were synthesized via both hydrothermal processing and precipitation methods. The novel pressureless two-step sintering technique (TSS), which exploits the difference in kinetics between the grain boundary diffusion and grain boundary migration to suppress accelerated grain growth in the final sintering stage while promoting densification, was applied for designing nanostructured CP bioceramics. The average grain size, density and phase composition were determined. The sintering behaviour and characteristics of the final ceramics are correlated with the characteristics of the starting nanopowders.

Experimental part

The starting chemicals used for the synthesis were $Ca(NO_3)_2\ 4H_2O$, 85 % H_3PO_4 and 25 % NH_4OH. The solution containing phosphate ions was added dropwise to the solution of calcium ions, under effective stirring, at T= 50 ºC, while pH was adjusted to 11 by the addition of ammonia. The white precipitate obtained was subsequently treated in different ways. HAp 1 was produced by boiling the precipitate for 10 min, aging of suspension for 24 h, filtrating, washing to pH=7 and drying overnight at 60 ºC. HAp 2 and HAp 3 were produced by hydrothermal treatment of the precipitate at 200 ºC. After reaching that temperature, the reaction mixture was quenched to the room temperature, washed to neutral conditions and filtrated. The starting Ca/P ratios of HAp 1, HAp 2 and HAp 3 were 1.67, 1.63 and 1.67, respectively. The obtained material was dried overnight at 60 ºC. All produced powders were characterized in order to determine the phase compostion, particle size distribution, morphology, Ca/P ratio and specific surface area (SSA) by XRD, Particle Size Analysis (PSA), FE SEM, XRF and the BET method, respectively.

The synthesized powders were calcinated, uniaxially compacted at 400 MPa into 6 mm Ø pellets. The sintering was performed via both conventional (CS) an two-step sintering (TSS) techniques at different temperatures in order to find out the best conditions for obtaining dense, nanostructured CP-based bioceramics.

Results and discussion

HAp 1

XRD pattern and FE SM micrograph in Fig. 1. a) and b) have shown that the synthesized powder has the pure hydroxyapatite phase, with the crystallite size of 15 nm and spherical morphology. The average particle size around 65 nm, which is in good agreement with PSA. The SSA was 78 m^2/g and Ca/P ratio was 1.67, which is considered to be stoichiometric Hap.

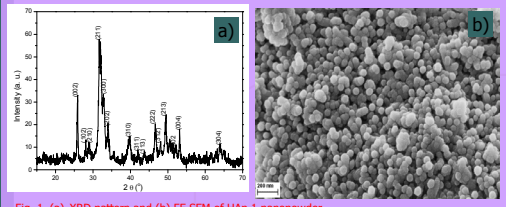

Fig. 1. (a) XRD pattern and (b) FE SEM of HAp 1 nanopowder.

The best conditions for TSS of HAp are found to be T_1=1150 ºC for 5 min and T_2=1050 ºC for 20 h. The final bioceramic material obtained was almost fully dense with an average grain size of around 400 nm. The XRD pattern in Fig. 2. a) shows that final ceramics is the pure Hap phase. In Fig. 2 (b), the FE SEM of its microstructure is shown.

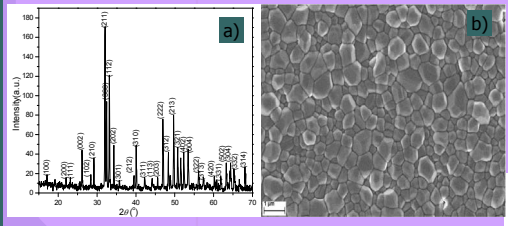

Fig. 2. (a) XRD pattern and (b) FE SEM of HAp 1 nanopowder processed via TSS at T_1=1150 ºC for 5 min, T_2=1050 ºC, for 20 h.

a) Powder characterization

HAp 2

XRD pattern and FE SEM micrograph in Fig. 3. a) and b) have shown that the synthesized powder has the pure hydroxyapatite phase, with the crystallite size of 20 nm and a slightly elongated morphology. The average particle size is around 84 nm, which is in good agreement with PSA. The SSA was 55 m^2/g and Ca/P ratio was 1.63, which is considered to be Ca-deficient Hap.

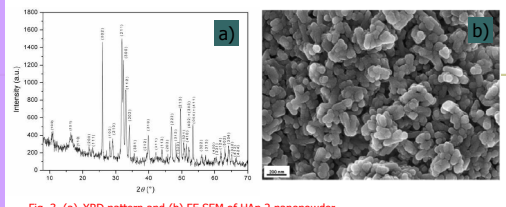

Fig. 3. (a) XRD pattern and (b) FE SEM of HAp 2 nanopowder.

b) Characterization of sintered ceramics

For HAp 2 nanopowder, both, CS and TSS were performed. After CS, 1h at 1200 °C, the final ceramics consisted of Hap, β-TCP and α-TCP, Fig.4 (a). Its average grain size is estimated to 1.4 μm, with uncontrolled grain growth and a non-uniform microstructure, Fig. 4 (b). On the contrary, when we employed the TSS experiment, with T_1=1150 ºC for 5 min, T_2=1050 ºC for 20 h, a biphasic system, containing only HAp and β-TCP, was produced, Fig. 4 (c). The average grain size was 375 nm, and it had significantly finer microstructure, Fig. 4 (d), which is favorable for the application in bone tissue reconstruction.

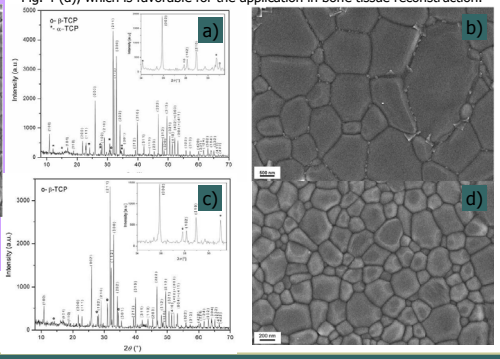

Fig. 4. (a) XRD pattern and (b) FE SEM of CS HAp 2 nanopowder, (c) XRD pattern and (d) FE SEM of HAp 2 processed via TSS at T_1=1150 ºC for 5 min, T_2=1050 ºC, for 20 h.

HAp 3

XRD pattern and FE SM micrograph in Fig. 5. a) and b) have shown that the synthesized powder has the pure hydroxyapatite phase, with the crystallite size of 19 nm and an elongated morphology. The width of particles was around 50 nm and their length was about 200 nm. The SSA was 58 m^2/g and Ca/P ratio was 1.66. The existence of some agglomerates could be noticed.

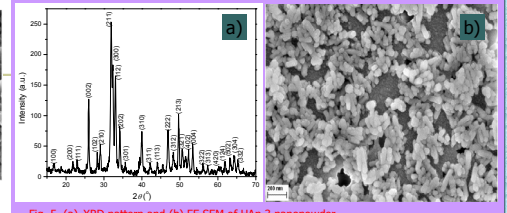

Fig. 5. (a) XRD pattern and (b) FE SEM of HAp 3 nanopowder.

For HAp 3 nanopowder TSS was performed at T_1=1150 ºC for 5 min,T_2=1050 ºC for 20 h, after which we obtained the pure HAp phase, Fig. 6 (a), and an average grain size of 250 nm, Fig. 6 (b). The existence of larger grains can be assigned to the presence of harder agglomerates in the synthesized powder, which influenced further sintering behavior, causing the coarsening of particles in the sintering process and differential sintering.

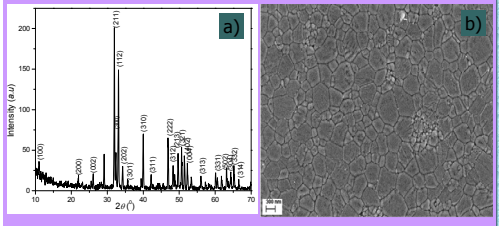

Fig. 6. (a) XRD pattern and (b) FE SEM of HAp 3 processed via TSS at T_1=1150 ºC for 5 min, T_2=1050 ºC, for 20 h.

Conclusion

In this study, three different HAp nanopowders were synthesized by chemical precipitation, HAp 1, and hydrothermal treatment of the precipitate at 200 °C, HAp 2 and HAp 3. The method of the synthesis significantly influenced the characteristics of the starting powder. Considering each nanopowder, it has been concluded that different synthesis routes yield different powder morphology. From chemical precipitation, spherical nanoparticles were obtained, while after the hydrothermal treatment an elongated morphology was formed, bearing in mind that the Ca/P ratio closer to stoichiometric leads to higher aspect ratio of particles. Further, it has been shown that two-step sintering method has significant advantages for obtaining nanostructured bioceramics, compared to conventional sintering. It leads to much finer microstructure, with smaller grains, but also lowers the sintering temperatures, which is advantageous in producing BCP ceramics, being very interesting from the point of view of combined bioactive/bioresobable properties. For Hap 1 almost fully dense, pure HAp bioceramics with an average grain size of 400 nm was obtained, with a uniform microstructure. For HAp 2 and HAp 3, BCP and HAp ceramics were obtained, with the grain size of 375 and 250 nm, respectively. It can be concluded that spherical morphology is favorable for the uniform final microstructure, while with elongated particles smaller grains are produced, which can be attributed to the synthesis procedure.

The obtained results imply that TSS can be successfully used as a processing route for the production of nanostructured ceramics. However, powder agglomeration and nonuniform green density still represent obstacles for inexpensive fabrication of nanostructured ceramics.