Full density calcium phosphate bioceramics from nanopowders by sintering

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INTRODUCTION

Synthetic calcium phosphate bioceramics belong to the group of the most perspective materials for bone tissue reconstruction. Chemical similarity with mineral part of the bones and teeth contributes to their excellent biocompatibility. Among many different calcium phosphates, hydroxyapatite (HAp) and beta tricalcium phosphate (β-TCP), are mostly used. HAp is bioactive material, meaning that attaches chemically to the surrounding tissue, while β-TCP is bioresorbable, allowing precipitation of biological carbonated HAp at the tissue/implant interface.[1] The main disadvantage of these materials is their brittleness, which excludes them from load bearing application. Mechanical properties could be enhanced by preparing of full dense materials by sintering process, with preserved fine-grained microstructure. However, sintering is associated with many complex and unpredictable processes, often yielding to the accelerated grain growth in the final sintering stage. Two-step sintering method (TSS), which is shown to be useful in obtaining full density fine-grained biphasic calcium phosphate (HAp+ β-TCP) materials [2] could be the promising approach in fabrication of dense fine-grained HAp. This method is founded on a different kinetics between grain boundary diffusion and grain boundary migration which are the main mechanisms of densification and grain growth, respectively.

In this study, HAp nanopowder is synthesized via hydrothermal processing of calcium phosphate precipitate. TSS method is applied to obtain full dense HAp material without accelerated and uncontrolled grain growth. Furthermore, Master Sintering Curve theory (MSC) is used to predict densification behavior for further planning of sintering strategies with this system. [3]

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 obtained white precipitate was subsequently placed in hydrothermal reactor and heated to 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 ratio was 1.67. The obtained material was dried overnight at 60 ºC. The produced powder was characterized in order to determine the phase compostion, particle size distribution (PSD), morphology and specific surface area (SSA) by XRD, Particle Size Analysis (PSA), FE SEM, TEM and the BET method, respectively.

The synthesized powder was calcinated, uniaxially compacted at 400 MPa into 6 mm Ø pellets. The sintering was performed via TSS technique. The data for MSC construction was acquainted by simple nonisothermally heating with 2, 10 and 20 °C/min. Consequently calculations were done in accordance with MSC theory. Relative density is calculated by dividing experimentally measured density values with 3.16 g/ccm, which is theoretical density (T.D.) of HAp.

RESULTS AND DISCUSSION

a)Characterization of synthesized nanopowder

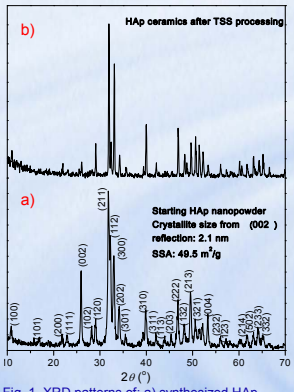

Fig. 1. XRD patterns of: a) synthesized HAp nanopowder b) HAp ceramics after TSS processing.

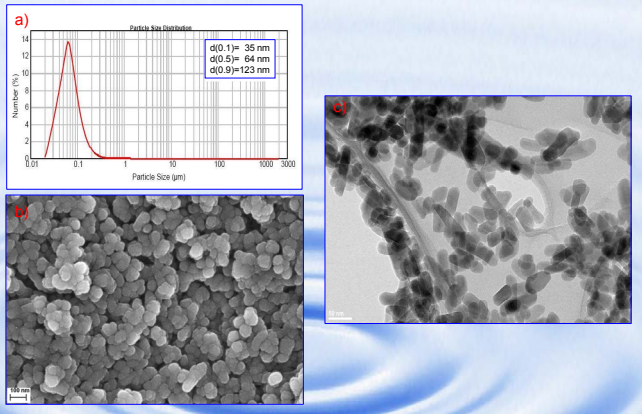

Fig. 2. a) PSD , b) FE SEM and c) TEM micrographs of synthesized HAp nanopowder.

b) TSS processed ceramics

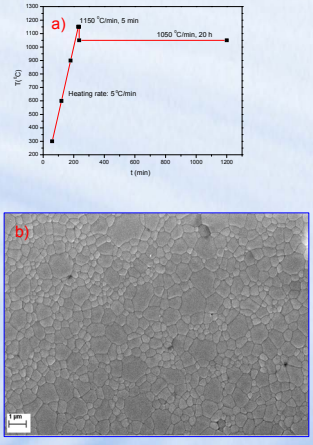

Fig. 3. a) The schematic representation of TSS approach and b) microstructure of polished and thermally etched surface of HAp ceramics processed via TSS.

c)*Modelling of sintering by MSC*

Background theory of MSC[3]

1. Based on combined stage sintering model.
2. Assumption of one dominant sintering mechanism.
3. Microstructural (density) and time-temperature parameters are placed on opposite side of equation: $\Phi(\rho)=\log\Theta(t,T(t))$.
4. A unique microstructural evolution to the sintering kinetics.
5. MSC can be used exclusively for a given powder and green body process.

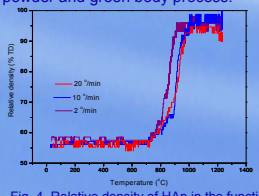

Fig. 4. Relative density of HAp in the function of temperature for different heating rates.

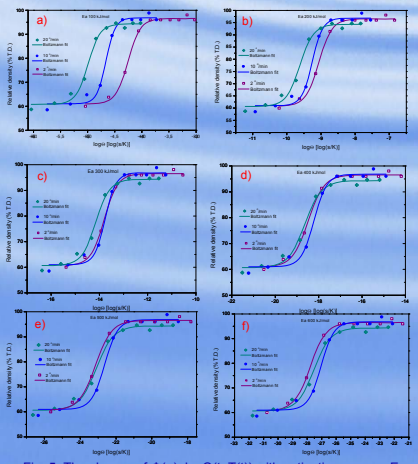

Fig. 5. The change of $\Phi(\rho)=\log\Theta(t, T(t))$ with activation energy, Ea: a) 100, b) 200, c) 300, d) 400, e) 500 and f) 600 kJ/mol.

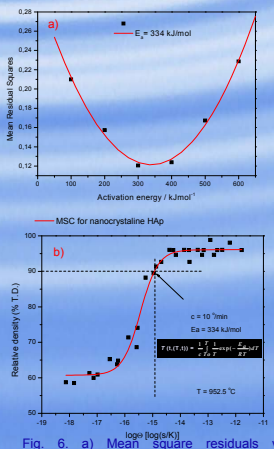

Fig. 6. a) Mean square residuals versus activation energy: minimum occurs at ~334kJ/mol; b) MSC for nanocrystalline HAp together with one validation point: for 90 % T. D. sample should be heated with 10°C/min to the 952.2 °C.

CONCLUSION

1. HAp nanopowder, with average particle size smaller than 50 nm is successfully synthesized by efficiently controlled hydrothermal processing of calcium phosphate precipitate.
2. Inexpensive, pressureless TSS approach was employed to obtain full dense HAp bioceramics with fine-grained microstructure.
3. For prediction of sintering behavior of the synthesized HAp nanopowder, MSC was constructed and activation energy for sintering is estimated to 334 kJ/mol.
4. Such created MSC is used to determine appropriate sintering path to obtain HAp bioceramics with desired microstructural characteristics.

REFERENCES

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3. H. Su and D. L. Johnson, Master sintering curve: a practical approach to sintering, J. Am. Ceram. Soc., 1996, 79, 3211-3217.