Precipitation synthesis and two-step sintering of hydroxyapatite nanopowders

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INTRODUCTION

Hydroxyapatite, (HAp), $Ca_5(PO_4)_3(OH)$, due to its excellent biocompatibility and osteoconductivity as well as close similarity to human bone structure, represents a promising material for hard tissue implantation. However, mechanical properties of synthetic HAp are not as good as those of natural bones and that limits load-bearing applications. It was found that nanostructured ceramics have much better mechanical properties, but final stage of sinterinig is always accompained with accelerated grain growth. An elegant way to suppress accelerated grain growth during final stage of sintering is provided by two-step sintering technique (TSS). This type of sintering is based on difference in kinetics of desirable grain boundary diffusion and undesirable grain boundary migration. The key elements in this method are: (1) heating to a high temperature T_1 to conduct first step sintering and to achieve a critical density ρ* to render pores unstable; (2) decreasing the temperature to T_2 to conduct sintering without grain growth at the lower temperature [1].

In this work, method of chemical precipitation was performed to prepare HAp nanopowder. Also, a few regimes of TSS were investigated to obtain best result and master sintering curve (MSC) for this powder was constructed to help in further improvement of characteristics of this bioceramics.

EXPERIMENTAL PART

HAp powder was prepared by chemical precipitation method [2]. Precursor chemicals used were $Ca(NO)_34H_2O$, 85% H_3PO_4 and 25% NH_4OH. Aqueous solutions of Ca^{2+} and PO_4^{3-} ions were made attaining starting pH values of both solutins at 10 by adding NH_4OH. Then, solution of PO_4^{3-} ions was dropwise added to solution of Ca^{2+} under vigorous stirring of 1000 rpm and such obtaiined milky slurry was kept at boiling for 10 minutes. The precipitate was washed, filtered, dried at 70 ºC for 6 h and finally grounded in agate mortar. Before sintering, ultrasound treatment of dried powder was performed in ultrasonic bath for 45 min to reduce the degree of agglomeration, followed by calcination on 500 ºC for 1h to evaporate moisture and again deagglomerated with ultrasound at the same conditions. Such obtained nanopowder was uniaxially pressed under 440 MPa into 13 mm ∅ pellets and two-step sintered. Green density of the sample, determined by Archimedes' principle, was 1,84 g/cm³.

The sample was heated to the first temperature with 6 ºC/min. Temprature range found to give the highest density with this nanopowder was 1100 ºC for T_1 and 1000 ºC for T_2 with attainment times to be 30 min and 20 h, respectively. The sample has been coolled down naturally between two temperatures. In order to find the optimum heating regime for densification and to estimate activation energy, Ea, for sintering of this nanopowder, we have constructed MSC. Pellets with ∅ 4 mm were nonisothermally sintered to 1200 ºC with constant heating rates of 5, 10 and 15 ºC/min, respectively. Experiment was conducted in heating microscope E. Leitz, Wetzlar, Germany.

As-prepared nanopowder as well as sintered pellets were characterized in sense of particle size distribution (PSD) (Mastrsizer 2000, Malvern Instruments Ltd. ,UK), XRD (Phillips PW 1050) and SEM (JEOL model JSM 5300).

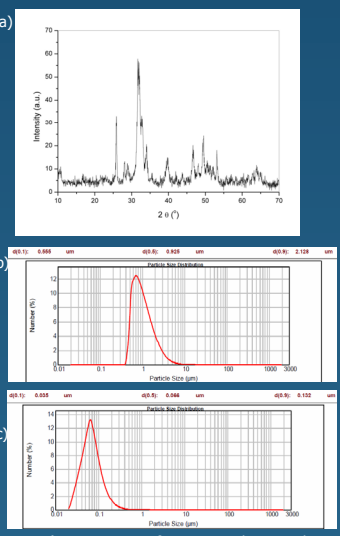

Fig. 1: a) XRD pattern of as-prepared Hap and its b) partcle size distribution; c) particle size distribution of the same powder after cycle: 45min ultrasound / 1h calcination at 500 ºC / 45min ultrasound deagglomeration.

Results and discussion

Fig.1a shows XRD pattern of as synthesized nanopowder. All reflections could be asignated to pure HAp. Due to high surface energy, obtained nanopowder was agglomerated and particle size distribution exhibits average particle size of 925 nm. After 45 min of ultrasoud dry deagglomeration of nanopowder, 1h of calcination at 500ºC in order to eliminate moisture which could make problems during sintering and finally one more time 45 min of ultrasound tretment, PSD was significantly changed with average particle size of 66 nm and very narrow PSD, Fig.1c. In our opinion, dry ultrasound deagglomeration treatment gave better results in decreasing of average particle size because that could irreversible break inter- and intra- aglomerate bonds, which is not completly possible into dispersion, because there exist closer contacts between particles.

After TSS regime, which we found the best (1100 ºC for T_1 and 1000 ºC for T_2 with attainment times to be 30 min and 20 h) of that nanopowder density of ceramics was 2,73 g/cm³ which is 86,4% of theoretical density for HAp (3,156 g/cm³). Fig 2.a shows SEM micrograph of fracture surface of sintered sample and on Fig1.d. XRD pattern at which it can be seen that at mentioned temperatures β-TCP phase arises. This observation implies on consideration of applications of the particular samples ,which should determine the best ratio of Ca/P in synthesized powders.

From construction of MSC we found that the activation energy Ea for HAp is 333 kJ/mol and that slower heating rate is optimal for densification.

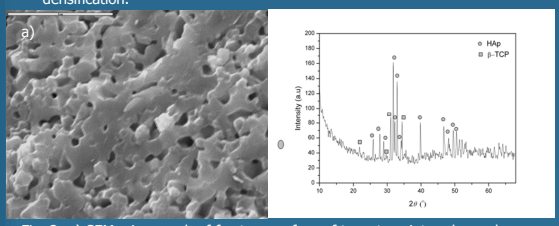

Fig. 2: a) SEM micrograph of fracture surface of two-step sintered sample and b) XRD pattern of that sample.

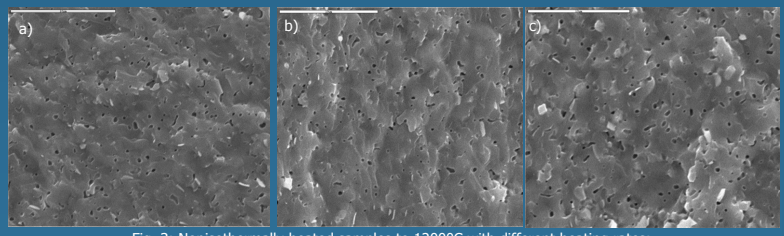

Fig. 3: Nonisothermally heated samples to 1200ºC with different heating rates: a) 5, b) 10 and c) 15 ºC/min.

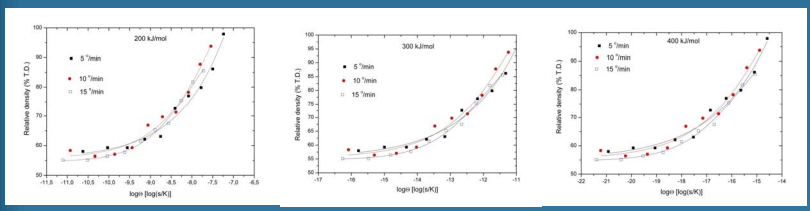

Fig. 4: $\Phi(\rho) = \log\Theta(t, T(t))$ for different activation energies, Ea.

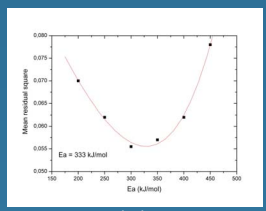

Fig. 5: mean residual square versus Ea
Ea=333 kJ/mol

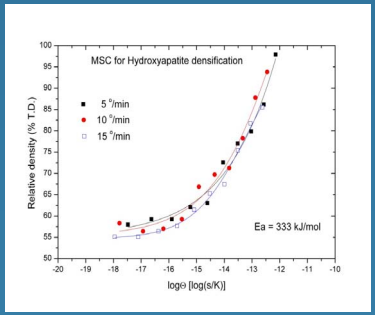

Fig. 6: MSC for HAp

CONCLUSION

From our results can be concluded that simple method of chemical precipitation followed by ultrasound deagglomeration of dried powder can successfully be used for synthesis of HAp nanopowder. However, to have high dense nanostructured ceramics particle size distribution sholud be completly uniform, because any local density gradient will seriously affect the final microstructure of ceramics. Also we estimated Ea for sintering of this HAp nanopowder to be 333 kJ/mol.

REFERENCES

[1] Chen, I. W. And Wang, X. H., "Sintering dense nanocrystalline ceramics without final stage grain growth", *Nature*,2000, **404**, 168-171.

[2] N. Ignjatović, D. Uskoković, "Biodegradable composites based on nano-crystalline calcium phosphate and bioresorbable polymers", *Advances in Applied Ceramics, Nanoceramics special issue*, **107**, 3 (2008) 142-147 .