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Synergistic effect of hydroxyapatite nanopowder's high crystallinity and non-ordered particles' boundary regions on low-temperature sintering

Miodrag J. Lukić, Ljiljana Veselinović, Smilja Marković and Dragan Uskoković

Centre for Fine Particles Processing and Nanotechnologies, Institute of the Technical Sciences of the SASA, Belgrade, Serbia

Introduction

* Fabrication of fully dense nanostructured hydroxyapatite is one way to get **reliable bone tissue implant for large defect repairs**.

* It is expected that nanopowders would enhance sintering behavior!

* Generally, what should be fulfilled?
  - -average particle size < 100 nm
  - -uniform particle size distribution
  - -specific surface area > 50 m^2/g
  - -spherical particles morphology

However, results are quite versatile!

Table I. Summary of the current results of the pressureless sintering of the hydroxyapatite.[1]

Synthesis method	Morphology	Size length/width (nm)	SSA (m^2g^{-1})	X_C (%)	Sintering method	Sintering temp. (°C)	Final relative Density (%)	Average grain size (nm)
precipitation	needle-like	100	58	low	CS	1250	97	10^3
precipitation	spherical	600	48	-	CS	1200	76.8	-
precipitation + milling	nanorods	50/15	120	-	CS	850	~99	83
neutralization	elongated	<100	15	80	CS	1215	92.3	10^3
neutralization	-	~100	90	-	CS	1200	98.7	>10^3
reverse micelle	rod-like	-	29	-	CS	1250	~86	>10^3
templating	spherical		39				97.5	
hydrothermal	elongated	70/20	-	-	CS	1200	85	-
precipitation	needle-like	150/40	-	high	TSS	1050 950	99	193
commercial	semirods	93/24	-	high	TSS	900 800	98.8	190
hydrothermal	slightly elongated	65/25	49.5	72	TSS	900 850	99.2	75

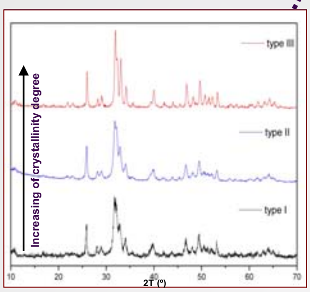
Where should we look for the potential explanations of very distinct sintering behavior?

Experimental part

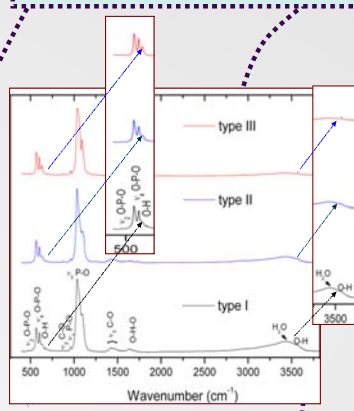
In this study, three types of hydroxyapatite nanopowder were prepared. The precursor chemicals used were $Ca(NO_3)_2$ and H_3PO_4 for hydroxyapatite types I and III, while for type II as a phosphate source $NH_4H_2PO_4$ is taken. Chemical precipitation was the basic reaction whereas hydrothermal processing was additionally employed in the case of type III. Materials characterization was performed by XRD, FTIR spectroscopy, scanning and transmission electron microscopy. Moreover, their sintering behavior was investigated by heating microscopy.

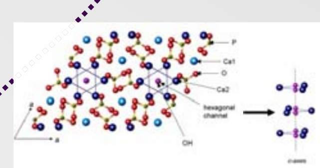
Results

XRD analysis: all systems are phase pure hydroxyapatite.

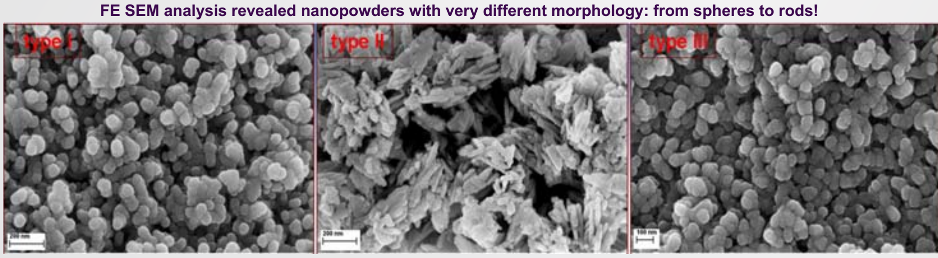


FTIR spectroscopy confirmed chemical purity, but also indicated difference between hydroxyl group vibration intensity implying different level of crystal ordering.

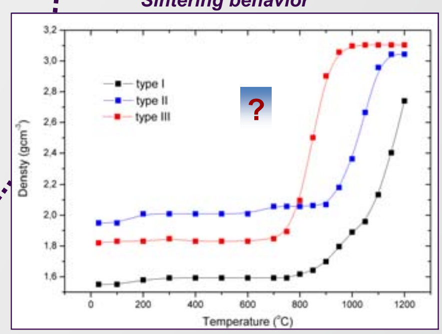




FE SEM analysis revealed nanopowders with very different morphology: from spheres to rods!

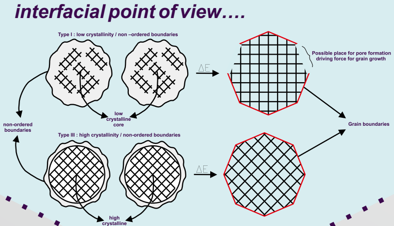


Sintering behavior

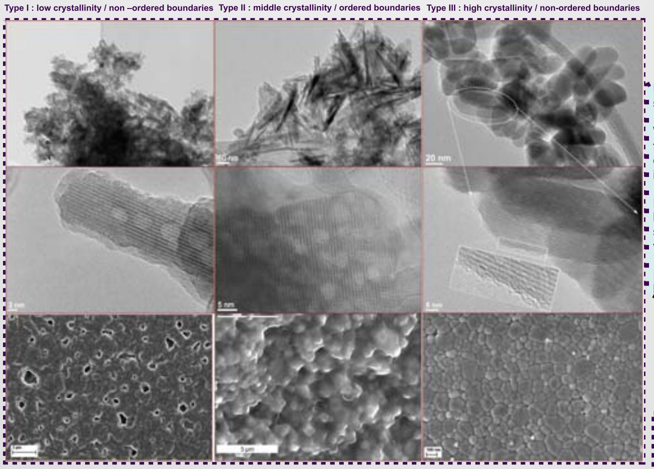


Discussion

…if the situation is considered from the interfacial point of view….



Type I : low crystallinity / non –ordered boundaries Type II : middle crystallinity / ordered boundaries Type III : high crystallinity / non-ordered boundaries



Conclusions

Hydroxyapatite nanopowders could be easily produced; however, they sinter quite differently!!!

We considered sintering behavior of three hydroxyapatite nanopowders from the point of view of particles boundary structure and overall crystallinity. Possibility to obtain fully dense nanostructured bioceramics is discussed.

Here is showed that highly crystalline particles with non-ordered boundaries are favorable for enhanced sintering since thermal energy supplied is mainly used for matter diffusion along grain boundaries which volume fraction is significant when deals with nanopowders.

Further grain boundary engineering should be done to prove these hypothesis...

References

1. Miodrag J. Lukic, Sreco Davor Skapin, Smilja Markovic and Dragan Uskokovic, Processing Route to Fully Dense Nanostructured HAp Bioceramics: From Powder Synthesis to Sintering, *J. Am. Ceram. Soc.*, xx-xx, (2012), DOI: 10.1111/j.1551-2916.2012.05376.x.

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