Hybrid composite materials with biofunctional properties

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As bioactive calcium phosphate ceramics hydroxyapatite is known as one of the most important biomaterials used for orthopedic and dental applications due to its chemical composition similar to that of bone and bioactive properties. It is relatively cheap, nontoxic, minimally resorbed, has an acceptable compressive strength, and could be well attached to hard tissues. Few studies for obtaining a hybrid metal-ceramic composite by powder metallurgy are presented in this paper. Some experimental analytical methods for characterization of the new obtained material have been used, as follows: FTIR, SEM, and EDAX. Results of the tests registered on the hybrid composites are evaluated and discussed properly.

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1. Introduction

This paper presents the experimental results obtained from investigation of hydroxyapatite and metalo-ceramic composites.

Materials used for obtaining metalo -ceramic composite was: hydroxyapatite as ceramic materials and stainless steel 316L - this type of steel used in medical implants like hip implant, joints, etc. [15]. Synthesis methods of hydroxyapatite are various, literature informations being plentiful in this area [3, 6, 7, 8]. In wet precipitation method, chemical reactions occur between calcium and phosphorus ions under controlled pH and temperature of the solution [1,2]. Usually precipitated powder is calcined at high temperatures in order to obtain stoichiometric structure of apatite [1,2]. For these studies we chose synthetic methods to obtaining hydroxyapatite, by wet precipitation at room temperature.

To improve chemical homogeneity of the reaction products was used titration and dilute solutions. An easy control of solution conditions is also necessary for wet precipitation method. In some cases, a good crystallization of hydroxyapatite occurs only around the ignition temperature of 1200^0C [3].

Aqueous precipitation is most often achieved by: reaction of a salt of calcium and alkaline phosphate, or reaction between calcium carbonate and hydroxide or phosphoric acid [3, 10, 11, 12].

Determination of free ions substituted apatite is fundamental, type and availability strongly influences osteoblast cell activity and therefore the entire process of bone remodeling. Ceramic particles obtained as mono and composite will be characterized as property specific ceramic. To highlight these properties we have considered that the following measurements: particle size distribution (by laser granulometry), thermal stability (thermogravimetric analysis, differential scanning calorimetry), chemical and mineralogical composition (infrared spectrophotometry) are important and will be detailed treated in this paper.

2. Experimental methods

In this study, hydroxyapatite was obtained by chemical precipitation method modified by Sung. Commercial chemical reagents (Chimreactiv, Romania) used: calcium nitrate tetrahydrate $Ca(NO_3)_2.4H_2O$ and dibasic ammonium phosphate $(NH_4)_2HPO_4$ were dissolved separately in deionized water by stirring. After adding $Ca(NO_3)_2$ over aqueous solution of $(NH_4)_2HPO_4$, the solution was shaken at room temperature for about 1 h until was obtained a milky precipitate, somewhat gelatinous which in turn was stirred for 1h in order to speed up the reaction mixture and blend. The obtained mixture was sintered at 100^0C for 24 hours. Then the precipitate was washed and filtered on a glass filter. After filtration, the sticky compacted product was dry in an oven at a temperature of 80^0C. In the figure 1 it is presented technological process for obtaining of hydroxyapatite powder by wet precipitation.

The powder was dried in a mortar and pestle and then calcined in alumina crucible at three different temperatures: 800^0C, 1000^0C and 1200^0C for 1h.

Table 1.

Method	Sample	Calcination Temperature (^{O}C)	Concentration $Ca(NO_3)_2 \cdot 4H_2O$:$(NH_4)_2HPO_4$ (M)
reflux after mixing	HAp 1	800	0.1:0.06
reflux after mixing	HAp 2	1000	0.1:0.06
reflux after mixing	HAp 3	1200	0.1:0.06

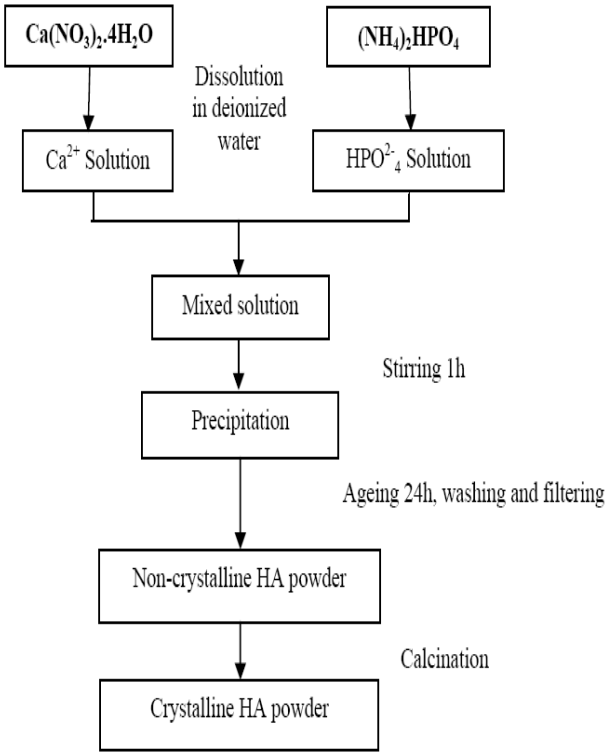

Fig. 1. Modified chemical precipitation route for HAp powder preparation. (Adapted from Sung)[3].

By varying the annealing temperature and maintaining the same molar concentrations and the same method of reflux after mixing, the best results were obtained at the temperature of 1000^0C, because only at this temperature was obtained hydroxyapatite as a single phase.

Literature about obtaining hybrid metal-ceramic composite by powder metallurgy is quite poor [4]. In his book, A Syewezyk and collaborators have obtained composite 316L/HAp with 5.10 and 15% hydroxyapatite, cold pressed with a pressure of 600 sqm and sintered at 1245^0C [5]. Taking this reference, we tried to obtain a new composite by changing proportions between steel and hydroxyapatite powders.

To obtain these composites has been performed a powdery mixture of 30% volume HAp and 70% vol. 316L stainless steel. After being mixed and homogenized the powders were pressed in a hydraulic press Otto Weber at a pressure of 90KN, after which the samples obtained were placed in a furnace for sintering. Sintering took place at a temperature of 1120^0C, in a protective atmosphere of H_2, 45 minutes kept hot and cold 40 minutes with a heating and cooling rate of 10^0C/min. Was made three cylindrical composite with 70% vol. 316L powder and 30% HAp with 10mm in diameter and 13mm in height.

2.1 Apparatus

Hydroxyapatite obtained by chemical precipitation at 1000^0C was characterized by FTIR analysis, thermal analysis and dimensional analysis of the particle. IR absorption measurements were performed using spectrometers SPECORD M80 (Carl Zeiss Jena, Germany) Perkin Elmer Spectrum GX (Perkin Elmer Inc.., USA) with TDS detector (deuterated triglycine sulfate) in KBr pellettes, resolution of 4 cm^{-1}, with 32 scans, operated both in transmission and in ATR device (total reflection attenuated).

Particle size measurements were performed with Zetasizer Nano ZS instrument. This tool performs particle size measurements using a process called Dynamic Light Scattering, DLS Particles suspended in a liquid constantly moving due to Brownian motion. DLS measures Brownian motion and correlated with particle size. This is achieved by illuminating the particles with a laser and analyzing the scattered light intensity fluctuations and uses them to calculate the particle size of the sample.

Metal-ceramic composites obtained in this paper were characterized by SEM, EDAX analysis and Shore D hardness. For SEM analysis was used a scanning type electron microscope Quanta Inspect F. Compositional microanalysis of AISI 316L stainless steel powder and particle morphology was determined by X-ray spectrometry with direct emission scanning electron microscopy equipped with EDAX analyzer type. For Shore D hardness, the samples were tested on a Zwick D 7900 durometer type7206.

3. Results and discussion

FTIR spectra of synthesized hydroxyapatite revealed the existence of specific absorption bands: the 3573-3570cm^{-1} band is corresponding to a sharp OH^- stretching vibration at 3432cm^{-1} corresponding to a wider OH vibration of water the band 1632 -1629cm^{-1} corresponds to a -OH vibration of adsorbed water, and the band from 1090cm^{-1}, 1050-1044cm^{-1}, 961-962cm^{-1}, 600-601cm^{-1} and 571cm^{-1} are corresponding vibration of PO_4^{3-} and group-632cm $^{-1}$ corresponding to -OH vibration. The 2003 cm^{-1} wave number is attributed to adsorbed CO_2 from the atmosphere, as shown in figure. The sample HAp2 subjected to calcination at a higher temperature than HAp1, namely 1000^0C, water content will decrease, and for the sample calcined at 1200^0C HAp3 water content increases more than HAp1 due to high reactivity of the powder thus obtained. Also broadening the absorption band at 1050cm^{-1} takes place with increasing calcination temperature HAps from sample 1 to sample 3 confirms that the sample appears as tricalcium phosphate reaction product. Research literature indicates that tricalcium phosphate is over 850^0C. In Fig. 2, three curves are shown FTIR performed on three types of hydroxyapatite, calcined at temperatures of 800^0C, 1000^0C and 1200^0C respectively.

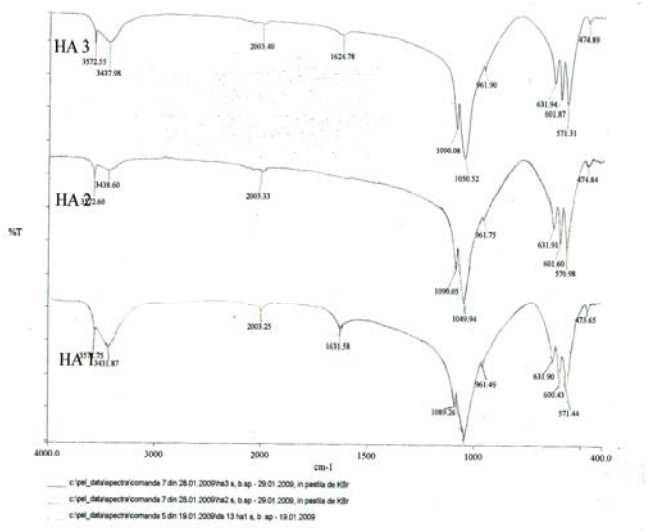

Fig. 2. FTIR analysis on the 3 HAp powders calcined at 800^{0}C, 1000^{0}C, 1200^{0}C.

FTIR tests were made to show the role of hydrogen and -OH group in the mechanism of adsorption. The only notable difference between these three spectra is the appearance of intense bands at 1624.7 cm $^{-1}$ and 1631.6 cm^{-1} respectively in samples of hydroxyapatite HAp 1 and HAp 3.

Dimensional analysis of hydroxyapatite particles was made in isopropyl alcohol, by using an aggregate grinding in the presence of alcohol, after the samples being ultrasonicated for 5 min in an ultrasonic bath (35kHz). Dispersions have acquired a white opalescent appearance, or precipitate. A few minutes after, they settled large aggregates that were collected evidence of metastable phase (top).

Is metastable in about an hour because it precipitates as well. The average size (mathematics) is 1800nm (1.8 microns).

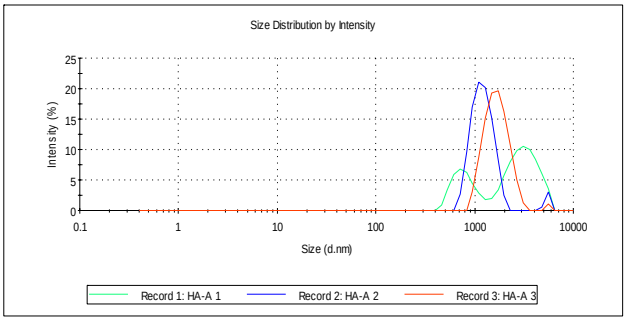

Fig. 3. Particle size distribution by intensity of the 3 records.

Taking into account the instability exhibited by a set of measurements to another (see the three sets of measurements on color), and changing the number of population (number of peaks) in the analyzed system the elementary particles in different forms of aggregation is resulting from sedimentation process.

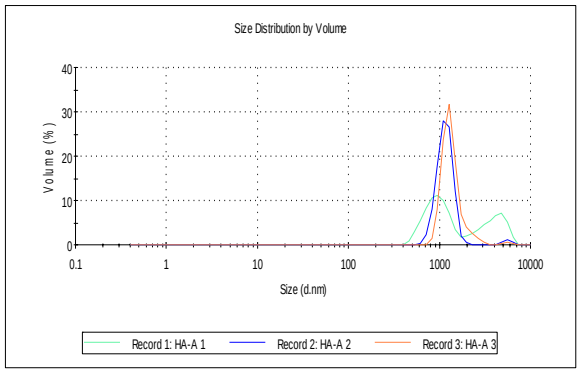

Fig. 4. Particle size distribution by volume of the 3 records.

The system contains over 6000 nm particles. Size distribution measurements were made on a single sample.

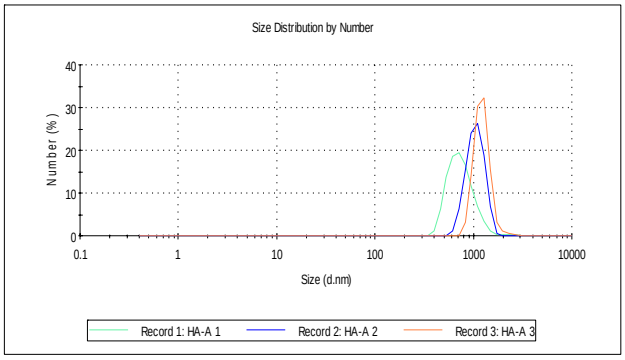

Fig. 5. HAp particle size distribution of the 3 records by number.

Data from the analysis of particle size distribution can be plotted as a histogram, as shown in figures, where the number of particles with a certain size and height are represented by a rectangle.

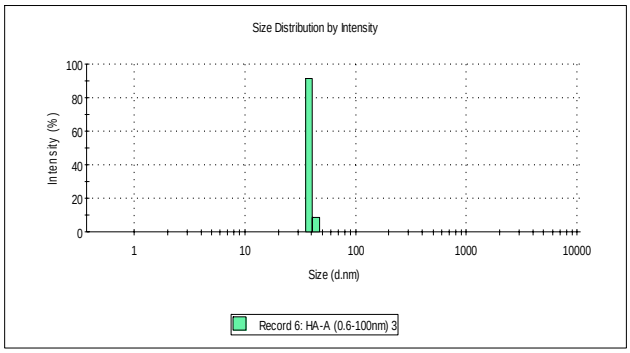

Fig. 6. HAp size distribution of nanoparticles in intensity.

Another method is to achieve a histogram representation whose area of a rectangle is proportional to the number of particles of a certain size.

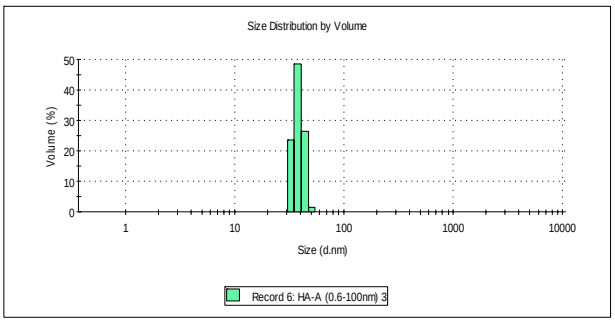

Fig. 7. HAp size distribution of nanoparticles by volume.

Cumulative distribution often provides a more accurate representation of the data. For hydroxyapatite powder was made a global analysis where reproducibility is better between sets of measurements, but measured particles seem more independent particles and not aggregates.

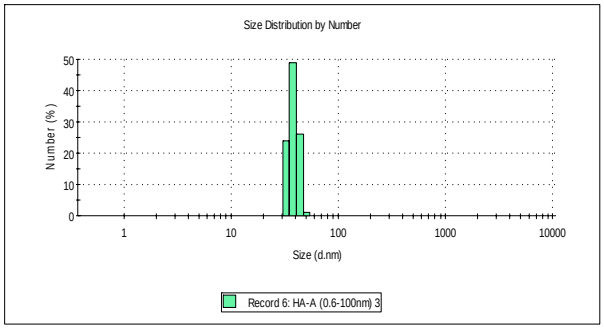

Fig. 8. HAp size distribution of nanoparticles by number.

Total dispersion in liquid occurs when the initial particle agglomerations are separated, resulting in the final mass of particles independent of each other. Preparing hydroxyapatite powders to determine the average size and size distribution was done in accordance with ISO 14887.

In the figure 9 is presented the image of metalo-ceramic composite obtained by mixture of 70% 316L stainless steel powder [15] and 30% HAp powder and relevant an aspects compact without high porosity materials. Applied method allowed us to obtain materials with a chemical composition, structure and specific porosity.

Fig. 9. Composites with 70% 316L and 30% Hap.

From the microscopic appearance of composite we can observe a relatively uniform distribution of stainless steel powders. This can be explained by the fact that the two types of powder mixing was done manually. Metal powders are like white formations, round, slightly dendritic, while the hydroxyapatites are dark.

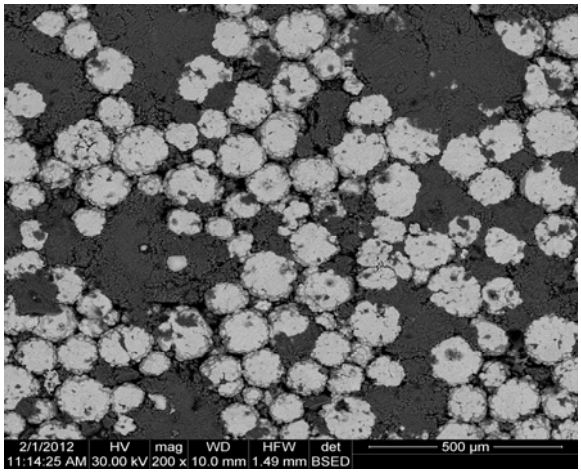

Fig. 10. SEM micrography of the composite with 70% 316L/ 30% Hap.

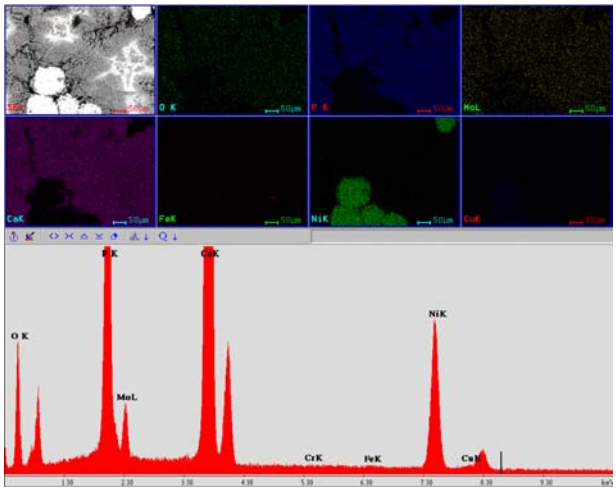

Fig. 11. EDAX for composit with 70% 316L and 30% HAp.

EDAX analysis of the composite give us the qualitative analysis of elements present in the composite.

The spectra reveal the presence of phosphorus and calcium specific to hydroxyapatite and the presence of elements such as Ni, Cu, Cr, Fe, Mo elements specific to stainless steel 316L. EDAX analysis of the composite with 70% 316 L and 30% HAp is shown in the figure 11.

The hardness of composites has been recorded for the mixtures of 70% 316L/30% HAp powder, and with a Shore D method, the values obtained being shown in the table below.

Table 2.

No.	Composite	HS D
1	70% 316L/30% HAp	71
2.	Human bone	85-95
3	Hydroxyapatite	81-88

3. Conclusion

For the composite 316L/HAp it was chosen the wet precipitation method because is more advantageous due to the easy synthesis way low working temperature, a relatively high percentage of pure product synthesis results and not so expensive installations.

Our results concluded to the following:

1. Analyzes by Fourier transform infrared spectroscopy showed that the best results have been obtained for the powder calcined at 1000^0C.

2. The possible elementary particles in the range 0.6 - 100nm which are captured global analysis of large aggregates obstructions. Such particles were found about 40 nm single-modes.

3. Compared with other composite previously obtained, we can observe that the material obtained by mixture of 70 % volume stainless steel powder have a specific porosity, is more compact and hence porosity decreases with increasing of amount the stainless steel. Pressure applied to compress composites had a considerable influence. Increasing the amount of HAps in the powder mixture leads to a decrease of the hardness and relative density of the composite 316L/HAp, with a significant increase in porosity. According to the literature, Shore hardness values for hydroxyapatite are between 81-88 HS D and for human bones between 85-95 HS D.

4. The results presented suggest that the composites obtained can be varied by choosing an appropriate chemical composition powder mixture.

References

[1] A. A. Poinescu, R. M. Ion, R. I. Van Staden et al. J. Optoelectron. Adv. Mater. **13**(2-4), 416 (2011).
[2] A. A. Poinescu, R. M. Ion, R. I. van Staden, et al., Advanced Topics In Optoelectronics, Microelectronics, And Nanotechnologies V, Book Series: Proceedings of SPIE-The International Society for Optical Engineering, **7821**, 78210B 1-6, DOI: 10.1117/12.882148, (2010).
[3] N. Monmaturapoj, Journal of Metals, Materials and Minerals, **18**(1), 15 (2008).
[4] A. Dudek, Archives of Foundry Engineering, Issn (1897-3310), **10**(3), 145 (2010).
[5] A. Szewezyk-Nykiel, M. Nykiel, Archieves of foundry engineering, ISSN 1897-3310, **10**(3), 235 (2010).
[6] K. Donadel, Laranjeira, C. M. Mauro, V. L. Goncavalves, Favere, T. Valredo, C de Lima, Joao and Prates Luiz H. M., Hydroxyapatite Produced by Wet-Chemical Methods, J. Am. Ceram. Soc. **88**(8), (2005).
[7] C. Garcia, S. Cere, A. Duran, Journal of Non Crystalline Solids **348**, 218 (2004).
[8] N. Angelescu, D. N. Ungureanu, A. Catangiu, V. Bratu, F. V. Anghelina, Metalurgia International, (4), 125 (2011).
[9] A. Ruban Kumar, S. Kalainathan, Cryst. Res. Technol., **43**(6), 640 (2008).
[10] Maria Helena Santos, Marise de Oliveira, Luciana Palhares de Freitas Souza, Herman Sander Mansur, Wander Luiz Gerais, Materials Research, **7**(4), 625 (2004).
[11] T. Anee Kuriakose, S. Narayana Kalkura, M. Palanichamy, D. Arivuoli, Karsten Dierks, G. Bocelli, C. Betzel, Journal of Crystal Growth 263, 517 (2004).
[12] A. Lopez-Macipe, 1 R. Rodriguez-Clemente, A. Hidalgo-Lopez, 1 I. Arita, M. V. Garcia-Garduno, E. Rivera, V. M. Castano, Journal of Materials Synthesis and Processing, 6(I), (1998).
[13] N. A. Zakharov, I. A. Polunina, K. E. Polunin, N. M. Rakitina, E. I. Kochetkova, N. P. Sokolova, V. T. Kalinnikov, Inorganic Materials, 40**(**6), 641 (2004).
[14] B. D. Ratner, A. S. Hoffman, F. J. Schoen, J. E. Lemons, Elsevier Academic Press ISBN-13:978-0-12-582463-7.
[15] F. V. Anghelina, G. Valerica Cimpoca, I. Pencea, V. Bratu, D. Ungureanu, C. C. Anghelina, Metalurgia International, (4), 17 (2011).

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