NAP-2013

# Biphasic Calcium Phosphate Composite for Biomedical Applications

L.B. Sukhodub[1,*], V.N. Kuznetsov[2,†], A.S. Stanislavov[2], N.N. Inshyna[1], A.I. Kulak[3], L.F. Sukhodub[1]

[1] *Sumy State University, 2, Rymsky Korsakov Str., 40007 Sumy, Ukraine*
[2] *Institute of Applied Physics, 58, Petropavlovskaya Str., 40000 Sumy, Ukraine*
[3] *The Institute of General and Inorganic Chemistry, 9/1, Surganova Str., 220072 Minsk, Belarus*

The paper describes the preparation of the biphasic (hydroxyapatite (HA) and tricalcium phosphate (TCP)) nanostructured calcium phosphate composite. The product was chemically synthesized from the solution which contained calcium acetate $Ca(CH_3COO)_2$ (0,167 mM), sodium dihydrogen phosphate $NaH_2PO_4$ (0,1 mM), sodium hydrocarbonate $NaHCO_3$ (0,02 mM). The calcium phosphate composite was formed at pH=11 with and without the addition of carbonate ions. The samples were analyzed using X-Ray diffraction after the heat treatment at 900°C for 1 h. The derived material contained HA and TCP phases with their contents change depending on the concentration of the carbonate ions in the solution. The mean crystallite size of the HA phase in (121) plane is 12 – 14 nm. Further studies will be directed to the using of the derived composite for the biomedical applications.

**Keywords:** Hydroxyapatite, Tricalcium Phosphate, Biphasic Composite, Heat Treatment, XRD, SEM.

PACS numbers: 87.85.J –, 87.64.Bx, 87.64.Ee

## 1. INTRODUCTION

Synthetic hydroxyapatite (HA) $Ca_{10}(PO_4)_3(OH)_2$ is widely used in medicine for treatment and replacement of the damaged bone tissues due to its closeness in chemical and physical structure to the inorganic component of the native bone. In past decade the replacement of biomaterial with newly created bone was accentuated in the course of the creation of biomaterials based on HA, with synthetic materials used as a source of necessary elements for bone tissue building. Thus the main requirements for biomaterials are their porosity, chemical composition, solubility, presence of the elements which diffuse from the material during resorption leading to easier bone regeneration. The biomaterial resorption function is important for its integration in organism. HA has a low level of solubility (solubility product $SP = 3 \cdot 10^{-116}$ [1]) and dissolves only in acid medium which is locally created by osteoclasts in an active bone resorption zone. It is surrounded by the fibroid capsule of the connective tissue in neutral or alkalescent intertissular liquid and remains undissolved which could lead to negative consequences. The transition to the biphasic composites is one of the means to improve the resorption of the materials based on HA which contain more soluble components, e. g. tricalcium phosphate (TCP) $Ca_3(PO_4)_2$, $SP = 0,2 \cdot 10^{-29}$ [1].

## 2. MATERIALS AND METHODS

### 2.1 Materials

The biphasic product which contains HA and TCP was derived during our studies. The output synthesis materials were calcium acetate $Ca(CH_3COO)_2$ (0,167 mM), sodium dihydrogen phosphate $NaH_2PO_4$ (0,1 mM), sodium hydrocarbonate $NaHCO_3$ (0,02 mM). Equal conditions for simultaneous interaction of $PO_4^{3-}$ and $CO_3^{2-}$ ions with $Ca^{2+}$ and $OH^-$ ions were provided by adding mixed solution of $NaH_2PO_4$ and $NaHCO_3$. The calcium phosphate composite was formed under pH = 11 and 10 M of NaOH aqueous solution at 80°C. The formed calcium phosphate suspension after aging for 24 h was carefully washed with deionized water and heated in a muffle furnace at 900°C for 1 h. The samples with and without the addition of $NaHCO_3$ were synthesized.

### 2.2 Methods

The crystallinity and structure of the synthesized samples were examined using an X-ray diffractometer DRON-3 (Bourevestnik, Inc., Saint-Petersburg, Russian Federation) connected to a computer-aided system for the experiment control and data processing. The current and the voltage of the X-ray tube were 20 mA and 40 kV respectively. All experimental data was processed by means of the program package DIFWIN-1 (Etalon PTC, Ltd., Moscow, Russian Federation). Identification of crystal phases was done using a JCPDS card catalog (Joint Committee on Powder Diffraction Standards).

The crystallite sizes $L$ were calculated using the Scherrer equation [2]:

$$L = \frac{K\lambda}{\beta \cos\theta}, \qquad (2.1)$$

where $K$ is the form coefficient ($K$=1), $\lambda$ is the wavelength, $\beta$ is the peak broadening, $\theta$ is the diffraction angle.

The quantitative phase analysis was done using the reference intensity ratio (RIR) method [3]:

$$C_i = \left( \frac{K_i I_i^{rel}}{I_i} \sum_{i=1}^{n} \frac{I_i}{K_i I_i^{rel}} \right)^{-1}, \qquad (2.2)$$

where $C_i$ is the concentration of the i-phase, $K_i$ is the

---

* l.sukhodub@gmail.com
† vkuznetsov.ua@gmail.com

corundum number of the i-phase, $I_i$ is the peak integral intensity of the i-phase, $I_i^{rel}$ is the peak relative intensity of the i-phase.

The Ca/P ratio was calculated using method described in [4]:

$$\frac{Ca}{P} = \frac{10 \cdot (100 - C_{TCP})/M_{HAP} + 3 \cdot C_{TCP}/M_{HAP}}{6 \cdot (100 - C_{TCP})/M_{HAP} + 2 \cdot C_{TCP}/M_{HAP}}, \ (2.3)$$

where $C_{TCP}$ is the TCP phase concentration (%), $M_{HAP}$ is the molar mass.

The scanning electronic microscopy (SEM) was used for studying the morphology of the samples. The beam voltage was 20 kV.

## 3. RESULTS AND DISCUSSION

The derived results show that the chosen solution composition for the HA synthesis with the organic component decreases the crystallinity of the resulting product compared to the composition with inorganic salt solutions (Fig. 1). The mean crystallite sizes of the HA phases in (121) plane in the heat treated at 600°C samples are 12 (without the carbonate ions addition) and 14 nm (with the carbonate ions addition) which approaches to the biological apatite, and at 900°C – 43 and 53,2 nm respectively. The phase concentrations and Ca/P ratios of the studied samples are shown in Table 1.
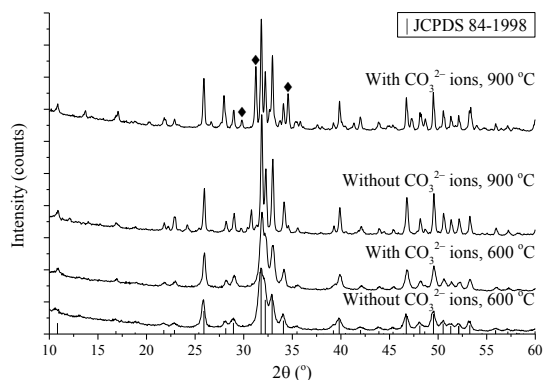


**Fig. 1** – X-Ray diffraction spectra of biphasic calcium phosphate composites of the different synthesis heat treated at 600 and 900°C; major TCP peaks are marked with ♦

**Table 1** – Phase concentrations and Ca/P ratios of biphasic calcium phosphate composites of the different synthesis

| Sample | HA | | TCP | | Ca/P, at. % |
|---|---|---|---|---|---|
| | JCPDS | Concentration, % | JCPDS | Concentration, % | |
| With CO₃²⁻ ions | 84-1998 | 65 | 51-422 | 35 | 1,64 |
| Without CO₃²⁻ ions | 84-1998 | 90 | 9-348 | 10 | 1,66 |

The formation of the significant portion of TCP after the heat treatment indicates that the crystallization of nonstehiometric apatite has occurred under the influence of the organic component, and also the presence of the defects in the crystal lattice due to the partial substitution of $Ca^{2+}$ ions with close in size $Na^+$ ions (0,99Å and 0,98Å respectively) which are present in the solution.

Additional local defects in the crystal lattice could've been induced by the incorporation of carbonate-ions which affect the biological behavior of the resulting product increasing its resorption degree.

The micrographs of particles and their conglomerates are shown in Fig. 2. The particles have the arbitrary shape and their sizes vary from 2 to 15 μm.
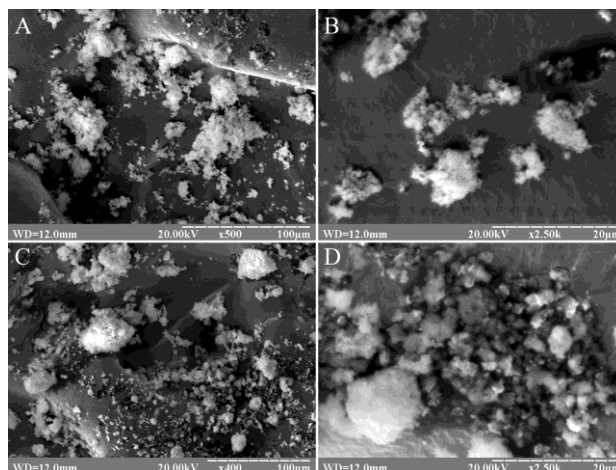


**Fig. 2** – Micrographs of particles and their conglomerates of biphasic calcium phosphate composites of the different synthesis heat treated at 900°C with (A, B) and without (C, D) the addition of carbonate ions

## 4. CONCLUSIONS

The changes of physical and chemical synthesis characteristics (solution composition, temperature, pH value) regulate the phase composition of the resulting biphasic calcium phosphate composite.

The sample synthesized with the addition of carbonate ions after the heat treatment at 900°C shows the increase of the crystallite sizes of the both phases in the major planes and the concentration of the TCP phase with the decrease of the Ca/P ratio.

The dependence of the resorption rate from the phase composition would be defined in future studies.

## REFERENCES

1. J.C. Elliott, *Structure and Chemistry of the Apatites and Other Calcium Orthophosphates* (London: Elsevier: 1994).
2. H.P. Klug, L.E. Alexander, *X-Ray Diffraction Procedures: For Polycrystalline and Amorphous Materials* (New York: Wiley: 1974).
3. F.H. Chung, *J. Appl. Crystallogr.* **8**, 17 (1975).
4. S. Raynaud, E. Champion, D. Bernache-Assollant, J.-P. Laval, *J. Am. Ceram. Soc.* **84** No2, 359 (2001).