PULBERI DE FOSFAT DE CALCIU OBȚINUTE PRIN METODA PYROSOL
CALCIUM PHOSPHATE POWDERS OBTAINED THROUGH THE PYROSOL METHOD

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Reducerea dimensiunilor particulelor, de la micro la nanometrii, permite dezvoltarea de noi materiale, cu proprietăți îmbunătățite. Metoda pyrosol este o metodă modernă de sinteză neconvențională de pulberi care poate conduce la obținerea de particule de dimensiuni de ordinul nanometrilor. Această metodă se bazează pe tehnica de piroliză a unui aerosol, obținut prin pulverizare cu ultrasunete.

Lucrarea de față descrie evoluția microstructurii pulberilor şi a compoziției odată cu variația parametrilor de sinteză. Folosind diferite materii prime, au fost sintetizate pulberi de hidroxiapatită (HAp) şi β-fosfat tricalcic (βTCP). Pentru a obține pulberi omogene şi fine de fosfați de calciu, au fost modificați următorii parametri experimentali: concentrația soluțiilor de materii prime, fluxul de gaz purtător, frecvența de vibrație ultrasonică a ceramicelor piezoelectrice, precum şi temperatura cuptorului sinteză.

Pulberile obținute au fost analizate cu ajutorul analizei termogravimetrice (TGA) şi analizei termice diferențiale (DTA), difracției de raze X şi microscopiei electronice de baleiaj. Mărimea medie a cristalitelor de pulberi a fost determinată din datele de difracție. Rezultatele arată că prin metoda de sinteza pyrosol pot fi obținute pulberi cu compoziții diferite, formate din particule sferice, cu o dimensiune de ordinul nanometrilor, care poate avea multiple aplicații medicale.

The decreasing in particle size, from micro to nanometer dimensions, allows the development of new materials, with improved properties. The pyrolysis method is a modern, unconventional synthesis method of various powders which leads to the preparation of very small (few nanometers) particles. This method is based on the spray-pyrolysis technique - pyrolysis of an aerosol obtained by ultrasonic spray.

The present paper describes the evolution of the powders microstructure and composition with different processing parameters. Using different precursors, phosphate powders - hydroxyapatite (HAp) and β-tricalcium phosphate (βTCP) - were synthesized In order to obtain homogeneous and fine powders of calcium phosphates the following experimental parameters were modified: the concentration of the solution of precursors, the flow of carrying gas, the frequency of piezoelectric ceramics ultrasonic vibration and the temperature of the pyrolysis furnace.

The obtained powders were investigated using Thermogravimetric Analysis (or TGA) and Differential Thermal Analysis (or DTA) measurements, X-ray diffraction and scanning electron microscopy. The average crystallite size of powders was also estimated from diffraction data. The results are emphasizing that by the pyrosol method can be obtained powders with various compositions, consisting of spherical particles, with size within the nanometer range, which may have many medical applications.

Keywords: *hydroxyapatite, β-tricalcium phosphate, spray-pyrolysis technique*

1. Introducere

Human calcified tissues (bones, teeth, cartilages) are composed, to a very large extent, of apatite crystals. Synthetic hydroxyapatite (HAp-$Ca_{10}(PO_4)_6(OH)_2$) is very similar to the composition of natural apatites. Regardless of the synthesis method used, very often the end products exhibit important compositional variations (relative percentage of hydroxyapatite phase and tricalcium phosphate), different morphology and texture, as well as variable porosity and grain size, resulting in different properties and consequently in different medical applications. Recently, the pyrolysis of an aerosol synthesis technique has been used to produce ultrafine particles with different compositions [1]. Its main advantage is that it has the potential to create particles for which the starting materials are mixed in a solution at the atomic level.

In this paper the synthesis of calcium phosphate ultrafine ceramic particles, by the pyrolysis of an aerosol is described. The evolution of their microstructure and composition with different processing parameters is also studied.

2. Experimental

2.1 Description of method

The phosphate based powders were synthesized by the spray-pyrolysis technique, using an ultrasonic atomizer. This technique is intermediate between the techniques of synthesis from a liquid phase and that of synthesis in the vapour phase. Three successive stages: the pulverization of solution, the transport of the aerosol and the pyrolysis, constitute the pyrolysis synthesis technique. The pyrosol process is based on the pyrolysis of an aerosol, produced by ultrasonic pulverization. The installation used is presented in Figure 1.

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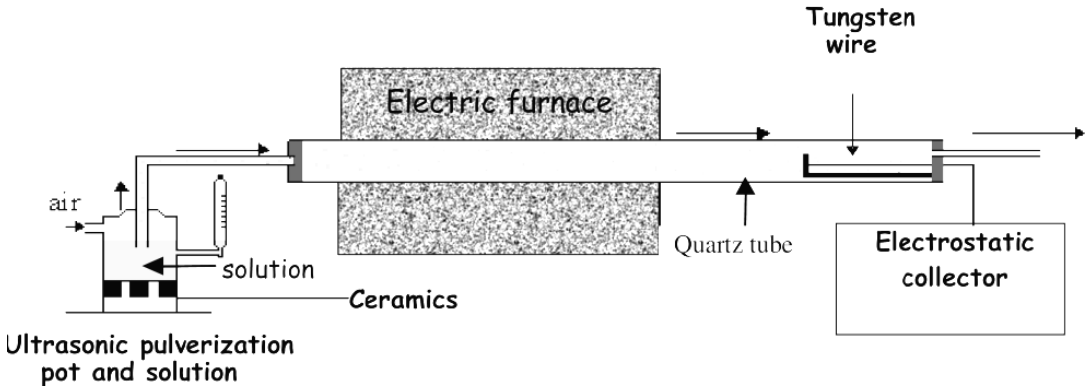

Fig. 1 - Pyrosol installation / *Instalația de pyrosol*

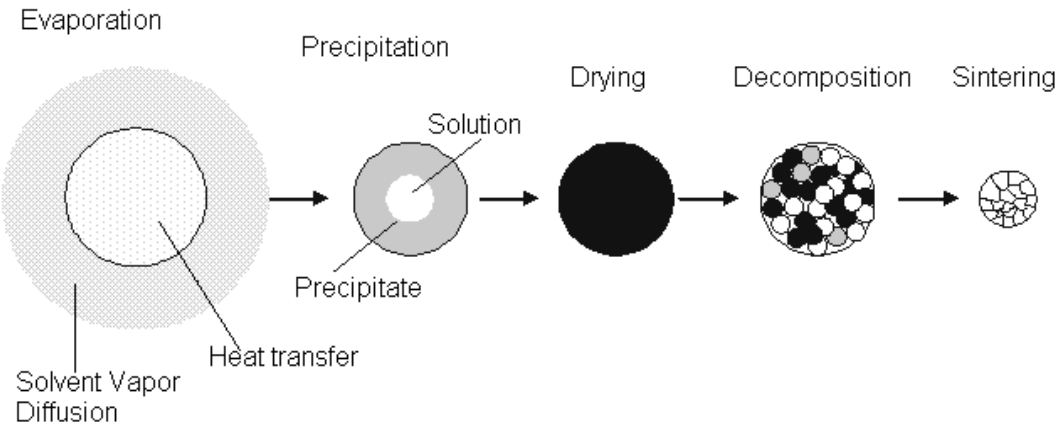

Fig. 2 - Stages of the pyrolysis process / *Etapele procesului de piroliză.*

The aerosol is produced due to the vibrations generated on the surface of a solution, by a beam of ultrasound directed towards the gas/liquid interface. The wave of ultrasound is generated by a piezoelectric ceramic. The wavelength of vibrations depends mainly on the frequency "f" of the ultrasound and the characteristics of the irradiated solution [2]. The average diameter of drops is inversely proportional to $f^{2/3}$. The aerosol thus formed is pulled by a carrier gas, whose flow is fixed, into a furnace carried at high temperature, in which the drops undergo a sequence of physicochemical transformations, described into detail by Messing and coworkers [1–6] (Fig. 2).

The high temperature causes the evaporation of solvent and allows the precipitation of the soluble species in the volume of a dense and spherical particle. At the exit from the pyrolysis installation, an electrostatic filter allows the recovery of powders. This filter consists of a molybdenum wire, held at high voltage (approximately 10 kV). One of the advantages of the pyrosol technique is that it is not necessary to thermally treat the powders to eliminate the volatile species, since the temperatures of pyrolysis are higher than the temperatures of decomposition of precursors. The important experimental parameters of the procedure of fabrication by pyrolysis are [1, 2]:

– the flow "D" of carrying gas;

– the frequency "f " of piezoelectric ceramics ultrasonic vibration;

– the temperature "T" of the pyrolysis furnace;

– the concentration "C" of the solution of precursors.

2.2 Experimental procedures

In this study, the influence of various synthesis parameters on the crystallinity and the composition of the reaction products were investigated. The precursor solution was made up of a stoichiometric mixture of $(NH_4)H_2PO_4$ and $CaCl_2{\cdot}2H_2O$ or $Ca(NO_3)_2$. The effect of the pyrolysis temperature was studied, in the range 600–1000°C, for the powder obtained from $CaCl_2{\cdot}2H_2O$, and also, for powders thermally treated at 1000°C, the influence of the nature of the precursor was studied. The hydroxyapatite powders were synthesized by pyrolysis of an aerosol produced from two precursor solutions A and B:

A { solution (0.05 mol L^{-1}) $CaCl_2 \cdot 2H_2O$; solution (0.06 mol L^{-1}) $(NH_4)H_2PO_4$

and

B { solution (0.1 mol L^{-1}) $Ca(NO_3)_2$; solution (0.06 mol L^{-1}) $(NH_4)H_2PO_4$

The experimental conditions are summarized in Table 1.

For the solution of precursors A, the flow rate and concentration were changed. The corresponding synthesis conditions are listed in Table 2. The experimental conditions are similar to those used for the synthesis of the powder 3, but at a rate two times lower (powder D/2), or with a concentration ten times lower (powder C/10).

The obtained powders were investigated through Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) measurements. The measurements were made using a SETARAM TAG 24, in air ambient, to 1300°C, using a ramp of heating and cooling of 10°/min.

X-ray diffraction analysis was performed using a diffractometer $\theta/2\theta$ Siemens D500, using CuK radiation, with scan step of 0.04° and couting time of 0.6 s/step, for diffraction angles 2 theta ranged between 20 and 60°, at room temperature.

SEM images were obtained by using a JEOL (JSM – 35) at 20KV, after metallization by carbon.

3. Results and discussions

3.1 X-ray diffraction

The as-synthesized calcium phosphate powders were characterized by X-ray diffraction. The X-ray diffraction patterns obtained on powders 1, 2, 3 and 4 are presented in Figure 3, for temperatures of pyrolysis of 600°C, 900°C and 1000°C, respectively.

In the case of the pyrolysis of synthesis carried out at 600°C (powder 1), the X-ray diffraction peaks are broad and uneven, in comparison with those of a powder synthesized at higher temperatures. Consequently, it can be concluded that a poorly crystallized calcium phosphate phase was formed at this temperature. An increase in the temperature of pyrolysis leads to diffraction peaks better defined, due to a higher crystallinity of powders. Whatever the temperature pyrolysis of the aerosol, the apatite type structure is recognizable, no other secondary phase being detected in powders 1, 2 and 3. For powder 4, it was identified β-tricalcium phosphate (JCPDS 09-0169) as the only phase. Consequently, it can be concluded that changing one of the precursors leads to the total change of the phase composition of the obtained powder.

The crystallite size is calculated using the Scherrer formula, starting from the results obtained by X-ray diffraction [8]:

$$L = 0.9\lambda/\theta \cos\theta_0 \qquad (1)$$

L – crystallite size (nm),
λ – incidental wavelength (nm),
θ – width at the middle height of the peak of diffraction, corrected with that of Si (radian) [or full width at half maximum (FWHM)],
θ_0 – angular position of the same peak degree).

The influence of gas flow and concentration of precursors are shown in Figure 4. For all experimental conditions the characteristic lines of hydroxyapatite are present, probably due to the nature of the precursor. However, it can be noted the enlargement of the most important peaks for powders D/2, C/10 and D/2C/10, comparing with powder 3.

The instrumental resolution was measured using Si as the reference powder (Rectapur Prolabo), whose grain size was 1 μm.

Table 1

Precursors and temperature of furnace / *Materii prime utilizate şi temperatura cuptorului de sinteză*

Powder no. *Simbol pulbere*	Temperature of furnace *Temperatura cuptorului* (°C)	Precursor / *Precursor*		
		$CaCl_2.2H_2O$	$Ca(NO_3)_2$	$(NH_4)H_2PO_4$
1	600	*	-	*
2	900	*	-	*
3	1000	*	-	*
4	1000	-	*	*

* used as precursor /*utilizată ca precursor,* - not used as precursor */ neutilizată ca precursor*

Table 2

Precursors and conditions of the pyrolysis synthesis / *Materii prime utilizate şi condiţiile experimentale de sinteză pyrosol*

Powder no. *Pulberea nr.*	Precursors / Concentration of solutions *Precursori / Concentraţia soluţiilor*		Flow of carrying gas *Debitul de gaz*
	$CaCl_2.2H_2O$	$(NH_4)H_2PO_4$	(L min^{-1})
3	0.05 mol L^{-1}	0.06 mol L^{-1}	6
D/2	0.05 mol L^{-1}	0.06 mol L^{-1}	3
C/10	0.005 mol L^{-1}	0.006 mol L^{-1}	6
D/2C/10	0.005 mol L^{-1}	0.006 mol L^{-1}	3

The width at mid-height and the position of peaks were measured by deconvolution of the diffraction lines, according to a pseudo-Voigt formula, using the Profile Fitting (Diffract – AT, Socabim, Paris) software. The Scherrer formula is applied to peaks (002) and (202) in the HAp spectra. The results obtained are presented in Table 3. One can observe that the size of the crystallites increases with the temperature of pyrolysis, due to the grain growth phenomena, accentuated by a higher thermal treatment temperature.

When the concentration of the precursor solution decreases, the crystallite size also decreases, but the effect is much higher with the concomitant decrease in concentration and flow (D/2C/10 powder).

Table 3

Average crystallite size calculated using the Scherrer formula, from diffraction data
Dimensiunea medie a cristalitelor calculate cu formula Scherrer, din difracția de raze X

Powder / *Pulbere*	1	2	3	D/2	C/10	D/2C/10	4
Average size of grains / *Dimensiunea medie a particolelor* (nm)	30	50	66	62	54	45	90

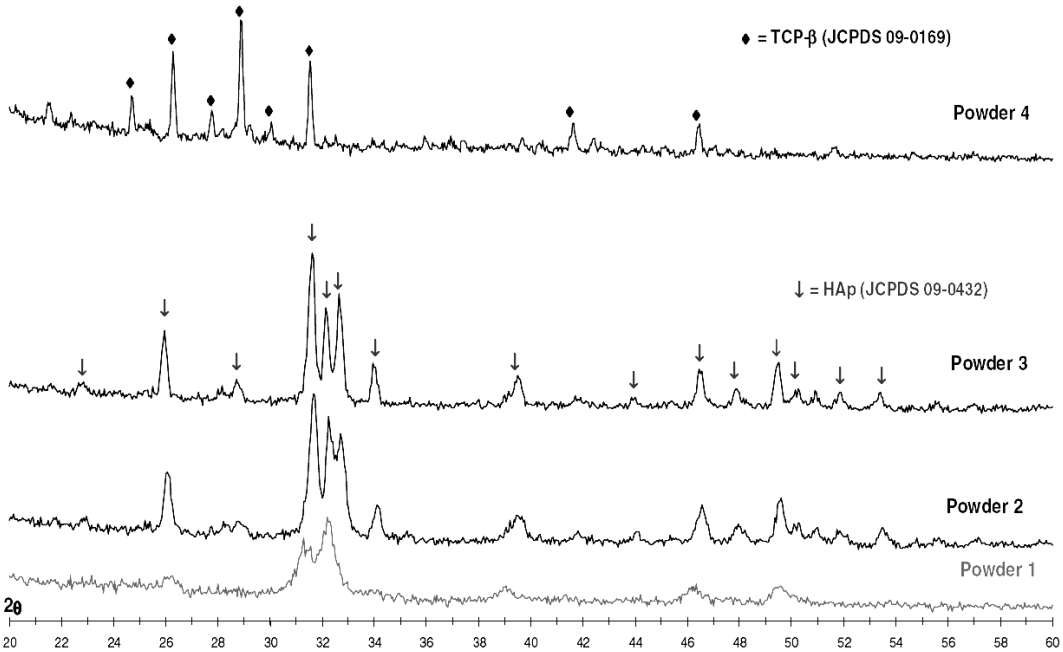

Fig. 3 - X-ray diffraction patterns of powders 1, 2, 3 and 4 / *Imagini de difracție de raze X pentru pulberile 1, 2 3 şi 4*

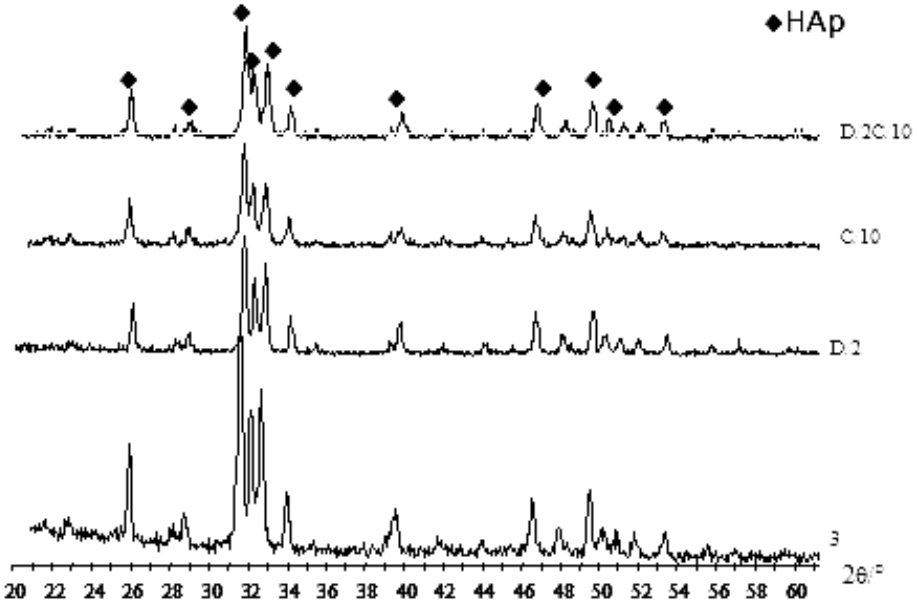

Fig. 4 - X-ray diffraction patterns of powders 3, D/2, C/10 and D/2C/10 / *Imagini de difracție de raze X pentru pulberile 3, D/2, C/10 şi* D/2C/10.

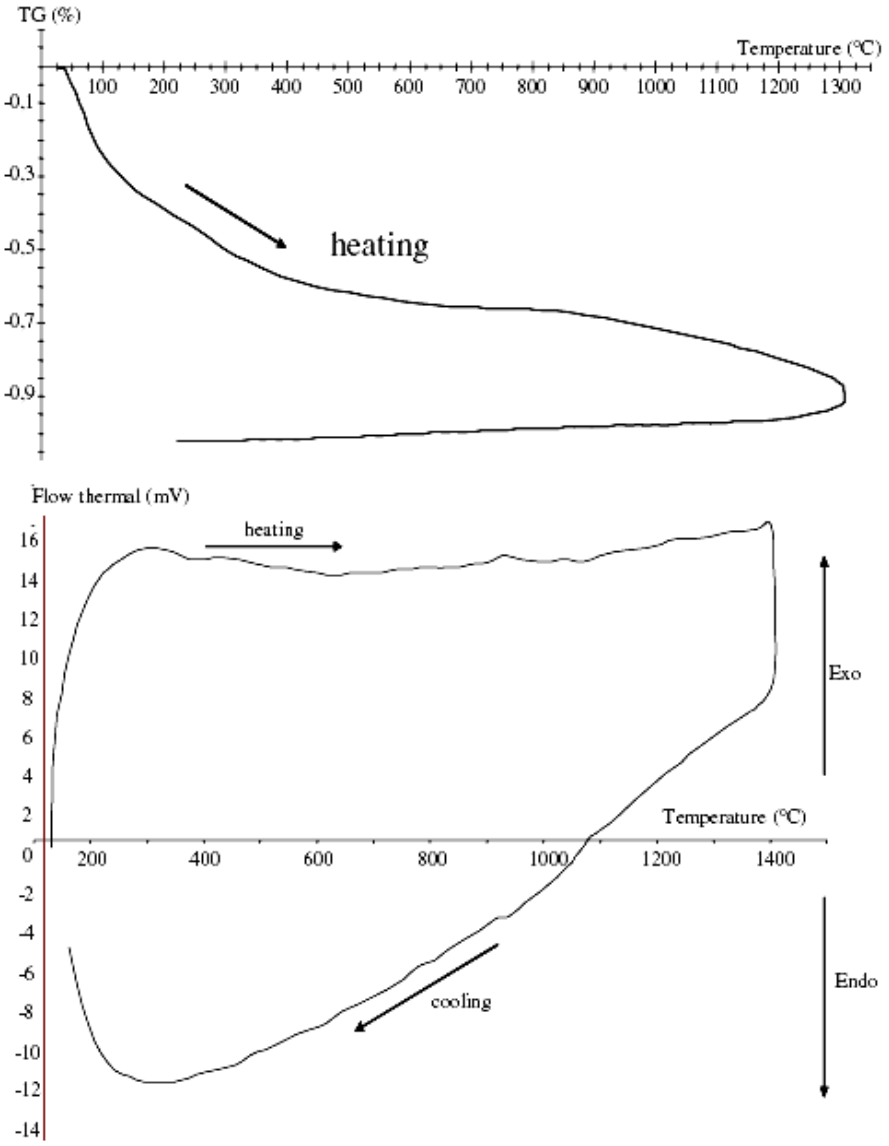

Fig. 5 - Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) of powder 1 / *Curbele TG şi ATD ale pulberii 1.*

3.2 Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA)

Thermogravimetric Analysis (TGA) and Differential Thermal Analysis (DTA) were carried out in atmosphere up to 1300°C, on powder 1. The results are presented in Figure 5. The TGA curve highlights a weak mass loss, of about 0.6% in weight, which takes place up to 500°C. Taking into account the range of temperatures, the reaction of dehydroxylation cannot be taken into account, so the variation observed should be due to the evaporation of water. Another weak mass loss is highlighted at 900°C, but it accounts for only 0.2% of the initial mass. A light dehydroxylation of the apatite phase can thus be considered [9]. An important result lies in the absence of any endothermic peak during heating and of any exo-thermic peak during cooling, which would have been likely to represent the decomposition of the hydroxyapatite into calcium phosphate [6, 10].

3.3 Scanning electron microscopy

The morphology of powders prepared through the pyrosol method was investigated by scanning electron microscopy. For the HAp powders synthesized starting from calcium chloride (powders 1, 2 and 3), the SEM images are presented in Figure 6.

In Figure 6a, corresponding to the powder obtained by pyrolysis at 600°C, the presence of spherical, porous, particles of sub-micrometric sizes can be observed. For higher temperatures of pyrolysis (Figures 6b and c), it can be observed the presence of particles with a shell morphology, very porous and very rough on the surface. The average size of particles is in the micrometric range (for the powder 2: $d_{average}$ = 1.6 μm; for the powder 3: $d_{average}$ = 1.71 μm and for the powder 4: $d_{average}$ = 2.55 μm). The size and morphology of powder 4 particles, elaborated starting from calcium nitrate and corresponding to the TCP

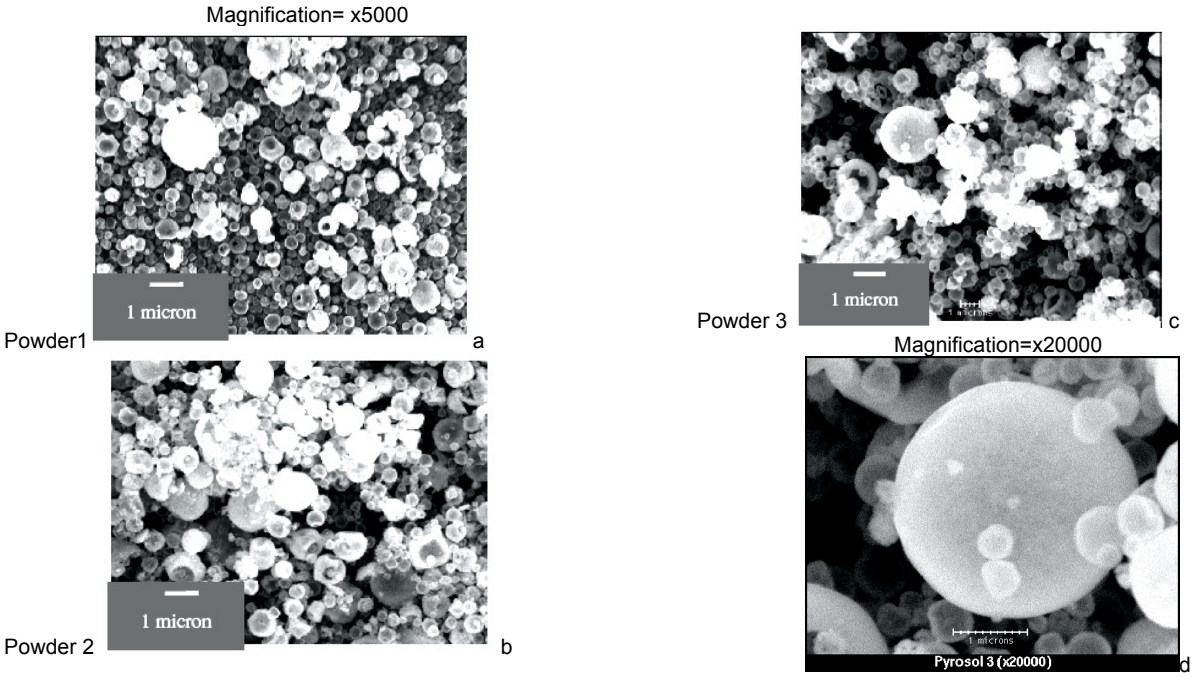

Fig. 6- SEM images of powders 1, 2 and 3 obtained at various temperatures of pyrolysis starting from calcium chloride solutions: (a) 600°C; (b) 900°C; (c) 1000°C (x 5000) and (d) 1000°C (x 20000) / *Imagini MEB ale pulberilor 1, 2 şi 3 obținute la diferite temperaturi de piroliză, utilizând ca materie prima soluția de clorură de calciu (a) 600°C; (b) 900°C; (c) 1000°C (x 5000) şi (d) 1000°C (x 20000).*

phase, are similar to those of HAp obtained in the case of powder 3, having undergone the same heat treatment during pyrolysis, at 1000°C (Fig. 7a, b). The larger particles are spherical, with deformations and large cavities, and they present a rough surface (Fig. 7b).

SEM images for powders D/2, C/10 and D/2C/10 are shown in Figure 8 (a, b and c, respectively). It is observed that the particle morphology is influenced by the gas flow and the concentration of starting solutions. Indeed, the particles are smaller in the case of powder C/10 and simultaneously become denser for the powder D2/C/10. In this case, we can say that a precipitation of the solute in the volume of the drop may have occurred, leading to the production of dense particles. The average particle sizes are in the range of 0.2 to 0.5 microns.

It is noticeable that higher dimensions of powders particles were determined through scanning electron microscopy, comparing to those corresponding to the crystallite sizes calculated from X-ray diffraction data, which indicates the polycrystalline nature of these particles.

4. Conclusions

In present paper the synthesis of calcium phosphate powders by the pyrolysis of an aerosol, starting from different precursors, was studied. The influence of the temperature of pyrolysis was also investigated.

If calcium chloride is used as a precursor, pure hydroxyapatite will be obtained. On the other hand, the predominant formation of tricalcium

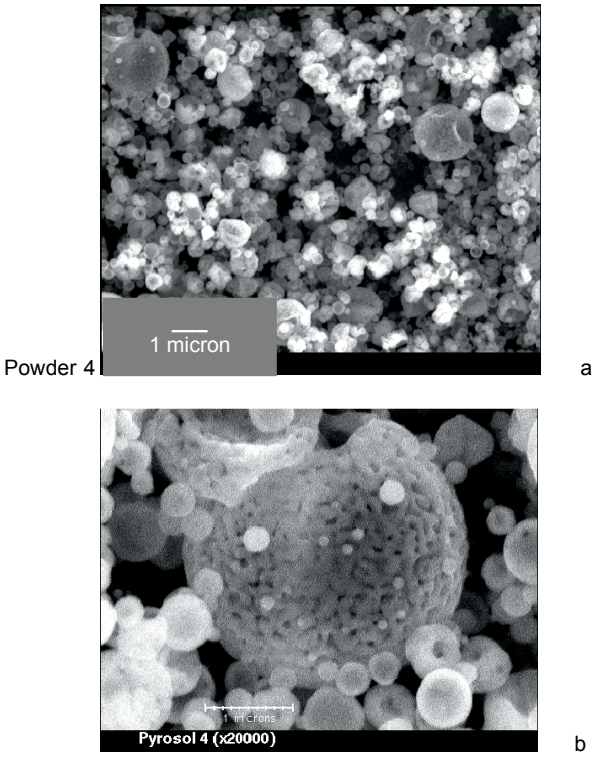

Fig. 7 - Scanning electron microscopy of powders 4 (*a: magnification = x5000, b: magnification = x20000*) / Imagini MEB ale pulberii 4 (*a: x5000, b: x20000*).

phosphate - β form is observed, if the precursor for calcium is calcium nitrate.

An increase of the temperature of pyrolysis has led to better crystallization of the HAp powders, but also to an increase of the particulate size.

The particles are spherical and porous, as was observed from scanning electron microscopy images. It might be concluded that the synthesis by pyrosol is a versatile method that allows the preparation of powders with various compositions, made up of spherical particles, with sizes in the nanometric range, which can have many applications.

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