

OBȚINEREA HIDROXIAPATITEI DENSE PRIN SINTERIZARE ÎN PLASMA DE SCÂNTEIE

OBTAINING THE DENSE HYDROXYAPATITE BY SPARK PLASMA SINTERING

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In this paper it is shown the obtaining of dense hydroxyapatite (HA) through the technology of sintering with spark plasma discharge (Spark Plasma Sintering-SPS). From hydroxyapatite powder obtained by the method of precipitation from solutions of salts have been sintered disc through the SPS to 1100°C, and 950°C for 5 minutes. In a conventional method of powder uniaxially pressing disks were obtained that were sintered at 950°C and 1100°C with landing 2 hours at final temperature. The samples obtained have been characterized by analysis of X-ray diffraction for the study of the composition and analysis of phases electronic microscopy (SEM) for revealing the microstructure. Samples of HA obtained by sintering the plasma discharge (SPS) ahead of those obtained by conventional process showed a dense structure with low porosity and physical-mechanical properties, improved hardness of at least 2.49 GPa and Young's modulus of at least 65 GPa.

În această lucrare este prezentată obținerea hidroxiapatitei (HA) dense prin tehnologia de sinterizare cu descărcare în plasmă de scânteie (Spark Plasma Sintering - SPS). Din pulberea de hidroxiapatită obținută prin metoda de precipitare din soluții de săruri s-au sinterizat discuri prin procedeul SPS la 950°C și 1100°C, timp de 5 minute. Din aceeași pulbere prin procedeul convențional de presare uniaxială au fost obținute discuri care s-au sinterizat la 950°C și 1100°C cu palier de 2 ore la temperatura finală. Probele obținute au fost caracterizate prin analize de difracție de raze X pentru evidențierea compoziției fazale și prin analize de microscopie electronică (SEM) pentru evidențierea microstructurii. Probele de HA obținute prin sinterizarea cu descărcare în plasmă (SPS) față de cele obținute prin procedeul convențional au prezentat o structură densă cu porozitate mică și proprietăți fizico-mecanice îmbunătățite, duritate de minim 2,49 GPa iar modulul Young's de minim 65 GPa.

Keywords: biomaterials, dense hydroxyapatite, SPS, hardness

1. Introduction

Currently, the use of phosphates of calcium in medical applications is very common and the great interest being implemented in various forms, depending on the body part that needs restoration. Hydroxyapatite ($\text{Ca}_{10}(\text{PO}_4)_6(\text{OH})_2$), HA), has been used widely for years for clinical applications like implants and coatings due to its chemical composition and excellent biocompatibility with natural bone, helping to rebuild bone.

HA presents a series of specific properties, i.e., it is non-toxic, non-inflammatory biocompatibility (no immunological defence reaction or undesirable inflammatory effects), osteoconductive (form a network and allow irrigation with blood), bioactive (allows the formation of interfacial bonds with weaving, favouring the emergence of new bone) [1,2].

Whereas, the HA is an important component in orthopaedic surgery and implantology should present mechanical properties similar to those of

hard bone tissue. That's why, in addition to the behaviour of the HA are important densification and methods of preparation of the powder, which can be obtained through: solid phase reactions, reactions of co-precipitation, precipitation, hydrothermal, sol-gel processes, combustion, pyrolysis and aerosol processes, etc. [3-7].

Various studies conducted on hydroxyapatite showed getting values of Vickers micro-hardness (HV) between 3.0 and 7.0 GPa and of low elasticity module (Young) between 44 and 88 GPa [4, 5, 8].

Densification of PAHS can be obtained through various techniques such as microwave sintering, hot pressing and sintering in spark plasma (SPS). Various studies have highlighted the possibility of improving mechanical properties with increasing density sintering [3-5]. However, one must consider the limit of stability at high temperature, because to 1000°C in vacuum HAP will decouple in tricalcium phosphate [4, 7].

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In the literature there are a few reports on the application of the technique of the discharge plasma sintering (SPS) for the production of dense ceramics for biomedical engineering. Compared to conventional sintering SPS makes it possible for low temperature sintering ceramics and sintering time shorter [5-9]. In this sense, the technique of plasma sintering (SPS), which is also known by the name of sintering technique in the field assisted (FAST), proved to be an effective technique, innovative unconventional for strengthening sintering the materials (metals, ceramics, composites, carbides, mesoporous materials, polymers, etc.)

Synthesis process is one of hot pressing changed the electrical current does not pass through an external heating system, so directly through the mould of pressing. Compared to conventional sintering SPS makes it possible for low temperature sintering ceramics and sintering of shorter duration [5-9]. In this sense, the technique of plasma sintering (SPS), has proved to be an effective technique for sintering densification of materials with structural characteristics. SPS sintering process resulting from the application of pulse electric current and of the effect of sintering in the plasma is achieved at low heating times and short process cycles with less than an hour. As a result you can get material compositions and properties previously unfeasible [9].

In this paper, based on the obtained powders by precipitation from solutions of salts [7] has pursued the investigation of Vickers micro-hardness for disks of dense HA obtained through both SPS technique and the conventional technique. Discs obtained were characterized morphological, structural and physical-mechanic.

2. Experiments

Of hydroxyapatite powder obtained by precipitation from solutions of salts [7] were obtained sintered discs with a diameter of 20 mm and a height of $3 \pm 0,5$ mm, through the process of sintering in vacuum plasma using an HP type D25 (FCT Systeme GmbH). The facility is equipped with a power source that produces a direct current pulses with a maximum intensity of 8 kA, at a voltage of 8 V after the mould has been introduced within the SPS installation was an initial pressure of 4 MPa.

Then, the pressure has been increased to 32 MPa and maintained constant until the completion of the treatment of sintering. Heating spare parts was done with a pulsed electrical current passing through powder and graphite mold. DC pulses were applied as follows: a pulse electric of 12 ms, pause 2 ms and a pulse for electric discharge. The heating rate was $100^\circ\text{C}/\text{min}$, temperature of sintering of 950°C and 1100°C , with

plateau five minutes at maximum temperature. After completion of the landing of sintering, cooling samples was achieved rapidly with a velocity of $100^\circ\text{C}/\text{min}$.

The same HAP powders were done by the conventional method, discs with a diameter of 20 mm and a height of 3 ± 0.5 mm. The discs have been pressed at 108 MPa. After drying at $105^\circ\text{C}/24$ h the samples were sintered at 950°C and 1100°C , with two hours plateau at maximum temperature.

The phase composition of samples obtained by the two methods was determined by x-ray diffraction in field the $2\theta = 10-60^\circ$ range, using $\text{CuK}\alpha$ radiation with Bruker-AXS, D8 in Advance diffractometer. For the textural and morphological investigations sintered samples PAHs were mechanically through polishing. The analyses were determined using scanning electron microscopy on a SEM-FIB, Auriga FESEM Workstation, Carl Zeiss. The micrographies were obtained with an electronic detector secondary at 50.00 kx and 2.00 kV voltage samples on samples polished. Density and porosity sintered material were determined by the method of Archimedes. Relative density was calculated as the ratio of the density of the sintered material and theoretical material density hectares (theoretical density of HA was considered $3.156 \text{ g}/\text{cm}^3$) [10].

Vickers hardness (HV) and the module of elasticity Modulus of sintered samples were determined by Oliver & Pharr, method at room temperature, using a piece of equipment for the determination of hardness (CSM Instruments). The device is equipped with a nanoindenter module with the diamond indenter Berkovich has the same report projected area and depth of the Vickers indenter. The measurements were carried out under the following conditions: Poisson's ratio of 0.27 indentation load of 300m, speed of indentation of 2000nm/min, speed of loading/unloading of 1500 nm/min, the hold time for the indenter to the maximum load of 15 seconds.

3. Results and discussions

3.1. The phase composition of samples

In Figure 1 are shown the X-ray patterns of sintered samples by SPS in a vacuum at 1100°C and 950°C for 5 minutes.

Figure 1a shows that at low temperatures (950°C) in the case of evidence obtained through the SPS a majority phase of hydroxyapatite with hexagonal structure (JCPDS No. 09-0432) without secondary phases of tricalcium phosphate (β -TCP). In Figure 1b it is observed that, with the increasing temperature of sintering at 1100°C , in addition to the phase of hydroxyapatite and β - $\text{Ca}_3(\text{PO})_2$ phases occur (JCPDS No. 09-0169).

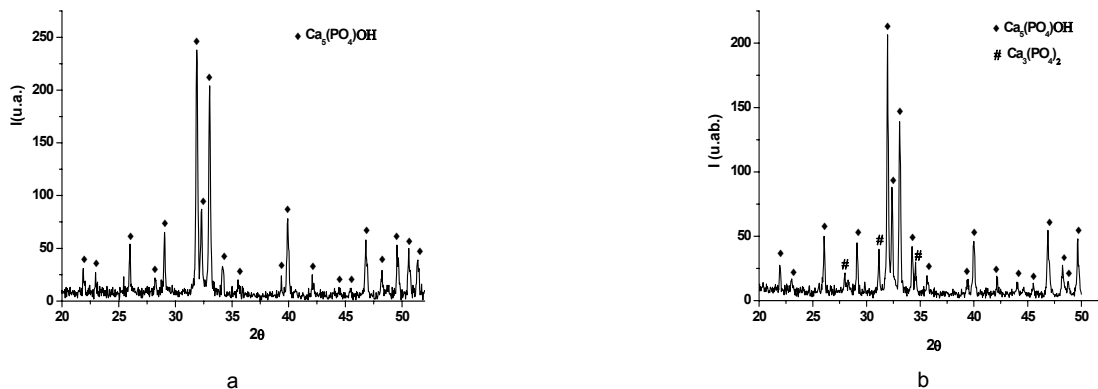


Fig. 1- XRD diffractions pattern of HA sintered at 950°C and 1100°C / Diffractogrammele XRD ale hidroxiapatitei sinterizate la 950°C și 1100°C.

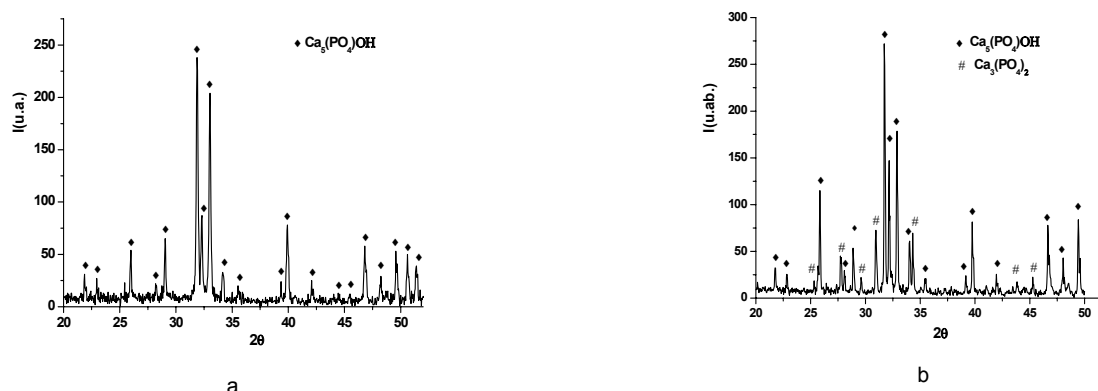


Fig.2 - XRD diffractions pattern of HA sintered at 950°C and 1100°C by conventional technologie / Diffractogrammele XRD ale hidroxiapatitei sinterizate la 950°C și 1100°C prin tehnica convențională.

Table 1

The average crystallite size for crystallized samples
Dimensiunea medie a cristalițelor pentru piesele cristalizate

The method used for processing Metoda utilizata de procesare	Temperature[°C] Temperatura [°C]	Dimensions of cristalites [nm] Dimensiuni cristalite [nm]
SPS	950	61.42
SPS	1100	68.80
conventional	950	56.46
conventional	1100	57.93

The results of analysis of diffraction for the samples obtained by the conventional method are shown in Figure 2. It is found that the X-ray patterns do not show major differences of phase composition being similar to the analysis of samples obtained by SPS.

The average crystallites size was calculated by using the formula for Debye-Sherrer and was determined in the range 56-68 nm. From the analysis of the data presented in Table 1 we can observe a slight increase in the size of crystallites with sintering temperature, increase regardless of the used processing method.

3.2. The microstructure of the sintered samples

The micrographs on the samples sintered by SPS were obtained by scanning electron microscopy after removing the graphite and polishing the samples. Figure 3a and 3b show the

micrographs image of the sample sintered at 950°C with a well densification with structure of spherical particles of nanometric dimensions. The microspores are distributed evenly with the size up to 400 nm. With increasing temperature, sintering structure is much denser, as shown in Figure 3c and 3d.

The micrographs of samples HA pressed by the conventional method are performed on the sample surface by electron microscopy and are shown in Figure 4. The samples sintered at 950°C shows a majority texture with large crystallites and the presence of intergranular pores, as shown in Figure 4a. The micrographs of samples sintered at 1100°C shows that with increasing temperature sintering it produce a slight increase a grains according to Figure 4c and 4d. This change in texture is associated with porosity, important property which influences the micro-hardness of sintered material.

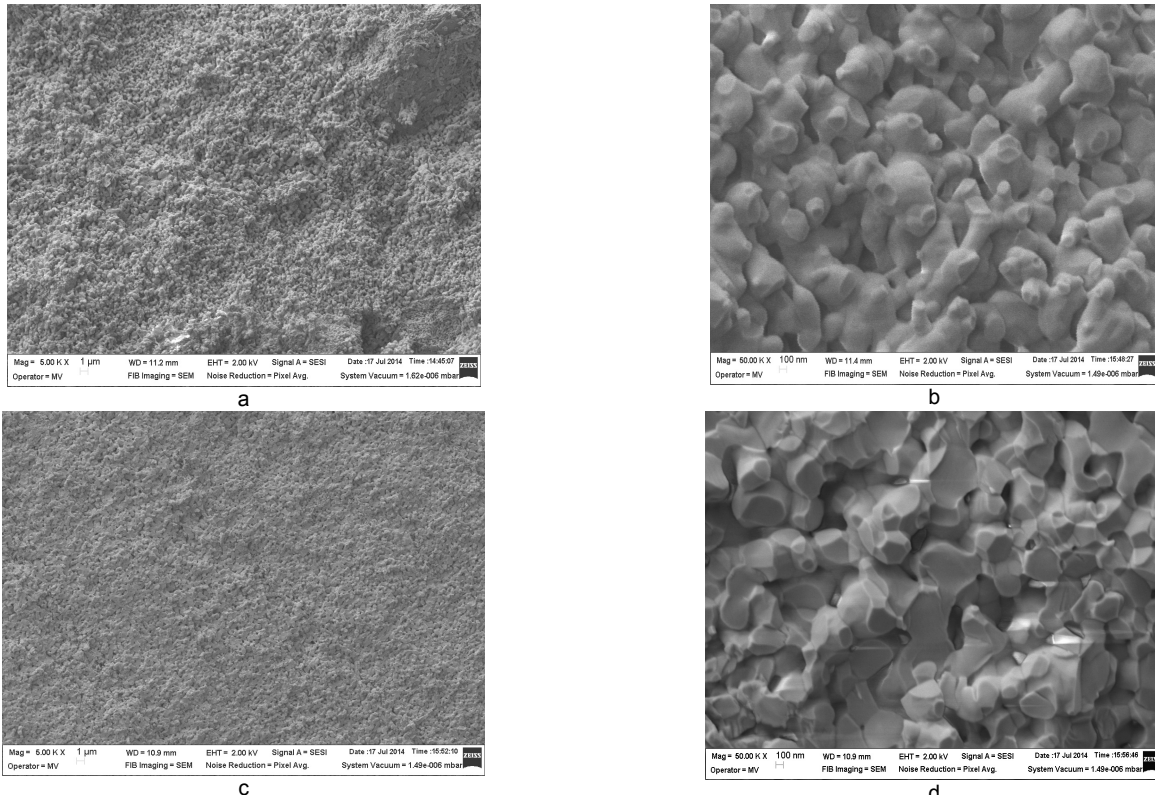


Fig. 3 - SEM micrographs of hydroxyapatite obtained by SPS: a) 950^oC b) 1100^oC / *Micrografii SEM ale hidroxiapatitei obținute prin SPS: a) 950^oC; b) 1100^oC.*

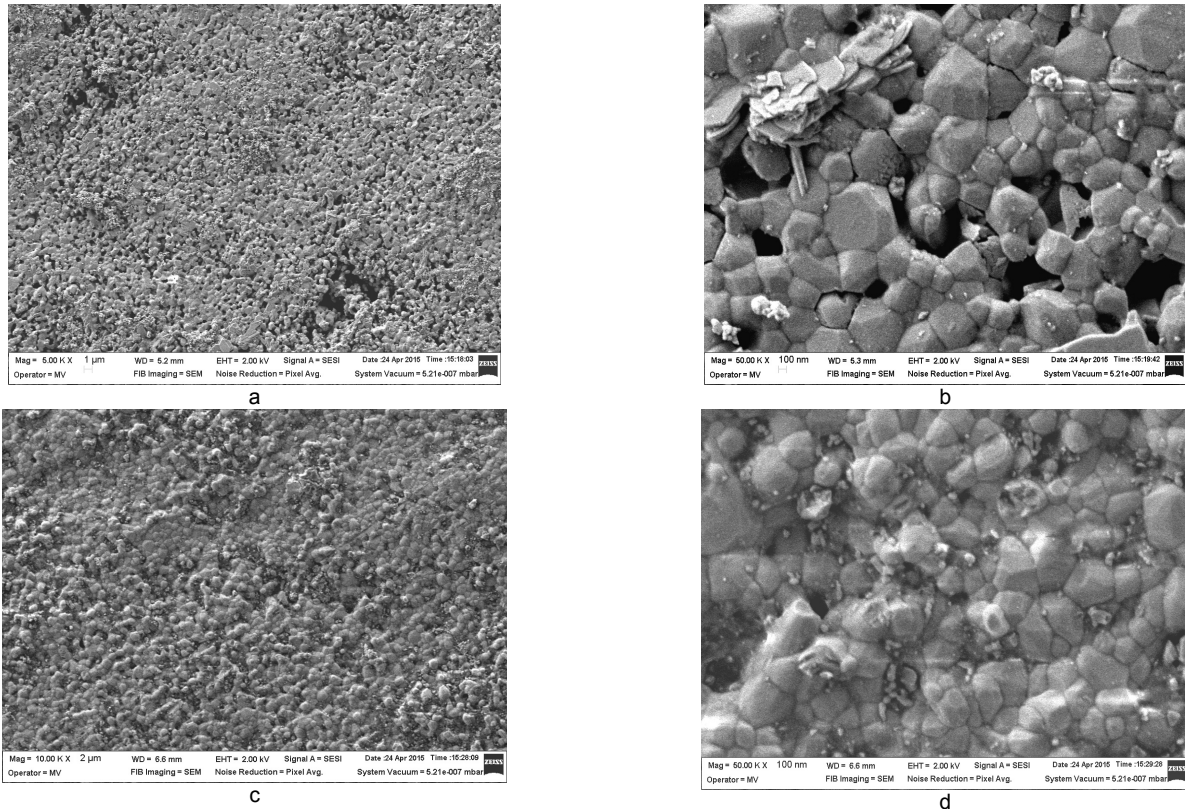


Fig. 4 - SEM micrographs of hydroxyapatite obtained by conventional method: a) 950^oC b) 1100^oC / *Micrografii SEM ale hidroxiapatitei obținute prin metoda convențională: a) 950^oC; b) 1100^oC.*

3.3. Physical and mechanical properties

In Table 2 the results of measurements of the physical and mechanical properties obtained

for sintered samples through the two methods at temperatures between 950 and 1100^oC.

Table 2

Physical and mechanical properties of the HA samples obtained by SPS and conventional method
Proprietăți fizico-mecanice ale probelor de HA obținute prin SPS și metoda convențională

Material type/Sintering temperature [°C]/Technique	Sintered density [g/cm ³]	Relative density [%]	Porosity [%]	Hardness Vickers (HV) [GPa]	Modulus Young's [GPa]
HA/950/SPS	2.93	92.8	7.20	2.49	65.37
HA/1100/SPS	2.89	90.75	9.25	5.17	129.68
HA/950/Conventional	2.54	80.48	19.52	0.25	13.26
HA/1100/Conventional	2.63	83.33	16.67	1.58	50.21

Analyzing the data, it appears that the relative density of the sintered samples at 950°C using the SPS, is close to the theoretical value, having a value of 92.8% and 7.2% porosity. After raising the temperature 1100°C, the densification of the sample, the presence of the compound β -TCP whose theoretical density is 3 g/cm³ [11], did not determine decrease mechanical properties.

Low porosity of parts obtained through SPS, influences positively micro-hardness and Young's modulus. In the literature, in the case of dense, hydroxiapatite for Young's modulus values are between 44 and 88 GPa and for hardness between 3.0 and 7.0 GPa [4,5]. As can be seen in the table 2, the results obtained are consistent with those reported in the literature.

With regard to the evidence produced by the conventional method, at 950°C they have a high porosity over 19% which causes a decrease in mechanical properties compared to the results obtained through the technique of SPS. Just in the case of samples through SPS once pressed with increasing temperature of sintering and mechanical properties values grow.

Good densification of powder of HA, produced by the SPS has been due to the combination of electrical discharge, heat resistance and the effects of applying pressure on HA powder. The electrical discharge, emission of energy is concentrated towards the HA particles which reach high temperatures. Fast heating rate used in the SPS process leads to increased wetting of the particles and at the same time avoids the agglomeration of the clusters of particles formed and kept at a temperature lower than in conventional processes [7, 12].

4. Conclusions

The results obtained show that the SPS technique play an important role in the signal processing of dense materials with low porosity due to the very short duration of sintering of approximately 30 min. Both samples processed through SPS at 950°C and shows good results from 1100°C terms of densification and mechanical properties. Sintered material to 1100°C manifesting the best mechanical properties, hardness Vickers is 5.17 GPa, modulus of elasticity of 129 GPa and a dense structure porosity of 4.7%. Although hydroxyapatite was easily decomposed to 1100°C with β -TCP formation, weren't influenced by mechanical properties.

It is observed a growth of crystals associated with porosity reduction in what is an important component influencing micro-hardness. The micro-hardness value decreases with increasing HA crystallite. All samples sintered densification is a high. Density and mechanical properties of hydroxyapatite samples were influenced by the sintering temperature.

Acknowledgements

The authors wish to thank to Phd. Eng. Gabriela Sbarcea, Phd.Eng. Virgil Marinescu and technician Iancu Ionica and Dorina Vlad for her technical support.

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