Structural analysis of PM hydroxyapatite-based biocomposites elaborated by two-step sintering

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The aim of the research is to develop bone grafts from biocompatible materials by powder metallurgy technology (PM). This paper presents the results of experimental research regarding the elaboration of some biocomposites by two-step sintering (TSS). The initial powder mixture consists of hydroxyapatite powders (30...50μm and <200 nm; 75 %mass) as matrix, respectively TiH_2 (<150 μm; 15-25 %mass) and $CaCO_3$ (5-10 %mass) as flowing agents and reinforcement precursor. The homogenization is performed in a Fritsch-Pulverisette 6 planetary mill (n=200 rot/min for 30 minutes). The green compacts, unilaterally cold compacted at 150 MPa, are submitted to the sintering treatment in a Nabertherm chamber furnace, type L5/12. The sintering parameters are: the 1st step = the sintering temperature, T = 900°C for 1 min, followed by the 2nd step = 800°C for t = 450, respectively 600 minutes. The paper follows the foaming agents and the influence of the sintering parameters on the bone implants structure. The biocomposites macrostructure analyzed by optical microscopy (OM) outlines the closed/open porosity type depending on the foaming agents' participation percentage. The structural analysis studied through SEM and EDX outlines the presence of the foaming reaction products of which TiO_2/Ti has positive effects and CaO has negative effects on the bone graft functionality.

1. Introduction

Hydroxyapatite (HAP) is the main inorganic component of the hard tissues (bone and teeth) of vertebrate animals and humans. For this reason HA has received considerable attention over the past three decades as an implant material showing excellent biocompatibility [1, 2]. Hydroxyapatite is the most important bioceramic materials due to its unique bioactivity and stability. But pure HAP is a type of material with low hardness. So, it cannot be used directly as an implant material [3, 6].

The selection of HAP as matrix is justified by its chemical compatibility with the bone, allowing the formation of successful deployment processes at the interface bone/graft.

The choice of the reinforcement of Ti is justified by the possibility of improving the mechanical characteristics of the graft by decreasing fragility HAP (frangible ceramic) and increasing wear resistance.

In this work are reported the results of the experimental research regarding the elaboration of some biocomposites by two-step sintering (TSS).

The primary materials used in the investigations are hydroxyapatite and titanium, as follows: HAP, having the role of matrix as it constitutes the common component of chemically with bone tissue to be grafted and Ti as a reinforcing element.

The selection of components is justified mainly by the biocompatibility which is characteristic to both materials. Also, the use of each of them in biomedical applications and experimental data of research [4-11] recommend the HAP materials and Ti biocomposites.

Aleksandra V. Byakova et al have studied the effect of the novel foaming agent, calcium carbonate in comparison with the conventional titanium hydride on structure and energy absorbing ability of the aluminium based foams [5].

In one study, Lee YI, Kim, YW and Mitomo, M. [12] have obtained nanostructured SiC of ceramic by sintering process in two steps. The samples were first heated at temperatures between 1700 and 1750ºC, and then cooled immediately and maintained for 8 hours at temperatures between 1550 and 1600ºC. The smallest size of the crystal grains was ~40 nm. The simplicity of the method makes it useful for making dense nanostructured materials, which will make a property of hardness, strength and wear resistance.

Isobe T. et al [13] prepared porous Al_2O_3 ceramics using a two-step sintering method. The average pore size and porosity of the obtained samples were 73 nm respectively 42%. The porosity was mostly constant at temperatures higher than 1300 °C. The T_1 and T_2 temperatures were set at 1150 °C, respectively 1000 °C for two-step sintering tests.

Mazaheri M., et al [14] applied two-step sintering (TSS) on nanocrystalline zinc oxide (ZnO) to control the accelerated grain growth occurring during the final stage of sintering. The results showed that the temperature of both sintering steps plays a significant role in densification and grain growth of the nanocrystalline ZnO compacts.

Wang et al [15] have developed a glass-ceramic bioresorbable calcium phosphate with interconnected macroporous structure.

The porosity obtained meets the requirements of adhesion and bone tissue regeneration. Moreover, the porosity is closely related to the conditions of the heat treatment to obtain the mechanical strength that makes the material lend itself biomedical applications.

In another study, Wang, XH and Deng, XY [16] have obtained dense $BaTiO_3$ samples of ceramic, having nanometric size and using the two-step sintering technology. The grain dimensions were obtained in the range of 8-500 nm, at a very low sintering temperature (900ºC).

In this work we report a methodology which can be used to develop bone grafts from biocompatible materials by powder metallurgy technology.

2. Materials and methods

2.1. Materials

In this study there were used commercial HAP powders with partical size 30-50 µm (HAPµ), as well as submicronic powder particals of HAP size < 200 nm (HAPn) and purity >99,99% produced by Sigma-Aldrich. As flowing agent it was used $CaCO_3$ produced by Sigma-Aldrich, with relative density 2,93g/cm^3 and melting point 800°C. Also as reinforcement precursor it was used TiH_2 powder of 100-150 µm size, purchased from Merch.

2.2. Methods and equipments

In this research, the calcinations, the drying and the TSS process of the samples was done in Nabertherm laboratory chamber furnace, type L5/12, at its maximum temperature of 1200°C, with protective gas connection.

The homogenization was performed in a Fritsch-Pulverisette 6. Compaction equipment was an A009 electromechanical computerized 100kN testing machine, equipped with TCSoft2004Plus software.

The physicochemical characterization of the HAP – based biocomposites was performed by Scanning Electron Microscopy attached with an X-ray detector (SEM/EDS), model Quanta Inspect S.

2.3. Samples preparation

2.3.1. Calcination

According to literature [7-9], the operation of calcination is primarily aimed at increasing the level of crystalline of HAP grains at the same time with the synthesis of CaO (by evaporation P) in order to decrease (until cancelled) resorption phenomenon of the HAP in contact with the bone.

In the research, the calcination of HAP is performed at 900 °C/1h, as shown in figure 1.
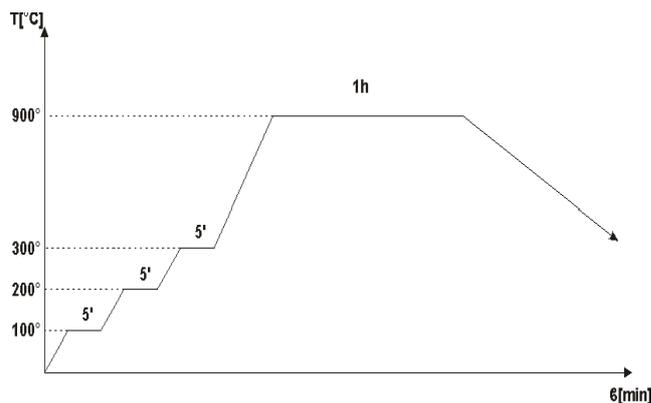

Fig.1. The graphical representation of the calcination process applied to HAP powders

2.3.2. Dosage

The chemical composition of the powders mixtures is presented in the table below.

Tab. 1. Chemical composition of the biocomposite powder mixture

Mixture code	Chemical composition [%mass]			
	HAPn	HAP µ	TiH_2	$CaCO_3$
1n	75	-	25	-
1µ	-	75	25	-
2n	75	-	20	5
2µ	-	75	20	5
3n	75	-	15	10
3µ	-	75	15	10

2.3.3. Homogenization

The homogenization is performed in a Fritsch-Pulverisette 6 planetary mill (n=200 rot/min for 30 minutes, in the protective atmosphere of Ar).

Operating conditions are figure 2: a bowl made of stainless steel with a capacity of 225ml, stainless steel balls with Ø5 diameter, the report ball-powder mixture being 2:1.

For the experiments, it was used ethylic alcohol in a proportion of 1 ml/1g powders mixture.

Homogenization in wet medium is recommended in what regards the uniform dispersion of the reinforcing element (TiH_2) in the matrix (HAP), especially since the matrix is composed of nano powders which have high caking tendency.

2.3.4. Drying

Drying of the powder mixture was held at 200 °C in air, over night.

The powders were maintained for several hours, is shown in Fig. 3.

This operation leads to the formation of conglomerates but powders, which will then be deagglomerated.

Fig.2. Macroscopic aspect of biocomposite in the state of homogenized mixture

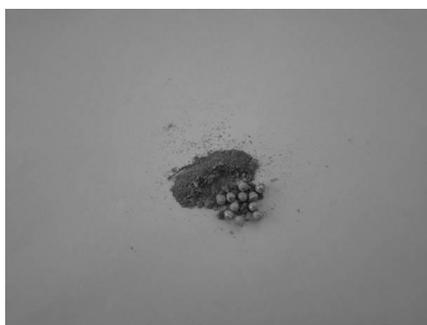*Fig.3. Drying of the biocomposite mixture HAP/Ti in the furnace after milling*

Fig.4. Macroscopic aspect of the biocomposite mixture

2.3.5. Deagglomeration of mixture HAP+TiH₂

Deagglomeration of HAP+TiH$_2$ mixture takes place in the planetary mill Pulverisette 6, in the atmosphere for one minute. Macroscopic appearance of the mixture after agglomeration is shown in figure 4. Finally, the powder mixture of milling balls is sorted in order to carry the sintering operation of bicomposites.

2.3.6. Addition of CaCO₃

CaCO$_3$ powders were weighed to realize the biocomposite HAP/TiH$_2$/CaCO$_3$ mixture, taking into account the dose ratio shown in Table 1.

Homogenization took place in a Fritsch-Pulverisette 6 planetary mill. Operating conditions are: report ball-powder mixture 2:1, speed mill 200 rot/min, homogenization medium-air, mixing time 10 minute.

2.3.7. Compaction the obtained mixtures

For compaction, it was used a cylindrical mold with the diameter of Ø=10 mm.

Compaction equipment was an A009 electromechanical computerized 100kN testing machine, equipped with TCSoft2004Plus software. It was used a pressing force of 150 MPa.

2.3.8. Sintering by TSS route

The aim of the research was to elaborate HAP-based biocomposites through TSS technology according to the following procedure: cold pressing of the compact powders in order to obtain biocomposites by sintering the compacts in two steps, Figure 5.

Argon atmosphere (99.98 % purity) was ensured during the whole sintering treatment.

The TSS technique was used with a 10°K/min heating rate until the 900°C temperature (first step), maintained for 1 minute, then followed by a quick cooling to the 800°C temperature (second step) and maintained for respectively 450 and 600 minutes.

The paper follows the influence of the foaming agents and of the sintering parameters on the structure of the bone implants. The structural analysis studied through SEM and EDX outlines the presence of the foaming reaction products: TiO$_2$/Ti and CaO with positive effects on the bone graft functionality.
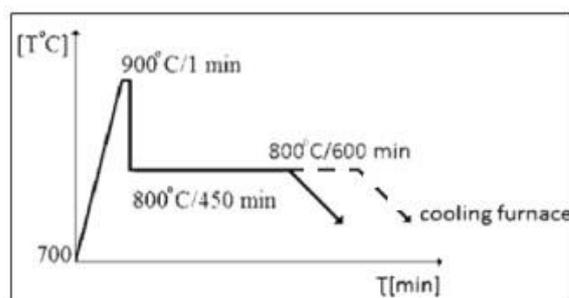

Fig.5. Graphical representation of the TSS process applied to HAP-based biocomposite

3. Results and discussions

These samples were then studied by electronic microscopy with EDS in order to outline the proceedings of diffusion processes during sintering.

The chemical composition of the sintered material is evidenced by the EDS analysis from Table 2.

From Table 2 it can be observed the following aspects:

Regarding the content of Ti

- High values of the Ti content are recorded for the biomaterials with HAPn matrix. The highest value is contained in the samples 1nI (16 %mass) represented in figure 6.

- Once with the 5 %mass $CaCO_3$ addition, in disadvantage of TiH_2, the Ti content from the sintered is decreasing, which is registered for the samples 2nI (Table 2).

- Comparing the sintered samples 2nI and 2µI from the Ti percentage point of view, it is noticed that the TSS treatment is encouraging a higher Ti content in the case of HAPn.
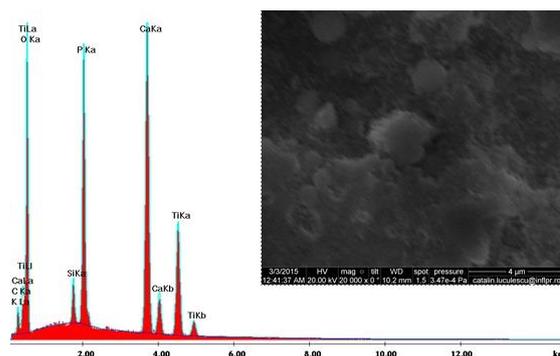

Fig. 6. EDS specter in zoom, SEM on the 1nI sample

Table 2. The chemical composition before and after the sintering of biocomposites samples

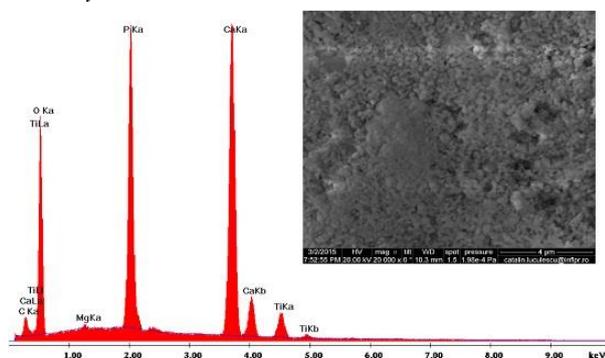| Sample code		Chemical composition [% mass]							
		green parts			TSS parts				
		HAP	TiH_2	$CaCO_3$	C	O	P	Ca	Ti
1	n I	75	25	-	4.29	40.74	12.25	26.72	16
	n II	75	25	-	6.07	40.50	11.27	27.63	14.44
2	n I	75	20	5	5.27	35.85	14.37	35.25	9.09
	µ I	75	20	5	4.73	36.76	17.47	35.84	4.99
3	µ I	75	15	10	4.74	37.14	16.44	36.37	5.07
	µ II	75	15	10	4.27	36.45	16.85	37.29	4.94

Legend:
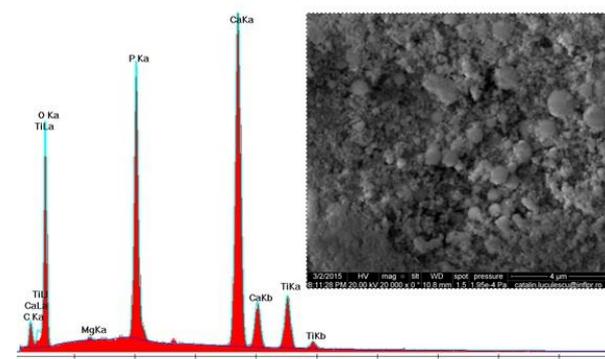*n= nanometric powder particles of HAP as raw material (<200 nm)*
µ = micron powder particles of HAP as raw material (30 ÷50 µm)
I – TSS cycle: $900^0C/1min + 800^0C/450min$
II – TSS cycle: $900^0C/1min +800^0C/600min$

- The Ti inferior limit (4,94 %mass) is registered in the 3µII samples

a)

b)

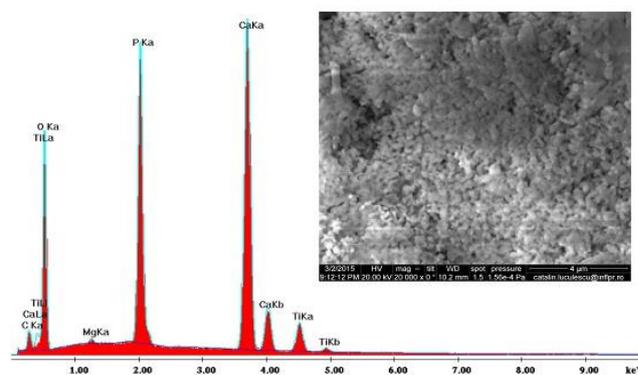*Fig. 7. EDS specter in zoom, SEM on the samples: a) 2µI, b) 2nI*

Fig. 8.EDS spectrul in zoom, SEM on the 3µII sample

Regarding the content of Ca

- High values of the Ca content are recorded for the biomaterials with HAPµ matrix. The highest value is contained in the samples 3µII (37,9 % mass) represented in figure 8.

- Once with the 5% $CaCO_3$ addition, in disadvantage of TiH_2, the Ca content from the sintered is increase, which is registered for the samples 3µI (table 2).

- Comparing the sintered samples 2nI and 2µI from the Ca percentage point of view, it is noticed that the TSS treatment is encouraging a higher Ti content in the case of

HAPμ.

- The Ca inferior limit (26,72 %mass) is registered for the 3nI samples.

Regarding the content of P

- High values of the P content are recorded for the biomaterials with HAPμ matrix. The highest value is contained in the samples 2μI (17,47 % mass) represented in figure 7. a).

- Once with the 10% CaCO$_3$ addition, in disadvantage of TiH$_2$, the P content from the sintered is increase, which is registered for the samples 3μII (table 2).

- Comparing the sintered samples 2nI and 2μI from the P percentage point of view, it is noticed that the TSS treatment is encouraging a higher P content in the case of HAPμ.

- The P inferior limit (11,27 %mass) is registered for the 1nII samples.

4. Conclusions

The HAP matrix is influencing the diffusion process as follows:

- the mirostructured matrix is encouraging the Ti high content (16 %mass for the 1nI samples), but instead it determines a reduced Ca content (26,72 %mass for the 1nI samples);

- the micronic matrix (HAPμ) determinesa high Ca percent (% mass) respectively P (% mass).

The foaming agent influences the structure of the studied biocomposites.

Thus, the biocomposites with TiH$_2$ contain maximum Ti and minimum Ca and P, no matter the 2nd step maintaining time, respectively I and II, 450'- 600'.

CaCO3 influences the Ca percentage as follows:

- in the case of 5 %mass CaCO$_3$ addition, the Ca percentage registeredin the sintered samples is influenced by the HAP powder dimension;

- in the case of 10% mass CaCO$_3$ addition, the Ca percentage registered in the sintered samples is not influenced by the maintaining time at 800°C (I or II).

The maintaing time influences the Ti, respectively P diffusion. Thus, at cycle I (450') were obtained Ti maximum values (16 %mass for 1nI), respectively for P (12,25 %mass for 1nI). Once with the increasing of the maintaing time at 600' (cycle II), Ti and P continueto diffuse in the biocomposite's volume.

The minimum values of 14,44 %mass Ti are registered for 1nII respectively P and11,27% mass for 1nII.

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