

The influence of the foaming agent on the mechanical properties of the PM hydroxyapatite-based biocomposites processed by two-step sintering route

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As bone tissue engineering applications, the studied biocomposites are processed by the powder metallurgy (PM) route. The powder mixture is made of hydroxyapatite submicronic powders (< 200 nm) respectively micronic (30-50 μm) as matrix and TiH_2 (100-150 μm ; 15-20 % mass.) as reinforcement's precursor as well as blowing agent. To increase the porosity by the space holder technique, CaCO_3 powder is added (5-10 % mass.). The homogenization step is performed in Pulverisette 6 ball mill ($n = 200$ rpm, time = 30 min.) followed by the cold compaction at 150 MPa. The green compacts are submitted to the two-steps sintering (TSS) route. Both foaming reactions developed in a manner specific to this composite system: the hydride dehydrogenation lead to TiO_2 (rutile) synthesis respectively the CaO was not synthesized along the CaCO_3 decomposition, and $\text{Ca}_3(\text{PO}_4)_2$ was formed. The compression tests of the researched biocomposites proved widened spectrum of mechanical behavior, from fragile to ductile, depending on the foaming agents content and decomposition reactions along the TSS technology.

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1. Introduction

The biocomposite materials represent a new class of advanced materials for bone reconstruction. Metallic /ceramic /and polymeric-based matrix are used for hard tissue grafting or implant [1-6].

For special applications, like cranial and vertebrae bone reconstruction, the biocomposite foams are the most recommended. The required demands focus on the similarity between the structure (porosity, density) and mechanical properties between the bone graft and natural bone.

The biocomposites based on hydroxyapatite (HAP), with chemical formula $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, have been research as foams for this purpose [7-12] due to its structural and functional similarity to the native bone. The pores structure (closed, interconnected and opened) as well as elaboration advances provide large spectrum of designing and processing.

The most known technological approaches are classified in solid-state by powder metallurgy (PM) technology [13-15], semi-solid [16] and liquid state processing [13, 17].

As far as the foaming technology concerns, the blowing and space holder routes are ones of the most used. The titanium hydride (TiH_2) is frequently used as blowing agent.

The hydride dehydrogenation reaction (starting at 400 and ending over 800 $^\circ\text{C}$) [13] leads to hydrogen releasing

resulting fine micro-pores [14] and $\text{Ti}(\alpha)$ synthesis in the material structure [18], which represents an advantage from the point of view of the biocompatibility characteristics. On the contrary, the space holder techniques via calcium carbonate (CaCO_3), beyond the high porosity generation by CO_2 releasing [19] between 650-900 $^\circ\text{C}$ [13, 16], it may bring structural and functional disadvantages by means of CaO synthesis that raises the biocomposite pH from 7 (neutral) up to 10 [8].

Under these circumstances, the mechanical properties of the PM HAP-biocomposite foams are strongly dependant on the foaming agents respectively foaming reactions initiated along the sintering treatments.

The sintering temperatures are correlated to the foaming temperature range for each foaming agent in order to optimise the foaming effect corresponding to cortical (dense) bone ($\sigma_{\text{UTS}} = 130\text{-}200$ MPa) respectively trabecular (porous) hard tissue ($\sigma_{\text{UTS}} = 1\text{-}100$ MPa) [20, 21].

The present research aims the processing of PM HAP-based biocomposite foams by means of TiH_2 and CaCO_3 foaming agents. The PM technological approach involved the two-step sintering (TSS) process which sintering temperatures (T1-TSS and T2-TSS) are related to the foaming temperature range of each foaming agent.

The compression tests monitored the G modulus and ultimate compressive strength which are explained by the structural phase composition of the HAP-based biocomposite foams.

2. Materials and methods

2.1 Materials

Two types of hydroxyapatite, $\text{Ca}_5(\text{PO}_4)_3(\text{OH})$, powder particles were used as matrix: micronic powders (Sigma-Aldrich, 30-50 μm , >90% purity) and submicronic powders (Sigma-Aldrich; <200 nm; 99,99% purity).

Titanium hydride (TiH_2) powders (Merck; 100-150 μm ; >98% purity) were used as Ti reinforcement precursor as well as blowing agent for the foaming process.

Calcium bicarbonate (CaCO_3) powders (2.93 g/cm^3 ; melting point 800 $^\circ\text{C}$; Merck) were used as space holder agent for the foaming process.

2.2 Equipments and characterisation

The heat treatments developed along the research (powders calcination, drying and sintering) took place in a chamber furnace laboratory scale Nabertherm, type L5/12, working at the maximum temperature of 12000C.

The calcination and sintering processed occurred in argon atmosphere (99.98% purity), with 150-200 ml/min. gas flow.

A planetary ball mill, Fritsch – Pulverisette 6 (P6), with stainless steel vials (250 ml) and balls (5 mm diameter), was used for powder mixtures wet homogenisation.

The cold compaction step for green parts elaboration developed on the A009 electromechanical-computerized 100kN testing machine, equipped with TCSOFT2004Plus software.

The sintered parts were microscopically analyzed by Scanning Electron Microscope (SEM), FEI Co., model Quanta Inspect S.

The structural composition of the samples was determined by the X-ray diffraction (XRD) using a Bruker

D8 advance diffractometer, with $\text{K}\alpha$ ($\lambda = 1.5418 \text{ \AA}$) radiation.

The mechanical compression tests of the sintered parts were performed on the universal mechanical testing machine INSTRON 3382, testing speed 0.5 mm/min and data acquisition rate 20 pct/min.

2.3 Experimental procedure

The HAP micronic and submicronic powder particles were calcinated in argon atmosphere, in the chamber Nabertherm furnace.

The heating rate was 10 $^\circ\text{C}/\text{min}$ up to 900 $^\circ\text{C}$ holded for 1 hour followed by the furnace cooling step in argon atmosphere.

The calcinated HAP powders were mixed and homogenized with TiH_2 particles, according to the experimental data presented in Table 1.

The wet homogenisation developed in the P6 planetary ball mill, in argon atmosphere, by 1ml ethanol addition for 1g powder mixture.

The balls: powder mixture ratio was 2:1. The mill speed was 200 rpm for 30 minutes as homogenisation time. The drying operation took place in the same Nabertherm furnace at 200 $^\circ\text{C}$ overnight time. The dried powder mixtures ($\text{HAP}+\text{TiH}_2$) were deagglomerated in the planetary ball mill P6 in air.

Subsequently, the CaCO_3 foaming agent was added to the ($\text{HAP}+\text{TiH}_2$) powder mixtures, according to the experimental data presented in Table 1.

The addition and homogenisation processes took place in the P6 planetary ball mill for 10 minutes, with 200 rpm and balls: powder mixture ratio of 2:1.

The samples are entitled using the acronym of the HAP matrix powder particles size – *SM* (submicronic, <200 nm) and *M* (micrometric, 100-150 μm) – followed by the CaCO_3 content [% mass] of the powder mixture.

Table 1. Chemical composition and experimental results of HAP-based biocomposite samples

Samples code	Chemical composition of green parts [% mass.]			TSS parts					
	HAP	TiH_2	CaCO_3	Phase composition			Mechanical properties		
				CaCO_3	$\text{Ca}_3(\text{PO}_4)_2$	TiO_2	G [MPa]	σ_{UTS} [MPa]	
<i>SM 5</i>	75	20	5	HAP	CaCO_3	-	TiO_2	998	135
<i>M5</i>					-	$\text{Ca}_3(\text{PO}_4)_2$		396	51
<i>SM10</i>					CaCO_3	$\text{Ca}_3(\text{PO}_4)_2$		634	38
<i>M10</i>									

The biocomposite green parts, about 1 g each, are cold compacted at 150 MPa in hard steel die of 10 mm diameter.

The TSS route was developed according to the thermal cycle presented in Fig. 1.

The TSS route is recommended in case of using submicronic powder particles to obtain nanostructured sintered parts.

The TSS advantage vs. the classic sintering (CS) consists in the possibility to control the material's porosity

and structural refinement by the means two steps developed in a conventional furnace.

The step 1, characterized by $T_{1-\text{TSS}} = 900^\circ\text{C}$ for a very short time (1 minute), allows the initiation of the diffusion processes between the matrix powder particles and reinforcements.

The second step, $T_{2-\text{TSS}} = 800^\circ\text{C}$ for 450 min. allows the densification process without grain growth development [22, 23].

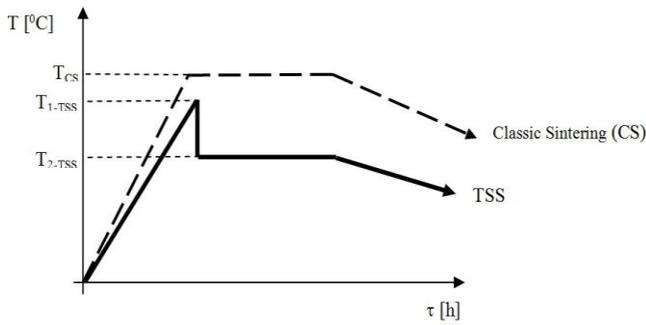


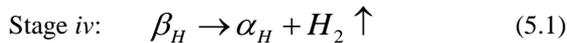
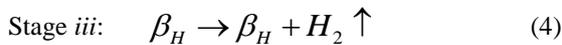
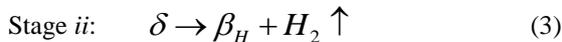
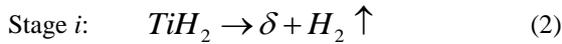
Fig.1 TSS thermal cycle for biocomposites processing.

3. Results and discussions

The titanium hydride belongs to the blowing agents' class, and the foaming reaction takes place as follow:



The dehydrogenation reaction starts at 4000C and ends over 8000C [13]. Liu et al. report four intermediary stages for TiH₂ become Ti, with continuously hydrogen releasing starting from the first dehydrogenation reaction [18]:



In this research, the dehydrogenation reaction brings many advantages. First, it acts as foaming reaction by H₂ releasing. Secondly, the hydride represents the precursor for Ti (α) synthesis which will perform as reinforcing component for the HAP matrix.

The experimental results show the effect of TSS technological parameters on the TiH₂ foaming reaction inside the HAP-based biocomposite system.

About the CaCO₃, this substance acts as space holder agent. During the foaming reversible reaction (6), the carbon dioxide is released while the calcium oxide remains into the material structure:



The advantage of pores formation by CO₂ releasing is counterbalanced by the basic character to the material brought by the CaO that rises the pH from neutral (<7) up to 10 when immersed in water [8].

For this research, the effect of TSS is studied in order to depict the development of reaction (6) with consequences on the mechanical behaviour of the HAP-based biocomposites.

The literature reports different foaming temperature ranges for CaCO₃. Kevorkijan et al. [13] mention 650-900⁰C while Haesche et al. [16] point out the range of 744-832⁰C.

The TSS technological parameters provide specific conditions to develop the foaming reactions of TiH₂ and CaCO₃. Thus, the reaction products will influence the mechanical behaviour of the studied HAP-based biocomposites.

The compression strength of the biocomposite samples was developed on the universal mechanical testing machine INSTRON 3382. The compression modulus (G) and ultimate tensile strength (σ_{UTS}) were determined. The experimental results of the mechanical testing are monitored and correlated to the XRD analysis ones in the Table 1. The mechanical behaviour of the HAP-based biocomposites is strongly dependant on the foaming reactions occurring along the TSS process. The 1st step temperature – 900⁰C corroborated with the 2nd step parameters, 800⁰C for 450 minutes provided specific foaming conditions for the both foaming agents: TiH₂ as blowing agent respectively CaCO₃ as space holder agent.

The most rigid biocomposite is processed from submicronic HAP foamed by 5% CaCO₃ (sample SM5). The highest compression strength, G = 998 MPa is accompanied by the highest ultimate compressive strength, σ_{UTS} = 135 MPa that corresponds to the cortical native tissue [20]. The TSS parameters allowed the complete TiH₂ dehydrogenation up to the stage of TiO₂ (rutile), as XRD analysis points out, according to the Table 1 and Figure 2. As far as CaCO₃ concerns, this foaming agent didn't completely decompose along the TSS route. It is supposed than less of 30% mass. of CaCO₃ addition decomposed during TSS, according to Gergely et al. [19]. Thus, the residual carbonate is present in the sintered HAP nanostructured matrix, Figure 3, providing the brittle mechanical behaviour of the biocomposite material.

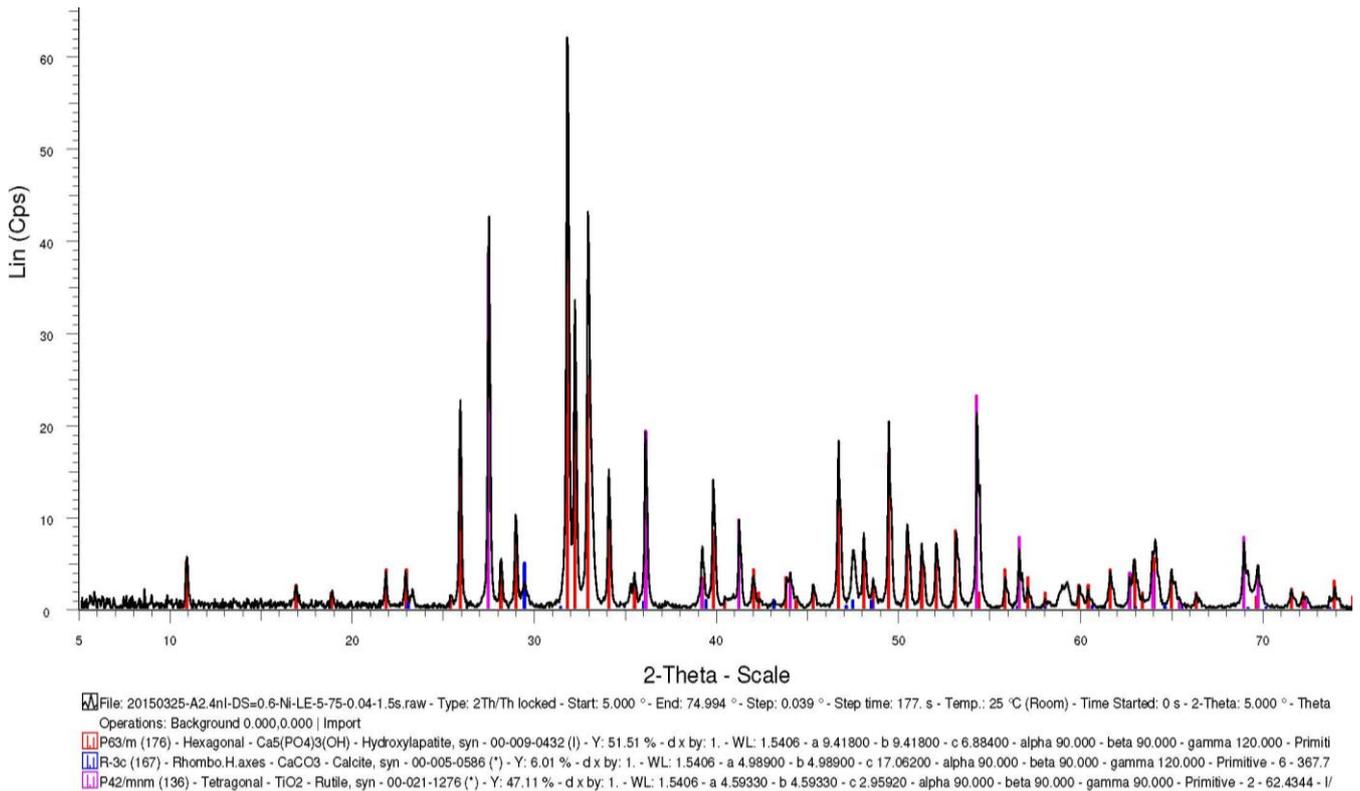


Fig.2 XRD pattern for SM5 sample processed by TSS.
The peaks reveal the phase composition: HAP, TiO₂ (rutile) and CaCO₃

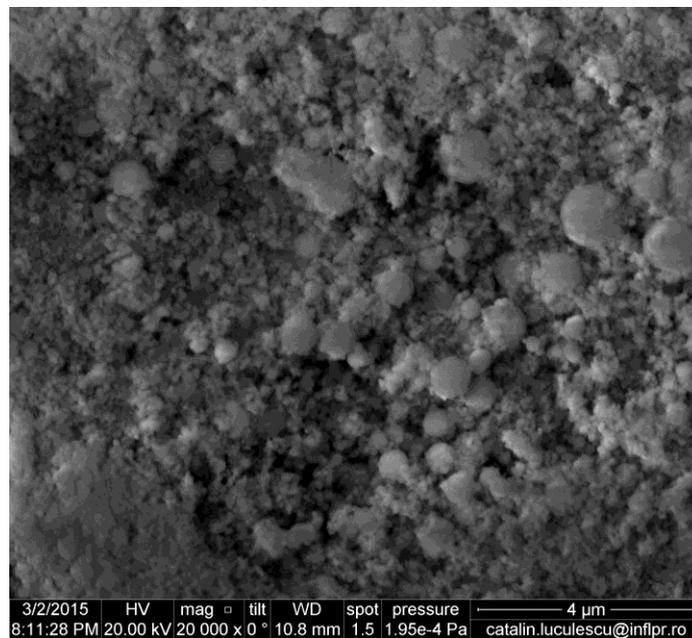


Fig. 3. SEM image of SM5 sample

A brittle-ductile behaviour of the studied biocomposites was registered in case of 10% mass. of CaCO₃ addition to the submicronic (SM10 sample) respectively micronic (M10 sample) HAP matrix.

This performance occurred due to the partial decomposition of CaCO₃ and the simultaneously synthesis of Ca₃(PO₄)₂. Both phases act as reinforcing

components, accompanied by TiO₂, for the HAP matrix, as Table 1 and Fig. 3 show. The mechanical experimental data confirms the brittle-ductile behaviour by $G = 634$ MPa respectively $\sigma_{UTS} = 38$ MPa. The compressive strength corresponds to the trabecular native tissue determined by Reilly [21] respectively more porous structure related to less rigid characteristic than the cortical tissue.

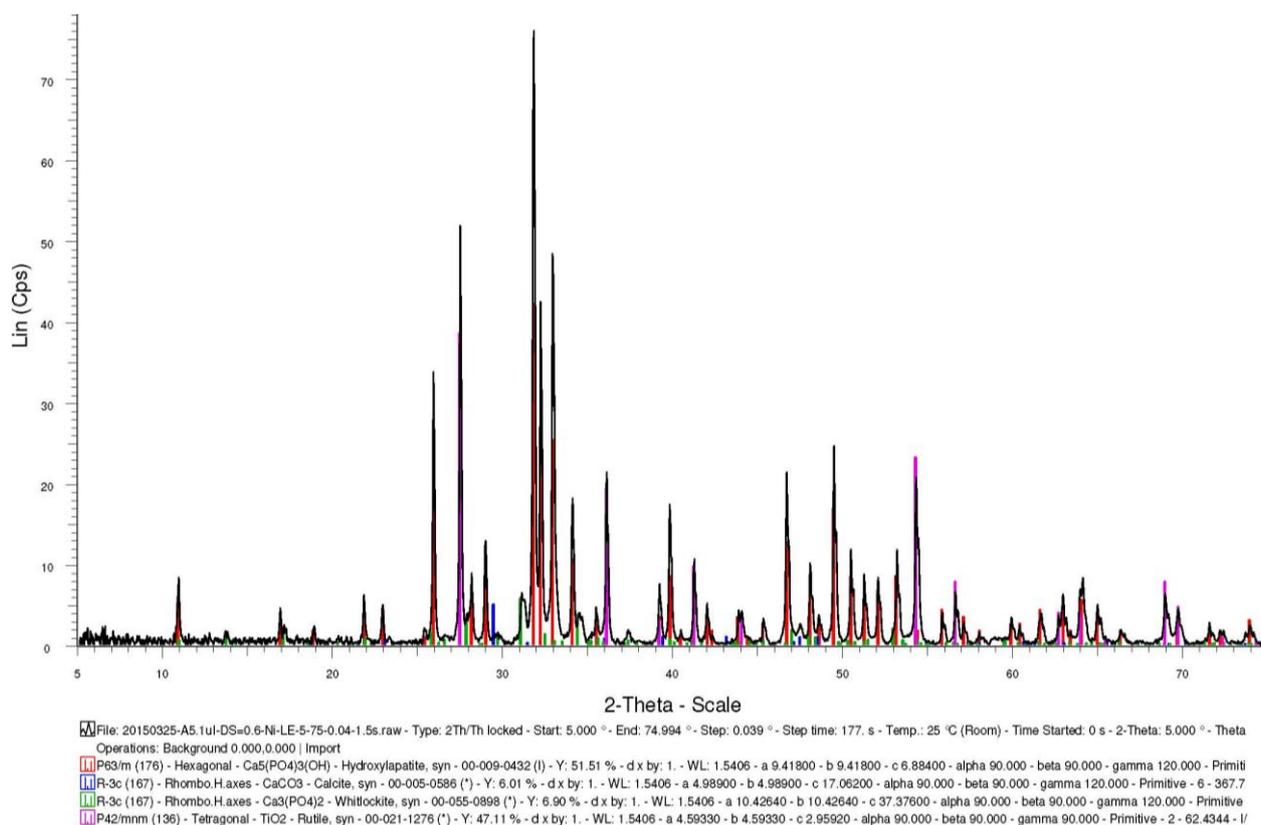


Fig.4 XRD pattern for M5 samples processed by TSS.
The peaks reveal the phase composition: HAP, TiO₂ (rutile) and Ca₃(PO₄)₂

4. Conclusions

The HAP-based biocomposites were processed by TSS route. As foaming technology, two simultaneously route were used: blowing technique via TiH₂ (15 and 20% mass.) respectively space holder technique using CaCO₃ (5 and 10% mass.). The TSS parameters (1st step: T1 = 9000C for 1 min.; 2nd step: T2 = 8000C for 450 min.) were correlated with the foaming temperature range for each foaming agent in order to obtain biocomposite foams with higher porosity.

The mechanical properties of the HAP-based biocomposites, determined by the compression tests, are influenced by the foaming reaction development. The foaming processes occurred in a different manner than the well-known ones. Thus, TiH₂ dehydrogenated up to TiO₂ (rutile) which is a biocompatible phase and brings advantage to the further in-vitro and in-vivo studies. The fragile performance of TiO₂ contributes to the entire biocomposites mechanical behaviour. On the other hand, CaCO₃ decomposed without CaO synthesis which is an advantage from mechanical behaviour point of view as well as for further in-vitro and in-vivo studies.

Also, the matrix (HAP) powder particles size as well as by the reinforcing components content (TiH₂ and CaCO₃) had a great control on the biocomposites' mechanical characteristics. The submicronic HAP powders partially obstructed the decomposition of 5% mass of

calcium carbonate that determined a fragile behaviour of the processed composites, containing residual CaCO₃ (G = 998 MPa; σ_{UTS} = 135 MPa) that corresponds to the cortical native tissue. By increasing the carbonate content up to 10% mass, the partial decomposition of CaCO₃ was more intense than for 5% mass. The samples contain residual CaCO₃ and synthesized Ca₃(PO₄)₂, providing a fragile-ductile behaviour (G = 634 MPa; σ_{UTS} = 38 MPa), similar to the native trabecular tissue. As far as the micronic HAP powders concern, they enhanced the complete decomposition of 5% mass of calcium carbonate. The ductile behaviour of the processed composites (G = 396 MPa; σ_{UTS} = 51 MPa) may be explained by the absence of CaCO₃ but only Ca₃(PO₄)₂ nearby HAP and TiO₂ phases.

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