Influence of Two Steps Sintering Parameters on Tribological Behaviour of Hybrid Hydroxyapatite-Based Biocomposites

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Abstract: The nanostructured biocomposites with hydroxyapatite (HAP) matrix reinforced by titanium (Ti), processed by two steps sintering (TSS) route in argon atmosphere, provide excellent wear behaviour when they are elaborated in specific sintering parameters. The wear tests, developed in steel ball-on-disc dry conditions, show low wear rates about $2x10^{-4}$ [mm^3/Nm] when the biocomposites are processed at 750...800^{0}C for 450...600 min. in comparison with high wear rates $7x10^{-4}$ [mm^3/Nm] in 700...750^{0}C for 300 min. as TSS parameters. The X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis outline the structural features that explain this wear behaviour.

Keywords: Biocomposites, nanostructures, two steps sintering route, wear.

1. INTRODUCTION

Nowadays, the biomaterials market overpasses the `80s trend which was just to replace/repair of the human body injured part. Thus, at the present time the 3rd class of biomaterials is strongly increasing, especially in the USA but also in the most developed European countries. The major demand to be fulfilled by the new biomaterials is to provide the self-healing effect by special mechanisms for integration into the human body and the nanostructure feature represents the key-solution for this demand [1,2]. In comparison with the conventional microstructured biocomposites, the nanostructured ones provide great advantages as far as concern the mechanical properties [3,4], dimensional stability [5] and osseointegration process [6].

One of the most representative biocomposites for hard tissue engineering applications is made of hydroxyapatite (HAP)-based matrix reinforced by titanium, entitled HAP/Ti. The advantages provided by the synthetic HAP, with chemical formula $Ca_{10}(PO_4)_6(OH)_2$ [7] are highly upgraded by its nanostructure feature as matrix [8] in combination with micrometric Ti particles as reinforcement component [9,10], hereinafter named hybrid biocomposites.

As far as the sintering treatment concerns, the two steps sintering (TSS) provides the great advantage of preserving the nanostructure feature of the sintered materials, in general, respectively HAP matrix. The TSS first step is characterized by a specific temperature (T_{1-TSS}), usually nearby the classic sintering (T_{CS}) and a very short dwell time (τ_{1-TSS}, about few minutes), just to afford the ignition reaction between the composite components. The TSS second step, that corresponds to the densification stage, is represented by an almost instantaneously temperature decreasing from T_{1-TSS} up to T_{2-TSS} and a particular dwell time, τ_{2-TSS} which is about several hours. The correlation between T_{2-TSS} and τ_{2-TSS} describes the well-known "kinetic window" concept [11] which allows the synthesis of the nanostructured materials with tailored porosity.

This research is focused on the HAP-based biocomposites characterisation from the point of view of their tribological behaviour in critical dry friction conditions. These biocomposites are processed by the powder metallurgy (PM) technology respectively the TSS as heat treatment. The correlation between the technological parameters (sintering time and temperatures) and the structural characteristics provided by the X-ray diffraction (XRD) and scanning electron microscopy (SEM) analysis contributes to the understanding of the wear behaviour of the hybrid biocomposites.

2. MATERIALS AND METHODS

2.1. Biocomposites Preparation

For the experiments, nanometric HAP powder particles (<200 nm; > 99,99% purity; Sigma-Aldrich; 75%wt.) and TiH_2 micrometric powder particles (< 150μm, water atomized; 25%wt.) are processed as homogeneous mixture as it is presented in other

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E-ISSN: 2409-5826/14

research [9, 10]. Compacted billets of 12 mm as diameter and 5mm as height are unilateral cold compacted for 90...150 MPa and then sintered by TSS technology. Figure **1** graphically presents the difference between the classic sintering (CS) and TSS from the point of view of the technological parameters. The major advantage of TSS vs. CS is the nanostructured materials manufacturing by a special management of the technological parameters, in the same conventional sintering furnace.

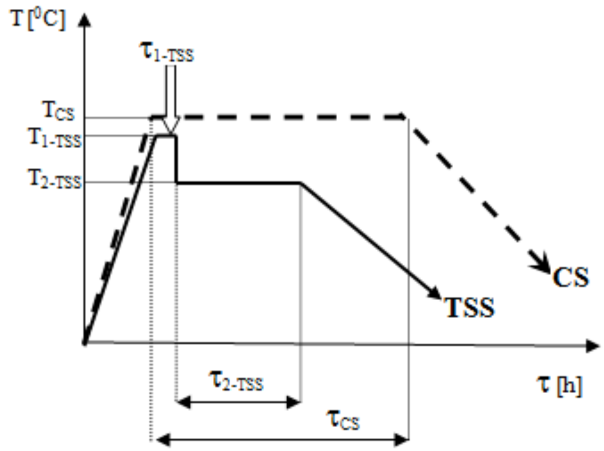

Figure 1: Schematic representation of TSS route (continue line) vs. classic sintering (CS) (dot line).

Table **1** presents the main technological parameters of the hybrid HAP-based biocomposites processing.

2.2. Biocomposites Testing

The dry wear tests have been performed on tribometer TRB 01-02541 (CSM Instruments S.A.). The testing parameters are: the ball-on-disc friction couple, the normal load 2N, 100Cr6 tool steel for the ball of 6 mm diameter, the sliding linear velocity = 1 cm/s. The evaluated parameters are the coefficient of friction (COF) and wear rate. The wear rates as well as the profile of the wear track are determined by the profilometer Surtronic 25 (M112/3522-01), Taylor Hobson Precision, using the following technical parameters: the roughness type, Ra; the cut-off = 0,8 mm; the evaluation length = 2...4 mm; the range = 100 mm. The experimental results on the COF and wear rate are presented in Table **1** and correlated to the experimental results obtained along optical microscopy and XRD analysis.

The optical biocomposite microstructure was analysed on inverted metallographic microscope Eclipse MA 100 (Nikon corporation, Japan) with NIS-Elements imaging software, version 3.03.

The XRD measurements were performed on the biocomposite sintered samples, with a Shimadzu XRD-6000 X-ray diffractometer, equipped with a vertical goniometer and a scintillation detector. The functioning parameters of the X-ray tube (A40-Cu type) were established at a voltage of 40 kV and a current of 30 mA. A continuous scan measurement has been chosen as operation mode in a geometry (θ/2θ) setting a scan rate of 2 [deg.min^{-1}] and a scan range from 10 deg. to 100 deg. Divergence slit was of 1.0000 deg, scattering slit was of 1.0000 deg, and receiving slit of 0.1500 mm.

3. RESULTS

The experimental results concerning the wear rate of the Hap/Ti biocomposites confirm a good behavior during the dry wear tests and they are comparable to those reported by Masmoudi *et al*. [12]. As far as the COF concerns, the technological parameters have a slight influence. However, there are some remarkable differences between the wear rates and the most important influence is registered by the kinetic window (the TSS 2nd step) parameters corroborated to the cold compaction pressure. The understanding of the tribological behavior is based on the structural composition of the sintered biocomposites which is presented in Table **2**.

According to the experimental results registered in Table **2** and corroborated with the wear results from Table **1**, the highest wear rate (7.7 x 10^{-4} Nm/mm^3) corresponds to the biocomposites processed at the lowest compaction pressure (90 MPa), the shortest sintering time ($\tau_{2\text{-TSS}}$ = 300 min.) and the lowest sintering temperature ($T_{2\text{-TSS}}$ = 700^{0}C). It seems that

Table 1: Technological Parameters for the Hybrid HAP-Based Biocomposites Processing and the Wear Tests Results

PM technology					Wear parameters		
Compaction pressure [MPa]	TSS parameters				Coefficient of friction (COF)	Wear rate [x10^{-4}] [mm^3/Nm]	Wear track area [μm^2]
	$T_{1\text{-TSS}}$ [^{0}C]	$\tau_{1\text{-TSS}}$ [min.]	$T_{2\text{-TSS}}$ [^{0}C]	$\tau_{2\text{-TSS}}$ [min.]			
90 - 150	900	1 - 10	700 - 800	300 - 600	0.3 - 0.36	2.2 – 7.7	289 – 2434

Table 2: Structural Composition of HAP/Ti Biocomposites Depending of the Technological Parameters of the Kinetic Window (TSS 2nd step)

Compaction pressure [MPa]	Kinetic window parameters		Structural phases of sintered HAP-based biocomposites	
	$T_{2\text{-}TSS}$ [^{0}C]	$\tau_{2\text{-}TSS}$ [min.]	Ca-based	Ti-based
90	700	300	Apatite, Ca	TiO2
	800	600	Apatite, Ca, Ca3(PO4)+H2O, Ca(TiO3)	TiO2
120	700	300	Apatite, Ca3P2, Ca(OH)2, CaP	TiO2, TiH2, Ti
	800	600	Apatite, Ca3(PO4)+H2O	TiO2
150	700	300	Ca(OH)2	TiO2
	800	600	Apatite	TiO2

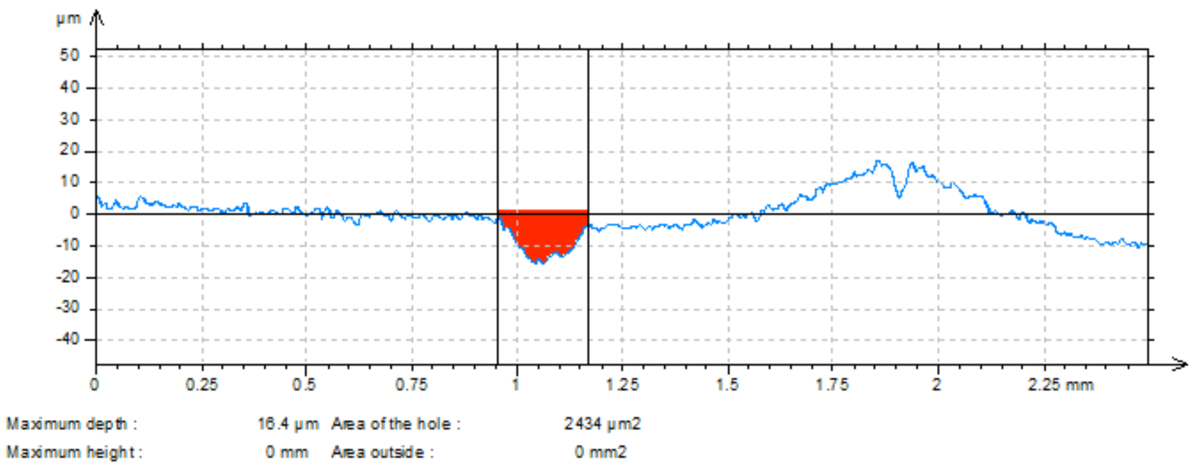

Figure 2: Wear track profile (coloured area) determined by Surtronic profilometer for the hybrid HAP-based sample compacted at 90 MPa and subsequently TSS 2nd step at 700^{0}C / 300 min.

the diffusion reactions between the composite components are incomplete and the obtained structural phases present low wear strength, confirmed by the largest wear track area of 2434μm^2, Table **1** and Figure **2**.

Another negative influence of these kinetic windows' parameters is the biocomposites cracking, as Figure **3** presents. Further research in this direction will focus on the thermal stresses which are possible responsible for this behaviour.

For a higher compaction pressure (120 MPa), more complex reactions occur between HAP and TiH_2 along the kinetic window and the wear rate improves respectively decreases.

The best wear rate respectively the lowest value (2.2 x 10^{-4} Nm/mm^3) corresponds to the highest compaction pressure (150 MPa) in relation with the highest parameters of the kinetic window: $T_{2\text{-}TSS}$ = 800^{0}C respectively $\tau_{2\text{-}TSS}$ = 600 min. The densification stage completes by the means of these technological parameters and, by consequence, the best wear behaviour may be explained by the presence of the apatite in combination with TiO_2 which is completely transformed from TiH_2, which is confirmed by the XRD patterns from Figure **4**.

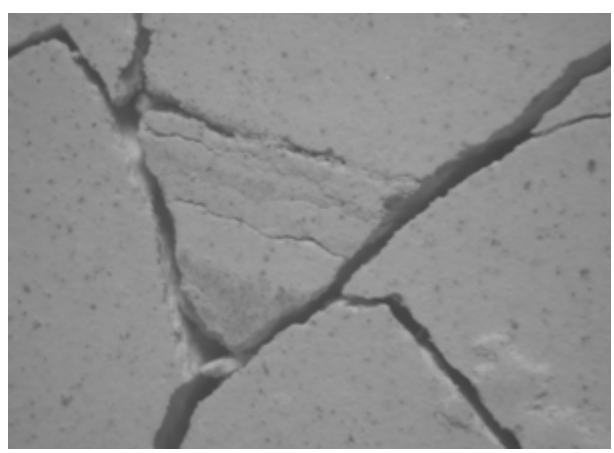

Figure 3: Optical macroscopic view of HAP/Ti compacted at 90 MPa and by TSS route with kinetic window's parameters: 700^{0}C / 600 min. (75X magnification).

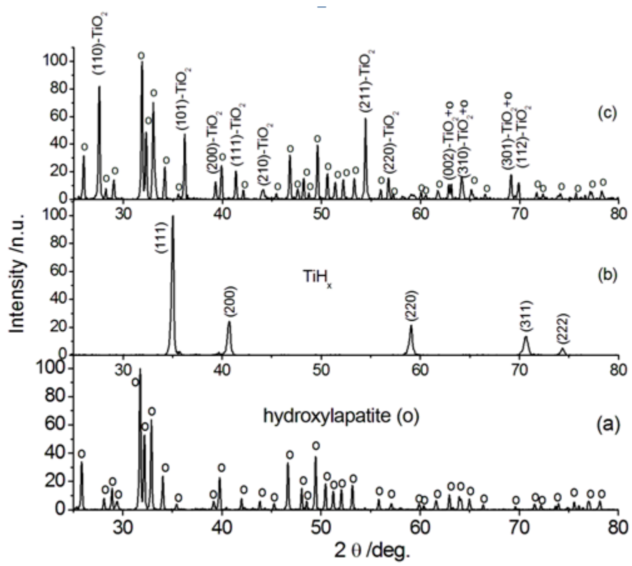

Figure 4: XRD pattern for: **a**) initial HAP powder particles; **b**) initial TiH_2 powder particles; **c**) as-sintered HAP/TiO_2 at 800^{0}C for 600 min. compacted at 150 MPa.

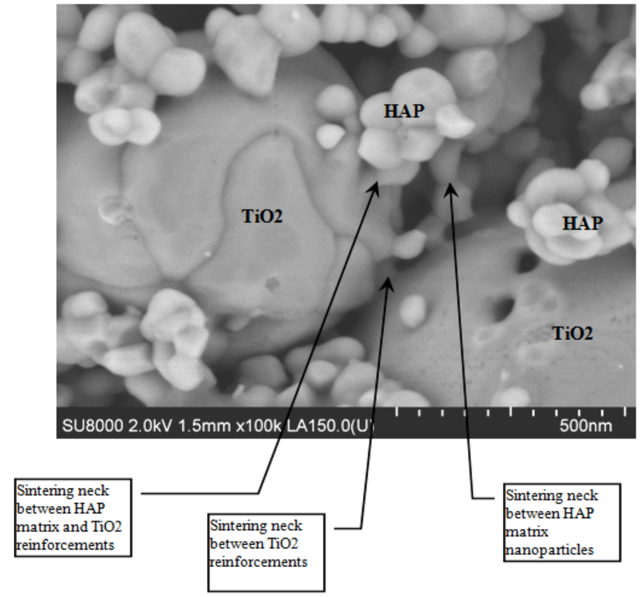

Figure 5: SEM aspects of hybrid HAP based biocomposites compacted at 150 MPa compaction and sintered by TSS 2nd step at 800^{0}C / 600 min.

Figure **5** presents the SEM aspect of the nanostructured HAP based biocomposites reinforced by TiO2 particles as a consequence of their compaction at 150 MPA and subsequently, at the TSS second step, at 800^{0}C / 600 min.

The TiO_2 presence enhances the wear behaviour and, by consequence, the wear track area is the smallest one (289 μm^2), Figure **6**.

4. CONCLUSIONS

The HAP/Ti hybrid biocomposites belongs to the new generation of the advanced hard tissue engineered materials. The manufacturing of the nanostructured HAP matrix reinforced by micrometric Ti particles is achievable due to the two steps sintering route.

The TSS advantages vs. the classic sintering comes from the close monitoring of the first step, which is responsible with the diffusion ignition stage, followed by the second one – the densification without grain growth effect. The last step is well-known as "kinetic window" and its technological parameters (temperature and time) were studied in this paper from the point of view of their influence on the HAP/Ti wear behavior.

The lowest values of the sintering time (300 min.) and temperature (700^{0}C) belonging to the TSS 2nd step

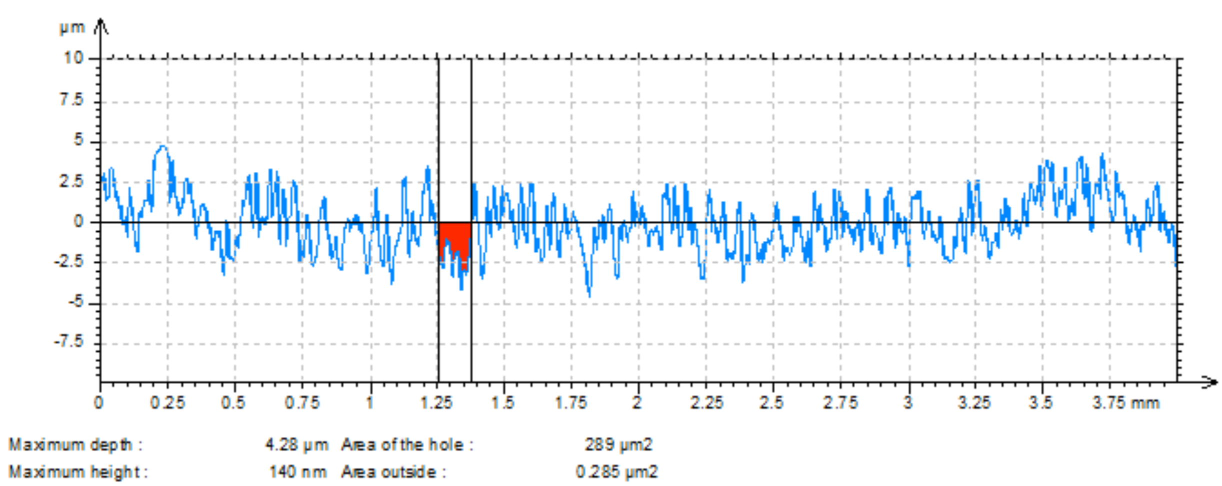

Figure 6: Wear track profile (coloured area) determined by Surtronic profilometer for the HAP/TiO_2 sample compacted at 150 MPa and subsequently TSS 2nd step at 800^{0}C / 600 min.

allow the diffusion processes occurring only partially, with potential consequences on the samples cracking. The wear behavior is low, confirmed by the high wear rates (> 7 Nm/mm^3) and it is corroborated with the smallest cold compaction pressure of the samples (90 MPa).

The highest sintering temperature (800^0C) and time (600 min.) of the "kinetic window", in combination with the highest compaction pressure (150 MPa) of the samples, lead to the complete oxidation of TiH_2 up to TiO_2 and thus the wear behavior improves. The wear rate decreases by three times than to former case respectively the wear track area by ten times.

ACKNOWLEDGEMENTS

The authors would like to express special thanks to Mr. Roland Schmidt from Hitachi High-Technologies Europe GmbH, which allowed the SEM observations at the European demo, application and training center for Hitachi electron microscopes in Krefeld, Germany.

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Received on 04-10-2014 Accepted on 23-10-2014 Published on 09-01-2015

DOI: http://dx.doi.org/10.15377/2409-5826.2014.01.02.5