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Titanium—hydroxyapatite porous structures for endosseous applications

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Materials for uncemented endosseous implants have to assure an as short as possible osseointegration time. Thus, a material with both surface bioactivity and a porous outer structure can become a preferred choice for this type of applications. This paper presents a class of titanium-base PM composites, reinforced with particulate hydroxyapatite. Raw materials were titanium powder, obtained through hydriding—milling—dehydriding, with the grain size of 63–100 μm, and sol-gel hydroxyapatite (HA) powder, produced by the reaction between $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$. Blends with 5 to 50% HA were prepared and pressed in a rigid die, producing single composition or gradual composition samples. The applied pressure was of 400, 500 or 600 MPa. Sintering was performed in vacuum, at 1160 °C. All samples, although well sintered, displayed swelling during sintering, due to diffusion into the matrix. The increase in volume is more severe for higher amounts of HA in the green compacts and for higher applied compaction pressure. Compacts with a gradual increase of the HA content are recommended from the functional and mechanical point of view, but the increase should be slow, not to produce interlayer cracks. The outer surface shows interconnected pores, suitable for the ingrowth of vital new bone.

1. Introduction

The time that passes from the surgical intervention till the stable fixation of uncemented endosseous implants is of major importance for the success of the operation. An unexpected mobilisation leads to the formation of a thick fibrous capsule around the implant, blocking the blood supply to the new bone and causing an early failure. This leads to the idea of maintaining the classic method of cementing implants. Although solving the early mobility problem, this is far from ideal: the method is suitable mostly only for orthopaedic implants; the intimate contact implant material—cement—bone can produce electrochemical reactions decreasing the biocompatibility; the generally used PMMA-base cement can be the place for interfacial cracks [1]. Biological fixation, using the growth of newly formed bone into the non-uniformities of the implant's surface is more suitable from the long—term biomedical point of view. A PM porous surface is favouring osseointegration. Titanium is the preferred choice for the quasi-bioinert material to produce implants with biological fixation, as it has proven a better biocompatibility in comparison to the other metals and alloys used in implantology [2, 3]. This is due to the stable oxide layer that insulates titanium surfaces from the tissue and is a good basement for the cascade cellular processes that precede the formation of bone, causing almost no inflammatory response after implantation [4]. Titanium was found the only metal biomaterial to osseointegrate [5, 6], as resulted from a 20 years dental surgery experience. In time, there were even assumptions on a possible bioactive behaviour [7], due to the slow growth of hydrated titanium oxide on the surface of the titanium implant that leads to the incorporation of calcium and phosphorus. The in time success rate of surgery related to titanium implants is still largely dependent on the size/shape of the implant, as well as on the general clinical conditions, and, sometimes, far from 100% [8–11]. As osseointegration starts with the cellular stage and continues with the nucleation of mineral and the structuring of the new vital bone, the overall required time is varying in a broad range. A proposed solution for a better control of osseointegration is the bioactive fixation. The most used material is hydroxyapatite, as the basic mineral in mature bone. Coating of metal implants with hydroxyapatite became a usual method, although it has some drawbacks: the toughness of hydroxyapatite is low ($K_{IC} \approx 1\,\mathrm{MPa\,m}^{1/2}$); during the coating stage (plasma sputtering, etc.), interfacial cracks can occur; the adherence metal/ceramic is low and can diminish in time. Hydroxyapatite was also found to disturb the proliferation and osteocalcin synthesis of human osteoblasts [12].

We propose, in this paper, porous titanium—hydroxyapatite composites as materials for uncemented endosseous implants, to summate the biological advantages of both components.

2. Materials and methods

Titanium powder (0.01%Fe; 0.01%Al; 0.001%Si; 0.05%Mg) with the grain size of 63–100 μm was used. The powder was obtained through the hydriding—milling—dehydriding process and the grains display a specific shape. The purity degree was assessed using the $\alpha \rightarrow \beta$ transformation temperature, by DTA (DTA/DSC Setaram Labsys DTA16). Alumina crucibles of 100 μl were employed for 100 mg samples. The temperature was calibrated according to the Curie temperature of nickel.

Hydroxyapatite (HA) was obtained through a sol-gel technique. The used reagents were $Ca(NO_3)_2 \cdot 4H_2O$ and $(NH_4)_2HPO_4$. $Ca(NO_3)_2 \cdot 4H_2O$ was dissolved in water at 90 °C, while $(NH_4)_2HPO_4$ was dissolved at the room temperature. The filtrate that resulted after mixing was washed with water at 40 °C, than dried in an oven for 2 h, at 110 °C. The gel was heat treated, first at 900 °C, for 3 h, then left to cool slowly, in the oven. A second heat treatment was performed at 1150 °C, for one hour, with oven cooling to 650 °C, then air-cooling. The obtained HA was milled and screened, in order to use a powder with the grain size of less than 100 μm.

Blends of titanium and 5, 10, 15, . . ., 50% HA were mixed in a turbula mixer for 30 min. Samples were pressed in a rigid die with the surface of 0.5 cm^2, without the use of any lubricant, with pressures of 400, 500 and 600 MPa, 3 samples for each experimental condition. Single composition samples, as well as multilayered ones were produced. In these cases, the stacking sequences were conceived for a continuous increase of the hydroxyapatite content. The green compacts were measured (0.01 mm precision micrometer) positioned separately in zirconia crucibles and subsequently vacuum sintered (10^{-6} torr) at 1160 °C for 60 min, with dwelling stages at 200, 600 and 800 °C, 30 min each. A part of the samples were cross sectioned by the middle of the generator, ground (180, 240, 320, 400, 600, 1000, 2000), polished with alumina (<0.5 μm), etched with Kroll's reagent, then studied through optical and electron microscopy, EDX (JEOL JSM–5600 microscope). XRD analysis was performed on HA powder and on sintered compacts on a Bruker D8 Advance diffractometer.

3. Results and discussion

The shape of the particles in the titanium powder follows two major patterns: compact particles (Fig. 1), sometimes with planar-faces, with rather sharp edges, and others, more spongy-like, with numerous microcavities (Fig. 2). Plate particles might rarely occur, together with hybrid- shaped ones (both compact and spongy).

The spongy/compact shapes of the particles in the Ti powder are caused by the non-uniform diffusion of hydrogen in the titanium raw material, during hydriding. This resulted in a non-homogeneous distribution of titanium hydride and Ti(H) solid solution throughout the raw material at this stage. The effects of the next stages of the technologic process of powder elaboration can be seen on the morphology of particles. During dehydrating, some of the particles were welded together, than the necks were broken during final milling (Fig. 1). Braking occurred even inside brittle particles, along basal slip planes. Spongy particles could be deformed during the final milling (Fig. 2).

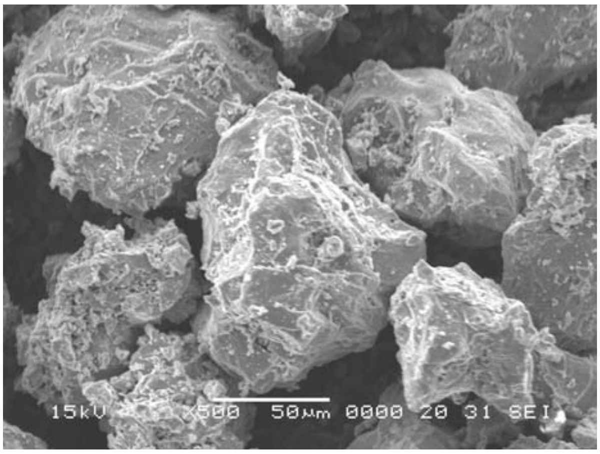

Figure 1 Compact—shaped Ti particles, with quasi-planar faces; some spongy regions and broken necks of former bonding to other particles.

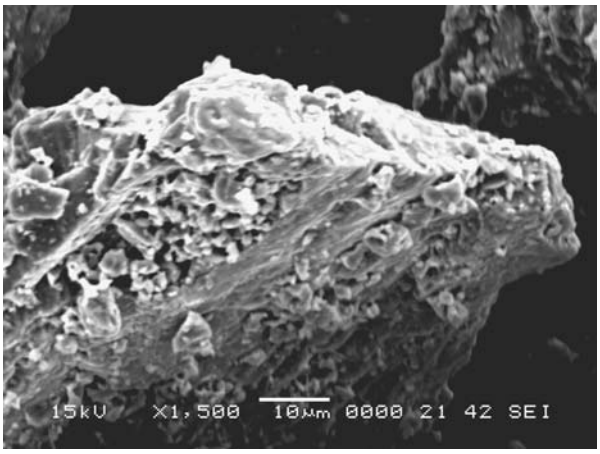

Figure 2 Spongy-like Ti particle.

The general aspect of the HA powder is of uneven particles, with sharp edges, as resulted after milling the brittle ceramic (Fig. 3).

The size fraction (63–100 μm) of the main component powder (Ti) was chosen in order to obtain a suitable pore size after sintering.

Some technologic properties were determined for the used titanium powder, Table I. Analysis was performed on the whole powder, as well as on two grain size classes separated from it: 63–80 and 80–100 μm. Flow rate, apparent density, fill ratio and porosity; tap density, compression ratio and porosity were determined. Tap tests were performed on a standard mechanical vibration machine. The bulk density of titanium was considered 4510 kg/m^3.

Flow rate is a major problem for this powder, due to the irregular shape of particles. For the coarser fraction (80–100 μm), the flow rate is better, but not enough.

TABLE I Technologic properties of the employed Ti powder

Size fraction [μm]	Flow rate V_{flow} [s/50 g]	Apparent density ρ_a [kg/m^3 $\times$ 10^3]	Compression Ratio C_a [%]	Fill porosity P_a [%]	Tap density ρ_v [kg/m^3 $\times$ 10^3]	Tap compression Ratio C_v [%]	Tap porosity P_v [%]
63–100	82.7	1.93	42.79	57.21	2.35	52.10	47.90
63–80	87.2	1.88	41.68	58.32	2.16	47.89	52.11
80–100	66.5	1.76	39.02	60.98	1.92	42.57	57.43

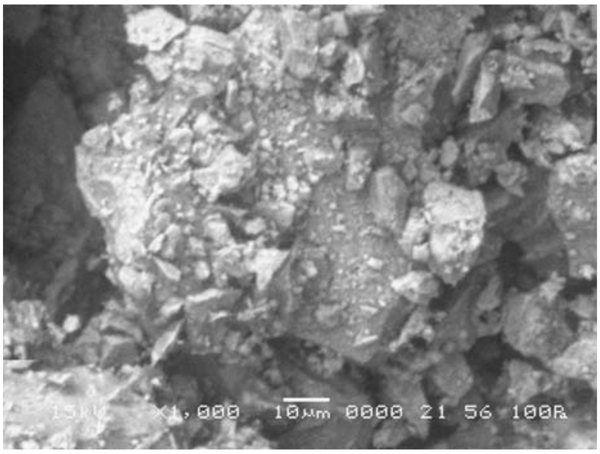

Figure 3 General aspect of raw HA powder.

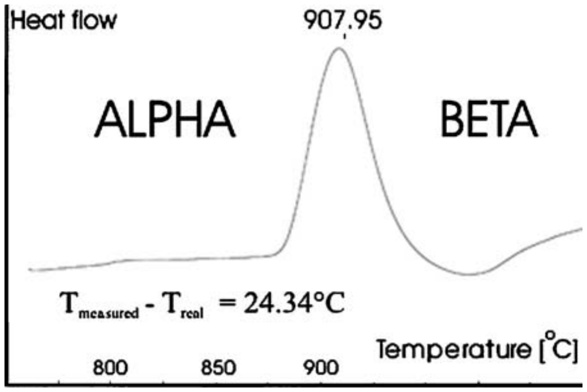

Figure 4 DTA pattern of the Ti powder (calibration by Curie temperature of Ni).

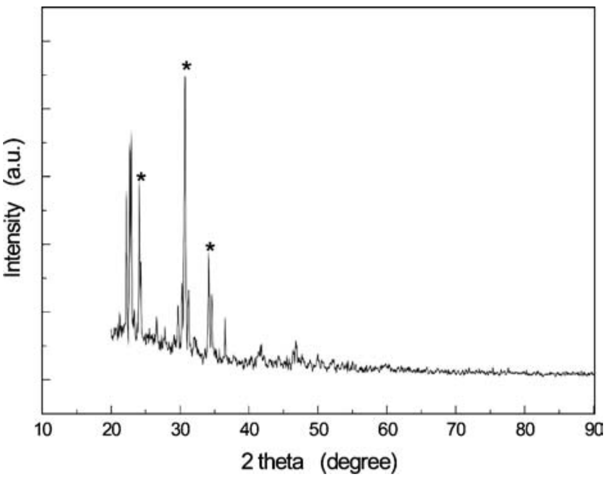

Figure 5 XRD pattern of raw HA powder (peaks at 2θ angles of 25.62°, 31.13° and 34°).

This means that the filling of dies has to be performed through a larger nozzle than usual. The compression ratio is better for the finer fraction, compared to the coarser one. The best density/compression ratio were obtained for the whole powder. If associated to flow rate, the whole powder was chosen as raw material for the following experiments. Although vibration induces a more advanced compaction, due to the problems relating to the filling of dies, we have chosen not to employ the method.

The properties of titanium are strongly dependent on the impurities content (gases are to be considered, mainly). The purity assessment of the raw Ti powder was performed by the $\alpha \rightarrow \beta$ transformation temperature (882 °C, according to ASM), strongly dependent mainly upon the content of α stabiliser impurities. Fig. 4 shows the exothermic curve, with the transition temperature at the raw value of 907.5 °C.

The measured values of the temperature were higher with 24.34 °C than the real ones, due to the thermal inertia, as determined after nickel's Curie point. Thus,

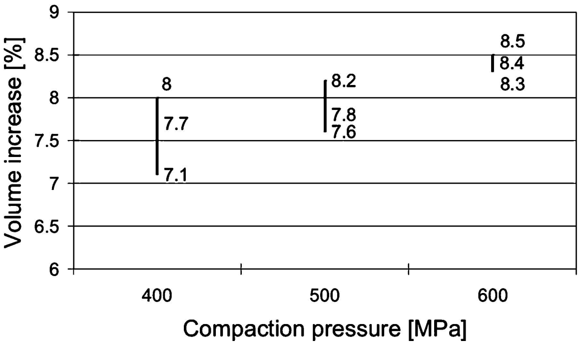

Figure 6 Volume variation of 5% HA samples after sintering.

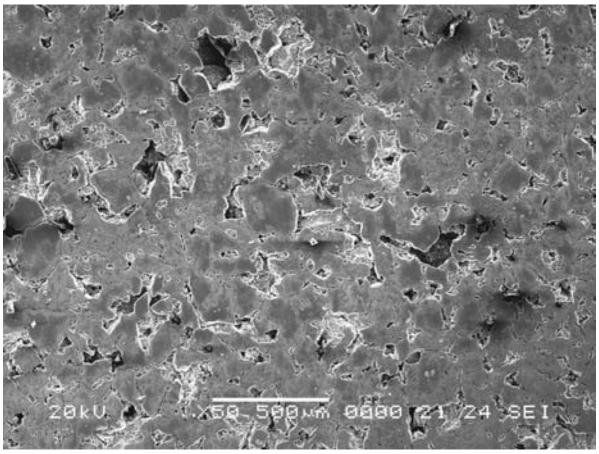

Figure 7 Sintered Ti – 5% HA sample (600 MPa compaction pressure), polished, etched (Kroll's reagent).

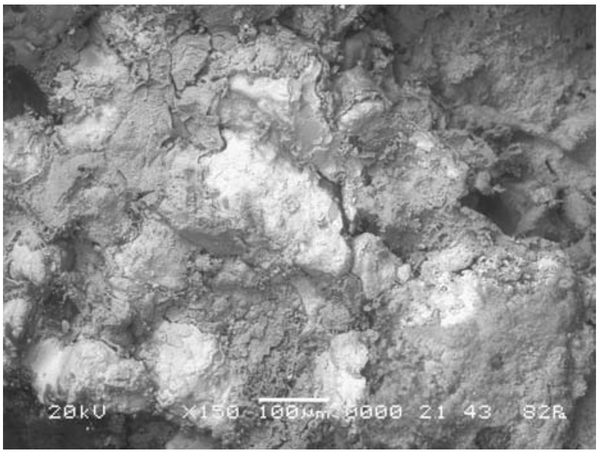

Figure 8 Surface of sintered Ti—50% HA sample, unpolished.

the calculated $\alpha \rightarrow \beta$ transition temperature was of 883.61 °C. The small difference to the standard 882 °C temperature (1.61 °C) reveals the purity of the Ti raw material.

The diffraction patterns performed on the employed HA powder, Fig. 5, are close to the data in literature, stating that the principal diffraction peaks of HA appear at 2θ values of 24.2° for reflection (002), at 30.8° (triplet) for reflections (211), (112) and (300), and at 34.0° for reflection (200) [13, 14]. The peaks of the HA powder employed in this study were at 2θ angles of 25.62°, 31.13° and 34°.

All samples displayed swelling during the sintering stage. Samples with 5% HA that were compacted using one of the three values of the applied pressure and subsequently sintered in the same batch were measured. Their increase in volume is shown in Fig. 6.

A higher pressure was shown to produce more swelling. While for 400 and 500 MPa the dispersion of values is broader, the 600 MPa pressure generated a much more even swelling among samples. The cause of swelling is the diffusion of calcium/phosphorus in the titanium matrix. The phenomenon was proven by subsequent EDX analysis. The effect of pressure over swelling shows that, by a higher loading of the grains in the metal matrix during the compaction stage, the diffusion coefficient of Ca/P in Ti increases. This is caused by the more numerous lattice defects induced by a more severe plastic deformation. The dispersion of the measured values of diameter/height is broader for smaller pressures. This is consistent with the fact that the pressure is transmitted unevenly through the column of powder inside the die (no added lubricant). A higher pressure (600 MPa in this particular case) leads

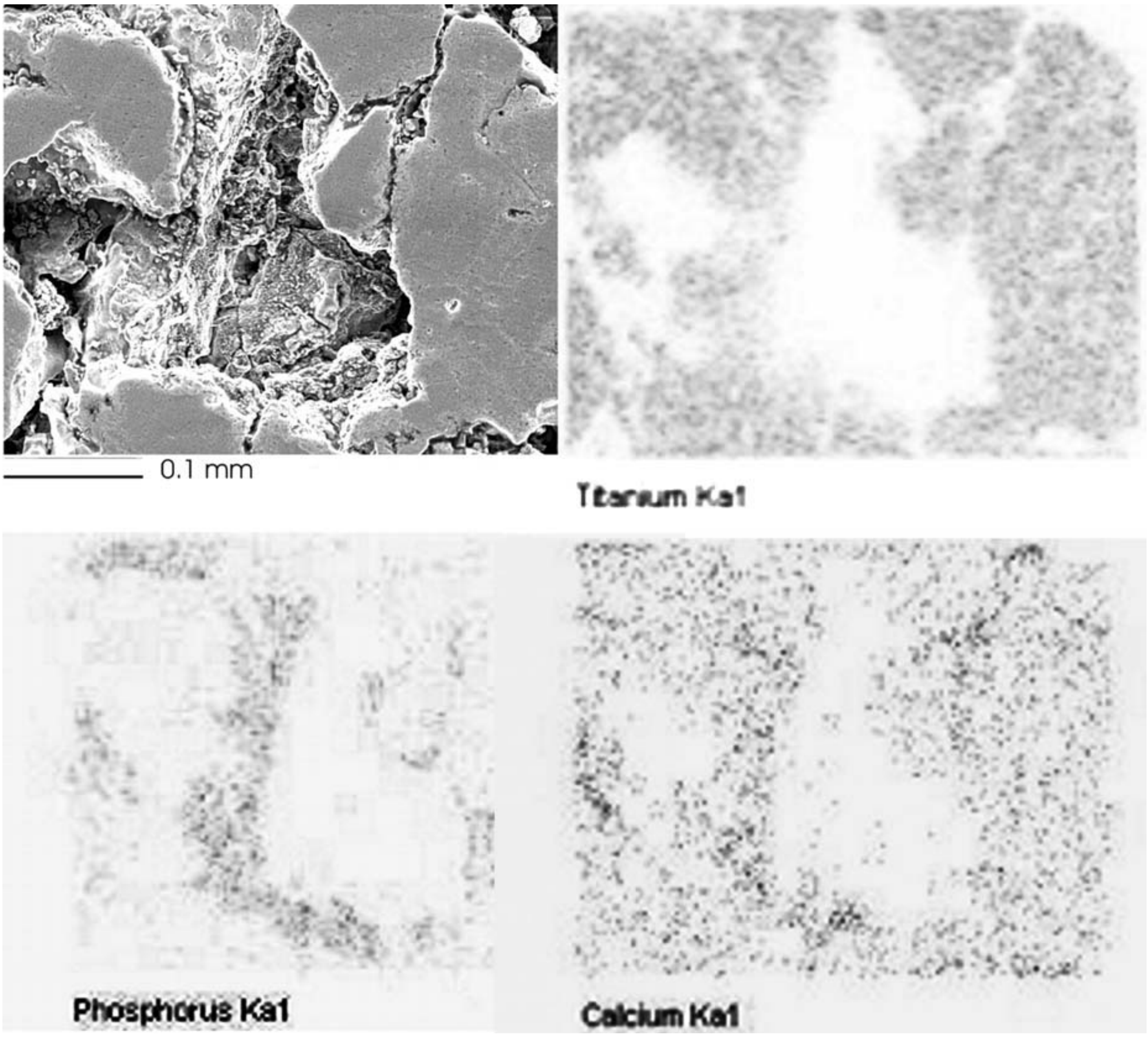

Figure 9 EDX elements distribution maps, 5% HA sintered sample, formerly pressed with 400 MPa.

to a more even pressure transmission in the entire green compact.

Fig. 7 presents an example of structure for the 5% HA sintered compacts.

Samples are well sintered, with a compactness increasing with the compaction pressure. During the grinding/polishing of samples, the ceramic component particles in the outer layer were pulled out and left craters in the surface of samples. This is well observed in the EDX elements map around these regions. If analysing the surface of samples, without passing through the cutting—grinding procedure, the position of the ceramic phase inside the compact can be seen, Fig. 8 (50% HA). The transition layer that can be seen at the interface between the matrix and the ceramic phase is believed to play a positive role in the overall mechanical stability of the compact.

The pores, with their bio-functional role, are important in what concerns osseointegration. The characteristic to be considered for a material used in endosseous implants is not the overall porosity (percentage of pores), but the aspect of pores.

The size of pores in the composite samples was estimated microscopically. As seen in Figs. 7 and 8, the pores are interconnected, with very irregular shapes/sizes. Large pores, with the main dimension comparable to 100 μm (the critical minimum size needed for the formation of a vital new bone), as well as smaller pores, could be seen. A higher compaction pressure applied to green samples reduced the sintered—state porosity.

The EDX analysis on polished samples has shown the diffusion of elements from the HA particles to the titanium matrix. Fig. 9 shows the distribution map of main chemical elements around a crater resulting from pulling out a ceramic particle (5% HA sintered sample, formerly pressed with 400 MPa). The diffusion of Ca is much more even inside the titanium grains, compared to P, that remained much less diffused, in the proximal region around the HA particle. Fig. 10 presents the distribution of Ca and P around a removed ceramic particle, on a sample that was formerly pressed with 600 MPa. Ca atoms remain well diffused inside the matrix. P was shown to diffuse in a more advanced manner compared to Fig. 9. Fig. 11 shows, comparatively, the relative amounts of the main elements in the areas shown in Figs. 9 and 10.

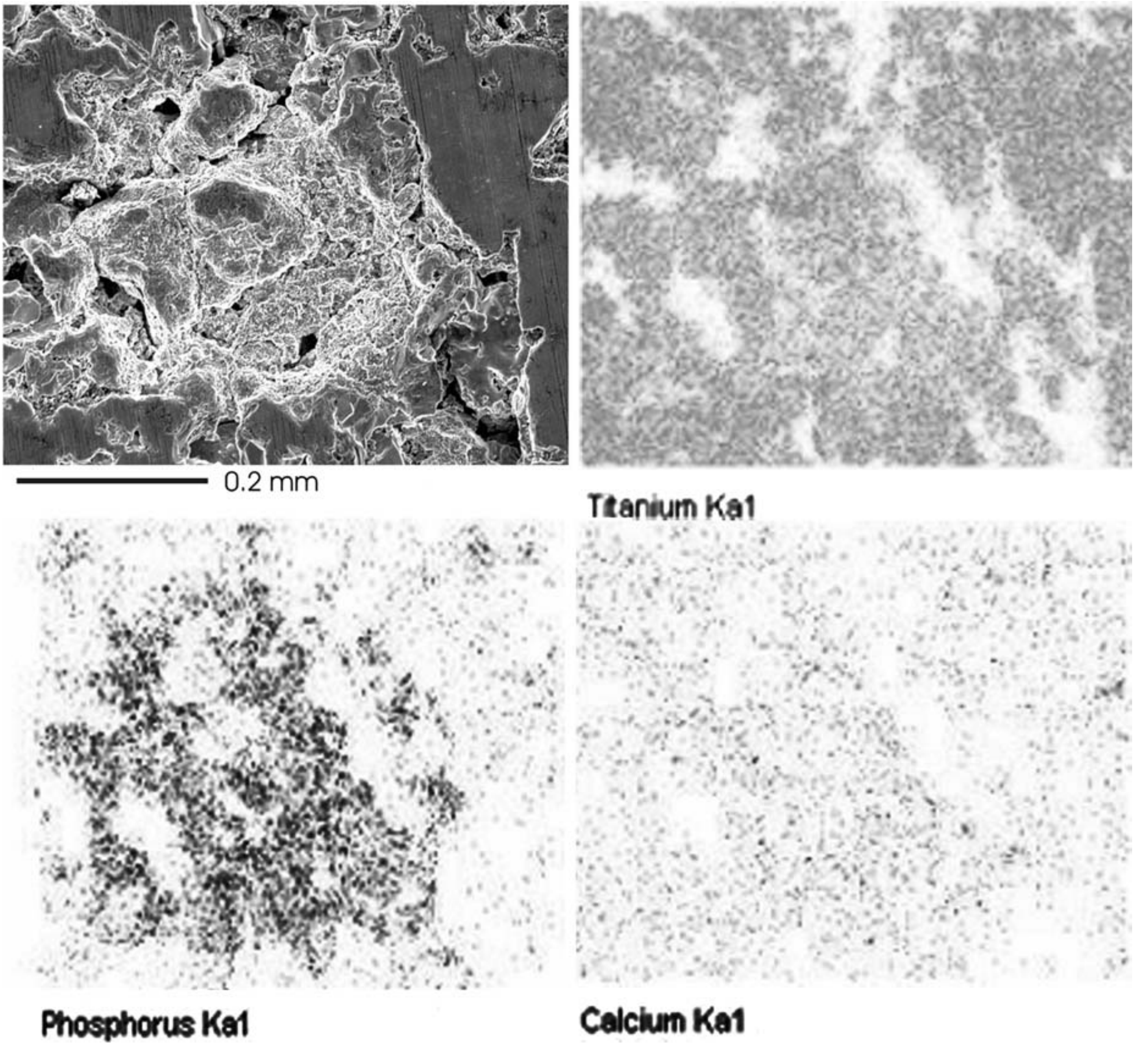

Figure 10 EDX elements distribution maps, 5% HA sintered sample, formerly pressed with 600 MPa.

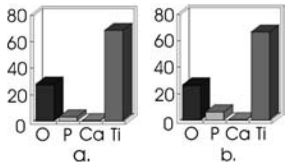

Figure 11 Comparison between quantitative results of EDX on 400 MPa. (a) vs. 600 MPa. (b) pressed samples (5% HA).

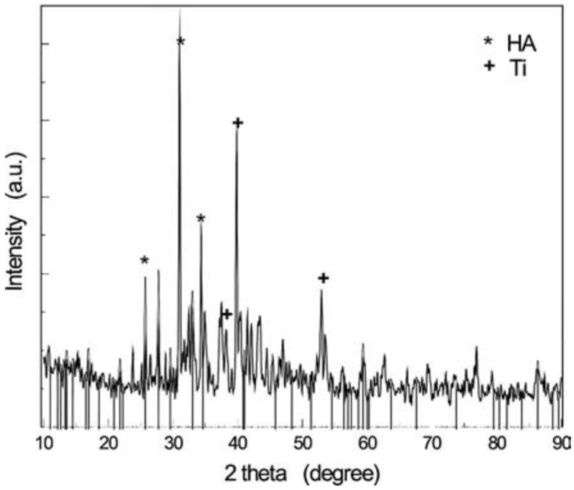

Figure 12 XRD pattern, Ti—HA composite (Ti peaks at 2θ angles: 38.25, 40.04 and 52.67°C).

The amount of diffused P in the Ti matrix is more important as the compaction pressure of samples was higher (600 vs. 400 MPa). This is consistent with the above conclusion that a higher pressure leads to a more advanced diffusion of elements from HA to the Ti matrix.

XRD analysis performed on sintered samples, Fig. 12, shows both components, Ti and HA in the final structure of the composite. The peaks that occur for 2θ angles of 38.25, 40.04 and 52.67° can be attributed to Ti [15], while the peaks for HA remain virtually the same as in Fig. 5.

The composition of green samples is the other key factor, together with compaction pressure. For a higher amount of HA, the diffusion process of Ca and P occurs in more numerous sites (around HA particles). The swelling effect is, then, more obvious, Fig. 13 (400 MPa, 30% HA).

For the gradual samples (with a later-to-layer increase in the HA amount), the swelling effect causes the limitation of the method. In the same sample (basically the same transferred pressure), that consists of several layers with various amounts of HA, the variations of volume are different (higher for the layers with more HA), causing stresses between layers. The interlayer stress is higher when the difference between the compositions of layers is higher. Transverse cracks can occur for differences of more than 5%.

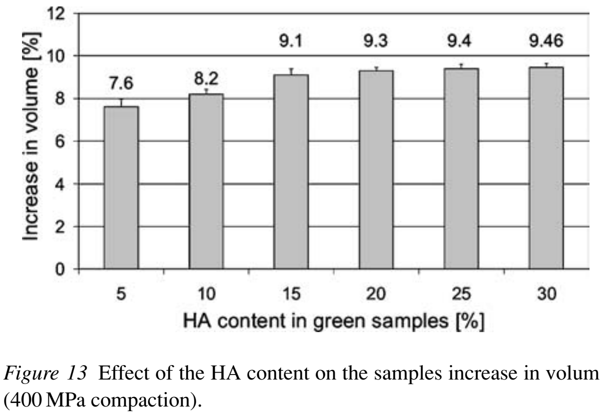

Figure 13 Effect of the HA content on the samples increase in volume (400 MPa compaction).

The gradual amount of HA is of particular importance for implants. The more HA at the direct bone—implant contact surface, the better the expected biocompatibility. On the other hand, the presence of HA has only a functional effect, as it decreases the mechanical properties. The more the HA content, the higher the brittleness. Thus, a structure with an as much as possible HA content in the areas in direct contact with bone and an as low as possible in the rest would be the most suitable. Unfortunately, it is not possible, as shown above, to decrease sharply the HA content, due to the risk of cracking. The samples with more than 30% HA display an excessive brittleness and, at 50% HA, the material is virtually unusable.

For every shape/size of implant, the couple pressure—stacking sequences can be optimised.

4. Conclusions

Porous PM Ti—HA composites (5 to 50% HA), using a Ti powder obtained by the hydriding-milling—dehydriding process and sol-gel HA, were obtained through a blending—pressing-sintering route.

A diffusion process of Ca and P in the matrix during sintering (1160 °C) causes the swelling of samples. The process is controlled by two parameters: compaction pressure and HA content. A higher pressure (over 500 MPa), as well as a higher amount of HA, lead to significant swelling.

The amount of HA is of major importance and has to be kept into severe limits: a too high amount (more than 30%) leads to excessive brittleness; a too low content in contact with bone is insufficient for the required bioactivity.

Gradual structures, with a high HA content at the surface and a low one in the interior, are the most suitable. The decrease of the HA content one layer to another has to be slow (highest rate of 5%), not to produce cracks as a result of the different swelling rates.

The outer pores are interconnected and suitable for the ingrowth of a new vital bone.

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