Microstructural characterization of PM Ti with dextrin addition for endosseous applications

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The aim of this research work was to study the microstructure of porous CP Ti with dextrin addition obtained by Powder Metallurgy, aimed for endosseous implants. Powder mixtures of CP Ti with 35 vol.% dextrin with different particle sizes were pressed with 400 MPa and sintered in two different conditions. The sintering behavior and microstructures were investigated by means of differential thermal calorimetry, optical microscopy and scanning electron microscopy. The results are helpful for the optimization of the processing cycle of Ti - dextrin powder mixtures.

1. Introduction

Ti and Ti alloys are widely employed in the medical field due to their excellent combination of good mechanical properties, good corrosion resistance, low density, biocompatibility [1, 2].

Porous structures gained an increased interest for endosseous applications as a consequence of their lower elastic modulus as compared to that of the compact material and therefore lower tendency to the stress-shielding phenomenon. Besides bulk structure, surface morphology and composition play an important role in the osseointegration process. A porous surface enhances the mechanical anchorage of the future implant with the surrounding hard tissue by the formation of the new bone in the surface pores [3]. To this aim, it was reported that the optimum pores size should be between 100 μm and 200 μm [4]. The chemical composition of the surface is also important since it strongly affects the bonding between the implant and the host hard tissue.

Different technologies may be employed to obtain porous structures, as conventional Powder Metallurgy (PM), Rapid Prototyping (RP) and others.

In PM practice, porogen agents or space holders are often used to obtain porous compacts with a designed porosity [4, 5]. However, it should be kept in mind that if porosity is beneficial for the osseointegration, it negatively affects the mechanical properties of the biomaterial. In consequence, a compromise ought to be found for each particular application. A possible solution could be the employment of porous compacts with a gradual porosity, which meets the requirements of the biomaterial both in term of osseointegration and strength [6, 7].

In our previous research, porous compacts of CP Ti were obtained by PM (pressing and sintering), using dextrin (($C_6H_{10}O_5$)$_n$) as porogen agent. Dextrin is an organic compound derived from starch. It may be easy

removed from the bulk material by solving it in water. The amount of dextrin and some of the processing parameters were optimized based on the microstructural characterization and mechanical behavior of the sintered compacts. It was found that an amount of 35 vol.% dextrin admixed to the base Ti powder, uniaxially pressed with 400 MPa and sintered at 1100ºC for 1 h in vacuum of $10^{-4} - 10^{-5}$ torr, resulted in satisfactory properties of the sintered compacts. No lubricant was used in order to avoid an eventual contamination of the samples, which might negatively affect the material biocompatibility. After pressing the powder mixtures, an additional operation ought to be introduced in the processing cycle aimed to remove the most part of the dextrin from the green compacts. It consisted in stirring the greens in water at a temperature of approximately 80ºC for 15 min., followed by drying in a heat chamber at 90ºC for 30 min. The as-prepared specimens were sintered at 1100ºC for 1 h in vacuum, with a heating rate of about 10ºC/min. During the heating step, an impairment of the vacuum level was noticed at a temperature between 350ºC and 400ºC. The as-sintered and surface conditioned specimens were tested both "in vitro" and "in vivo" [8].

The purpose of the present study was to get a deep understanding of the microstructure of PM Ti compacts with dextrin addition, for a further optimization of their processing. The results would further allow an accurate characterization of as-sintered specimens in terms of biocompatibility.

2. Experimental

The CP Ti powder (with a purity higher than 99.5%) obtained by hydration-milling-dehydration process with powder particles size lower than 45 μm was used as base material to produce cylindrical specimens with 10 mm

diameter and about 4 mm height, as indicated in Fig.1. The used Ti powder contained same TiH_2 as detected by XRD analysis, resulted from the obtaining process [8].
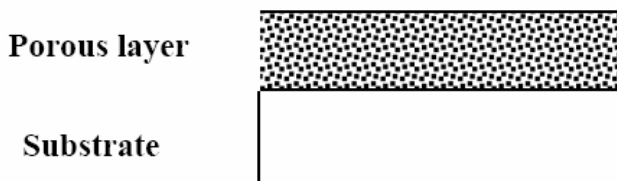

Fig. 1. Design of the studied specimens

For the substrate only Ti powder was used. The porous layer was made of mixtures of Ti with 35 vol.% dextrin with different particle size, as follows: < 100 μm, between 100 μm and 160 μm, > 160 μm. The powders were pressed at a same time in a closed die with 400 MPa. The most part of dextrin was removed from the greens by stirring them in water at about 80°C for 15 min. The pressed compacts were subsequently dried in a heating chamber at 90°C for 30 min. Sintering was carried out in two different conditions:

- **cycle A**: at 1200°C for 1h, in vacuum of 10^{-5} torr, heating rate of 5°C/min., with a soaking stage at 450°C for 2 h, in a lab furnace;

- **cycle B**: at 1300°C for 1h, heating rate of 5°C/min., in vacuum of 10^{-5} torr up to 500°C then in Ar, with two soaking stages at 600°C and 1000°C respectively, for 20 min. each, in an industrial furnace.

It should be underlined that the differences between the two sintering are as follows: heating profiles, of a primary importance in the frame of this research, and sintering temperature, less considered in the present study. Cycle A characterized by the presence of the soaking stage during heating should be more beneficial than cycle B with regard to the dextrin removal.

Metallographic samples were prepared as according to the standard procedure. Etching was carried out with Kroll reagent. The microstructures were analysed with the help of an Olympus GX51 optical microscope and a JEOL 5600LV scanning electron microscope, equipped with EDS. Ti powder and Ti - dextrin mixture were subjected to differential scanning calorimetry using a Labsys Setaram equipment. The powders were heated up to 1200°C with a heating rate of 10°C/min. in Ar atmosphere.

3. Results and discussions

3.1 Thermal analyses

DSC curves of Ti and Ti-dextrin mixture are shown in Fig.2 and Fig.3 respectively. The first endothermic peak displayed by both curves at temperatures lower than 100°C was related to the removal of moisture from the powders. Decomposition of dextrin is indicated by the endothermic peak at a temperature between 250°C and 260°C [9].

The endothermic events at about 331°C displayed by the DSC curves of both Ti and Ti - dextrin mixture correspond to the reduction of TiH_2 as according to the reaction (1):

$$TiH_2 = Ti + H_2 \qquad (1)$$

The formation of rutile, TiO_2, the stable form of Ti oxide at temperatures higher than 600°C [10], is evidenced by the presence of the peak at about 556°C in Fig. 2 and the peak at about 590°C in Fig.3.
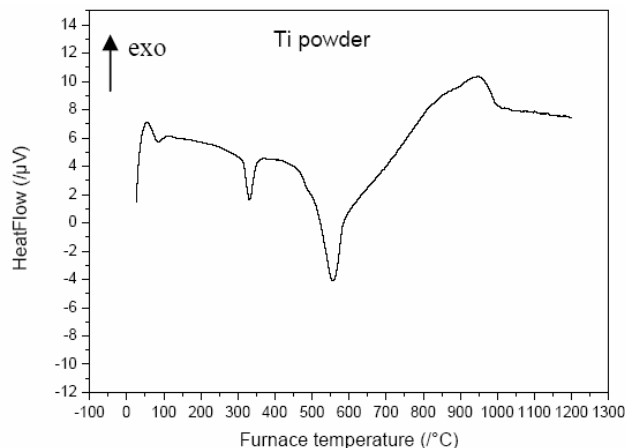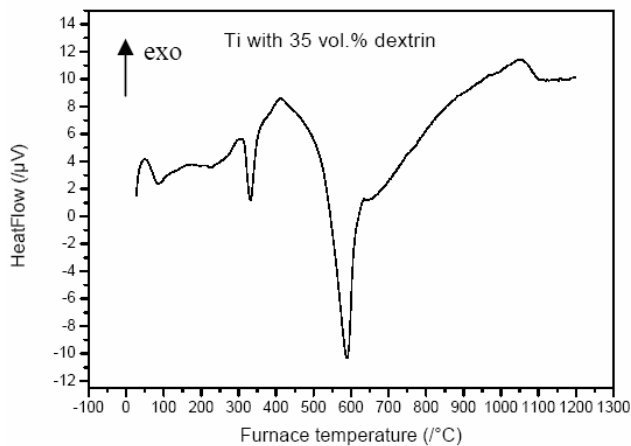

Fig.2. DSC curve of Ti powder


Fig.3. DSC curve of Ti-dextrin powder mixture

3.2 Microstructure

The microstructures of samples prepared with dextrin of different particles size and sintered as according to cycle B, as example, are shown in Fig.4. The pores size increased with the mean particle size of the admixed dextrin powder, as expected. Irrespectively to the sintering conditions, macrocracks were found in the porous layer of specimens prepared with dextrin larger than 160 μm. Based on this observation, for the further experimental trials only dextrin with particle size lower than 150 μm will be employed.
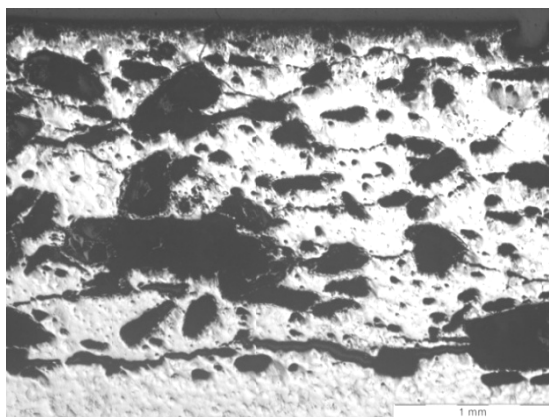
Delamination between the substrate and porous layer was noticed in some of the produced samples, Fig.5. This was attributed to the different elastic expansion of the porous layer and substrate after ejection from the compacting die (spring back), which depends, among others, on green density, powder grade, etc.
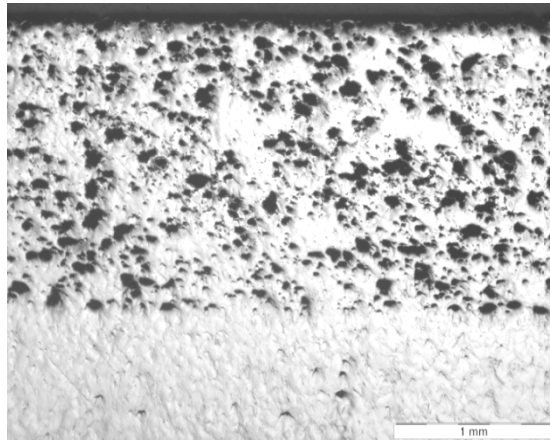
a)
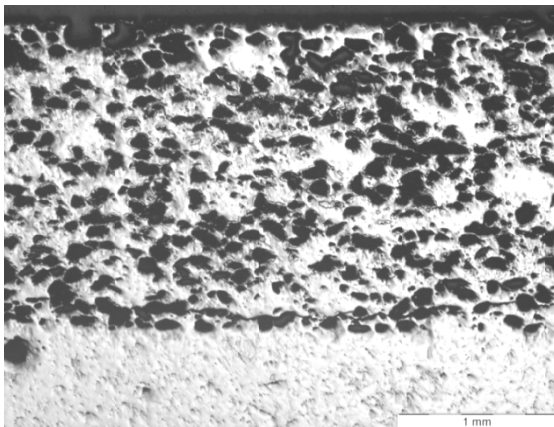
b)

c)

Fig.4. Microstructure of the porous layer of the sintered specimens, cycle B. Unetched. a) Ti with dextrin < 100 μm ; Ti with dextrin in range of 100 μm – 160 μm; c) Ti with dextrin > 160 μm.
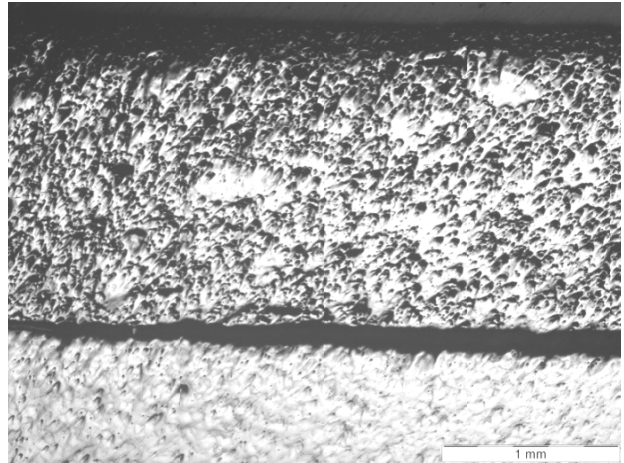
Fig.5. Delamination of the porous layer in a sample of Ti with dextrin < 100 μm sintered with cycle A.

Even in unetched condition, the microstructure of the as-sintered porous layers displayed the presence of a brighter phase/compound, indicated by the arrow in Fig. 6. The appearance in the unetched microstructure suggested that its hardness is higher than that of the matrix. It was detected in the whole porous layer, excepting the approximately 500 μm below the surface.

The etched microstructures of samples sintered with cycle A, Fig.7, displayed mainly echiaxial α Ti grains with few intergranular phase. A continuous layer with a thickness lower than about 10 μm was noticed on the surfaces of the porous layer of the as-sintered sample, Fig.7b.
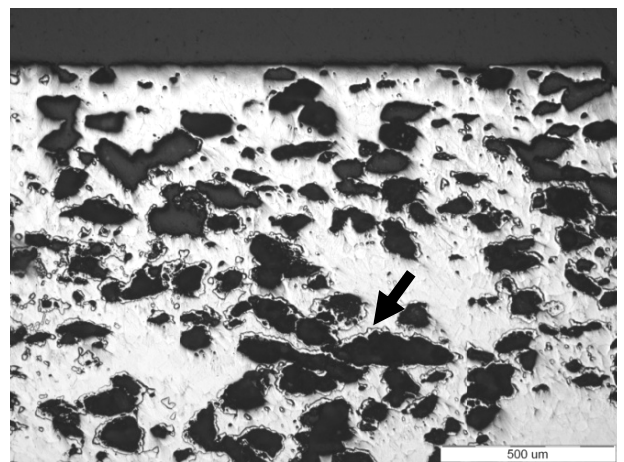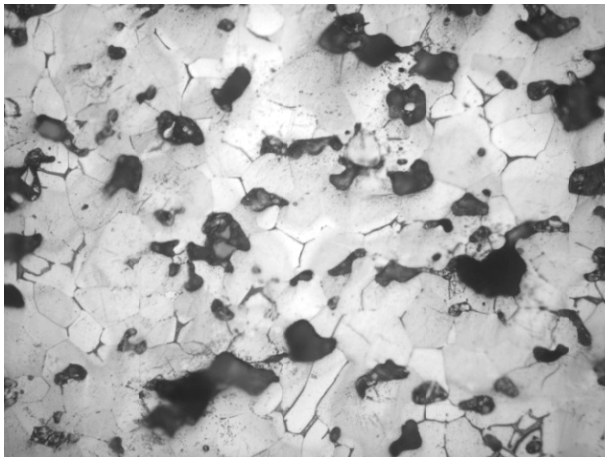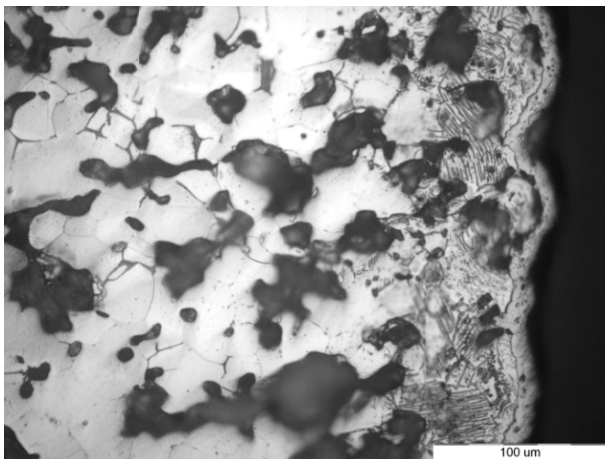

Fig.6. Microstructure of the porous layer of the sintered specimens, cycle B. Unetched. Aspect of the brighter phase/compound, indicated by the arrow.

a)

b)

Fig.7. Etched microstructure of a sample sintered with
cycle A: a) overview of the porous layer; b) surface of
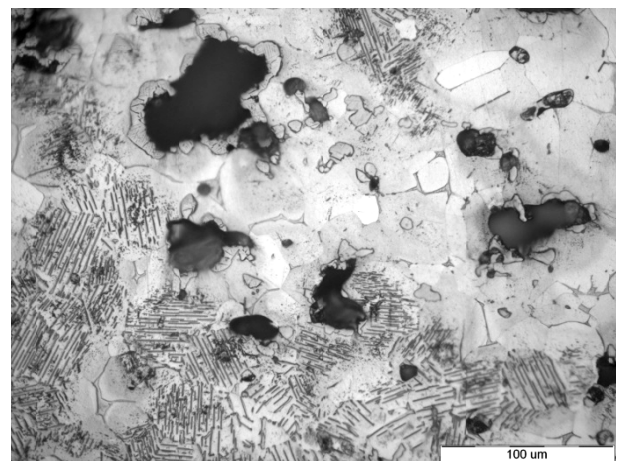the porous layer.

Samples sintered with cycle B, Fig.8, have an α phase microstructure in the substrate, similar with samples sintered with cycle A. The porous layer displayed areas with echiaxial α grains with some intergranular phase and areas with acicular (α + β) grains, the last being observed in the microstructure of the samples sintered with cycle A only just in the neighborhood of the surface thin layer, as shown in Fig.7b.

The phase noticed even before etching was found to be present in larger amounts in samples sintered with cycle B than in samples sintered with cycle A. It formed mainly around the pores. Its aspect was very similar with the appearance of the continuous thin surface layer observed on the surface of the as-sintered specimens and consequently it was assumed to be of the same type. The distribution in the microstructures of the sintered samples suggested that its formation was related to the

decomposition of the remnant dextrin from the pressed samples, during sintering. Similar microstructural details were observed in the samples studied in our previous work. XRD analyses performed on the surfaces of the as-sintered specimens indicated the presence of a TiOCN like phase whose amount increased with the percent of the admixed dextrin [8]. With regard to the qualitative chemical composition, based on the chemical compositions of the matrix and that of dextrin, it was expected to contain Ti, C and O. The presence of N was somehow surprising.
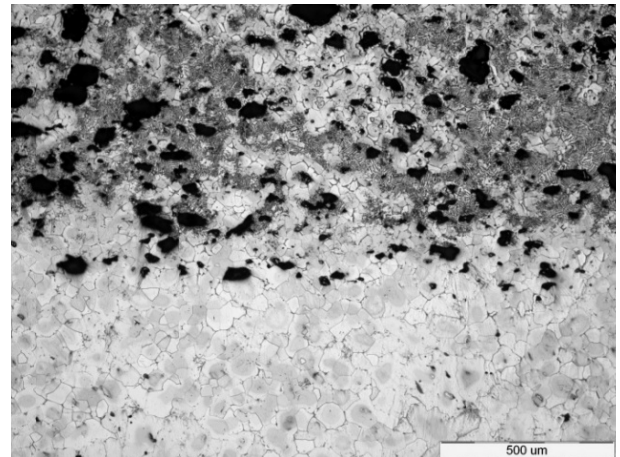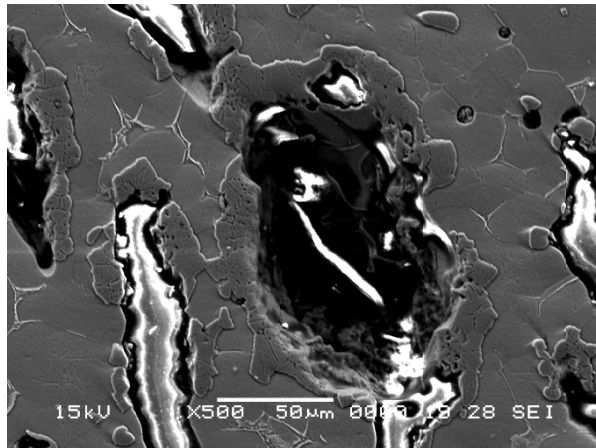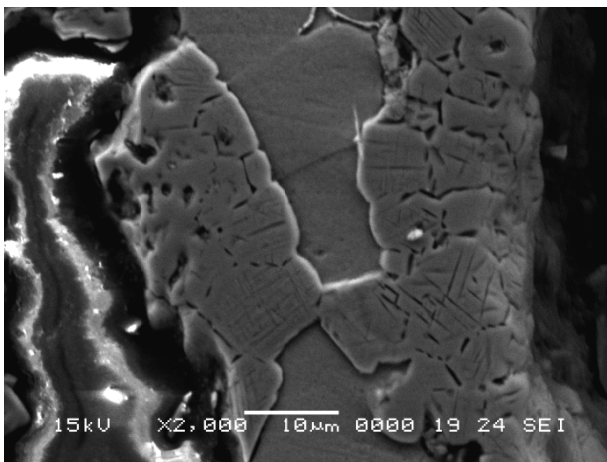

a)

b)

Fig.8. Etched microstructure of a sample sintered with
cycle B: a) overview; b) porous layer.

The SEM images of the microstructure of a sample sintered with cycle B are shown in Fig.9.
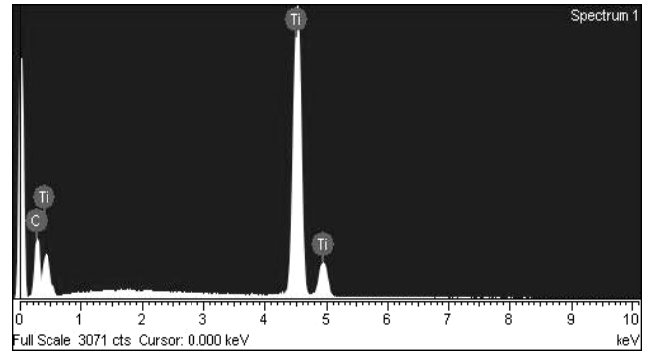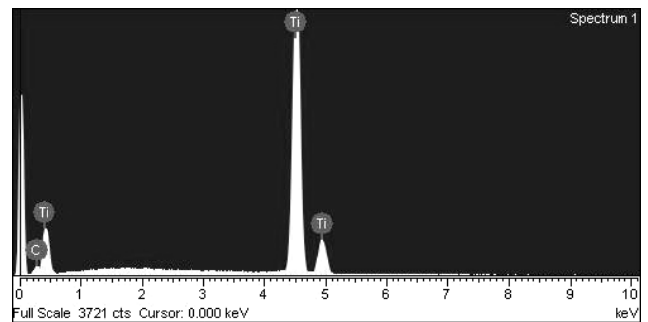
a)

b)

Fig.9. a) Microstructure of the as-sintered sample, SEM image; b) higher magnification.

a)

b)

c)

Fig.10. EDS analysis on: a) the phase around the pores; b) the matrix, α Ti grain; c) the matrix, intergranular phase.

The EDS analyses performed on the different microstructural constituents are given in Fig.10. The phase around the pores contains Ti and C, Fig 10 a), the last being detected in a higher amount than in Ti matrix, Fig 10 b). Based on this result, it could be speculated that this phase might have α Ti enriched in C. As reported in the literature, the maximum solubility of C in α Ti is about 0.4 wt.% at 920°C, it slightly decreases with the temperature. A maximum of 0.2 wt.% C could be dissolved in β Ti at temperatures higher than 920°C. Formation of Ti$_2$C in the C rich areas could also be considered [11].
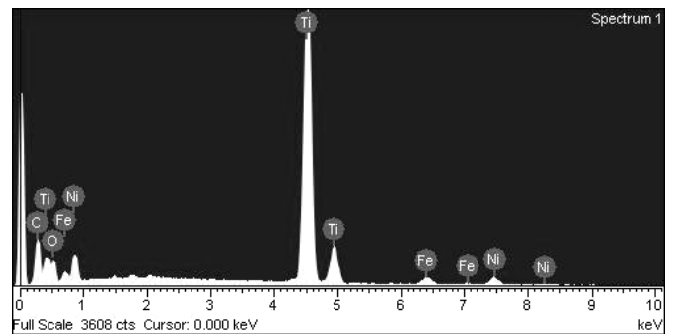
The intergranular phase displays, besides O and N which are α stabilizing elements, Fe, which is β stabilizer. Additionally, C appears to be present in a higher amount than in the matrix, Fig. 10 b). It could be therefore assumed that at the grain boundaries, β phase might also be present.

It results that, if not properly removed, the remnant dextrin may give rise to the formation of C containing phases in the microstructure of the sintered samples, as Ti$_2$C, TiOCN like compounds and possibly α Ti with a higher amount of C. These phases were located mainly around the pores and on the surface of the as-sintered samples. Bearing in mind that the surface chemical composition plays an important role in the osseointegration of the future implant, the impact of its presence on the biocompatibility of the studied materials needs to be further defined.

However, the studies carried out in the present research have shown that a proper heating profile with a soaking stage at approximately 400°C in vacuum allowed a better removal of the remnant dextrin, resulting in a

lower amount of this C containing phase in the microstructure of the as-sintered materials.

4. Conclusions

Porous CP Ti structures with a designed porosity are possible to be obtained by a proper selection of the dextrin particle size;

Dextrin powder with a mean particle size lower than 150 μm will be used for obtaining porous structures;

An efficient removal of dextrin could be helped by a proper heating ramp during sintering; a low heating rate up to about 400°C followed by a soaking stage at this temperature are recommended to this aim;

Future research work was planned in order to assess the impact of the microstructural features on mechanical properties, wear resistance and biocompatibility.

References

[1] M. Geetha, A. K. Singh, R. Asokamani, A. K. Gogia, Progress in Mater. Sci. **54**, 397 (2009)

[2] C. Popa, V. Candea, V. Simon, D. Lucaciu, O. Rotaru, Stiinta Biomaterialelor, Biomateriale metalice, Ed. UTPress, Cluj-Napoca (2008).

[3] L.M. Reis de Vasconcellos, Daniel de Oliveira Leite, F.O. Nascimento, L.G. Oliverira de Vasconcellos, M. Lima de Alencastro Graca, Y.R. Carvalho, Med. Oral Patol. Oral Cir. Bucal **15**, 407 (2010).

[4] S. Sobieszczyk, Adv. Mater. Sci. **10**(2) (2010).

[5] W. Niu, G.B. Qiu, Q. Wang, Mater. Sci. Eng. A **506**, 148 (2009).

[6] C.E. Wen, Y. Yamada, A. Nouri and P.D. Hodgson, Mater. Sci. Forum **539-543**, 720 (2007).

[7] M. Thieme, K.P. Wieters, F. Bergner, D. Scharnweber, H. Worch, J. Ndop, T. J. Kim, W. Grill, J. Mater. Sci.: Mater. Med. **12**, 225 (2001).

[8] I. Gligor, PhD Thesis, Technical University of Cluj-Napoca, Cluj-Napoca (2011).

[9] D. Predoi, Digest J. Nanomater. Biostruct. **2**(1), 169 (2007).

[10] E. Gemelli, N.H.A. Camargo, Rev. Matér. **12**, 525 (2007).

[11] ASM Metals Handbook, vol.3, 9th Edition, ASM International USA (1990).

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