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Titanium and Ti-13Nb-13Zr Alloy Porous Implants Obtained by Space-Holder Technique with Addition of Albumin

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Abstract. Titanium and its alloys are the main metals studied as porous metallic implants by their excellent mechanical properties and biological interactions. Production methods of porous metallic materials are based on powder metallurgy (PM), because it allows the manufacturing of parts with complex shapes and dimensions close to the finals (near-net shape), and the addition of alloying elements reaching a satisfactory structural homogeneity, and porosity. The pore production by space-holder technique constitutes of mixing organic compounds with metal powder, which when removed by thermal treatment prior structures are kept in place. The objective of this study is to obtain porous implants of commercially pure titanium (cpTi) and Ti-13Nb-13Zr alloy by PM with space-holder technique and albumin as an additive. For the processing of the samples were used hydride titanium powder (TiH_2) to obtain cpTi samples, and metal powders of Ti, Nb and Zr in the stoichiometric proportions for obtaining the alloy samples. The samples were prepared by mixing the metallic powder to the albumin (30wt%) and filling a silicone model that was pressed isostatically (140 MPa). The thermal treatment was performed in an oxidizing atmosphere (350°C/1h) for the decomposition of organic material. The sintering was performed at a temperature of 1300°C (1h/cpTi, 3h/Alloy) in high vacuum furnace (10^{-5} mBar) to all samples. The calculated porosity showed a significant difference between the samples cpTi (40%) and alloy (60%). The samples surface characterization showed very rough with high specific surface area. Samples of cpTi presented formation of necks arising from sintering. In the alloy samples were observed homogenous microstructure with the presence of α and β phases composing the Widmanstätten structure. It is possible to conclude that the same amount albumin allowed the formation of pores in the microstructure of cpTi and alloy although in different proportions, without harming the sintering of both and allowing diffusion of the alloy elements.

Introduction

Biomaterials based on titanium and its alloys are widely used in orthopedics and dentistry due to their excellent mechanical properties and biological interaction. However, there are some problems with the use of titanium as implant material. The high stiffness when compared to the surrounding bone can cause problems of stress and subsequent dislocation of the implant [1]. Thus, the difference in modulus between the bone (10-30 GPa) and the metallic biomaterials (100 GPa to cpTi) has been identified as the reason of implant loss [2].

To address this problem have been developed osteoconductives porous materials for bone regeneration. The advantage of using materials with interconnected porous structure is the ability to allow a biological anchorage to the surrounding tissues through the bone ingrowth through the pores. Furthermore, the value of elastic modulus can be adjusted to match to the trabecular bone, thereby preventing bone resorption at the interface of the implant [2].

Investigations on porous materials that allow bone growth began in the 1970s involving ceramic materials, polymers and metals. Although the ceramics have excellent corrosion resistance, the porous ceramic structures cannot be used in conditions subject to loads due to its intrinsic fragility.

The porous polymeric systems face the same difficulties in relation to mechanical stress, this has led to more intense research for the processing of metals, especially titanium [1,3].

The obtaining of porous metals has been investigated since 1943, when B. Sosnik [2] obtained metal foam by adding mercury to molten aluminum. The concept of biomedical applications using porous metals was later investigated by Weber and White (1972), indicating osseointegration [2]. Currently there are various techniques for obtaining porous metallic material, which uses the powder metallurgy (PM) as a base. This technique allows the production of parts with complex shapes and dimensions close to the finals, near-net shape, avoiding the step of machining [4]. The manipulation of the metals in the form of particulate allows the addition of elements reaching a satisfactory structural homogeneity, and interconnected porosity. Some methods use the metals in the hydrogenated form since it reduces the formation of oxides during processing [5,6].

A simple technique to produce pores using space maintainers, is called space-holder, which are generally organic compounds mixed with metal powder, when it is treated to removed this organic compounds from the structure, the space previously occupied by them retains its form leaving a pore in place. Examples of mainly used organic compounds are hydrogenated ammonium carbonate, urea, gelatin and sodium chloride. The powder particles TiH_2 mixed with ammonium carbonate hydrogenated, pressed and sintered in a high vacuum oven (1300°C/2h) form samples with 44-62% porosity [7]. While the addition of urea powder TiH_2 provides structural pores average 360μm, with a porosity of 36% [8].

The albumin, which is used to obtain porous ceramics, presents characteristics of low cost and biocompatibility and can be a promising organic compound to be used in processing metals also [9]. Based on this natural protein, this study aimed to apply space-holder technique to obtain porous metallic implants by PM.

Experimental Procedure

Hydrogenated titanium (TiH2) powder and metallic powder of titanium (Ti), niobium (Nb) and zirconium (Zr), were used in this study. Those powders were characterized as for: morphology by scanning electron microscopy (SEM) (Philips XL 30); crystalline phases by X-ray diffraction (XRD) (DMAX 2000, Rigaku) with Cu-Kα radiation; particle size distribution by granulometry (CILAS, granulomer – 1064); mass deviation by thermogravimetry (SHIMADZU 60WS). For the processing of the samples were used hydride titanium powder (TiH_2) to obtain cpTi samples, and metal powders of Ti, Nb and Zr in the stoichiometric proportions for obtaining the Ti-13Nb-13Zr alloy samples. The albumin was also characterized by particle size distribution and mass deviation.

The studied technique involves pores formation by space-holder, using the metal powder mixing with albumin. The ratio used was 30wt% of albumin from the total solids, which were mixed in an alumina mortar. Cylindrical silicon molds were filled with the mixed powder and isostatic pressed (140 MPa). The samples were thermal treated in an oxidizing atmosphere at 350°C for 1 hour with heating rate of 1°C/min. This thermal treatment was necessary for the decomposition of organic material and removing carbon from the same. The samples were sintered in a furnace of tungsten heating element with high vacuum (10^{-5} mBar), 1300°C for 1 hour to the cpTi samples and 3 hours to the alloy samples.

The control group represented by dense samples, were obtained by isostatic pressing (140 MPa) the metallic powder in the silicon mold, sintered in the same conditions and machined, without albumin or any other space-holder element.

Sintered samples were characterized for density by Archimede's method (ρ), morphology by SEM; crystalline phases by XRD with Cu-Kα radiation; and surface topography by roughness analysis (SJ-201, Mitutoyo). The apparent porosity was calculated according to the standards of ASTM C20-00 [10].

All sintered samples underwent a cytotoxicity test to enable their use as an implantable biomaterial, to perform the test, extracts of samples and toxic positive control were incubated with CHO-k1 cells, the positive control used was phenol solution 0.3% and for negative control cpTi. According to ISO-10993-5 (1993).

Results and Discussion

In powder metallurgy, morphology and size of the powder used is very important to the sintering process. The morphology analysis performed by SEM of TiH_2 showed particles of irregular shapes (Fig.1 A4). By the particle size distribution, the average particle diameter was ~43 μm.

Analyzing the Ti particles (Fig.1 A3) was possible to observe the high irregular shape, yet more rounded than Nb particles, which have sharp angles (Fig.1 A2). Zr particles are those that are closer to the spherical shape (Fig.1 A1). The particle size distribution by granulometry showed the average particle diameter was ~120 μm to Ti, Nb ~36 μm and Zr ~5,5 μm.

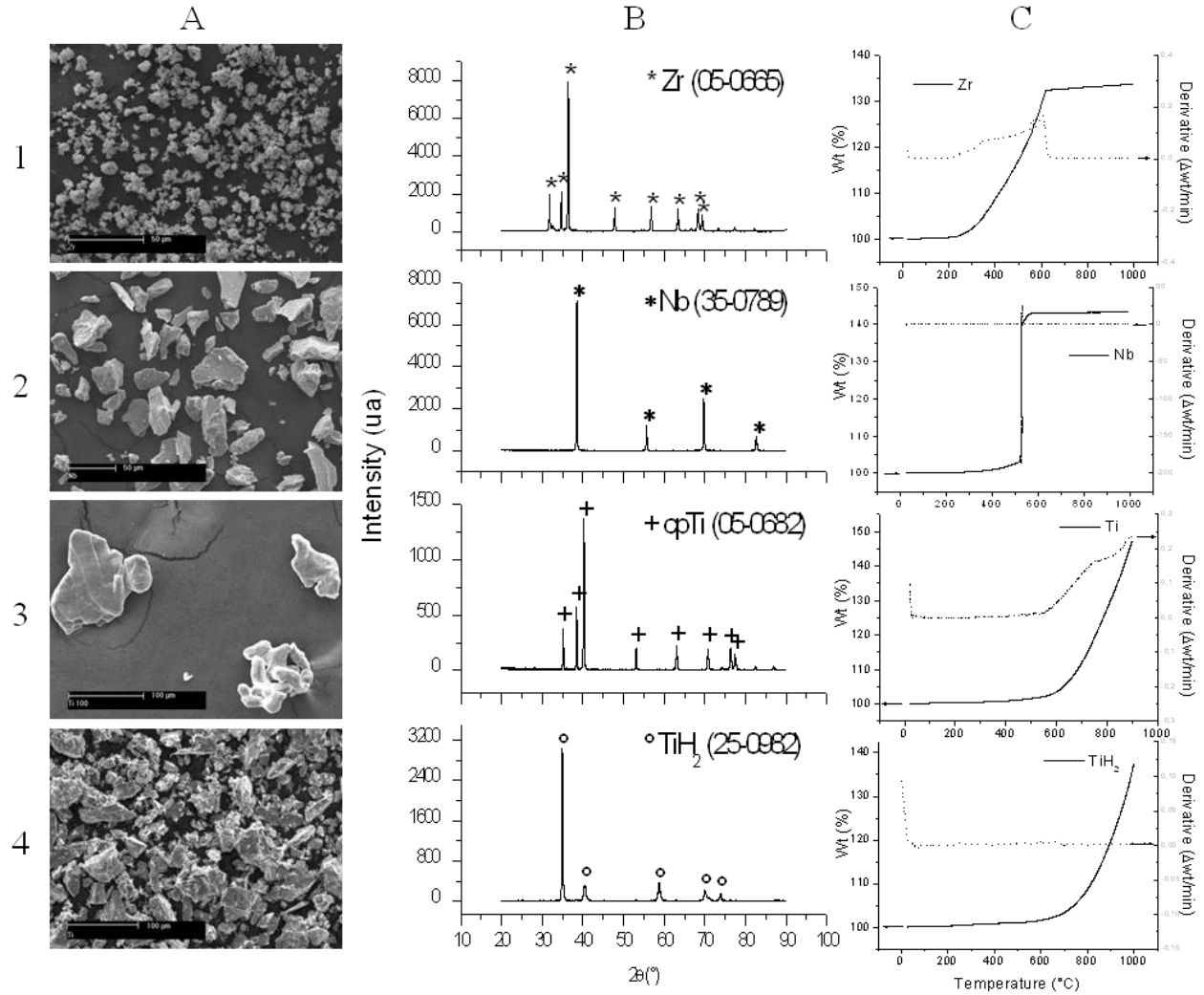

Figure 1. A) Powder morphology by SEM. B) Powder crystallography by XRD. C) Powder thermogravimetry. Respectively to: 1) Zr, 2) Nb, 3) Ti and 4) TiH_2, powders.

To confirm the crystalline phase of the raw material powder (TiH_2 ,Ti, Nb, Zr), XRD analysis was performed and only TiH_2 phase, Tiα-phase, Nb and Zr were found respectively (Fig.1 B4, B3, B2, B1). The use of hydrogenated powder facilitates the processing of porous material, because metallic powder can suffer oxidation at high temperature in an oxidizing atmosphere. As the mechanism of pore formation is the result of organic material degradation with rising temperature, it is necessary to perform the thermal treatment in an oxidizing atmosphere for the removal of natural polymers added before sintering in vacuum. The behavior of the hydride and all metallic powders was analyzed by thermogravimetric analysis, which promoted the air-oxidation of metals according to the rising temperature. The oxidation of metallic cpTi begins at 500°C, as temperature rises there is significant mass increase (Fig.1 C3). On the other hand the oxidation of particulate TiH_2 begins at 700°C, hence it has greater stability than metallic cpTi (Fig.1 C3). This happens because prior to the oxidation the particulate TiH_2 needs to dehydrogenate, process which took place at ~600°C. The Nb is stable up to

approximately 500°C, with a significant gain mass at this temperature. This characteristic indicates that the thermal treatment up to 500°C does not affect the oxidation of the metal and provides a good operating range (Fig.1 C2). Differently to, is the case of Zr, which when close to 300°C begins oxidation because particles with high surface area have a higher reactivity (Fig.1 C1).

The same analysis was done for albumin alone, using a heating rate of 10°C/min to 800°C in an oxidizing atmosphere. Were observed three main stages of mass loss. The first, relating to the loss of free water contained in the material occurs in up to ~ 100°C, ~ 10% of weight loss. The second stage, refers to the loss of structural water and decomposition of organic material to CO_2. The third stage occurs at ~ 600°C by consuming all the material. It was observed during the test the formation of a "browning" layer on the surface of albumin which prevented the release of the mass in the form of CO_2. From ~ 530°C, this layer disrupted, allowing the release of gases (Fig.2 A).

Based on the results obtained by thermogravimetric analysis, the samples were thermal treated at 350°C for 1 hour, with heating rate and cooling of 1°C/min in an oxidizing atmosphere.

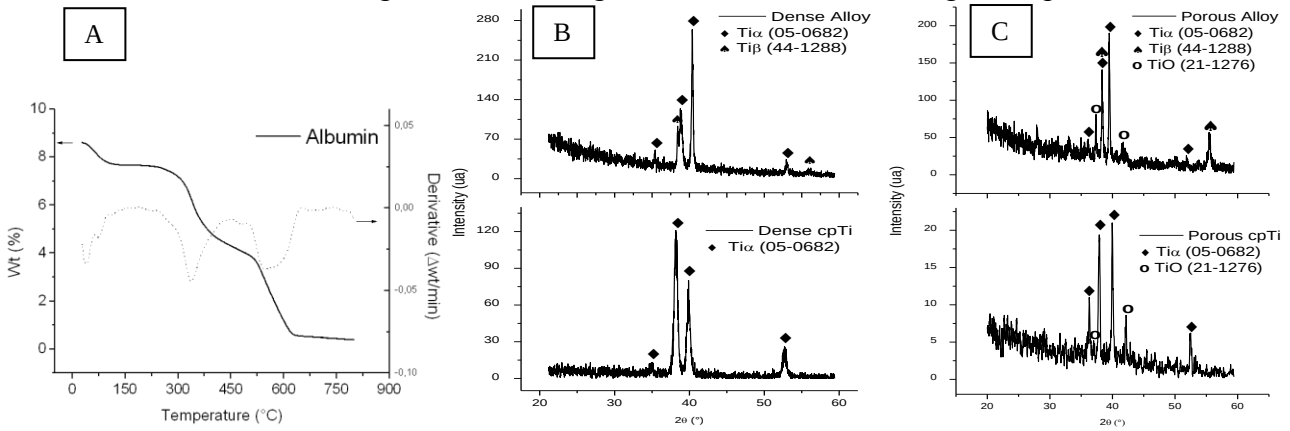

Figure 2. A) Albumin thermogravimetry. B) XRD of sintered dense samples. C) XRD of sintered porous samples

After sintering, there was present only one phase, the α-phase in the structure of cpTi dense samples, it means that all hydrogen had gone away during sintering (Fig.2 B). The alloy dense samples showed only α and β phases in the structure as expected (Fig.2 B). The porous samples showed the TiO phase, that may be related with the increased surface specific area (Fig.2 C).

Regarding to the microstructure of the dense samples it was possible to observe by SEM the formation of closed scattered porosity evenly distributed, this kind of porosity is the expected result of processing by conventional powder metallurgy (Fig.3 B, C), and the alloy samples showed more porous than samples of cpTi, also confirmed by apparent porosity (Table 1). Still, through image analysis was possible to observe the formation of Widmanstätten structure, which represents the structural homogeneity with the formation of β phase in the α matrix of the alloy samples (Fig.3 C).

In order to compare the topography of samples, machined dense samples were used in this study as control, representing most commercial implants. The machined surface can be observed in Fig.3 A. Besides the image evaluation, the results of roughness analysis, showed that porous implants have a rougher surface than most of the implants used commercially (Table.1). The topography of the implant is a factor that directly influences the quality and success of osseointegration, thus the implant surface roughness is a desirable feature and with PM to achieve it, there is no need of further processing to obtain it, as needed for surface treatments.

The values of apparent porosity of samples obtained by PM with use of space-holder (albumin) were calculated after sintering. There is significant difference among porosity values when using different metal powders, the mean porosity was ~40% to cpTi porous samples and ~60% to Alloy porous samples (Table 1).

Table 1. Porosity and roughness of the samples.

Sample	cpTidense	cpTi porous	Alloy dense	Alloy porous
Apparent porosity	1%	40%	9%	60%
Roughness [Ra]	0,15µm	4,64 µm	0,5 µm	6,16 µm

The sintering parameters used for this study were very efficient, there was successfully formation of necks between particles of cpTi, and the resulted shape was roundish, as shown on implant surface (Fig. 4B). Although the porosity acts as a physical barrier for the proper diffusion of alloy elements, a homogeneous structure can also be observed in the porous samples of the alloy. The β stabilizing elements (Nb and Zr) are well distributed in the α matrix (Fig. 5C), observed by the Widmanstätten structure. The small mean particles size of the beta stabilizing elements provided a good penetrability for alloying, also combined with the increased dwelling time of 3 hours.

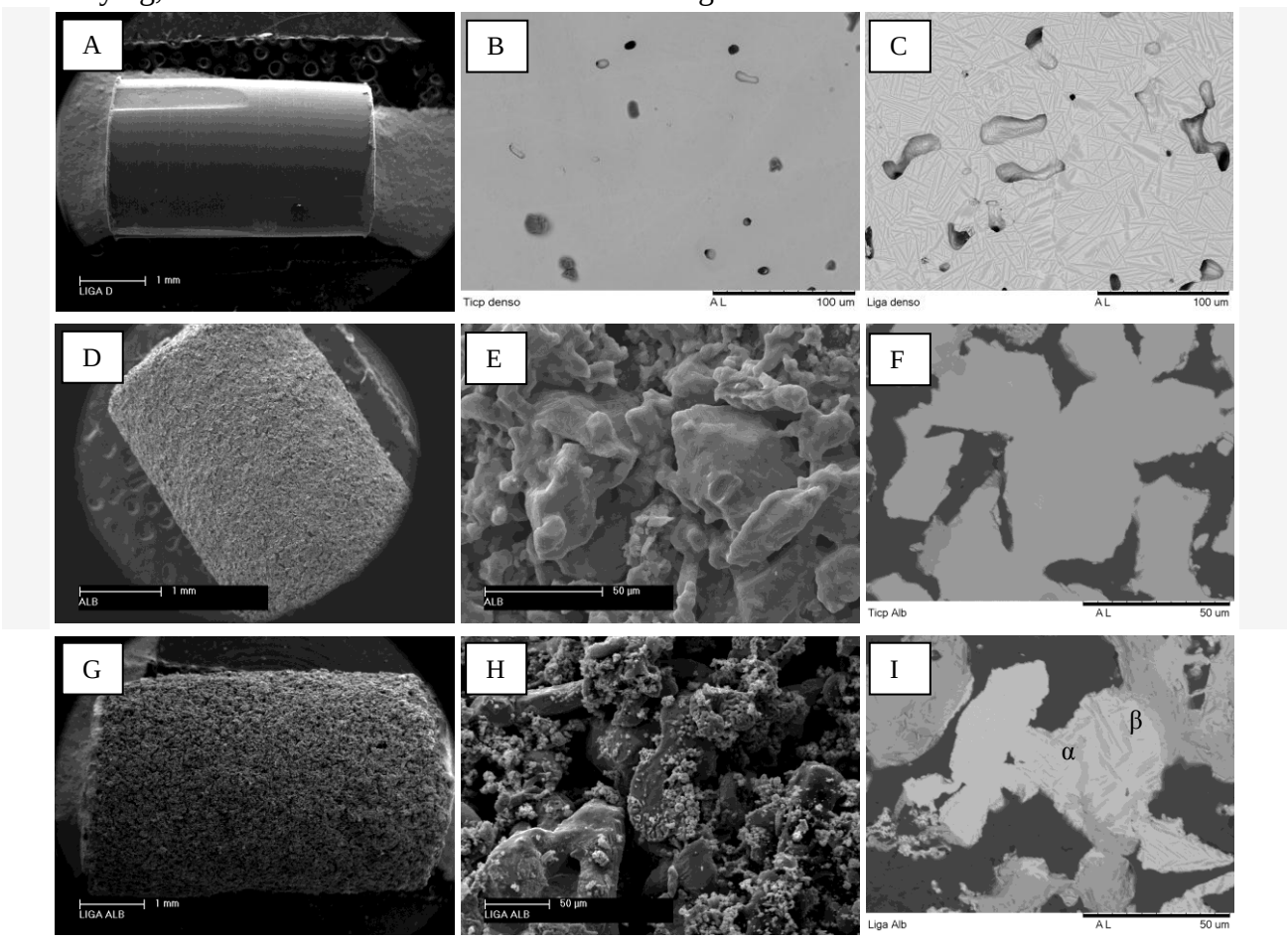

Figure 3. SEM images. A) Representative machined dense sample, low magnification. B) Microstructure of the cpTi dense sample. C) Microstructure of the Alloy dense sample. D) cpTi porous samples, low magnification. E) cpTi porous surface morphology. F) cpTi porous microstructure (polished). G) Alloy porous samples, low magnification. H) Alloy porous surface morphology. I) Alloy porous microstructure (polished) showing phase α and β.

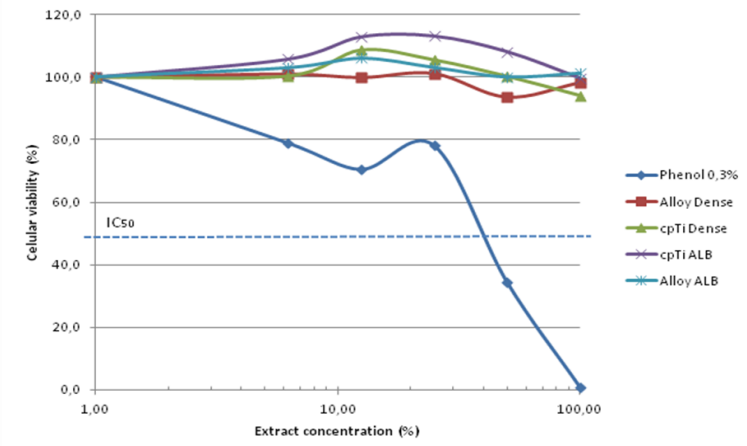

Figure 4. Cytotoxicity test.

To validate the process of biomaterial obtaining, cytotoxicity assay were performed, in which it determines the biological response of mammalian cells in vitro using appropriate biological parameters. To this test, the intercept of the curves analyzed with the index of cytotoxicity ($IC_{50\%}$) determined the degree of toxicity of the sample. In the graph (Fig.6), the curve obtained for each sample correlates the average percentage of living cells as a function of concentration of the extract used. From the test none of the samples tested had the IC less than 50%, only the positive control presented cytotoxicity. Despite all the handling process of metals for obtaining the implants with different structures, none showed cytotoxicity, enabling the implant samples as well their obtaining process to perform *in vivo* assays.

Conclusions

It is possible to conclude that the same amount albumin allowed the formation of pores in the microstructure of cpTi and Alloy, although in different proportions, without harming the sintering of both and allowing diffusion of the alloy elements.

Although the different phase formed by addiction of albumin, no sample showed cytotoxicity, enabling their use *in vivo*.

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