Production and Characterization of Porous Titanium applied in Biomaterials

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Abstract: The development of materials with a porous titanium surface has been widely studied in the field of biomaterials due to the excellent biocompatibility, high corrosion resistance and combination of high strength with low density. Another relevant fact is that porosity allows bone tissue growth. However, the high reactivity in liquid state ends up hindering titanium fusion, so an alternative is the powder metallurgy (PM).The aim of this work was to produce porous titanium samples by conventional PM. Porous samples was characterized by porosity and microstructure (optical microscopy - OP and scanning electron microscopy SEM), crystaline phase (X- ray diffraction –XRD), mechanical properties (three point bending test) and cytotoxic test. The results showed the presence of alpha phase, a decrease in the elasticity modulus, increase in average pore size and samples exhibited no toxic effects.

Introduction

Titanium and alloys has been widely used in biomaterials, because complies to biocompatibility requirements and combines low density with high mechanical strength and high corrosion resistance. Pure titanium has been used in dental implants, screw and hip joints, due to lower mechanical loads when compared to orthopedic implants [1]. However, some studies [1,2] indicate that Young´s Modulus of pure titanium (201GPa) is higher compared to the bone tissue (around 10-30 GPa) and may result in stress shielding of the implant. Studies suggest that this discrepancy can be a factor for implant failure [1].

As the porous surface increases the Young´s Modulus decreases, which favors the regeneration of bone tissue and affords anchoring to the biological tissue. Currently, powder metallurgy technique is among the available processes to obtain whole components of porous titanium or coatings [3]. The advantages over other processes are cost and a superior processing route, considering the suitability for the envisioned application. In this paper is presented detailed characteristics of porous samples obtained by conventional powder metallurgy technique, aiming applications on the production of biomaterials.

Material and Methods

Initially the powder of commercially pure titanium grade 1 (Cp-1) was obtained by way of hydrogenation-dehydrogentation (HDH) process (Fig.1) with a 45μm mean particle size. The following composition of titanium powder was determined by infrared and thermal conductivity tests: 0.0 4 C, 0.02 N, 0.06 H, 0.08 Fe and 0. 03O (% wt).

The powder was then uniaxially pressed under 400 MPa in a cylindrical steel mold, followed by a sintering process carried out in high vacuum condition (10^{-6} torr) at 1100 (batch 1) and 1150 ºC (batch 2), applying heating rates of 10°C/ min.

All the sintered specimens were mechanically polished with 600, 800 and 1200 grit with a SiC paper, followed by polishing with 6, 3 and 1 μm diamond suspension. After polishing, the samples were cleaned in ultrasonic bath and etched by contact with Kroll´s reagent, consisting of 2,5mL HNO_3, 5mL HF and 42,5mL H_2O.

The microstructure was examined by optical microscopy and X-ray Diffraction. Pore size distribution was analysed using a quantitative software NIS-Elements D 3.2 on optical micrographs with 200 X magnification without etching. The maximum bending strength and stiffness was determined on six rectangular specimens, three for each sintering temperature. The samples size averaged 32,00 X 12,88 X 6,24 (mm). Three point bending test was performed in ISTRON 4400R with a speed of 5X 10^{-4} m/s, as recommended by ASTM E290-97a [4]**.**

The maximum bending strength (TRS) and Young ´s Modulus (E) were calculated by expression (1) and (2), respectively.

$$TRS = \frac{3 * P * L}{2 * b * h^2} \tag{1}$$

Where P is load in Newton, L is distance between supports (25m), b is specimen width and h is thickness.

$$E = E_0 \frac{(1-p)^2}{(1+K_E * p)} \tag{2}$$

Where E is Young ´s Modulus of the porous material in GPa, E_0 is longitudinal Young´s Modulus for a pore free material in GPa, P is porosity (%) and $K_{e=}$ 2-3ν, ν- Poisson's rate.

The last evaluation procedure was cytotoxicity. The sintered samples were added to culture medium and incubated for 48 hours at 37 °C with 5% CO_2 atmosphere, followed by extract dilution. The samples were then sprayed with supravital dye composed of tetrazolium compound (MTS) and an electron coupling reagent (PMS), followed by a two hours incubation. The amount of surving cells was then measured by spectrophotometry method.

Results and Discussion

Fig. 1 shows SEM micrographs of commercially pure titanium (Cp-Ti). The structure presents surface porosity (Fig. 1a) and roughness characteristic of the HDH process (**Fig. 1b**).

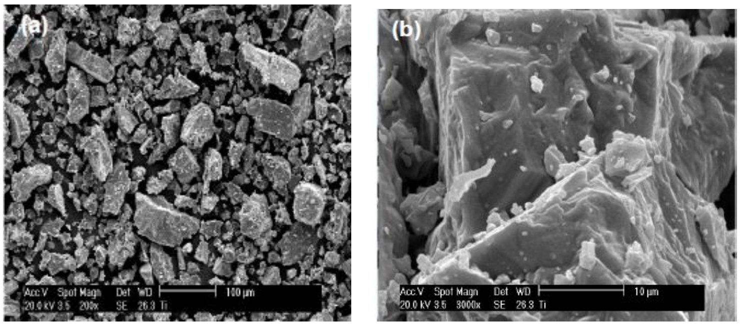

Fig 1. SEM micrograph of titanium hydride-dehydride powder: (a) angular particles; (b) particle roughness .

Fig. 2 presents the microstructure after the sintering process. It can be observed that hexagonal compact phase and residual pores dominate the microstructure. Although alpha to beta transformation has occurred during the sintering process, only alpha phase was observed at room temperature, due to the cooling speed. In addition, the material didn´t contain any alloying elements suited to stabilize the beta phase [5].The X-ray diffraction patterns of specimens sintered at 1100°C and 1150°C are shown in **Fig. 3,** confirming the sole presence of α-phase.

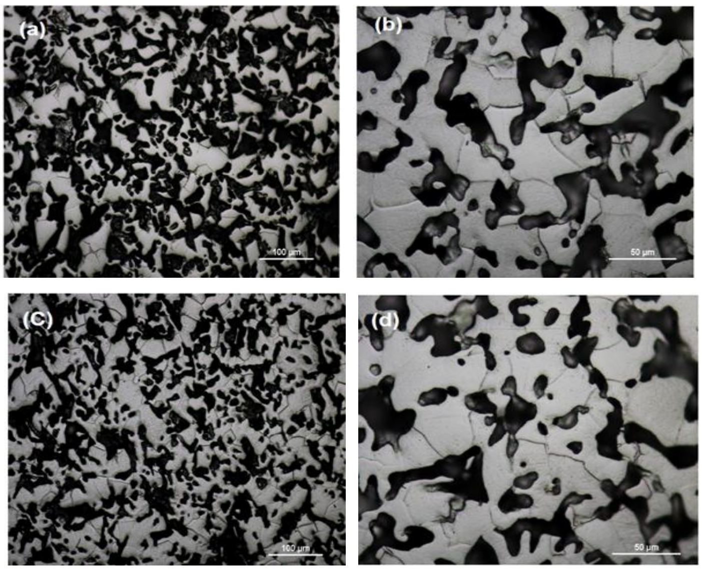

Fig 2. MO micrographs of porous sintered titanium at: (a),(b) – (Batch 1 -1100°C); (b), (C)- (Batch 2 - 1150°C).

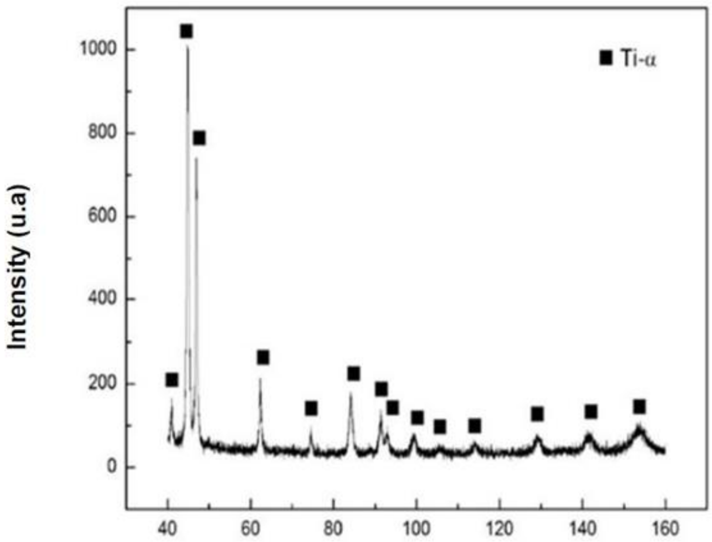

Fig 3. XRD pattern of porous sintered titanium at 1100 and 1150°C.

According to the analysis performed by NIS-Elements software, the average interconnected pore size was in 110-140μm interval (**Fig. 4**). This specific range can promote bone ingrowth, which provides a strong bond with the implant. In addition, it can afford enough space for vascularization and proliferation of new bone tissue, improving osteointegration [6].

Although earlier studies reported that optimal range of porosity for metallic biomaterials lies in 100 - 500 μm, Turrer and Ferreira [7] has showed recently that a 50-100μm interval produced superior resistance to infections processes.

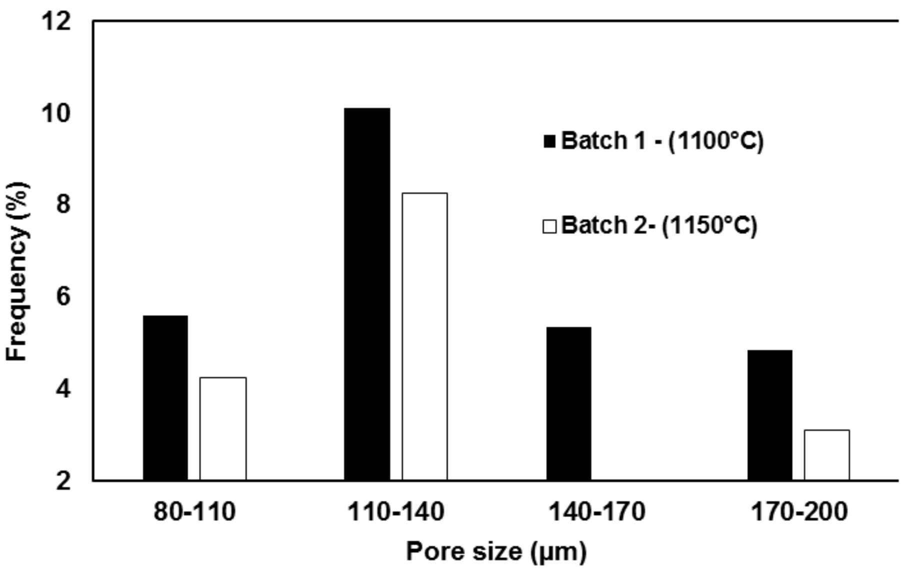

Fig 4. Relationship between frequency and pore size for sintered titanium at 1100 and 1150°C.

As expected, the mechanical properties on the samples of batch 2 were higher than samples of batch 1 (**Table. 1**). Higher sintering temperatures favors migration of atoms allowing the growth of sintering necks, resulting in a drop in both porosity and pore size [8]. On the other hand, the average stiffness on the samples of batch 1 was lower than batch 2, representing 66 % of the solid titanium (102 GPa). Therefore, powder metallurgy can be considered an efficient alternative to obtain biomaterials more akin to bone tissue, regarding stiffness [9,10].

Table 1. Bending strength and modulus elasticity of sintered specimens

Samples	Bending strength (N/m^2)	Modulus of Elasticity (GPa)
Batch 1- (1100°C/ h)	238 ± 13	66,67
Batch 2- (1150°C/ h)	252 ± 3	70,49

Even though titanium has been accepted as biocompatible for a long time, the HDH process commonly uses ciclohexane, which is known to be cytotoxic [6,11].

Figure 5 shows that citotoxicity index (CI) is higher than 50%, suggesting that the porous sample didn´t show toxic effects. The ciclohexane is eliminated during the sintering process.

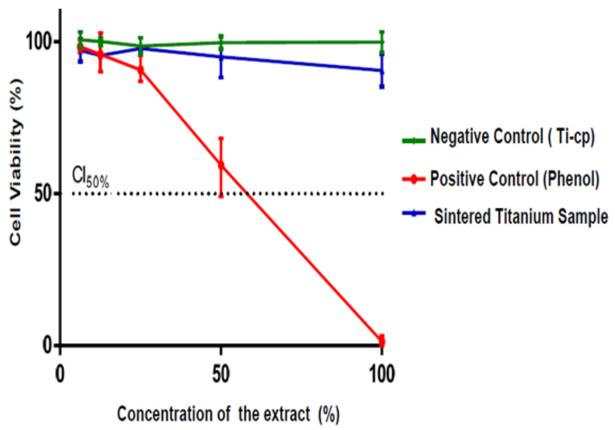

Figure 1. Graph of Cell Viability (%) versus Concentration of Extract (%) for sintered porous titanium.

Conclusions

The results supports that the powder metallurgy technique can effectively produce porous specimens for biomedical applications. Samples showed pore sizes within the range considered optimum to achieve adequate stiffness and osteointegration. Finally the resulting material is not cytotoxic.

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