PREPARATION AND CHARACTERIZATION OF TITANIUM SCAFFOLDS

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Abstract. *Combining knowledge of the areas of materials science and engineering, biology, pharmacy and medicine, parts with three-dimensional surfaces, called scaffolds are created for storage, drug delivery and as an osteoinductive material. These scaffolds can be produced in various biomedical accessories such as implants, valves, stents, and prostheses, among others. Among the materials used, we have the titanium and its alloys. In this work porous scaffolds of titanium alloys (Ti-Sn-Nb_2O_5) were produced from the by plasma sintering process. The technique of plasma was used for the production of these scaffolds aiming to obtain a material with a porous surface and a dense core, without the need to use space – holder. Ti alloys (90% and 80%), Sn (5%, 10% and 15%) and Nb2O5 (5%, 10% and 15%) were mixed and pressed. After the pressed pellets were sintered by plasma during 2 hours. We used argon and hydrogen during the sintering process. The samples in the first stage were characterized as to porosity, microhardness and scanning electron microscopy to observe whether there was the interconnectivity of pores. Through the sintering process was possible to obtain scaffolds with a porous surface (30.54% to 66.83%) and a core with low porosity (7.44%). The microhardness of the materials obtained ranged from 282,91 to 210,14 Hv. By scanning electron microscopy was possible to observe the pore size and interconnectivity of the porous layer of the scaffolds obtained. We observed that the time of sample preparation by sintering the plasma is much smaller than in conventional sintering.*

Keywords*: Titanium, Tin, Oxide of niobium, scaffolds, plasma.*

1. INTRODUCTION

Porous titanium scaffolds are promising materials for biomedical applications. This type of material has osteoconductive properties, i.e., facilitates the migration of osteoblasts around the implant site helping the healing process (Vasconcelos et. al., 2008).

Titanium scaffolds have been used to facilitate and / or allow bone growth in the porous structure. This bone growth provides a strong interaction between implant and bone tissue. The three-dimensional pore should preferably be interconnected to provide sufficient space for the attachment and proliferation of new bone tissue and to facilitate the transport of fluids through the material. These porous structures have many applications ranging from acetabular hip prosthesis, dental implants, osteosynthesis plates permanent and invertebrates disks (Blom, 2007).

However the use of pure titanium for the production of these scaffolds makes this artifact expensive and thus inaccessible to a wide range of people. That is why titanium has been used in combination with other elements such as molybdenum (Mb), tantalum (Ta), zirconium (Zr), tin (Sn) and niobium (Nb). Among the most prominent leagues has the Ti-Sn-Nb because of their excellent biocompatibility (Caram, 2009).

These alloys must be biocompatibles, have high mechanical strength, low modulus of elasticity, in order to monitor the flexibility of the bone. The high modulus of elasticity limits the natural deformations of the femur, which can cause bone degeneration (Caram, 2009).

Several methods have been investigated for the production of these scaffolds, including the technique of powder metallurgy, which seems to be particularly advantageous because of its processing route and cost. In powder metallurgy, the pores depend on the compression of the particles, of decomposition of particles space-holder and diffusion of the solid state in the sintering stage (Taddei et. al., 2004).

One technique that has shown significant results for the production of these scaffolds is the sintering process. Studies carried out revealed that samples sintered by plasma show a porosity gradient between the surface in contact with the plasma and core of samples (Alves Jr. et. al., 2003).

When a material is immersed in plasma is exposed to a complex environment where the material surface will be influenced mainly by radiation and bombardment of ionic species, the latter being responsible for the thermal peaks. The heat peaks in turn, are responsible for heating locally of high intensity modifying the structure of the material. (Souza Jr. et. al., 2002). The intensity of the surface porosity of the material varies according to the parameters of system such as pressure and configuration of electrodes (Galvão, 2007). The layer of material affected by bombardment was called by Galvão et.al. (2007) of zone affected bombardment - ZAB.

In heat treatment of solid materials the ZAB presents itself as a microstructure different to the rest of the sample, in the sintering of porous materials this layer has with a higher porosity than the rest of material structure (Galvão et. al., 2008).

In this work scaffolds titanium alloys (Ti-Sn-Nb_2O_5) were produced from the sintering process, in order to obtain a material with a porous surface and a dense core, without the need to use space-holder for the formation of pores in order to use them as a biomaterial.

2. EXPERIMENTAL

The following materials, titanium (Ti-90 and 80), tin (Sn-5, 10, 15) and niobium oxide (Nb_2O_5 - 5, 10, 15) (%wt.) in powder form, were used in the preparation the scaffolds of Ti, "Tab. 1".

Table 1: Composition of samples

Nomenclature	Symbols	Weight composition
Sample 1	A1	90%Ti – 5%Sn – 5%Nb_2O_5
Sample 2	A2	80%Ti – 15%Sn – 5%Nb_2O_5
Sample 3	A3	80%Ti – 5%Sn – 15%Nb_2O_5
Sample 4	A4	80%Ti – 10%Sn – 10%Nb_2O_5

For the process of sintering, the powders were mixed and compressed to obtain samples green. We used a mold and a hydraulic press, the load applied on the mold was 13 tons for 30 seconds. After pressing, sintering was conducted at 900 º C for 2 hours under an atmosphere of argon (Ar) and hydrogen (H_2).

The plasma reactor for sintering of the samples of Ti alloy consists of a borosilicate glass chamber with a cylindrical shape, having two electrodes at both ends. The camera is equipped with thermocouple, vacuum pump, pressure sensor, continuous power source and gas supply system "Fig.1". In all the sintering has been used total flow of 20 sccm gas (17 sccm of Ar and H_2 3 sccm) at a pressure of 6 mbar.

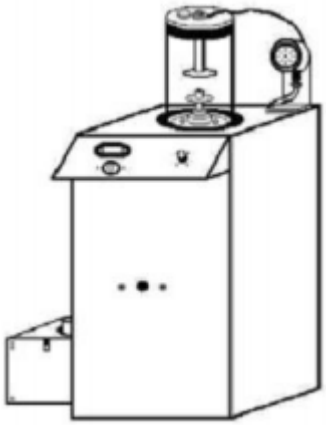


Figure 1: Schematic of plasma reactor used for sintering.

In the sintering process was used hollow cathode configuration, in which the samples were placed between the cathodes, thus increasing the efficiency of treatment. A model of hollow cathode used in the workplace was a bulkhead 35 mm in diameter suspended by a tripod it was made of stainless steel with a height of 6 mm between the surface of the substrate and the ceiling of the cathode "Fig 2".

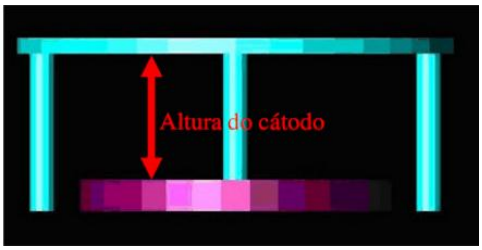


Figure 2: Configuring the hollow cathode used in this work.

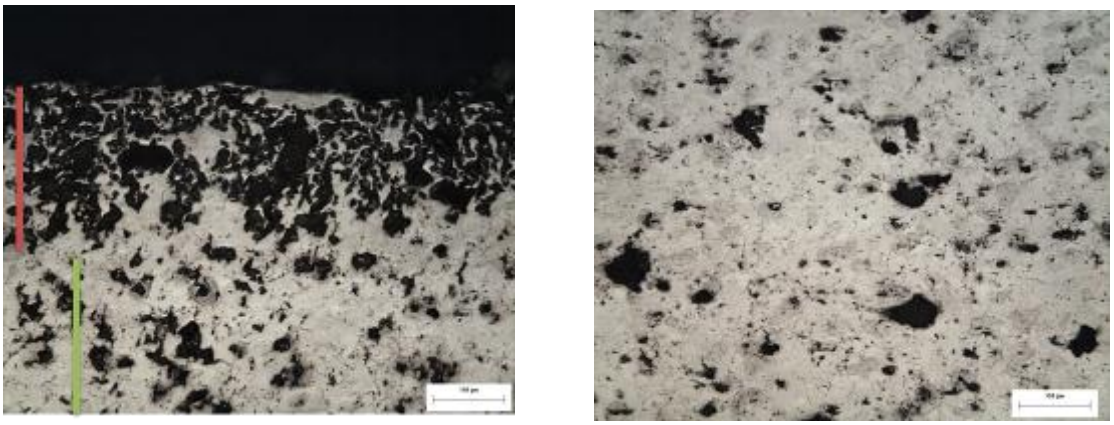
The samples were sintered after being subjected to the process metallographic sanding (sandpaper ranging from 220 to 2000 mesh) and polished (solution of colloidal silica with hydrogen peroxide). For image analysis was used BX60M OLYMPUS microscope equipped with a camera for image acquisition. The images were analyzed with the aid of Image Pro Plus 6.0 software.

Calculation of percentage of porosity was carried out as follows: first the image was divided into two regions for analysis - edge and core - then the porosity was calculated in each region. The sum of the total porous area was divided by the total area of the region analyzed and multiplied by 100 to obtain percentage values. Moreover, it was also possible to measure the thickness of the porous layer and observe presence or absence of interconnectivity of pores, for this we used a scanning electron microscope Philips XL-30-ESEM (SEM).

For Vickers microhardness of sintered specimens and polished, we used the equipment brand Panambra HVS model 1000, using a 50g load, for a time of 15 seconds. Measurements were made from edge to edge sample, with 250 microns spacing between measurements. Noting as well the difference in hardness between the core and edge.

3. RESULTS AND DISCUSSION

Samples treated by Plasma showed different degrees of porosity for different compositions. The sample A1 showed a surface layer with high porosity (56.42%) known as the porous layer or area bombardment after this layer there is a decrease in porosity. In relation to this core appears more dense with porosity of 7, 44% “Fig. 3a and 3b”.

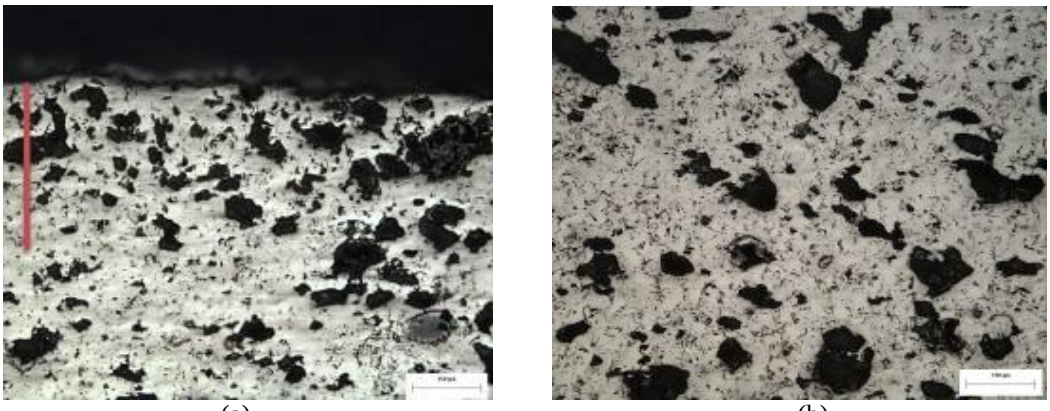


(a) (b)

Figure 3: In "Fig. a" has the image of the edge of the A1, the area marked by the red bar is called the porous layer, in the area marked by the green bar to the porosity was found to be 18, 13%. In “Fig. b” the core of sample (200x, increase).

The area that has the highest porosity is called ZAB where there is the largest bombardment of particles with the material as told by Galvão et. al., thus forming a porous material and a more compact core.

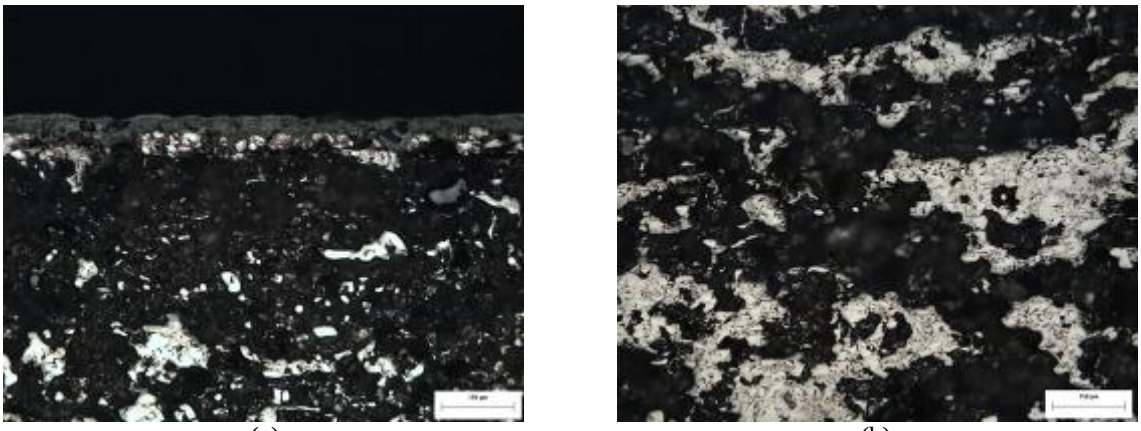
The sample A2 presented a homogeneous porosity in the surface of the material (30,54%) and an increase of the porosity in the nucleus of the sample (18,23%) in relation to the sample A1. This must have happened due to the decrease in the amount of Ti and increase of Sn in the preparation of the sample “Fig. 4”.



(a) (b)

Figure 4: In "Fig. a" image from the edge of the A2, the area marked by the red bar is the ZAB. In "Fig. b” the core of sample. (200x increase).

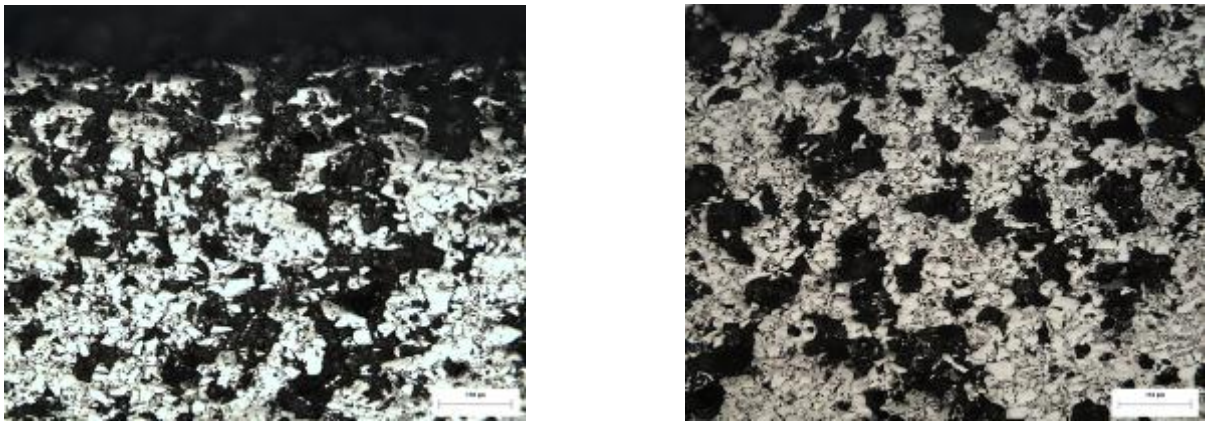
Comparing sample 2 with sample A3 the amount of Ti remained the same, but there was a decrease in the amount of Sn and increasing the amount of Nb_2O_5 so the material showed a high porosity in both surface (66.83%) as in nucleus (58.80%) "Fig 5".



(a) (b)

Figure 5: Fig. a" edge of A3 sample. In "Fig. b" is observed core (200x, increase).

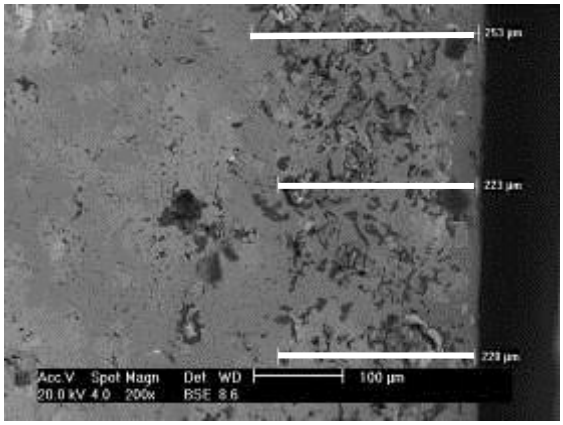
The samples A2, A3 and A4 have same amount of Ti, but the amount of Sn and Nb_2O_5 was modified. Resulting in samples with little difference in porosity between the surface and core "Fig 6. In relation to the porosity of the sample A1 the edge porosity of this sample was smaller than A4, while core sample A4 showed a higher porosity than the core sample A1, comparing the porosity of the edge of the sample A2 and A4 practically there are not difference but the core sample A4 was much more porous than the core sample A2 this may have occurred because the sample A4 had double of niobium oxide sample A2. The sample A3 had much more porous than all other samples, probably due to the decrease in the amount of Ti and Sn and the increase of Nb_2O_5.



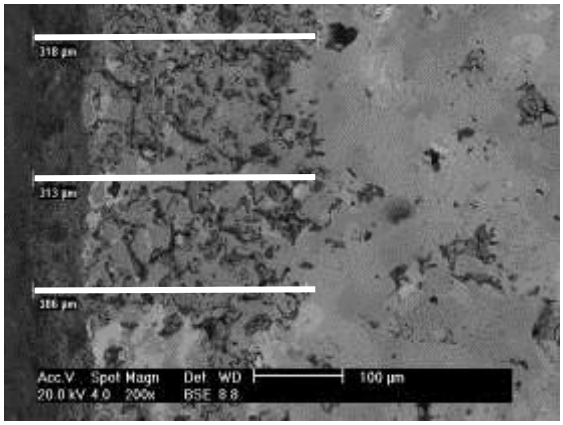
(a) (b)

Figure 6: "Fig. a" edge of the sample 4. In "Fig. b" the core. (200x increase).

In relation to thickness of the porous layer present in these samples. These varied both in relation to amount of material used in each sample as well as compared to side that was in contact with the sample port and the side of the plasma. In sample A1 the porous layer is thicker in side of the plasma than in side sample port as shown in "Fig 7.



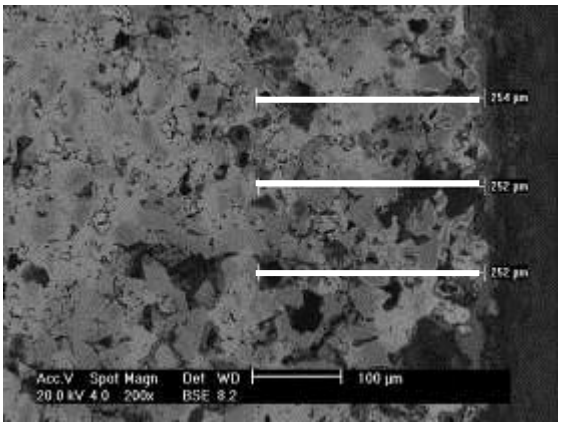
(7a)



(7b)

Figure 7: Measurement of the thickness of the porous layer by scanning electron microscopy of the A1. The "Fig "show the side that was in contact with the sample port and "Fig b" shows the side facing the plasma, i.e., the area affected by the bombing (ZAB).

In A2 sample the coating is thinner than sample A1 and there is no great difference in thickness between the side in contact with sample port and the side of the plasma "Fig 8". This demonstrates that variation in amount of Ti and Sn used in two samples influenced the formation of this porous layer. In relation to sample A3 this did not present a porous surface layer as highlighted in the sample A1 and is therefore not possible to measure this layer "Fig 9".



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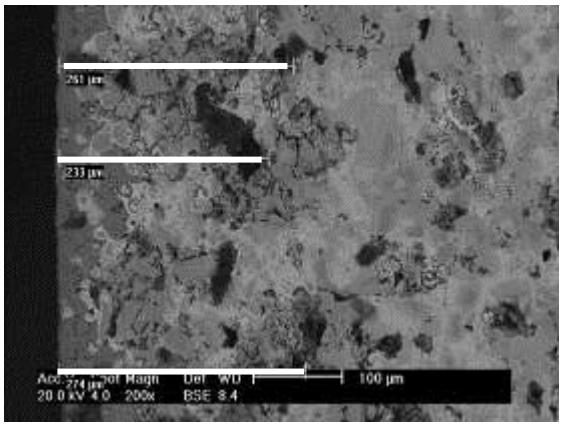
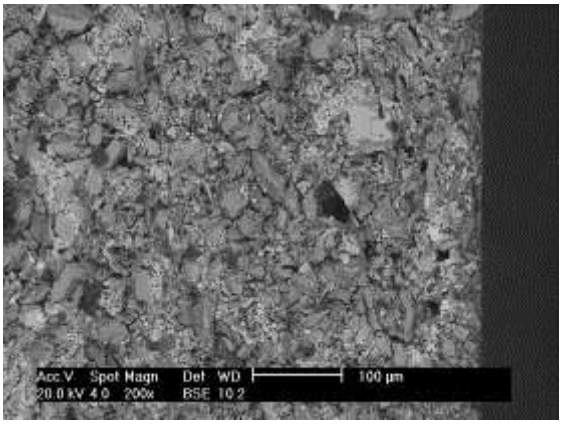
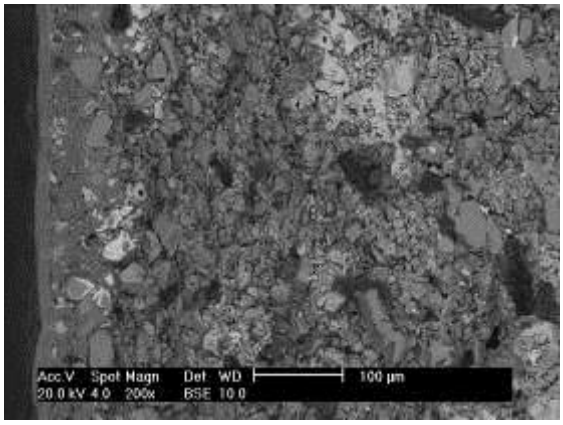


(b)

Figure 8: Measurement of the porous layer thickness of sample A2. "Fig. a" side door of the sample and "Fig b" side of the plasma.



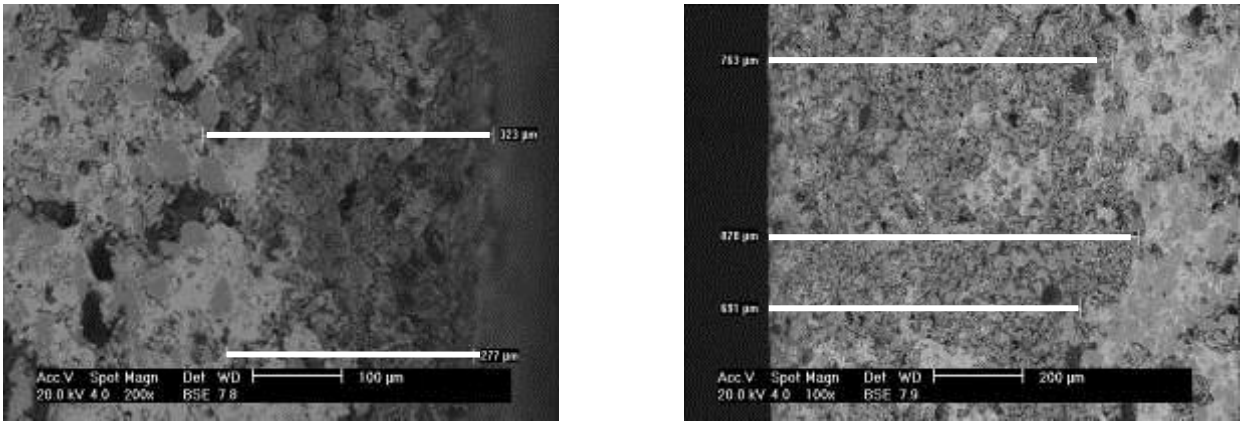
(a)



(b)

Figure 9: "Fig. a" side of the sample port and "Fig. b" side of the plasma.

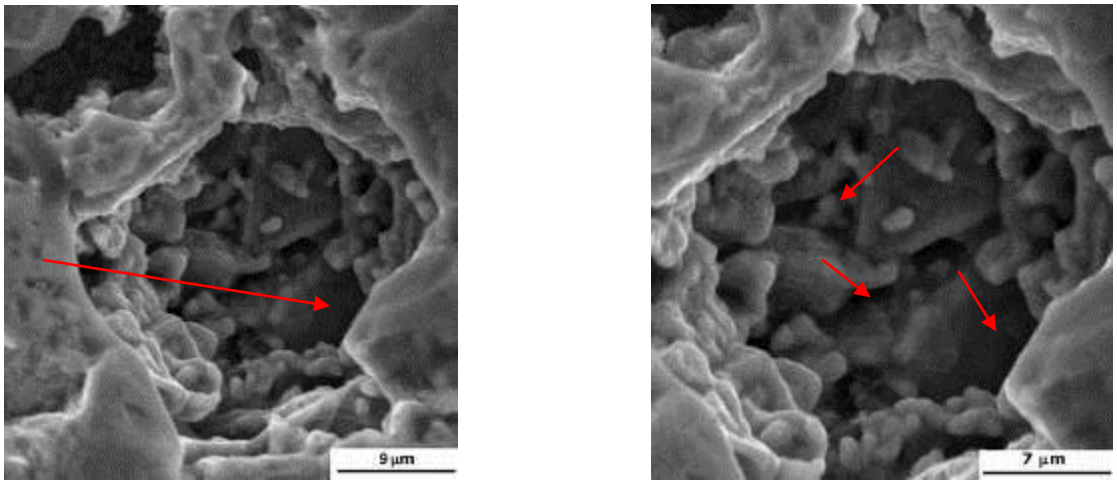
The greater porous layer was observed in A4. This may have occurred due to decreased amount of Ti and increasing the amount of Nb2O5 and Sn relative to other samples "Fig 10.



(a) (b)

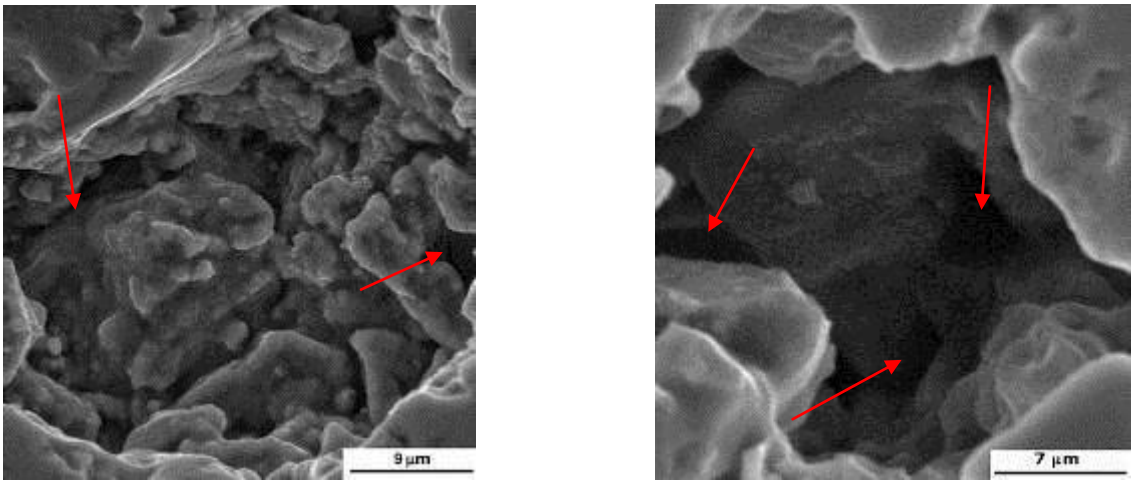
Figure 10: "Fig. a" porous layer side sample port, "Fig. b" porous layer side of the plasma.

By scanning electron microscopy (SEM) was possible to verify whether there was interconnectivity between the pores existing in the samples. Both the sample A1 and A2 was possible to confirm the interconnectivity between the pores "Fig 11 and12.



(a) (b)

Figure 11: "Fig. a" pores of the sample A1 an increase of 3500x, "Fig. b" inside pore look showing other pores in its interior increased 5000x.



(a) (b)

Figure 12: "Fig. a" pores of the sample A2 increased 3500x. "Fig. b" an increase of the pore 5000x.

In samples A3 "Fig. 13a" and A4 "Fig 13b" also observed the formation of pores, however it was noted that much of the pores on behalf of the trainees were not complete densification of the particles due to the high concentration of niobium oxide and low concentration of Sn.

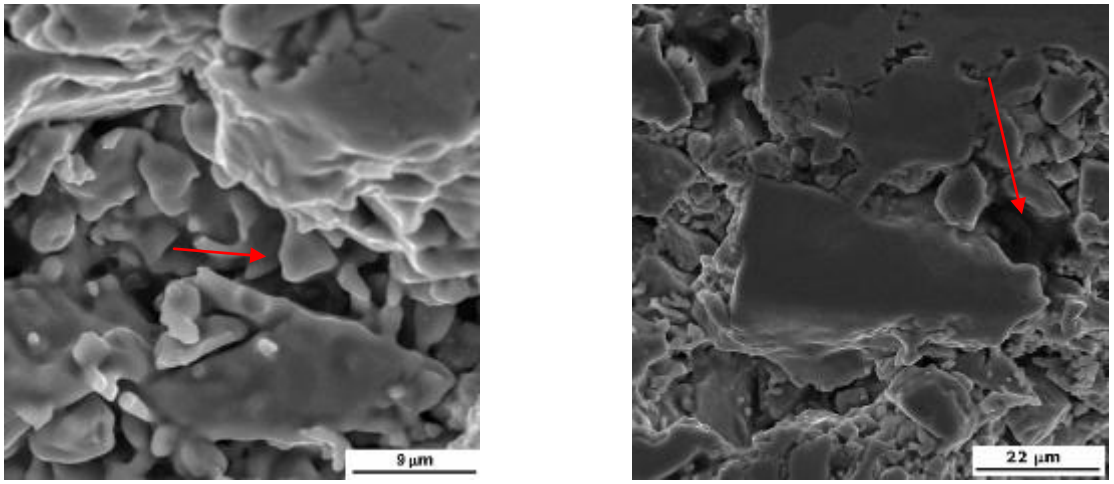


Figure 13a: Sample 3 with increase of 3500x

Figure 13b: Sample 4 with increase of 1500x

The porosity and interconnectivity of pores in samples is important because it may allow the mechanical anchoring of the biomaterial to be implanted and promote tof cell growth and induce the cells to produce extracellular matrix components (Machado et. al., 2006).

In microhardness tests, there were major differences between edge and core of samples. In "Fig 14 "shows the microhardness from the edge of the samples, we observe that the edge of the samples with higher amounts of Ti (90%) have greater hardness than the other samples that contain a lower amount of Ti Another observation to be made about this chart is that the greater the proportion of niobium oxide hardness minor of edge.

Among the samples analyzed in edge microhardness test to sample A1 that had higher amounts of titanium (Ti 90%) showed the highest hardness "Fig 14. When we reduced the amount of Ti, using only 80% of Ti in the case of other samples (A2, A3, A4), there was a decrease in hardness of these samples in relation sample A1, ie the amount of Ti used in preparing the samples influenced the hardness of them.

Noting the "Fig 14 " the A3 sample has lowest hardness, this is due to an increased amount of Nb_2O_5 in the sample.

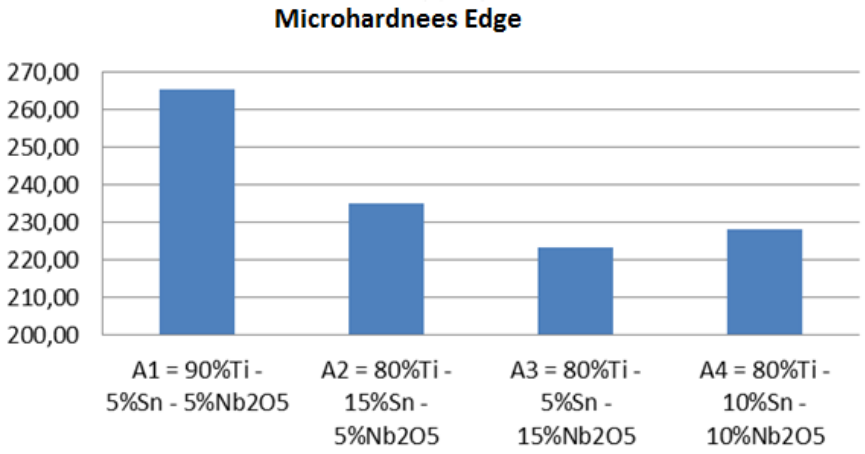


Figure 14: Profile of microhardness of edge of sample

Microhardness tests in core "Fig 15 ", the samples had a different behavior from that found in" Fig 14. In the graph of microhardness of the core is observed that even a sample showing a higher amount of Ti, it had a higher hardness in the core. However the sample of greatest prominence in this trial was that a higher amount of Sn, this is due to the flow of Sn for the core sample through the capillary, which during the cooling step is solidifcava, thus increasing the core hardness of the sample 2, another factor that influenced hardness was quantity of Nb2O5 in this sample that was less than in samples 3 and 4.

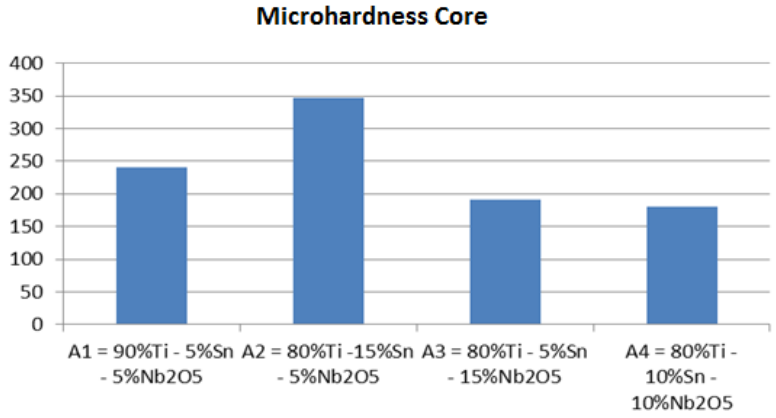


Figure 15: Profile of microhardness of core of samples.

4. CONCLUSION

The sintered by hollow cathode plasma was effective for producing parts with a more porous surface and a denser core. Furthermore, it was possible to obtain samples with interconnectivity between the pores, these interconnections favor the formation of tissues in the form of an organized network, with wide application in tissue reconstruction. The proportions of the elements Sn and Nb2O5 used to produce these scaffolds of Ti influenced in the porosity of the material, hardness and sintering time.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

Alves Jr., C.; Hajek, V.; dos Santos, C. A., 2003. “Thermal behavior of supersolidus bronze powder compacts during heating by hollow cathode discharge. Materials sci. and engineering A., vol.348, p. 84 – 89.

Blom, A., 2007. "Which scaffold for which application?", Mini-symposium: Fracture healing. Current orthopaedics, Vol 21, pp. 280-287.

Caram, R., 2009. "Unicamp desenvolve ligas de titânio". 10 junho. 2009 <http://blog.projetistasbrasil.com>.

GALVÂO, N.K.A.M. Determinação do perfil térmico em amostras de aço AISI M35 imersas em plasma. 2007, (Dissertação de Mestrado). Programa de pós-graduação em ciências e engenharia de materiais da Universidade federal do Rio Grande do Norte – UFRN

Galvão, N.K.A.M.; Costa, B.L.S.; Mendes, M.W.D.; de Brito, R.A.; Souza Jr. C.F; Alves Jr., C (2008). "Structural modifications of M35 steel submitted to thermal gradients in plasma reactor". Journal of Materials Processing Technology, Vol. 200, Issues 1-3, p. 115-119.

Machado, J. L. M., Benderovics, G., Santos, L. A., 2006. "Obtenção de suporte para engenharia de tecidos utilizando-se cimento de α-Trifosfato de cálcio(α-TCP)". Anais do Congresso Brasileiro de Ciência e Engenharia de Materiais, Vol.1, Foz do Iguaçu, Brasil.

Souza jr, C.F.; Sinka, v.; Alves jr, C.; Hajek, V., 2002. "Avaliação das grandezas térmicas durante o aquecimento de sólidos imersos em plasma". Anais do Congresso Brasileiro de Ciência e Engenharia de Materiais, Vol.1, Natal, Brasil.

Taddei, E. B., Henriques, V. A. R., Silva, C. R. M., Cairo, C. A. A., 2004. "Sinterização a vácuo da liga Ti-35Nb-7Zr-5Ta". Revista Brasileira de vácuo, vol. 23, n 2, 67-72.

Vasconcelos, L. M. R., Oliveira, M.V., Graça, M. L. A, Vasconcellos, L. G. O., Carvalho, Y. R., Cairo, C. A. A., 2008. "Porous titanium scaffolds produced by poder metallurgy for biomedical applications". Materials Research, vol. 11, nº 3, 275 – 280,

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