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EXPLORATORY STUDY OF Ti-35Nb OBTAINED BY POWDER METALLURGY

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Abstract. *To be applied as permanent implant material in the human body requires that it present a range of properties and characteristics that includes compatibility in physical and mechanical terms with the tissue to be replaced, biocompatibility and excellent resistance to the corrosion. In the case of metallic materials to be used in orthopedic implants, some titanium alloys can attend satisfactorily these requirements, such as β -type titanium alloys, such as the one used in this study. Such alloys have high hardness, excellent corrosion resistance and young's modulus values close to the bone, and are composed of non-toxic and biocompatible elements. Titanium alloys can be obtained by melting processes in inert atmosphere or by powder metallurgy processes from the elementary powders, which is a viable alternative because it is possible to make pieces with complex geometries and dimensions close to the ends, with good surface finish. In addition, the sintering temperatures used are low compared to other metallurgical processes, and simple design furnaces with lower energy consumption can be used. The main results show that there was cold sintering of the niobium grains in the compacted samples at high pressures and also the occurrence of deformation twins in the particles of titanium.*

Keywords: *Titanium alloys, Powder Metallurgy, High Pressure.*

1. INTRODUCTION

The application of a material as permanent implant in the human body requires that this material present a set of properties and characteristics that includes physical and mechanical compatibility with the tissue to be replaced, biocompatibility and resistance to corrosion (Polmear, 1995). In the case of metallic materials to be used in orthopedic implants, it can be seen that some titanium alloys can satisfy these requirements satisfactorily and can be used in the manufacture of metal plates and screws.

Between the metallic materials used as implants are Ti-6Al-4V alloy, stainless steel and Co-Cr-Mo based alloys (Leyens and Peters, 2003). The Ti-6Al-4V alloy is the main representative of titanium alloys $\alpha + \beta$ and for several years was used extensively in the manufacture of implants in the biomedical field, replacing pure titanium, due to the higher mechanical resistance of the components made with this alloy (Eisenbarth et al., 2004).

New alloys are being developed for the substitution of vanadium in the Ti-6Al-4V alloy, because vanadium is toxic and can cause damage to the implanted health (Eisenbarth et al., 2004). Aluminum can also be harmful and may cause disorders in the implanted neurological system (Silva et al., 2004). These are some adverse aspects of $\alpha + \beta$ alloys that have led to increased use of β -titanium alloys as materials for the manufacture of orthopedic implants.

In addition to the presented, should also be considered the Young's Modulus of the material to be implanted, because when materials with Young's Modulus higher than to the human bone are used for the preparation of implants, there is insufficient transference of the tension to the bone, being able to generate bone degradation and consequently osteoporosis (Tarr et al., 1983). In extreme situations, bone degradation associated with osteoporosis can lead to femoral fracture.

Materials such as stainless steels and Cr-Co-Mo alloys have high Young's Modulus, close to 200 GPa and values higher than 240 GPa, respectively. Therefore, to avoid bone degradation, the Young's Modulus should be similar to that of bone (20 to 40 GPa, (Tane et al., 2008)). Thus, β -titanium alloys, as studied in this work, become attractive, because the Young's Modulus presented by them can vary from 55 to 85 GPa (Niinomi, 1998) and the substitution of vanadium by niobium as a β -stabilizer element is justified by niobium to be biologically inert. In addition, niobium is an element that when added to titanium has the property of reducing the Young's Modulus of this element, which makes it important in obtaining new titanium alloys for biomedical applications (Santos, 2006).

Titanium alloys can be obtained by conventional melting or by powder metallurgy. The process of powder metallurgy can be divided into four main parts, being: obtaining the powders and their classification, mixing, compaction and sintering. Powders can be obtained in various forms, among them hydride-dehydration (HDH). The classification of the powders can be done by using vibrating sieves and the mixing of the powders is done in proportions determined according to the chemical composition of the alloy. The compacting process is performed using presses and dies, and the compacting pressures vary with the different materials to be used, with the characteristics of the metallic powders and with the amount of the lubricant added to the powders mixture (White, 1998). Sintering occurs at temperatures below the melting point of the base metal of the alloy (Chiaverini, 1986).

In this context, the aim of this work is to evaluate the microstructural and mechanical behavior the Ti-35Nb alloy compacts produced under pressures up to 2000 MPa.

2. EXPERIMENTAL PROCEDURES

Initially titanium and niobium elementary powders were classified by sieving using Tyler Series sieves mounted on a magnetic sieve shaker. After this classification, the powders were weighed on analytical balance, 35% by weight of each sample corresponding to the niobium and 65% by weight corresponding to the titanium, and then the powders were mixed in rotating cylinders for 48 h in order to allow homogenization of the alloy.

After mixing, the uniaxial pressing of the powders was carried out under variable pressures, considering the pressures of 400, 600, 800, 1000, 1500 and 2000 MPa, using a hydraulic press. Then the metallographic preparation of the green compacted was carried out, consisting of sanding, using silicon carbide sandpaper 220, 400, 600, 800, 1000 and 1200, followed by polishing using DP-PLUS polishing cloth and colloidal silica (OP-S), both from Struers. The chemical attack was performed using the following reagent 100 ml H₂O, 10 ml HNO₃ and 5 ml HF, in varying times of 3 to 10 seconds. The characterization was performed using optical light microscopy, Vickers hardness (microhardness) and measurements of Young's Modulus by ultrasonic method.

3. RESULTS

The results obtained for the characterization of the titanium and niobium powders and also the results of the Ti-35Nb alloy after uniaxial compaction at pressures equal to 400, 600, 800, 1000, 1500, and 2000 MPa are presented below.

3.1 Characterization of titanium and niobium powders

After the classification of the titanium and niobium powders individually, the characterization of these powders was performed. This characterization was performed in two steps: verification of the morphology and size of the powders of each element by optical light microscopy and measurements of the apparent density of the powders.

The results regarding the average size of the powders of the metals involved are qualitative, being an estimate. The measurements were performed considering the largest dimension presented by the particles. Thus, the titanium powders have an average size corresponding to $190 \pm 43 \mu\text{m}$ and the niobium powders have a size corresponding to $207 \pm 65 \mu\text{m}$.

The powders used were those that passed through the 100 mesh sieve but were retained in the 200 mesh sieve. Correspondence can be made to the size of the powders retained in each sieve, and the powders of 100 mesh passed powders of less than or equal to $149 \mu\text{m}$, and in the 200 mesh sieve, powders with a size greater than $74 \mu\text{m}$ were retained. The correspondence between the sieve designation (mesh number) and the corresponding size in μm can be verified in Chiaverini (2001).

When comparing the size of the measured powders with the one corresponding to the sieve used, it is verified that the obtained data are in agreement with the range of sizes expected for the powders (149 to $74 \mu\text{m}$), because according to the microscopic analysis of the powders of both materials, they are irregularly shaped, and the titanium powders have a more uniform size (Fig. 1a) and the niobium powders have a larger aspect ratio (length greater than the width), as shown in Fig. 1b.

The apparent density measurements were performed by measuring the mass presented by each material considering a predetermined volume. According to the apparent density measurements, the density of the titanium powders is equal to 1.99 g/cm^3 and the niobium is equal to 4.14 g/cm^3 . Comparing with the theoretical density of these materials, $d_{\text{Ti}} = 4.5 \text{ g/cm}^3$ (Lampman, 1998) and $d_{\text{Nb}} = 8.57 \text{ g/cm}^3$ (Lambert, 1998), apparent density was found to be lower than these, this is due to the fact that the initial powders occupy more volume, since they do not present compaction, having many empty spaces among the dust particles.

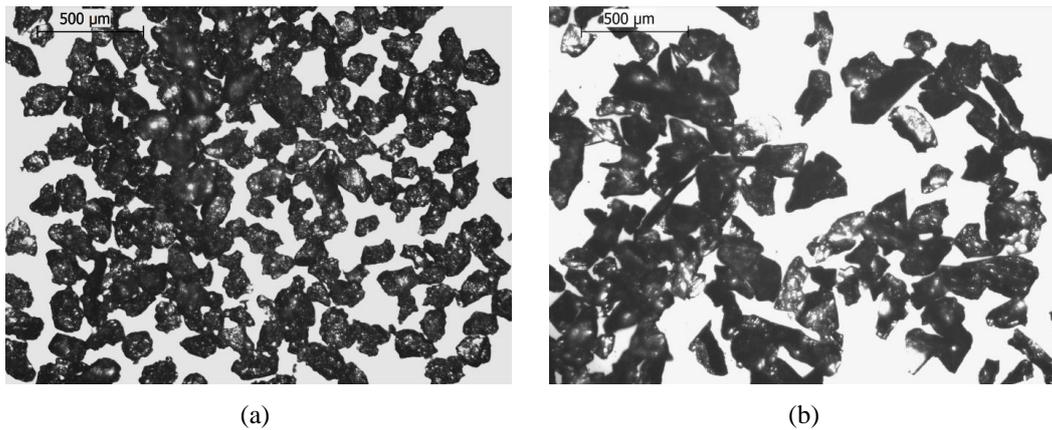


Figure 1. Powders of: (a) titanium; (b) niobium.

3.2 Characterization of green compacted

After the characterization of the titanium and niobium elementary powders, was weighed according to the chemical composition of the alloy and then the mixing in a rotate drum for 48 hours, to guarantee the compositional homogeneity followed by compression in a die using a hydraulic press. The pressures used were equal to 400, 600, 800, 1000, 1500 and 2000 MPa.

Figure 2 shows micrographs of Ti-35 Nb alloy compacted at 400, 600 and 800 MPa, and these compacting pressures are considered low pressures. In a general way, samples compacted at low pressures, presented the presence of porosity and was also verified that the titanium powders showed deformation twins after compaction, in details in the Fig 2d. According to Humphreys and Hatherly (2004), the deformation of materials with hexagonal close-packed structure (hcp), as well as titanium, is due to this crystalline lattice have less symmetry and also less slip systems than the cubic structures. This mode of deformation is more significant in low tensions.

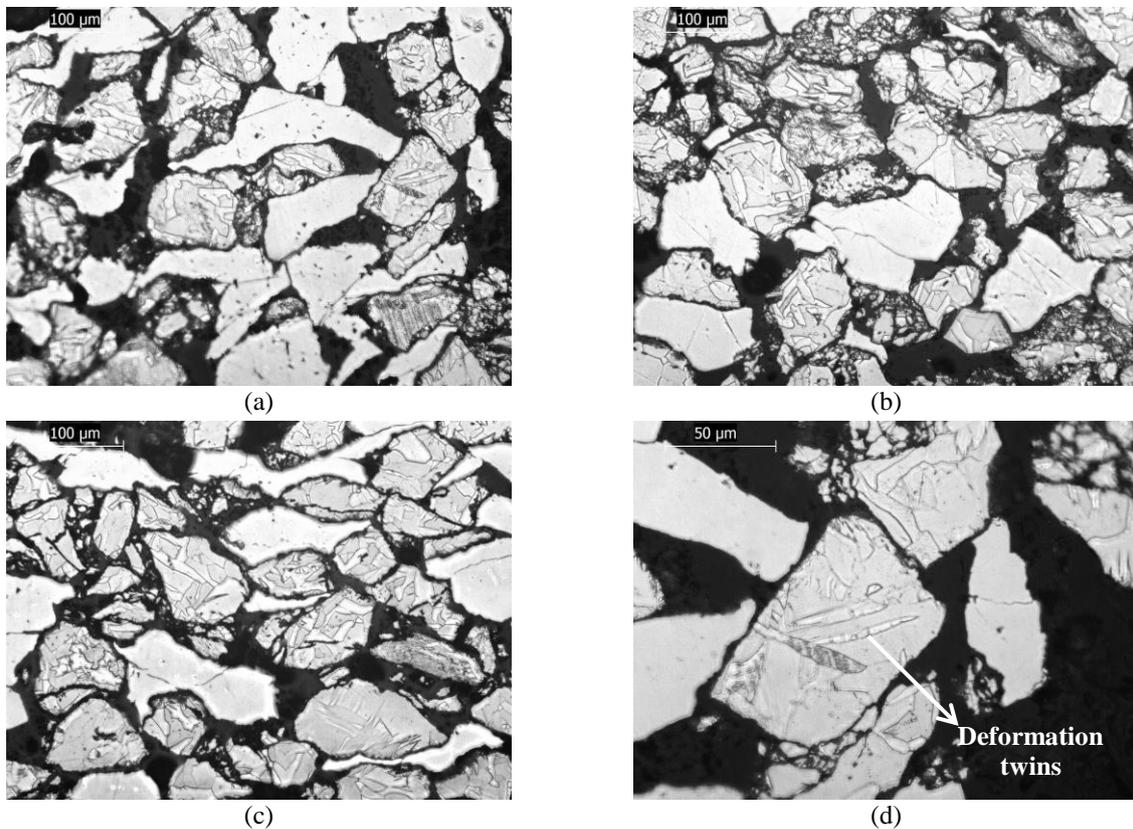


Figure 2. Micrograph of Ti-35Nb alloy compacted uniaxially at: (a) 400 MPa; (b) 600 MPa, (c) 800 MPa; (d) 400 MPa, the arrow indicates deformation twins presented by compacted titanium powders.

Niobium powders showed shape change, due to the imposed plastic deformation, being this behavior more evident in the compacted samples at 800 MPa. It was also verified that the titanium powders fractured during the compaction, which did not occur with the niobium, evidencing the greater ductility of the niobium.

The main results of the compressed samples at high pressures of 1000, 1500 and 2000 MPa, show a significant reduction in the size and quantity of pores identified in the microstructure of the compacts. Furthermore, titanium grains also presented deformation twins, and some fractured during compaction. In accordance with Padilha and Siciliano (2005), in the metals hcp, due to the restrictions for occurrence of deformation by sliding, the twinning becomes an alternative form of deformation.

Niobium grains in the Ti-35Nb alloy compacted at high pressures also showed a shape change, which is more evident than in the compacted samples at low pressures. This behavior of the niobium grains occurs due to the fact that it presents a body-centered cubic structure with a centered body (bcc), and, therefore, has more slip systems available for the occurrence of plastic deformation, being therefore more ductile than the titanium, preferably deforming by slipping (Humphreys and Hatherly, 2004).

Figure 3 shows micrographs of Ti-35Nb alloy compacted at 1000 and 1500 MPa. The observed samples continue to present porosity, as well as those compacted at low pressures, but there is a decrease in the area related to the pores, such pores being the dark regions of the micrographs.

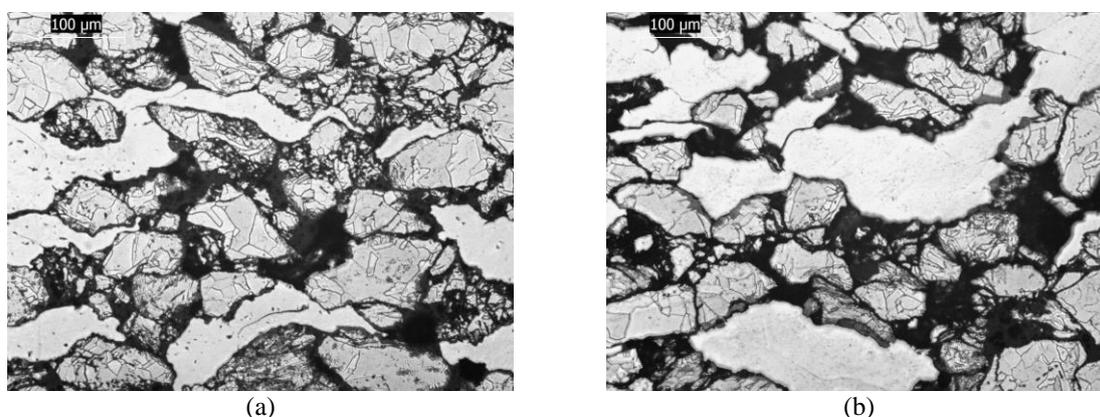


Figure 3. Micrograph of Ti-35Nb alloy compacted uniaxially at: (a) 1000 MPa; (b) 1500 MPa.

In compacted samples at pressures of 1500 and 2000 MPa, the niobium powders have a tendency to connect by cold sintering. This behavior may be related to the higher compaction pressure used and also to the intense plastic deformation suffered by the niobium. Titanium powders fractured more intensely in the compacted samples at 2000 MPa and there was a decrease in the quantity and size of the pores in the samples analyzed. Figure 4 presents details of an area of sample compacted at 2000 MPa, in which the niobium particles exhibited bonding points by cold sintering.

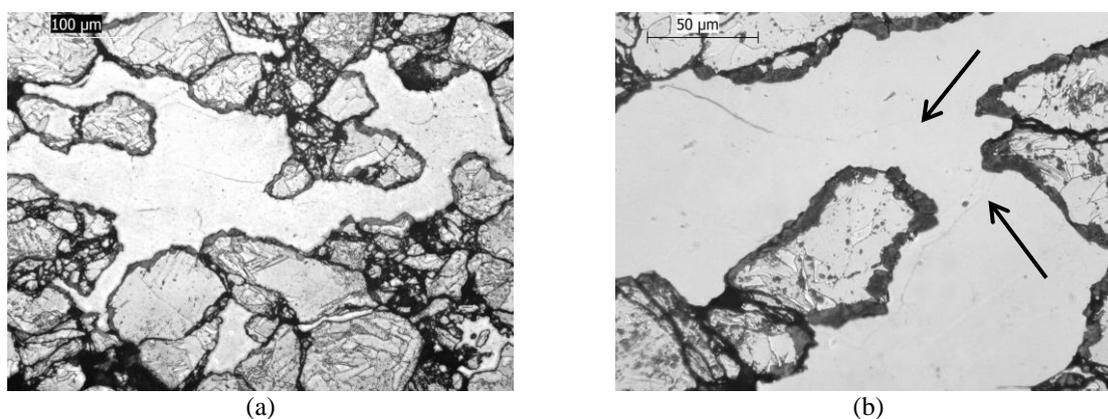


Figure 4. Micrograph of Ti-35Nb alloy compacted uniaxially at 2000 MPa: (a) general view; (b) detail of cold sintering points of niobium powders, indicated by arrow.

Vickers hardness measurements showed that as the compaction pressure was high, the measured Vickers hardness values also increased, this behavior was observed for the two elements involved, since measurements were made on each element. This can be explained by the greater mechanical energy supplied to the material during compaction, causing greater densification of the powders and consequently greater plastic deformation of the powders. It is also verified that the niobium presented less hardness than the titanium, which explains its shape change during the compaction, since it presents with less hardness, being thus more ductile, corroborating with the presented results.

Table 1 presents the results of Vickers hardness measurements of samples compacted uniaxially. The hardness values presented refer to 10 measurements performed on individual titanium powders and 10 measurements performed on individual niobium powders.

Table 1. Results of Vickers hardness measurements of Ti-35Nb alloy compacted uniaxially at 400, 600, 800, 1000, 1500 and 2000 MPa.

Compacting pressure (MPa)	Vickers hardness (Mean \pm Standard deviation)	
	Titanium	Niobium
400	170 \pm 19	102 \pm 14
600	188 \pm 18	113 \pm 6
800	200 \pm 13	121 \pm 8
1000	233 \pm 12	126 \pm 8
1500	235 \pm 13	133 \pm 5
2000	254 \pm 9	141 \pm 6

Several attempts were made to measure Young's modulus using an ultrasonic method. During the trials it was verified that there was no clear pattern of ultrasonic waves, which made the use of this method unfeasible. This fact can be related to the numerous pores presented by the compacted samples, since these are empty spaces and when the ultrasonic wave hits the same, it immediately returns to the equipment, which does not allow the obtaining of a clear wave pattern to obtain the Young's modulus. Thus, this technique proved to be inadequate for the determination of this mechanical property in the compacted samples. The next step of this work is to perform sintering on compressed samples, and it is expected that with the higher densification of the material it will be possible to obtain clearer wave patterns and, consequently, obtain the Young's modulus of the material.

4. CONCLUSIONS

According to the results obtained can be concluded that in the samples compacted at low pressures, the presence of porosity is higher, decreasing as the compression pressure increases. It was also verified that high pressures favor the occurrence of mechanical twinning in the particles of the titanium powders and also their fracture, as well as changes in shape of the niobium particles, due to the plastic deformation of the powders occurred during the compacting. It was also verified that niobium powders have a tendency to connect by cold sintering at pressures from 1500 MPa, these points being created during the cold compaction process, which was not observed in the compacted samples at the other pressures studied. Furthermore, high pressure was main responsible for the increase of the densification in the Ti-35Nb alloy samples. Vickers hardness measurements showed that as the compaction pressure was high, the measured Vickers hardness values also increased, this behavior was observed for the two elements involved, since measurements were made on each element. Ultrasonic method was not adequate to obtain the Young's modulus in the compacted samples.

5. ACKNOWLEDGEMENTS

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6. REFERENCES

- Chiaverini, V., 1986. *Tecnologia Mecânica – Processos de fabricação e tratamento - Vol II*. McGraw-Hill, São Paulo, 2nd edition.
- Chiaverini, V., 2001. *Metalurgia do pó: Técnicas e produtos*. Associação Brasileira de Metalurgia e Materiais, São Paulo.
- Eisenbarth, E., Velten, D., Müller, M., Thull, R., and Breme J., 2004. "Biocompatibility of β -stabilizing elements of titanium alloys". *Biomaterials*, Vol. 25, pp. 5705-5713.
- Humphreys, F. J. and Hatherly, M., 2004. *Recrystallization and related annealing phenomena*. Elsevier, 2nd edition.

- Lampman, S., 1998. Wrought Titanium and Titanium Alloys. ASM Metals Handbook, Vol 2 – Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, 9th Edition.
- Lambert, J. B., 1998. *Refractory Metals and Alloys*. ASM Metals Handbook, Vol 2 – Properties and Selection: Nonferrous Alloys and Special-Purpose Materials, 9th Edition.
- Leyens, C. and Peters, M., 2003. *Titanium and Titanium Alloys*. Wiley-VCH.
- Niinomi, M., 1998. “Mechanical properties of biomedical titanium alloys”. *Materials Science and Engineering A*, Vol. 243, pp. 231-236.
- Padilha, A. F. and Siciliano Jr, F., 2005. *Encruamento, recristalização, crescimento de grão e textura*. Associação Brasileira de Metalurgia e Materiais (ABM), São Paulo, 2nd edition
- Polmear, I. J., 1995. *Light Alloys - Metallurgy of the Light Metals*. Arnold Ed., 3rd edition.
- Santos, D. R., 2006. *Obtenção da liga Ti-35Nb por metalurgia do pó para utilização em próteses ortopédicas*. Ph.D. thesis, Faculdade de Engenharia de Guaratinguetá, Universidade Estadual Paulista, Guaratinguetá, Brasil.
- Silva, H. M., Schneider, S. G. and Moura Neto, C., 2004. “Study of nontoxic aluminum and vanadium-free titanium alloys for biomedical applications”. *Materials Science and Engineering C*, Vol. 24, pp. 679-682.
- Tane, M., Akita, S., Nakano, T, Hagihara, K., Umakoshi, Y., Niinomi and Nakajima, M. H., 2008. “Peculiar elastic behavior of Ti-Nb-Ta-Zr single crystals”. *Acta Materialia*, Vol. 56, pp. 2856-2863.
- Tarr, R. R., Clarke, I. C., Gruen, T. A. and Sarmiento, A., 1983. *Comparison of loading behavior of femoral stems of Ti-6Al-4V and cobalt-chromium alloys: A Three-Dimensional Finite Element Analysis, Titanium Alloys in Surgical Implants*. American Society of Testing Materials.
- White, D. G., 1998. *History of Powder Metallurgy*. ASM Metals Handbook, Vol. 7 - Powder Metal Technologies and Application, 9th edicion.

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