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CHARACTERIZATION OF Ti-35Nb ALLOY OBTAINED BY POWDER METALLURGY USING HIGH PRESSURES

Thailler Machado Nunes da Silva
Hayka Cristina Vieira
Sérgio Renato da Silva Soares
Alexandra de Oliveira França Hayama
Universidade Federal de Rondonópolis, Engenharia Mecânica, Avenida dos Estudantes, 5055, Cidade Universitária, Rondonópolis – MT, 78736-900.

Abstract. *The present work presents the results of the microstructural characterization of the Ti-35Nb alloy obtained by powder metallurgy, using uniaxial pressing and high pressures. Beta-type titanium alloys, as alloy studied in this work, are formed by biocompatible elements and can be used as materials for manufacturing of orthopedic implants. These alloys can be obtained by melting processes or by powder metallurgy, this being a viable alternative, because is possible to manufacture parts with complex geometries, with dimensions close to the final and good surface finishing. In this context, the objective of this work is to evaluate the microstructural and mechanical behavior of the beta-type titanium alloy, Ti-35Nb (% by weight), obtained by powder metallurgy using uniaxial pressing and high pressures (1000, 1500 and 2000 MPa, followed by sintering in inert atmosphere. The main results show that high pressures favor the occurrence of mechanical twinning in the particles of titanium powders and also their fracture, as well as changes in the shape of the niobium particles, due to the plastic deformation that occurred during compaction. After sintering, the occurrence of recrystallization of the titanium particles was verified, with a tendency of union between the particles that fractured during the compaction.*

Keywords: *Powder Metallurgy, Titanium alloys, High pressures, Sintering.*

1. INTRODUCTION

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

Among the materials used in the manufacture of orthopedic implants are stainless steels and alloys based on chromium, cobalt and molybdenum. The choice between one or the other type of material is based on technical aspects and also on economic factors. Regarding the properties presented by these materials, they exhibit a Young's modulus sometimes higher than that of human bone 20-40 GPa (Tane et al., 2008). While stainless steels have a modulus of elasticity close to 200 GPa and Cr-Co-Mo alloys, values greater than 250 GPa. Regarding β-type titanium alloys, the Young's modulus can vary from 55 to 85 GPa (Niinomi , 1998).

In the case of the existence of a metallic rod implanted in the femur and with different elastic characteristics, there is restriction regarding the transference of mechanical efforts to the bone, which can generate bone degradation and, consequently, osteoporosis (Tarr et al. 1983). In extreme situations, bone degradation associated with osteoporosis can lead to fracture of the femur.

Type β titanium alloys are composed of non-toxic and biocompatible elements, such as niobium, and have suitable properties to be used as permanent implants in the human body, such as corrosion resistance and biocompatibility. They can be obtained by melting processes in an inert atmosphere or by powder metallurgy processes from elementary powders, which is a viable alternative, because it is possible to manufacture parts with complex geometries and dimensions close to the final ones, still presenting good surface finish. In addition, the sintering temperatures used are low compared to other metallurgical processes, and can be carried out in simple design furnaces, with lower energy consumption (Chiaverini, 1986).

Powder metallurgy is one of the processes that has grown the most in recent decades, and this is due to the fact that it is an economical, fast process that can be applied to the production of large-scale parts. This process does not require the fusion of the material, only the use of pressure (compaction) and heat (sintering) (Chiaverini, 1986).

The powder metallurgy process can be divided into four main parts: obtaining the powders and their classification, mixing, compacting and sintering. Powders can be obtained in several ways, including: atomization, electrolysis and milling. The classification of powders can be done by sieving, using vibrating sieves and the mixture of powders is done

in proportions determined according to the desired chemical composition. The compaction process is carried out using presses and dies, and the compaction pressures vary with the different materials to be used, with the characteristics of the metallic powders and with the amount of lubricant added to the powder mixture (White, 1998). Sintering occurs at temperatures below the melting point of the base metal of the alloy (Chiaverini, 1986).

Within the presented, the aim of this work is to evaluate the microstructural and mechanical behavior of the Ti-35Nb alloy (% by weight), obtained via powder metallurgy using uniaxial pressing and high pressures (1000, 1500 and 2000 MPa), followed by sintering at 800°C for 60 min.

2. EXPERIMENTAL

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

After mixing, the uniaxial pressing of the powders was carried out at high pressures, considering the pressures of 1000, 1500 and 2000 MPa, using a hydraulic press for this, giving rise to the green compact, that in the sequence were sealed in quartz tubes under vacuum. Sintering was carried out at temperatures of 800°C for 60 min, followed by air cooling.

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 H_2O, 10 ml HNO_3 and 5 ml HF, in varying times of 3 to 10 seconds. The characterization was performed using optical light microscopy and Vickers hardness (microhardness). Ten microhardness measurements were performed, using a load equal to 0.98 N for 20 seconds.

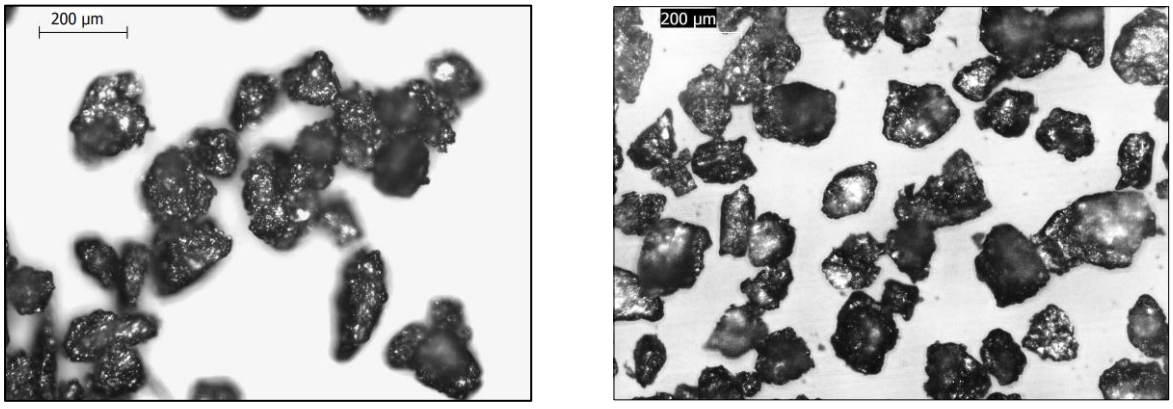
3. RESULTS AND DISCUSSION

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 1000, 1500 and 2000 MPa followed by sintering at 800°C for 60 min 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 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 ± 43 µm and the niobium powders have a size corresponding to 207 ± 65 µm. The obtained data are in agreement with the range of sizes expected for the powders, 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 (Figure 1a) and the niobium powders have a larger aspect ratio (length greater than the width), as shown in Figure 1b.



(a) (b)

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

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/cm3 and the niobium is equal to 4.14 g/cm3. Comparing with the theoretical density of these materials, dTi = 4.5g/cm3 (Lampman, 1998) and dNb = 8.57 g/cm3 (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.

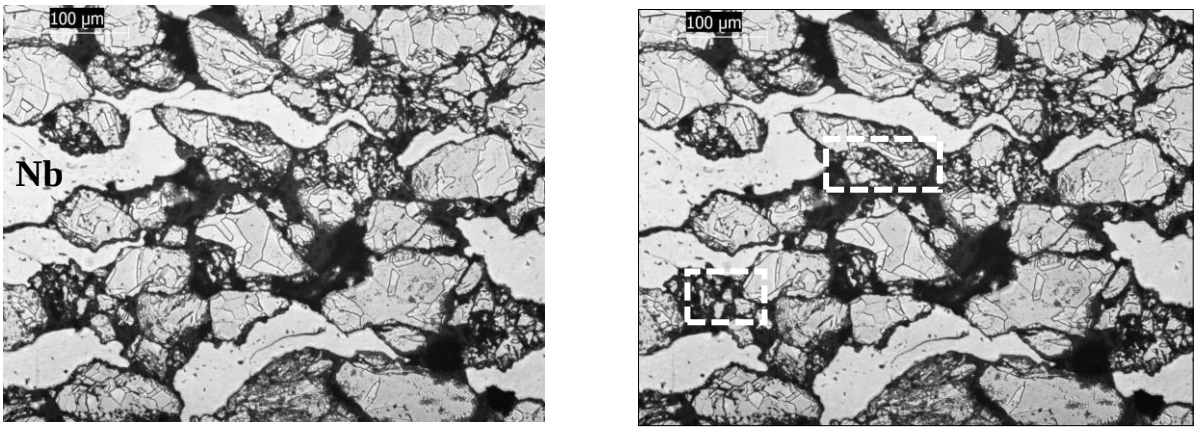
3.2 Characterization of green compacted

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 1000, 1500 and 2000 MPa.

Figure 2a shows micrograph of Ti-35Nb alloy compacted at 1000 MPa. It is verified the presence of porosity (dark regions) and also individual grains of niobium and titanium. It was found that the titanium grains showed deformation twins and also some of them suffered fracture during compaction. The niobium grains changed shape due to plastic deformation caused by the higher compaction pressure, this characteristic is shown in Figure 2b. Comparing the results of titanium and niobium microstructures presented (Figures 2a and 2b) observed that the first material is more fragile. The fracture of titanium grains and consequently the reduction of their starting size combined with the deformation of the niobium grains is a strong indication that the pressure can dynamically contribute to the increase in the compaction of these materials.

Regarding the deformation twins presented by titanium powders, it is known that the deformation of materials with a compact hexagonal structure (HC), as well as titanium, is due to the fact that this crystalline lattice presents less symmetry and also a smaller number of slip systems than cubic structures (Humphreys and Hatherly, 2004), therefore, in HC metals, due to restrictions on the occurrence of deformation due to slip, mechanical twinning becomes an alternative form of deformation (Padilha and Siciliano Jr, 2005).

Niobium showed a more evident change due to the fact that it has a body-centered cubic crystal structure (CCC), and thus, it has more slip systems available for the occurrence of plastic deformation, and is therefore more ductile than titanium, deforming preferentially by slip (Humphreys and Hatherly, 2004).



(a) (b)

Figure 2. Micrograph of Ti-35Nb alloy uniaxially compacted at 1000 MPa showing: (a) compacted titanium and niobium powders; (b) highlighted some fractured titanium powder particles

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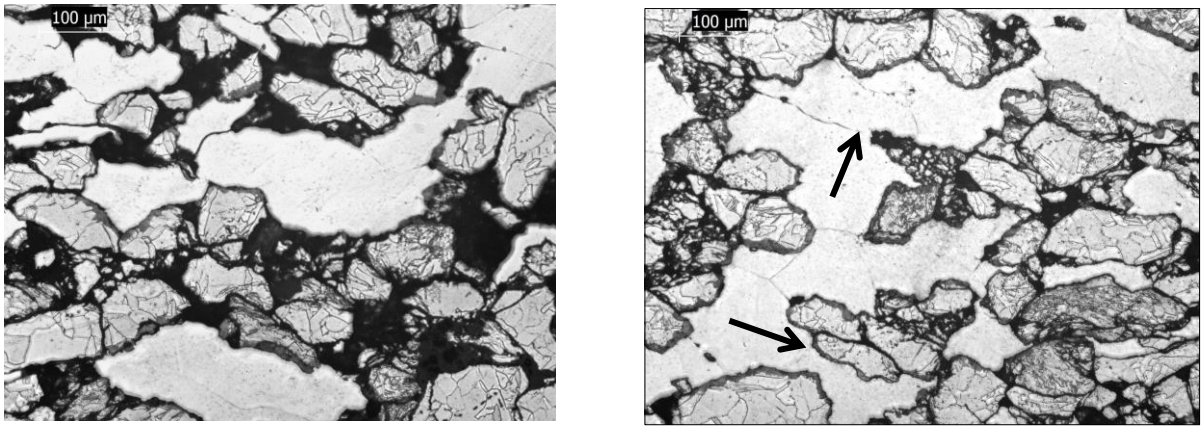
In compacted samples at pressures of 1500 and 2000 MPa, the niobium powders have a tendency to connect by cold sintering. This behavior may be related to the higher compaction pressure used and also to the intense plastic deformation suffered by the niobium. Titanium powders fractured more intensely 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 3a presents micrograph of compacted sample at 1500 MPa. The observed samples continue to present porosity, as well as those compacted at 1000 MPa, but there is a decrease in the area related to the pores, such pores being the dark regions of the micrographs. Figure 3b presents micrograph of compacted sample at 2000 MPa, showing details of an area in which, the niobium particles exhibited bonding points by cold sintering. Additionally, observed that the evolution of the compacted microstructure is consistent with the gradual increase in the compaction pressure. Additionally, was observed that the evolution of the compacted microstructure is consistent with the gradual increase in the compaction pressure. Samples compacted at 2000 MPa are in the final sintering stage and this characterizes a cold sintering of the compacted microstructure. The main driving force for sintering compacts was not temperature but, unlike conventional sintering processes, high pressure (Gutmanas and Rabinkin, 1979).



(a) (b)

Figure 3. Micrograph of deformed samples compacted at: (a) 1500 MPa; (b) 2000 MPa, showing cold sintering points of niobium powders, indicated by arrow.

Vickers hardness measurements showed that hardness values increase according to compaction pressure, this behavior was observed for the two elements involved, since measurements were made on each element. The compacts produced under 2000 MPa are those that presented the highest microhardness values. This indicates that the increase in the average value of this mechanical property depends simultaneously on the degree of cold densification and hardening present in the compacted microstructure of these materials. The latter is probably the main responsible for the increase in microhardness in the grain of each of these materials. 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 1000, 1500 and 2000 MPa.

Compaction pressure (MPa)	**Vickers hardness (Mean ± Standard deviation)**	
	Titanium	**Niobium**
1000	233 ± 12	126 ± 8
1500	235 ± 13	133 ± 5
2000	254 ± 9	141 ± 6

3.3 Characterization of sintered samples

The surface of the sintered samples presented no oxidation. In general, according to the microstructure analysis of the samples sintered at 800°C for 60 min, there is the occurrence of recrystallization of the titanium particles, as there is a microstructural change when compared to the microstructure presented by the compacted (deformed) sample, and the particles meet with equiaxed grains (about equal dimensions in all directions), which are typical of recrystallized materials.

It is known that during the recovery process there is no modification of the deformed structure, with only a decrease and distribution of the density of defects in the structure, while in recrystallization, there is the nucleation of new grains with a different shape from the deformed material, which are equiaxed (Padilha and Siciliano, 2005).

The recrystallization process occurs by nucleation of recrystallized grains and growth of these nuclei, being a diffusional process. The appearance of recrystallization nuclei occurs in places with higher accumulated deformation energy, such as in the contours of deformed grains (Humphreys and Hatherly, 2004).

Regarding niobium grains, in compacted samples it is possible to visualize the contour regions between them, which is not possible in sintered samples, as the contour was eliminated due to the occurrence of atomic diffusion, linking the particles in such a way as to make them a single larger size than those found in the green compact.

Regarding the titanium particles that fractured during compaction, as seen in the micrographs of the green compacts, there was also a tendency to unite them due to atomic diffusion.

The microstructure of the Ti-35Nb alloy sample that was compacted at 1000 MPa and sintered at 800°C for 60 min is shown in Figure 4. According to the analysis using light optical microscopy, it appears that there was atomic diffusion between the niobium and titanium grains separately, but there was no union of the titanium grains with those of niobium, and therefore there was no diffusion layer between the two metals. It is also verified that recrystallization of titanium particles occurred, since the grains in its interior no longer present deformation twins, as what happened in the compacted samples, but present equiaxed grains, typical of the recrystallization process, as already mentioned.

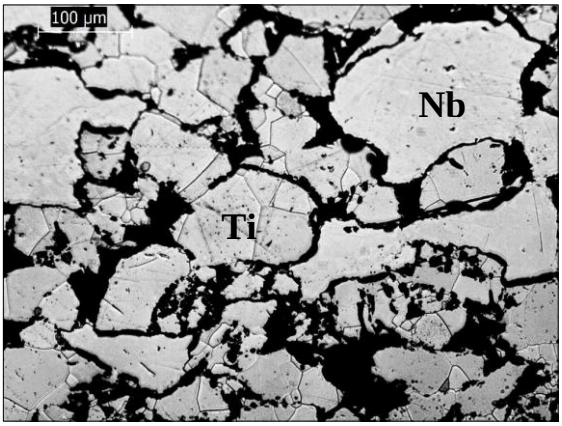
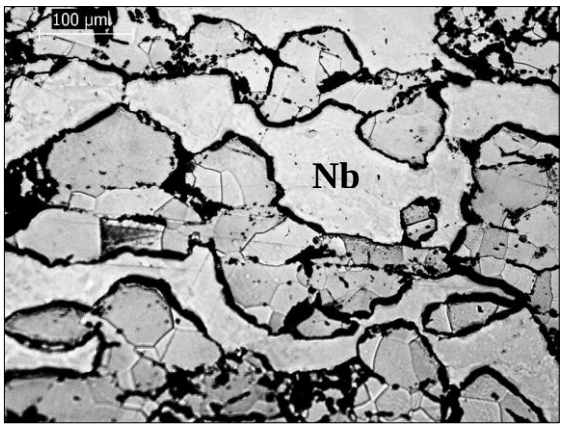


Figure 4. Microstructure of Ti-35Nb alloy compacted at 1000 MPa and sinterized at 800°C/60 min.

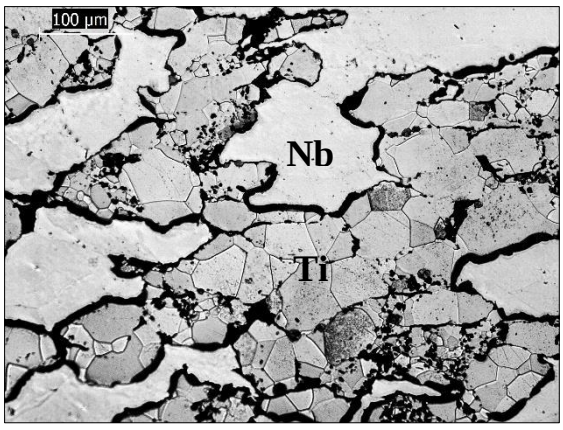
The microstructure of the sample compacted with a pressure of 1500 MPa and sintered at 800°C for 60 min is shown in Figure 5a. It appears that the union of niobium particles through atomic diffusion was more effective and niobium particles that came together to form a single, larger particle. Comparing the results presented in the Figures 2 and 5a was observed on the one hand, that the temperature was insufficient to increase the densification of the produced compact at 1000 MPa, but sufficient to reduce its hardening degree.

The micrograph of sample that was compacted at 2000 MPa and sintered at 800°C/60 min is showed in the Figure 5b. Can be verified that the atomic diffusion process was facilitated, which provided greater bonding between both niobium and titanium grains. The diffusion effect was more marked on the titanium grains. As previously observed, there was no diffusion between the titanium and niobium grains together. Titanium grains are recrystallized.

In the compacted condition, welding points were found, which occurred due to friction and slip of one particle in relation to others during compaction, this fact contributed to the union of niobium grains in the sintered sample was more effective. Note that inside the niobium grains formed there are no contours, which confirms the occurrence of the union of several grains to form a single one. Regarding titanium, there was a recrystallization of the grains and also the union by atomic diffusion of some grains, this union being less marked than that of niobium grains. Comparing the results previously presented in the sintering microstructure with the one shown in Figure 5b, it was observed that the temperature was sufficient both to increase densification and to reduce the degree of hardening present in the microstructure previously compacted at 2000 MPa.



(a)



(b)

Figure 4. Microstructure of Ti-35Nb alloy compacted at: (a) 1500 MPa and sinterized at 800°C/60 min; (b) 2000 MPa and sinterized at 800°C/60 min.

The results of the Vickers hardness measurements (microhardness) presented refer to the average of 10 measurements performed. In general, it is verified that the samples sintered at 800°C showed that there was a decrease in hardness in relation to the green compact, and this behavior was observed for all pressures studied and also for both titanium and niobium, as stated. in Table 2.

This decrease in titanium hardness values observed in samples sintered was due to the recrystallization of the material, which can be confirmed by the microstructure, because during the recrystallization process a large number of dislocations are annihilated and the consequent softening of the material, with the formation of new grains with low density of dislocations and with equiaxed shape (Humphreys and Hatherly, 2004).

With regard to niobium particles, it is not possible to specify which phenomenon is occurring, whether recovery or recrystallization, since it was not possible to visualize the microstructure of the niobium particles with the chemical attack used, as emphasis was placed on titanium and also if it had if the formation of a diffusion layer between titanium and niobium occurred, such chemical attack would be efficient in revealing the resulting microstructure. Comparing the results in Table 1 with those presented in Table 2 was noted that the mean microhardness values shown in Table 2 were significantly reduced. This is mainly due to the elimination of the degree of hardening present in the compacted microstructure and total dependence on a highly densified microstructure, typical of the final sintering step.

Table 2. Results of Vickers hardness measurements of the Ti-35Nb alloy samples uniaxially compacted at 1000, 1500 and 2000 MPa and sintered at 800/60min.

Condition	**Titanium**			**Niobium**		
	Vickers hardness (Mean ± Standard deviation)			**Vickers hardness (Mean ± Standard deviation)**		
	1000 MPa	**1500 MPa**	**2000 MPa**	**1000 MPa**	**1500 MPa**	**2000 MPa**
800°C/60min	176 ± 20	187 ± 17	186 ± 10	78 ± 8	87 ± 6	87 ± 5

4. CONCLUSIONS

According to the results obtained can be concluded that the high compaction pressure 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.

In a dynamic way, the high pressure contributed, via simultaneous or non-simultaneous action, to the deformation, welding, hardening and fracture of the ductile materials used in this study and made it possible to obtain a highly densified sample. The sample compacted at 2000 MPa and sintered at 800ºC was the one that presented a microstructure in the final stage of sintering.

Encapsulation in quartz tubes under vacuum proved to be efficient during the heat treatment, as there was no surface oxidation of the samples during sintering. In general, according to the microstructure analysis of the samples sintered, there is the occurrence of recrystallization of titanium particles and niobium particles, the contour between the particles was eliminated due to the occurrence of atomic diffusion, binding the particles together in such a way as to make them a single particle of larger size than those seen in the green compact. Still referring to the titanium particles that fractured during compaction, there was a tendency to unite them also due to atomic diffusion.

The results of the Vickers hardness measurements (microhardness) showed that in samples sintered there was a decrease in hardness in relation to the green compact, and this behavior was observed for all pressures studied and also for both titanium and niobium, this fact is related to the occurrence of recrystallization.

In the samples highly densified and cold sintered (without temperature) the predominant hardening mechanism to obtain a high average hardness value was the degree of deformation (hardening level).

5. ACKNOWLEDGEMENTS

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