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MICROSTRUCTURAL AND MECHANICAL CHARACTERIZATION OF THE Ti-25Ta-25Nb ALLOY FOR BIOMEDICAL APPLICATIONS

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Abstract: Metallic biomaterials are usually used for replacing the function of hard tissues and also can be used in the manufacturing of biomedical prostheses and implants. Among of the metallic biomaterials stand out the titanium and titanium alloys due great characteristics like biocompatibility. The Ti-25Ta-25Nb alloy is considered a titanium-β alloy of great interest for biomedical application due presents great characteristics like low modulus of elasticity. This present study evaluated the mechanical, microstructural and electrochemical properties of the Ti-25Ta-25Nb alloy after processing using severe plastic deformation (rotary swaging). The alloy was obtained in an arc voltaic melting furnace with an inert atmosphere of argon gas from sheets of pure metals (titanium, niobium, and tantalum). The ingots were heat treated and worked by cold rotary swage (severe plastic deformation). Optical microscopy was used to evaluate the microstructure of the alloy at each processing stage. Traction tests and microhardness were used to evaluate the mechanical behavior of the alloy. Electrochemical analysis (open circuit polarization and potentiodynamic polarization) was used to evaluate corrosion resistance. The ternary alloy showed presence of β phase at each processing stage and 55 GPa of Young's modulus. Also was observed a great corrosion resistance in comparison with comercial alloys. The results showed that the Ti-25Ta-25Nb alloy presented excellent results with this method of processing, therefore being feasible for biomedical applications that's involving plastic deformation to do components.

Keywords: Biomaterials, Titanium alloys, Biomedical applications.

1. INTRODUCTION

The use of biomaterials in biological systems has increased in recent years searching through studies the development of new materials that efficiently satisfy the employment for which it will be attributed to it. Biomaterials may be of natural or synthetic origin, and may be used indefinitely in the total or partial replacement of biological tissues, which time is relative to their composition, function and complexity. They must be defined as biocompatible so that they can be used in a biological environment such as the human body (Kulkarni et al., 2014). They present a set of properties and characteristics which include physical and mechanical compatibility with the biological tissue to be replaced or biomechanical or biological function to be performed, high biocompatibility and excellent corrosion resistance (Oliveira and Nanci, 2004).

The application of metals and metal alloys in the biomedical area requires a set of different properties, such as biocompatibility and mechanical properties, combination of resistance to wear and low modulus of elasticity, and resistance to corrosion in the body environment (Williams, 2009). In this way, titanium and its alloys have been used as materials for surgical implants due to their resistance to the effects of body fluids, excellent tensile strength, flexibility and high resistance to corrosion (Al-Zain et al., 2010).

Due to its low density, mechanical strength and biocompatibility titanium is one of the few materials that meets the requirements necessary to be used as a biomaterial (Anderson et al., 2013). However, the formation of the passive film on the surface of titanium alloys is not stable and can be destroyed locally in some specific environments, which allows the process of corrosion and consequent release of the result of the reaction in the inserted medium, causing possible harmful effects to the body (Sui et al., 2007).

An interesting property of titanium is allotropy, which can be defined as the ability of the material to exhibit two or more different crystal structures. At room temperature the titanium has a compact hexagonal crystal structure, called the alpha phase, which is stable up to 883°C. Above this temperature the structure becomes cubic with a centered body, which is called the beta phase. In general, titanium alloys can be classified as alpha (α), alpha plus beta (α + β) and beta (β) (Leyens, 2003).

Over the last decade, a great increase of researches has been observed aiming the development of materials that have optimized properties, such as low modulus of elasticity, high mechanical resistance, besides having composition free of toxic and non-allergenic elements (Rack and Qazi, 2006). The elastic modulus is considered a key property and therefore the development of β-type titanium alloys can be a great alternative in the area biomedical, because the closer to the bone module (17-28 GPa) the better the compatibility of the material in substitution for a function (Yang and Zhang, 2005). The modulus of elasticity should be closer to the bone due to the effect called stress shielding. This effect is characterized by the heterogeneity in the transfer of load between the implant and the bone, which is caused by the difference between its elastic modulus, resulting in an insufficient load that the bone can withstand, which can lead to bone resorption, failure of the implant , and even the appearance of a new fracture (Niinomi and Nakai, 2011).

One of the first titanium alloys were composed of nickel and titanium (NiTi), bringing as differentiated properties the shape memory and superelasticity, fact and reason to be applied until today, in the manufacture of orthodontic appliances, stents and clips (Gerke et al., 2009). However, the use of NiTi alloys reported cases of allergy due to nickel hypersensitivity (contact dermatitis). Due to this nickel cytotoxicity problem, new titanium-based alloys have been developed to increase the degree of safety of the materials used in the various biomedical areas (Arciniegas et al., 2013).

Other one titanium alloy was the Ti-6Al-4V alloy, initially used in military and aerospace applications, started to be used in the biomedical area due mainly to its excellent mechanical resistance and considerable resistance to corrosion. As for the NiTi alloy, the Ti-6Al-4V alloy presented problems of cytotoxicity caused by the release of aluminum ions through the result of passive layer breakdown and reaction of the body fluid with the alloy substrate that can cause damage in cells of the nervous system. Another problem linked to cytotoxicity is the presence of vanadium, which is both toxic in the elemental state and in the oxide form (Walker et al., 1998).

Because the Ti-6Al-4V alloy has more disadvantages than advantages, new titanium alloys without vanadium and aluminum have been studied in recent years for biomedical applications.

Takahashi et al (2002) evaluated the effect of thermal treatment on the microstructure and the addition of tin in Ti-16Nb-4Sn alloys. Which led to the conclusion that the heat treatment has a strong influence on the phase transformation of the alloy and that the transformation temperature martensitic reaction decreased with the increase in tin content, noting that for each addition of 1% tin the martensitic transformation temperature decreased by about 120°C.

The corrosion behavior of Ti-16Nb-5Sn and Ti-18Nb-4Sn alloys was evaluated by Rosalbino et al (2012), which showed very satisfactory results, showing that these alloys formed a passivation layer spontaneously, as well as NiTi alloys. However, the passivation layer formed by the ternary alloys proved to be stronger than the NiTi alloy.

A new alloy containing Ta and Nb was proposed by Bertrand et al. (2010; 2013). The use of these elements is due to the high biocompatibility and capacity to promote the reduction of the modulus of elasticity. In the proposal of Bertrand et. (2010; 2013), of a ternary alloy composed of Ti-25Ta-25Nb using cold rolling process, were able to verify that in the alloy occurs the stabilization of the β phase after thermal treatment of solubilization, due to the presence of tantalum and niobium elements. Besides that, they verified a phenomenon of double flow in the elastic region during the performance of a tensile test, due to the variation in the modulus of elasticity characterized by the transformation of the β phase into α''. Such phenomenon is undesirable for the manufacture of orthopedic prosthesis because it allows for fractures (Li et al., 2008). However, due it exhibits superelastic behavior due to martensitic transformation, it may be an interesting alloy for orthodontic applications.

The purpose of this work was to develop, produce, process and characterize a titanium alloy containing Ti and Nb (Ti-25Ta-25Nb alloy) by using a new processing route: melting in arc furnace, cold working by rotate swaging and heat treatment, for biomedical applications.

2.   MATERIALS AND METHODS

The alloy was obtained from commercially pure titanium plates (Ti CP, grade 2), tantalum (99.9%) and niobium (99.98%) which were previously cleaned by a chemical pickling process, with the aim of removing all surface impurities. Then the metal was weighed according the alloy composition (Ti-25Ta-25Nb wt%) in an analytical balance.

Then the metals were weighted according to the composition of the alloy on an analytical balance. After that, the metals were subjected to melting process in an electric arc (generated by potential difference between a tungsten electrode and the copper crucible) furnace with an inert atmosphere of argon gas and copper crucible, being the melting furnace and the crucible cooled with water.

The ingots were subjected to a homogenization heat treatment at 950°C in a tubular furnace with vacuum atmosphere (with argon gas cleaning process) with a heating rate of 10°C/min, temperature maintenance for a period of 24 hours, followed by cooling in furnace. After the heat treatment, the ingots were subjected to a cold rotary forging to

a final diameter of 10 mm. Subsequently to the swaging, was made a solubilization heat treatment at 850°C in a tubular furnace with vacuum atmosphere with a heating rate of 10°C/min, maintaining temperature for 2 hours, followed by rapid cooling in water.with the same conditions before forging.

2.1. Microstructure Characterization

For microstructural characterization was used four conditions or stages of processing: as cast (after melting process), homogenized (after homogenization heat treatment), forged (after rotate swaging process) and solubilized (after final solubilization heat treatment).

The samples were transversally sectioned in an automatic machine with diamond disk, being for the optical microscopy the samples were embedded in resin and for X-ray diffraction not embedded. They were grinded with silicon carbide sandspaper (from #80 to #2000), polished with colloidal silica and oxalic acid solution 3% and cleaned in ultrasonic bath with acetone. The microstructure was obtained with Kroll's reagent and evaluated by Epiphot, Nikkon. And the phases formed were evaluated by using a PANalytical-Empyrean diffractometer operated at an accelerating voltage of 40 kV, a current of 30 mA, scanning speed of 0.2°/s with Cu Kα radiation and scan angle from 30 to 120°.

2.2. Mechanical characterization

The mechanical characterization was made for microhardness on samples after the optical characterization and for tensile test after machining of specimen after solubilization heat treatment.

The microhardness test was performed in samples by using a microhardness tester HMV 2t. Vickers square based diamond pyramid with an angle of 136° between planes was used, load of 50 grams (490.5 μN) for 15 seconds. The results of microhardness were supplied by the device after measurements in a diagonal of the dents produced for each specimen. Vickers microhardness of each sample was determined as the arithmetic mean of the readings.

The specimens for tensile test were made using the ASTM E 8M Standard. The specimens were subjected to a uniaxial tensile loading along their axes. The tests were performed using a speed of 0.5 mm / min in a mechanical test machine, MTS, 632.24C-50.

2.3. Electrochemical characterization

To analyze the corrosion resistance of the alloy was taken from a sample of the condition after solubilization heat treatment used in the XRD analysis. The sample was sanded, bind to a copper rod and embedded in epoxy resin.

The electrochemical characterization of the alloy was based on an electrochemical cell consisting of three electrodes: the alloy (working electrode), saturated calomel (Pt, Hg / Hg_2Cl_2 / KCl_{sat}) (reference electrode) and high purity graphite (contra-electrode) . The working electrode, with exposed area of 1 cm^2, was sanded in a rotary polishing machine with SiC emery paper (# 100 to # 600). All the electrochemical tests were performed after immersion in a thermostated bath with a temperature of 38°C composed of NaCl and NaF with concentrations of 0.15 and 0.03 mol. L$^-$^{1}. The equipment used was the Potenciostat / Galvanostat EG & G INSTRUMENTS Princeton Applied Research (PAR) Model 283 aided by the software 352 SoftCorr III.

3. RESULTS AND DICUSSIONS

3.1. Microstructural characterization

Figure 1 shows the diffractogram for the alloy processing route. Figure 1a shows a dendritic microstructure, typical of monophasic alloys subjected to rapid cooling, due to the rapid cooling of the copper crucible surrounding the metals during the melting process. Figure 1b also shows the presence of the dendritic microstructure, but it is noted that there is contrast difference, which characterizes the phase transformation. Figure 1c shows the deformation of the grains due to cold forming process severity. And in Figure 1d, it is possible to observe the tension and deformation relief in the microstructure generated by the process of cold rotary deformation and also the reduction of grain size resulting in a fine microstructure.

X-ray diffraction analysis showed the predominance of the presence of the β phase for all the conditions evaluated according to the peaks shown in figure 2. It is also possible to observe that as cast condition was the only one that presented the presence of another phase which could also have been observed in Figure 1a, by the difference in contrast between the β phase (light gray) and the α phase (dark gray) . It is also observed that the heat treatment of homogenization was sufficient to convert the α phase to β. Besides, it is observed that different phase transformations do not occur during the other stages of alloy processing even after the different thermal treatments performed, proving the study carried out by Bertrand et al. (2010), where the stability of the β phase was observed in the Ti-25Ta-25Nb ternary alloy due the presence of the niobium and tantalum elements.
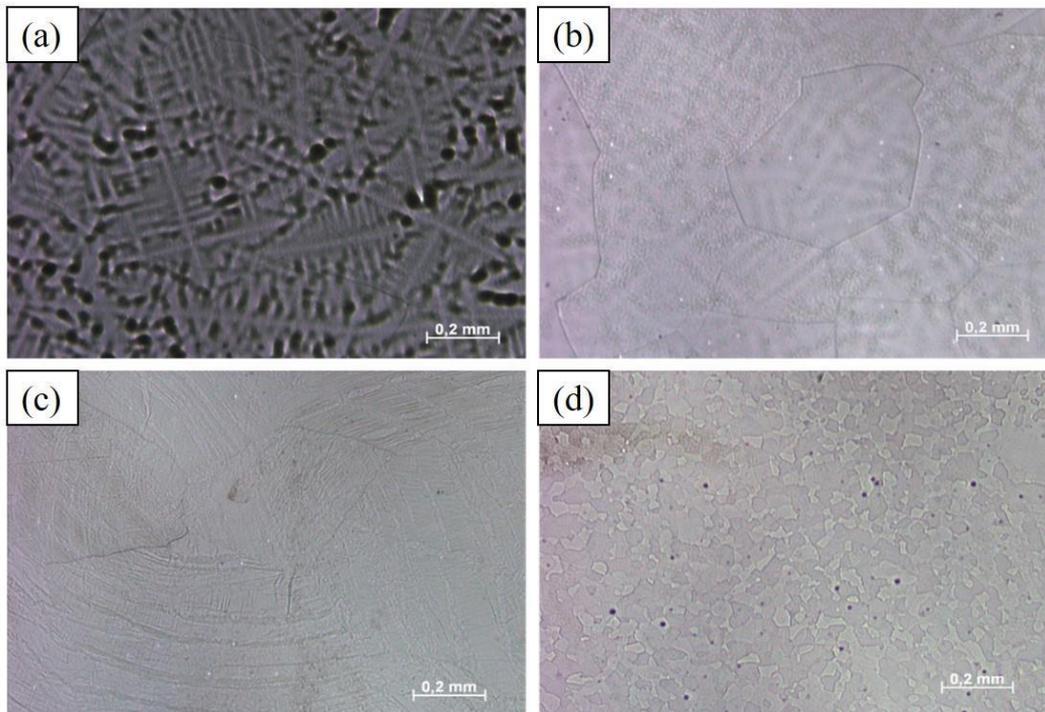
Figure 1. Micrograph of the Ti-25Ta-25Nb alloy: (a) as cast; (b) after homogenization (950°C for 24 hours); (c) rotary swaging; (d) solution heat treatment (850°C for 2 hours and quenching)
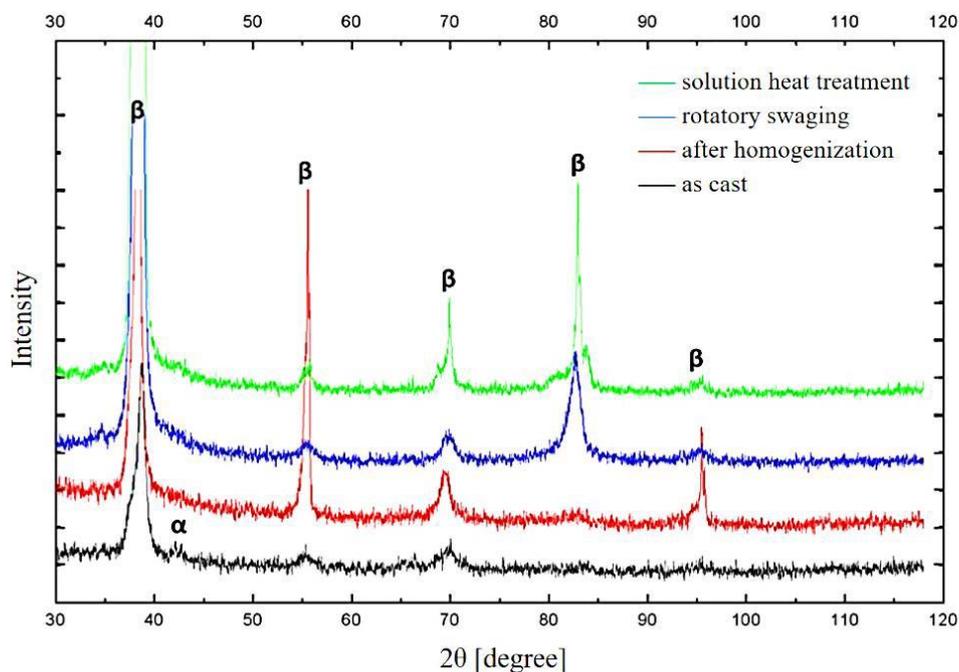

Figure 2. XRD spectra of the Ti-25Ta-25Nb alloy for each step of processing

The microhardness test results are shown in Table 1. The values obtained for the as cast conditions and after heat treatment of homogenization are very close, 256 and 255 HV, respectively. This is due to the fact that there has been a small recrystallization of the grains and conversion of the alpha phase to beta, this fact that can be observed in the micrograph of both conditions, figures 1a and 1b. After the rotative swaging process was observed a hardness increase for 273 HV, due to this process causing a severe deformation, resulting in the creation of a tensile zone in the microstructure. For the heat treatment of solubilization can be observed the reduction of hardness to 166 HV, due to the predominance of beta phase and absence of work hardening.

The values found in this study are lower than the NiTi alloy (280 HV) and Ti-6Al-4V alloy (341 HV) and higher than Ti-25Ta- 25Nb alloy (145HV) obtained by Bertrand et al (2010). The difference for the value obtained by Bertrand et al (2010) is due to the high deformation generated by rotatory swaging.

Table 1. Experimental results from microhardness test.
Average results of 12 random measure.

Condition of processing	Microhardness (HV)
As cast	256 ± 8
After homogenization	255 ± 8
Rotatory swaging	273 ± 15
Solution heat treatment	166 ± 6

Table 2 shows the results obtained through the tensile test. From these, it can be verified that the presence of the β phase of the titanium gives the ternary alloy a "double-flow" effect, reason why in the elastic region can be observed two values of yield stress. According to Li et al. (2008) this phenomenon corresponds to the critical value of the stress required to transform β into α " and this effect may not be beneficial during the use of these alloys in applications involving fillers, for example prostheses. Aiming at the application of the alloy, a reduced modulus of elasticity is observed when compared to Ti CP (105-110 GPa) and Ti-6Al-4V (113 GPa). Which is much closer to the modulus of elasticity of bone in the human body that can range from 10 to 30 GPa, reducing the effect of stress shielding increasing the reliability of the material when used as an implant.

Table 2. Experimental results from tensile test
Average results of 2 specimens.

Mechanical properties	Ti-25Ta-25Nb
σ_σ (MPa)	530
σ_e (MPa)	210 / 480
E (GPa)	55
ε (%)	20

Figure 3 shows the curves obtained from the open circuit polarization process. It can be observed that the curve referring to the ternary alloy is more positive in relation to the titanium CP, being therefore considered more noble. The fact that one material is more noble than the other does not necessarily mean that it exhibits greater resistance to corrosion. The more positive value observed in the OCP curve indicates the formation of more stable species, usually oxides, which in turn has as a characteristic a better formation of the passive layer under the surface of the material. Due to the lack of alloying elements, Ti CP presents the formation of a more compact oxide, which makes it more protected, whereas the titanium alloys form porous oxides, creating regions more susceptible to corrosion.

Figure 4 shows the potentiodynamic polarization curve for Ti CP and Ti-25Ta-25Nb. The obtained results of this curve are shown in Table 3. Observing the obtained electrochemical parameters it is possible to verify that the current density of the ternary alloy presents higher value than the Ti CP, which leads to a small association and consequently conclusion. That if the corrosion current density is associated with the speed with which the material suffer corrosion in a given enviroment, it can be concluded that due to the lower value of Ti CP, the Ti-25Ta-25Nb alloy presents a higher resistance to corrosion, since presents a lower breaking speed of the passive layer formed on its surface. Bertrand et al. (2010) studied the Ti-25Ta-25Nb alloy, revealing low rates of corrosion density (jcorr), which characterizes this material as very stable.

Corrosion rates and consequent ion release were lower for the Ti-25Ta-25Nb alloy than for the Ti CP, and the tantalum and niobium elements exhibit the same beneficial effects. All these characteristics demonstrate that alloys containing elements with titanium, tantalum, and niobium are indeed promising for long-term use as biomaterial.
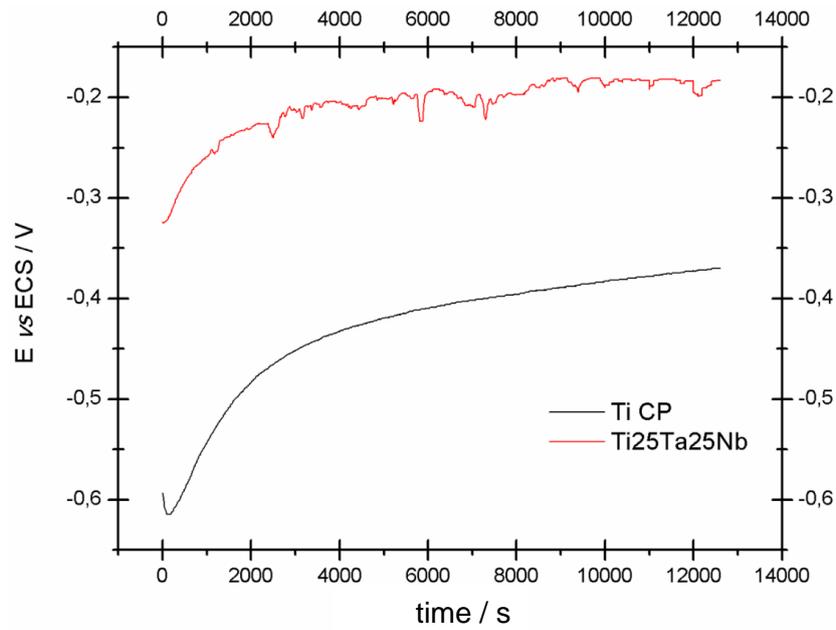
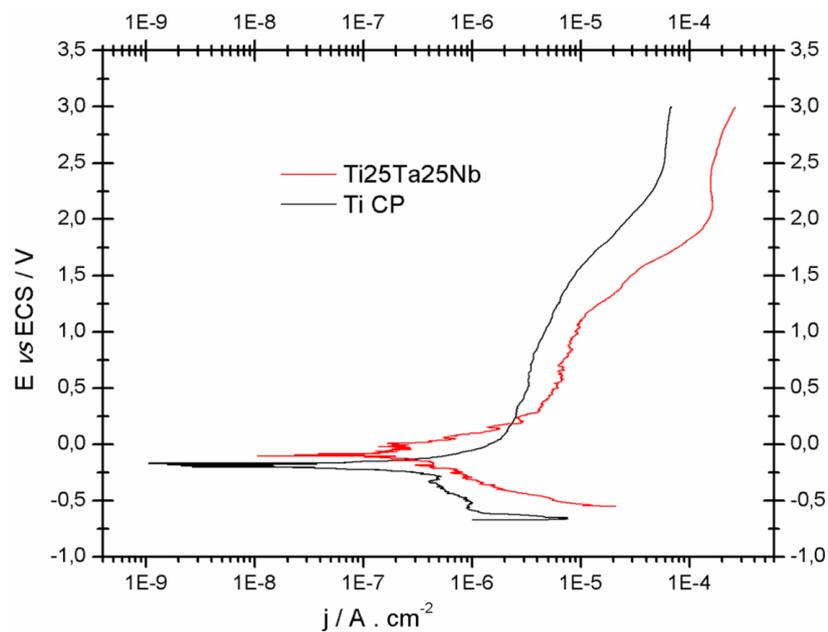Figure 3. OCP analysis of ternary alloy Ti-25Ta-25Nb and Ti CP.

Figure 4. Potentiodynamic polarization curve for Ti CP and Ti-25Ta-25Nb.

Tabela 3. Electrochemical parameters extracted from the potentiodynamic polarization curve
Average results of 2 tests

Eletrochemical parameters	Ti CP	Ti-25Ta-25Nb
E_{corr} (mV)	-187,9	-96,85
j_{corr} (A/cm^2)	$1,948 \times 10^{-7}$	$9,564 \times 10^{-7}$

4. CONCLUSIONS

- Microstructural analysis proved the predominance of the β phase.
- According to the XRD, only the as cast condition showed the presence of the α phase.
- The heat treatment of homogenization was sufficient to transform the α phase into β.

- Rotary swaging did not change the phases present in the structure, but caused severe deformation of the grains.
- The solubilization heat treatment was sufficient to promote the stress relief in the microstructure, removing the deformation of the grains, giving rise to a structure containing β phase predominance.
- The mechanical tests showed results of modulus of elasticity and microhardness lower than Ti CP and other titanium alloys. Therefore, for the biomedical application the alloy in study is more appropriate because it reduces the effect of stress shielding due they present values of mechanical properties closer to the bone.
- The corrosion test has proven that the Ti-25Ta-25Nb alloy is more resistant to corrosion when compared to other titanium alloys.

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