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TRIBO-MECHANICAL BEHAVIOR OF Ti-25Nb AND Ti-25Nb-25Ta DUE THE ADDITION OF BETA STABILIZERS ELEMENTS

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Abstract. *The mechanical and tribological properties of the commercial pure titanium (Ti-cp), Ti-25Nb and Ti-25Nb-25Ta alloys for biomedical applications were investigated. Metallographic analysis and patterns of X-Ray diffraction indicate that the Ti-25Nb alloy is composed by ($\alpha+\beta$) phases, and the Ti-25Nb-25Ta alloy by β -phase. The results obtained by instrumented indentation technique showed that the addition of beta stabilizer elements in alloys decreases the elastic modulus values and increase the hardness values of both alloys, comparing to cp-Ti. The coefficient of friction, performed in reciprocating tribometer against WC ball, showed that the Ti-25Nb-25Ta alloy presented higher values compared to others metals, and showed higher wear rate. Worn tracks revealed abrasive and adhesive wear for all metal. However, a severe abrasive wear was observed for Ti-25Nb alloy, whereas a severe adhesive wear for Ti-25Nb-25Ta. All results showed that mechanical and tribological properties depend on the alloys microstructure ($\alpha+\beta$ or β) and the addition of beta stabilizer elements (Nb and Ta).*

Keywords: β -titanium alloy, $\alpha+\beta$ -titanium alloy, mechanical properties, wear, coefficient of friction

1. INTRODUCTION

Titanium and its alloys are the metals used to produce metallic biomaterials due to high biocompatibility, better mechanical properties and corrosion resistance when compared to stainless steel (316 L) and CoCrMo alloy (Geetha *et al.*, 2009; Cordeiro and Barão, 2017). However, the cp-Ti has low strength and poor wear resistance. These limitations of the Ti can lead to the formation of wear debris that result in the inflammatory reaction causing pain and loss of implants due to osteolysis (Rashdan *et al.*, 2013; Hussein *et al.*, 2015).

The alloy frequently used for orthopedic prostheses is the Ti6Al4V. However, some authors have shown toxic effects due to the release of aluminum and vanadium ions (Hussein *et al.*, 2016; Geetha *et al.*, 2009). Vanadium (V) can accumulate in some parts of the body, such as bones, kidneys and liver, the presence of V ions in human tissues can change the kinetics of enzyme activity associated with the inflammatory response of cells. The presence of aluminum (Al) increases the potential for the development of Alzheimer's disease (Geetha *et al.*, 2009; Cordeiro and Barão 2017).

Many studies are being conducted in the development of new alloys, specifically the β -Ti alloys containing Nb, Mo, Zr, Sn or Ta, which are considered nontoxic, corrosion resistant and have mechanical properties suitable for biomaterials applications (Cordeiro and Barão, 2017; Mohammed *et al.*, 2014). The addition of beta stabilizer elements can reduce the elastic modulus, which facilitates the transfer of charge, avoiding damage to bone cells and the effect of stress shielding that tends to induce a loss of bone mass (Mohammed *et al.*, 2014; Niinomi, 2008).

The recent publications of new β -type alloys are focused on the analysis of alloy manufacturing process in relation to microstructure, crystalline structure, mechanical properties and effect of annealing. This occurs because the new alloys have a complex mechanism of phase transformation, which depends of manufacturing, such as melting procedures, annealing and cooling rates. Alloys with different mechanical and physical properties can be obtained (Lütjering, 1998).

However, few studies analyze tribological properties in new β -Ti alloys (Farokhzadeh and Edrissy, 2016; Setti and Rao, 2013; Xu *et al.*, 2013a). The knowledge of tribological mechanisms is fundamental to develop of new biomaterials, because debris generated as wear products can cause local and systemic reactions adverse in the host leading to inflammation of the surrounding tissue, osteolysis, loosening or implant fracture (Rashdan *et al.* 2013; Hussein *et al.*, 2015).

In this work, the influence of beta stabilizer elements (Nb and Ta) in the Ti-25Nb and Ti-25Nb-25Ta alloys was studied concerning to the microstructure, mechanical properties (elastic modulus and hardness) and tribological properties (friction coefficient, wear rate), and the results were compared with cp-Ti.

2. METHODOLOGY

The alloys Ti-25Nb and Ti-25Nb-25Ta (%wt.) were prepared from Ti (grade 2), Nb (99.7% purity) and Ta (99.8% purity). In order to obtain $\alpha+\beta$ and β type alloys different procedures of manufacturing of alloys was employed. The fusion process was the same for both alloys, it was used an arc melting furnace with copper crucible and water-cooled, non-consumable tungsten electrode and an argon-controlled atmosphere.

For the Ti-25Nb alloy, the cooling was done in furnace at rate of 5°C/min. After that, the Ti-25Nb alloy were submitted to heat treatment (1000°C/24 h) in an ultra-vacuum furnace to relieve the residual stress resulted by melting process. The ingots with 25% wt. of Nb were obtained after melting process, which were submitted again at the same heat treatment to recrystallize the microstructure of the material modified by forging. From the ingots, samples were obtained with 9 mm diameter and 2 mm thickness.

After fusion process the ingots of the Ti-25Nb-25Ta were subjected to a solubilization heat treatment at 950°C/24 h in a tubular furnace, with slow cooling in furnace. Following the solubilization heat treatment, the ingot was subjected to cold rotary forging (swage) until a final diameter of 10 mm was obtained. Then, a solubilization heat treatment was carried out at 850 °C/1 h, with the fast cooling in water. The ingots with 50% Ti, 25 % f Nb and 25 % Ta (%wt) were obtained after melting process with 10 mm diameter, and from which discs with 2 mm thickness were obtained.

For the microstructural analysis, the samples were prepared following standard metallographic techniques used for Ti and its alloys and etched with a Kroll's reagent. After that, the microstructures were examined by optical microscopy (FV10i - Olympus). The alloys phases were determined by X-Ray diffraction (Shimadzu XRD-7000), operating at 40 kV and 20 mA, Cu K α radiation, in Bragg-Brentano geometry (2 θ - 20° to 80°) in step scan of 2°/min.

The hardness and elastic modulus of cp-Ti and alloys were obtained using an instrumented indenter (UNAT - Zwick-Roell/Asmec), following the Oliver-Pharr method [4]. It was used a Berkovich tip and a maximum load of 500 mN.

Friction coefficient of alloys was investigated using a linear reciprocating tribometer (CSM). Tests were performed at room temperature under unlubricated condition. Tungsten carbide ball (6 mm diameter) was used against the cp-Ti, Ti-25Nb and Ti-25Nb-25Ta alloys. It was applied 1 N normal load, a sliding speed of 0.5 cm/s, half-amplitude of 2 mm and 675 number cycles, in air at room temperature. The worn regions after the wear tests were examined using SEM (TESCAN VEGA 3 LMU). Wear rate was obtained measuring the tracks profiles with a nano profilometer (Dektak XT - Burker).

3. RESULTS AND DISCUSSION

3.1 Microstructural characterization and phase identification

Fig. 1 shows the microstructures of alloys. The Ti-25Nb alloy (Fig. 1a) had an acicular-shaped and Widmanstätten structures. This array is characteristic by applying a slow cooling rate from β -phase to $(\alpha + \beta)$ phase (ASM International, 2015). When the Ta element was added in alloy, the microstructure changed to entirely β -phase in the Ti-25Nb-25Ta alloy (Fig. 1b).

Fig. 2 shows the X-ray diffraction peaks for alloys. The Ti-25Nb alloy showed peaks of $(\alpha + \beta)$ phases. Due to the low amount of element beta stabilizer, β -phase was not completely stabilized. The Ti-25Nb-25Ta alloy showed only β -phase. The addition of 25% wt. of Ta in the Ti-25Nb was effective to retain completely the β -phase.

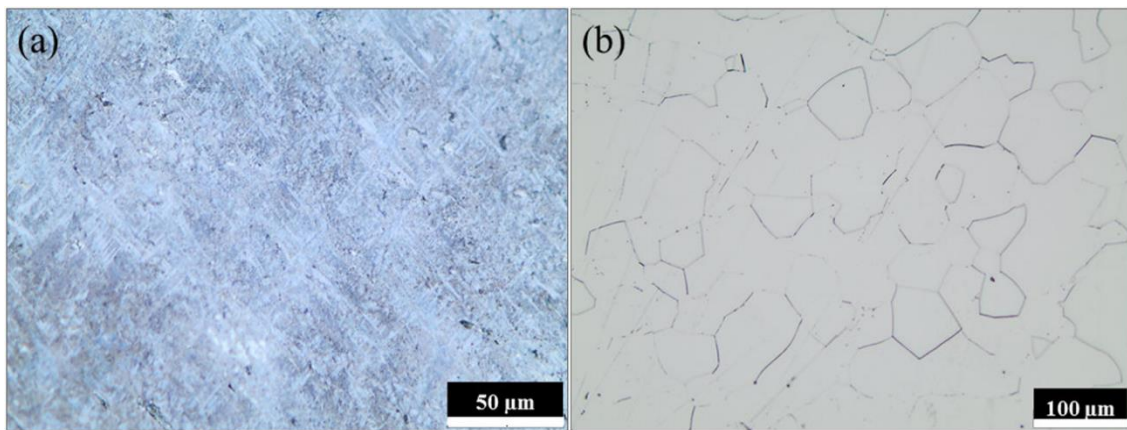


Figure 1. Optical micrographs of homogenized alloys (a) Ti-25Nb and (b) Ti-25Nb-25Ta

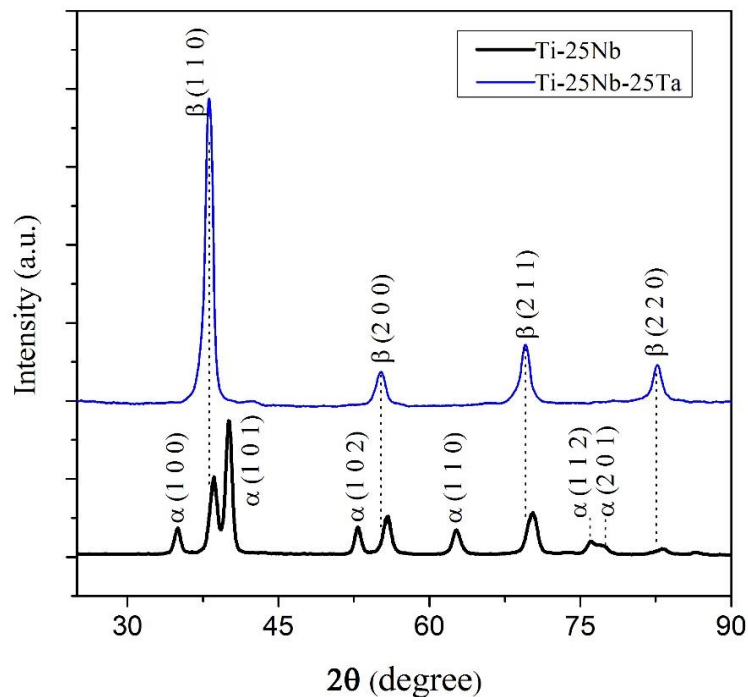


Figure 2. XRD peak intensities (arbitrary units) for Ti-25Nb and Ti-25Nb-25Ta alloys

3.2 Mechanical Properties

Table 1 shows the results obtained by instrumented indentation technique for cp-Ti and alloys. The addition of beta stabilizers elements not only change the microstructure of the alloys, but also improve the mechanical properties. It is well known that the increase of the beta phase can increase the hardness and reduce the elastic modulus (Cordeiro and Barão, 2017; Niinomi, 2008). Therefore, as expected the hardness of both alloys was higher than cp-Ti, due mechanisms of solid solution and phase precipitation hardening. The elastic modulus of both alloys was lower than cp-Ti, being that the Ti-15Nb-25Ta alloy presented lower elastic modulus, due the body-centered cubic structure of the β -phase.

The results shown on the fig. 1-2 not only are related to the addition and/or amount of beta stabilizers elements, but also with the manufacturing process of alloys. For example, the control of the conventional aging treatment allows obtain the strengthening and larger elastic modulus of β -type titanium alloys; although some alloys showed values below 80 GPa (Niinomi *et al.*, 2012). For alloys that apply a severe cold rolling or severe cold swaging, it is possible obtain lower elastic modulus and can be highly effective in increasing the strength. However, under the last circumstances, the high strength of severely deformed metals is achieved by compromising ductility (Okulov *et al.* 2017). As a result, a severe plastic deformation can be observed for beta alloys (Okulov *et al.* 2017).

Therefore, the knowledge of alloy manufacturing process is fundamental to predict the behavior of the mechanical and tribological properties of alloys. As a result of the addition of beta stabilizer elements and manufacturing process of the alloys analyzed in this work, it was obtained a higher hardness for Ti-25Nb and a lower elastic modulus for Ti-25Nb-25Ta.

Furthermore, the hardness of material may prewise the abrasive wear, but is not a great measure for wear resistance because two or more mechanisms for wear can be in the wear process, such as abrasive, adhesive or oxidative wear (Lee *et al.*, 2015).

However, the data of the elastic modulus and hardness can predict wear behavior and integrity of novel materials; using different correlations these measurements, as summarized by de Souza *et al.*, 2017.

Table 1. Mechanical properties of the cp-Ti, Ti-25Nb and Ti-25Nb-25Ta alloys.

	Sample		
	cp-Ti	Ti-25Nb	Ti-25Nb-25Ta
Elastic Modulus (GPa)	103.9 $\pm$ 1.7	84.2 $\pm$ 3.0	56.0 $\pm$ 3.5
Hardness (GPa)	1.93 $\pm$ 0.50	3.20 $\pm$ 0.20	2.21 $\pm$ 0.30

3.3 Tribological Properties

Fig. 3 shows the friction coefficients behavior as a function of the number of cycles. For cp-Ti the coefficient of friction goes through a run-in period of about 125 cycles and then a steady-state value for this sample is achieved around 0.8. A steady state value of the coefficient of friction between 0.8 and 0.9 is established for Ti and Ti-25Nb alloy, and between 1.0 and 1.4 for Ti-25Nb-25Ta alloy. The fluctuations of the coefficient of friction observed for all samples can be attributed to debris being trapped, ejected, and recycled in and out the sliding contact (Lee *et al.*, 2015).

The addition of Nb in Ti matrix was not effective to change the friction coefficient, but when β -phase was completely stabilized due the addition of Ta it was observed a higher value to friction coefficient. These results are in agree with (Xu *et al.*, 2009b), they do not observed significant changes for the coefficient of friction for Ti-Nb alloys compound with 5%, 10%, 15% and 20% of the Nb.

Furthermore, under unlubricated conditions the presence of surface oxides of metal determine the friction behavior of metals in air (Lee *et al.*, 2015; Rashdan *et al.*, 2013). Therefore, the native oxide film of the Ti-25Nb-25Ta alloys was not sufficient to support the sliding of the WC ball, being continuously fragmented and contributed for the higher friction coefficient. Whereas, probably, Ti and Ti-25Nb have a similar oxidative layer, thus they showed a similar friction coefficient (Xu *et al.*, 2009b). For Ti and Ti-Nb alloys that the effects of phase/structure of alloys are determinant for mechanical properties (as observed in table 1), but it is insignificant for corrosion behavior, which have relation with native oxides of alloys (Lee *et al.*, 2002).

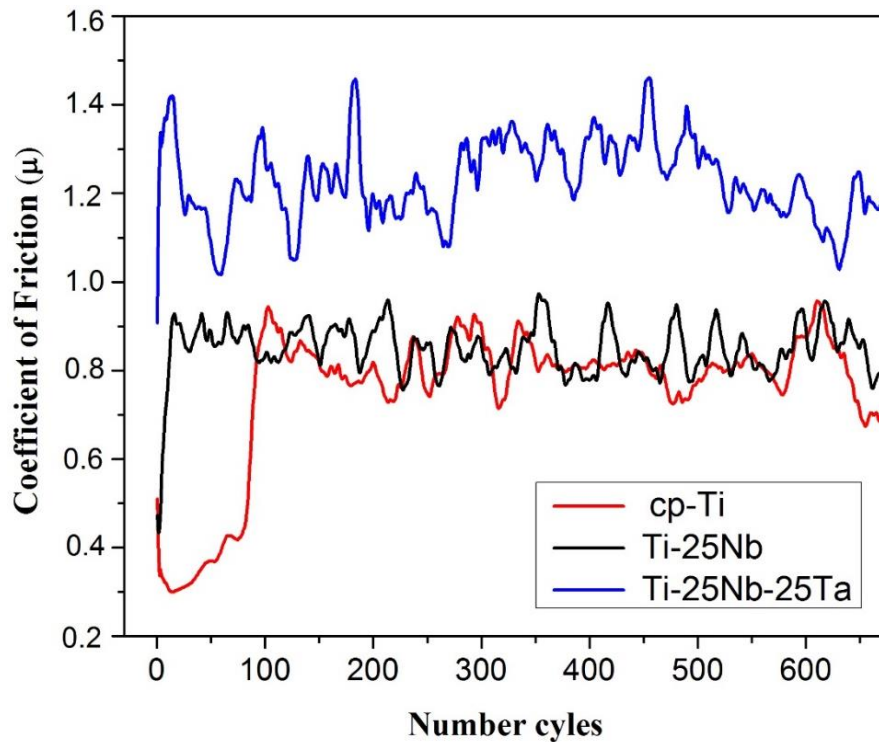


Figure 3. Variations of friction coefficient of samples against WC ball in function of number cycles

Fig. 4 shows SEM images of worn surfaces after tribological tests. Fig. 4a shows that a severe embrittlement occurred on the surface of cp-Ti after wear, showing a large number of grooves and elements that characterize adhesive wear, as indicated in the fig. 4a. Observing the SEM image (fig. 4b), there is evidence of predominance of abrasive wear on the surface of the Ti25Nb alloy and elements that characterize adhesive wear. The surface of the Ti-25Nb-25Ta alloy (Fig. 4c) showed a few grooves in the direction of sliding and adhesive wear was much stronger than other metals.

The features of wear can be relational with the hardness (table 1), and are in agreement with relations between elastic modulus and hardness reported by (de Souza *et al.*, 2017). The Ti-25Nb alloy has the higher hardness that reduces the adhesive wear when compared to cp-Ti. The hardness values for Ti and Ti-25Nb-25Ta do not showed significant differences, thus, a same behavior wear (abrasive and adhesive) was observed. These results are in accordance with (Xu *et al.*, 2013a) that observed an adhesive wear predominating for Ti-15Mo-xNb alloys when increase the amount of the β phase.

Besides that, the Ti-25Nb-25Ta alloy was manufactured by swage process that causes severe plastic deformation for beta alloys (Okulov *et al.*, 2017). Cross-section view of tracks worn was reported by Farokhzadeh and Edrissy, 2016 for Ti-10V-2Fe-3Al (near- β titanium alloy) and Ti-6Al-4V ($\alpha+\beta$ titanium alloy), which showed that the plastic deformation occurs along the elongation of β particles in the sliding direction.

Table 2 showed the wear rate calculated for Ti and Ti alloys. It was observed that the increase of the beta phase causes an increase of the wear rate. The higher wear rate observed for Ti-25Nb-25Ta can be associated with the severe plastic wear, as reported by Xu *et al.*, 2013a and Farokhzadeh and Edrissy, 2016. In the same way, the presence of β phase in Ti-25Nb alloys leads to higher wear rate than cp-Ti, which is compound only by α -phase.

Table 2. Wear rate of cp-Ti and Ti alloys

Sample	Wear rate ($10^{-3} \cdot \text{mm}^3/\text{N.m}$)	Standard deviation ($10^{-3} \cdot \text{mm}^3/\text{N.m}$)
cp-Ti	0.63	0.01
Ti-25Nb	0.99	0.01
Ti-25Nb-25Ta	2.63	0.46

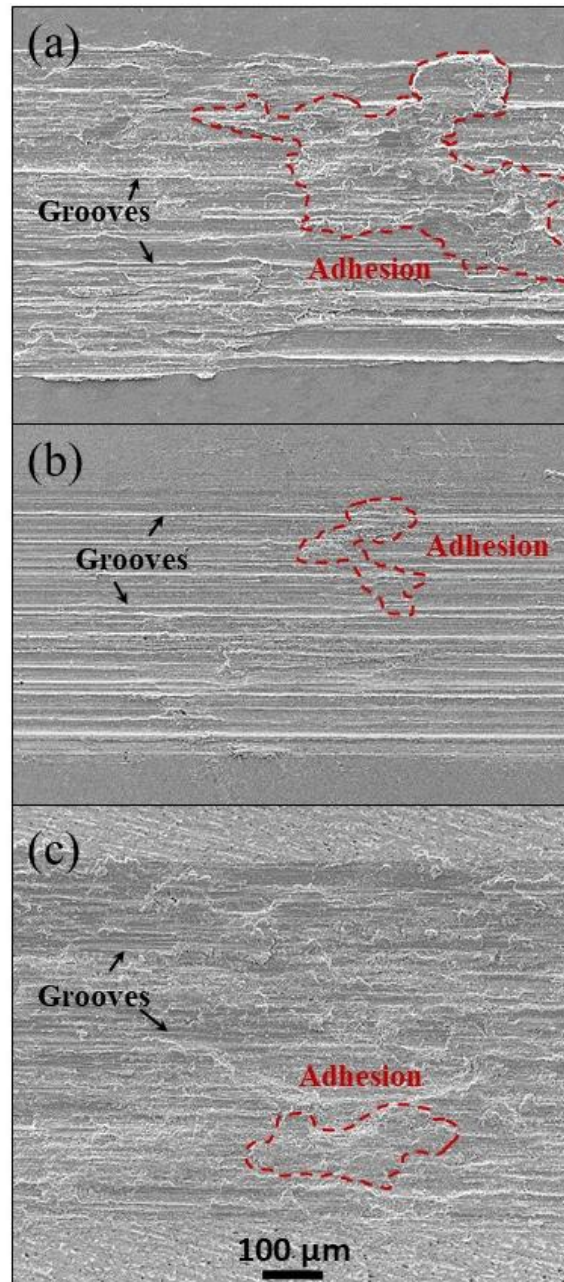


Figure 4. SEM images of worn surfaces after tribological tests: (a) cp-Ti, (b) Ti-25Nb and (c) Ti-25Nb-25Ta

4. CONCLUSIONS

The results of metallographic analysis and XRD patterns showed that Ti-25 Nb alloy is composed of ($\alpha + \beta$) phase, and the Ti-25Nb-25Ta by the β -phase.

The instrumented indentation tests showed higher values of hardness to alloys than cp-Ti, and lower modulus of elasticity to alloys due to the addition of the stabilizer beta elements.

The coefficient of friction had a similar behavior for cp-Ti and Ti-25Nb alloy. The Ti-25Nb-25Ta alloy had a higher coefficient of friction and higher wear rate, probably owing to the characteristics of the native oxide of alloys.

Worn tracks revealed abrasive and adhesive wear for all metal. However, a severe abrasive wear was observed for Ti-25Nb alloy, whereas a severe adhesive wear for Ti-25Nb-25Ta. The wear rate increase with increase the amount of the β -phase, so the Ti-25Nb-25Ta had the higher wear rate.

Therefore, the microstructure, mechanical and tribological properties depends on the addition of beta stabilizer elements.

5. ACKNOWLEDGEMENTS

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