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EVALUATION OF MICROSTRUCTURAL PROPERTIES OF TI-6AL-7NB ALLOY FOR BIOMEDICAL APPLICATION

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ABSTRACT

The choice of metallic materials for use in orthopedic and dental implants is made by evaluating physical, chemical and biocompatibility properties. Among these materials we highlight titanium-based alloys, such as those from the Ti-Al-Nb system, which have high chemical stability and biocompatibility attributed to the presence of niobium. Among these materials we highlight titanium-based alloys, such as those from the Ti-Al-Nb system, which have high chemical stability and biocompatibility attributed to the presence of niobium. Surface characterization was performed using XRF, SEM, XRD and XPS techniques. It was observed a uniform structure and distribution of the α - equiaxial phase involved by the β phase in the grain boundaries, besides the formation of alkaline titanate hydrogel by the chemical attack of the NaOH solution on the surface. The results obtained allowed making some considerations about aluminum and niobium contents, giving the Ti-6Al-7Nb alloy adequate characteristics for use in implantable biomedical devices.

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INTRODUCTION

Titanium for its biocompatible characteristics and titanium-based alloys are considered the most attractive metallic materials for biomedical applications. The commercial Ti – 6Al – 4V alloy for some time and until today has been the material of choice for orthopedic and dental applications (MANJAIAH; LAUBSCHER, 2017; NIINOMI *et al*., 2014). However, the lack of knowledge of the answer the biological effect of bone tissue to Ti alloys has not been fully elucidated. The Ti-6Al-4V alloy despite its high mechanical and corrosion resistance, became questionable for containing toxic elements (BOLZONI *et al*., 2012; CREMASCO *et al*., 2011). After years of research, in mid-1985, the Ti-6Al-7Nb alloy was presented as a biomaterial of excellent biocompatibility and high strength[5,6] being approved and standardized by ASTM F1295 in 1992 (GALLEGO *et al*., 2012); standard that covers chemical, mechanical and metallurgical requirements of the production of the alloy in question to be used in the manufacture of surgical implants. Literature reports state that this alloy presents good biological responses (BOLZONI *et al*., 2012, 2013; FONSECA *et al*., 2017).

In order to replace the vanadium element, the Ti-6Al-7Nb alloy, considered a substantially harmless materialwhich in turn has good properties such as Ti-6Al-4V, in addition to lower toxicity, property attributed to niobium that acts as a β-phase stabilizing element, presenting excellent biocompatibility, and aluminum as responsible for the solid strengthening of titanium(BOLZONI *et al*., 2013; EL-HADAD; SAFWAT; SHARAF, 2018; GALLEGO *et al*., 2012). The mechanical properties of the Ti-6Al-7Nb alloy are strongly affected by the microstructure, whose refining increases both strength and toughness.(KIZUKI; MATSUSHITA; KOKUBO, 2014; REN *et al*., 2014). The present study aimed to evaluate the physicochemical interactions that encompass a surface activation of the commercial metallic alloy Ti-6Al-7Nb by thermochemical treatment with NaOH, since such activation aims to attach chemical substances coming from the inorganic part of the bone and which favors its interaction with the implantable device.

MATERIALS AND METHODS

Substrate preparation: The Ti-6Al-7Nb alloy (SANDINOX) in cylindrical shape was sectioned longitudinally to obtain samples with dimensions of 20 mm in diameter and 2 mm in thickness. Afterwards, the samples were sanded and polished and to reveal the microstructures a chemical etching with Kroll reagent was used: 1HF 85% /1HNO_3 65%/100 H_2O (v/v).

Surface activation

Topography and surface roughness: The surface of the Ti-6Al-7Nb alloy was prepared with a SiC/180 mesh sandpaper, then cleaned in a solution of alcohol and acetone for 30 minutes in ultrasound, washed with distilled water and dried.

Thermochemical treatment: NaOH: Samples with sanded surfaces were immersed in a NaOH solution (5.0 mol.L-1) for 24 hours at 60 °C, then dried in an oven for 3 hours at 60 °C.

Physical-Chemical Characterizations

X-ray fluorescein spectrometry (XRF): The Ti-6Al-7Nb alloy was analyzed in an Energy Dispersive X-Ray Fluorescence Spectrometer (EDX-800 RayNy), brand Shimadzu.

Scanning Electron Microscopy (SEM): Micromorphological analyzes of the Ti-6Al-7Nb alloy were performed in the cross section of the Ti-6Al-7Nb samples, and performed with a JEOL-JSM Microscope, model T-330 A.

X-ray diffraction: For the identification of the present phases, the following were used: X-ray diffractometer SIEMENS D5000, with angular scanning between 10 and 50º, in Bragg-Brentano assembly, using Cu radiation ($k_{\alpha}1$) and X-ray diffractometer by Rigaku brand , model D/MAX System – 2100/PC, using copper Kα radiation (1.5405A) with Ni filter for K_{β} radiation with an ULTIMA theta-theta goniometer with a speed of 2 degrees min-1 being the source of K_{α} radiation accelerated copper with a potential of 40kV and a current of 20 mA and angular sweep between 10º and 50°, in the Bragg-Brentano assembly.

X-ray excited photoelectron spectroscopy (XPS): The surfaces of the Ti-6Al-7Nb alloy thermochemically treated with NaOH were characterized in a Kratos Analytical Spectromicroscope, model XSAM HS.

RESULTS AND DISCUSSION

Topographic evaluation (SEM) of the Ti-6Al-7Nb alloy: Figure 1 shows the SEM analysis of the Ti-6Al-7Nb alloy. It was observed a very uniform microstructure and distribution of the α - equiaxial phase involved by the β phase in the grain boundaries, characteristics of materials treated thermo-mechanically. Figure 2 (a, b) shows the surfaces of the Ti-6Al-7Nb alloy before and after treatment with the NaOH solution and presents a passivevery stable layer of titanium oxide that forms over the alloy spontaneously to environmental exposure. Figure 2 (b) shows a partially crystallized microporous layer featuring a layer of crystalline sodium titanate ($Na_2Ti_5O_{11}$) and rutile (TiO_2).

X-ray fluorescence spectrometry: Table 1 shows the concentrations of the alloy elements within the maximum ranges allowed by the ASTM (American Society for Testing and Materials) standards specific for applications in biomaterials.

X-ray diffraction: Figure 3 shows the analysis of the X-ray diffractogram where the non-detection of the alloying elements Al and Nb is observed due to their low mass concentration of 6 and 7%, respectively, and the lack of standard sheets that can measure the alloy under study showing peaks referring to metallic Ti, corresponding to the sheet 44-1294 (JCPDS, 2003). The passive layer of titanium oxide that is formed on the alloys, even without treatment, is very stable. However, this TiO_2 layer can react with a NaOH solution and form an alkaline titanate hydrogel on the surface,(KIZUKI; MATSUSHITA; KOKUBO, 2014; OH *et al.*, 2014) being dehydrated and stabilized as a sodium titanate partially crystallized after treatment at 60ºC for 3 hours. The reaction that takes place on the titanium oxide layer is represented by the following equations, which show a corrosive attack of hydroxyl on TiO_2 producing hydrates on the alloy surface:(KAZEK-KĘSIK *et al.*, 2018; KIZUKI; MATSUSHITA; KOKUBO, 2014; MOHAMMED *et al.*, 2015)

Table 1. Chemical composition of Ti-6Al-7Nb alloy (%m/m). Oxygen (O), Nitrogen (N), Carbon (C), Hydrogen (H), Tantalum (Ta), Iron (Fe), Aluminum (Al), Vanadium (V), Niobium (Nb), Titanium (Ti)

Elements (% máx)	Ti-6Al-7Nb	Ti-6Al-7Nb (ASTM F1295-97a)
O	-	0.20
N	-	0.05
C	-	0.08
H	-	0.009
Ta	-	0.5
Fe	0.14	0.25
Al	6.5	5.5-6.5
V	-	-
Nb	7.17	6.5-7.5
Ti	Control	Control

Source: survey data

Table 2. Values of Binding Energies (eV) of the Components of the main photoelectric peaks. The percentages in parentheses refer to the relative amounts of each component of the respective peak

Specimentest	Link energy (eV)			
	C 1s	O 1s	Ti 2p3/2	Na 1s
Ti-6Al-7Nb/ NaOH	284.8 (70%) 286.4 (17%) 288.6 (13%)	529.9 (80%) 531.8 (11%) 533.2 (4%) 535.4 (4%)	458.5 (100%)	1071.5 (92%) 1074.3 (8%)

Soude: Survey data

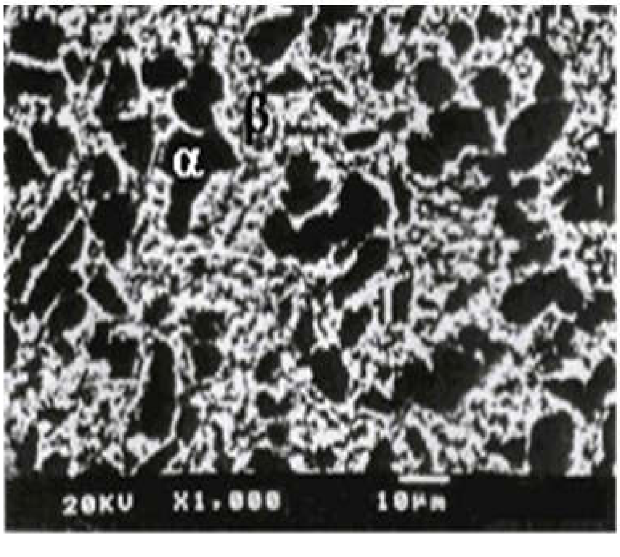

Figure 1. Micrograph of Ti-6Al-7Nb alloy

$TiO_2 + OH^- \rightarrow HTiO_3^-$

$TiO_2.nH_2O + OH^- \Leftrightarrow HTiO_3^-. nH_2O$

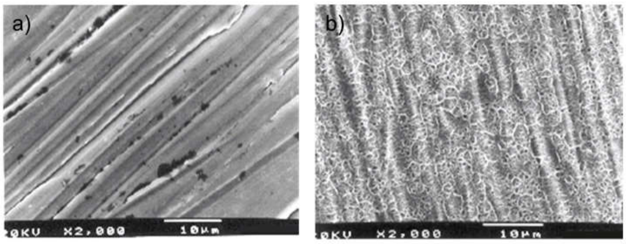

Figure 2. SEM of Ti-6Al-7Nb alloy surface before (a) and after (b) thermochemical treatment with a NaOH solution.

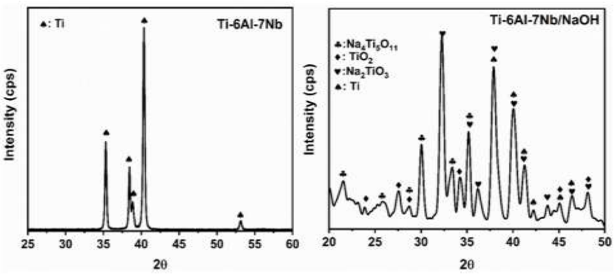

Figure 3. X-ray diffractograms of Ti-6Al-7Nb and Ti-6Al-7Nb/NaOH alloy

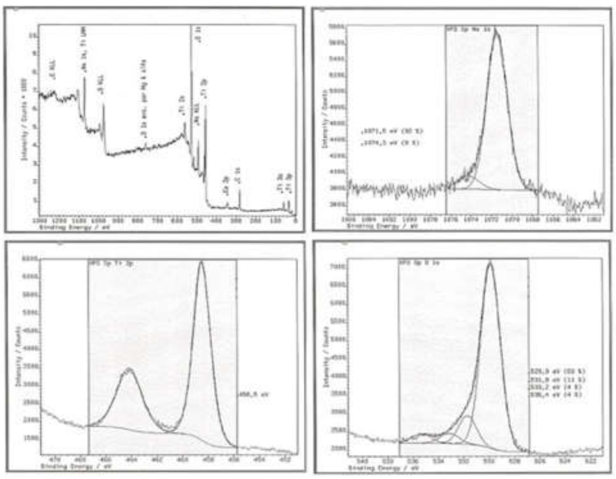

Figure 4. XPS spectra of the Ti-6Al-7Nb alloy surface attacked with a 5 mol.L-1 NaOH solution

X-ray excited photoelectron spectroscopy (XPS): Figure 4 corresponds to the XPS spectra of the elements found on the surface of the NaOH/Ti-6Al-7Nb samples and its analysis is shown in Table 2, where it is observed binding energies of Na 1s and Ti 2p3/2, 1071.5 eV and 458.5 eV.XPS analyzes on Ti-6Al-7Nb alloy without etching were not performed because the objective was to understand the transformations that occurred on the surface treated with NaOH. To obtain the multifunctional properties of Ti alloys, their surface can be enriched by additional techniques and substances that favor the formation of a layer with biologically active substances.(KAZEK-KĘSIK *et al*., 2018). The study supports researchers on the morphological appearance of the alloy surface where it shows a microporous layer composed of an alkaline titanate hydrogel formed during the alkaline/thermal treatment and can be characterized as a partially crystallized sodium titanate layer containing small amounts of a mixture of crystalline sodium titanates ($Na_2Ti_5O_{11}$) and rutile (TiO_2). (GIL *et al*., 2002; KIZUKI; MATSUSHITA; KOKUBO, 2014; MOHAMMED *et al*., 2015). During treatment with sodium hydroxide the titanium oxide that protects the surface is partially dissolved to form an alkaline solution due to the corrosive attack of the hydroxyl groups. (GIL *et al*., 2002; KIZUKI; MATSUSHITA; KOKUBO, 2014; MOHAMMED *et al*., 2015). According to Feng *et al*., the binding energies 458.22 eV and 458.39 eV are associated with the formation of TiO_2. Oxygen on the titanium surface in a wet environment can exist in three states:

TiO_2, basic Ti-OH and acidic Ti-OH or H_2O.(EKKERT *et al*., 2018; FENG *et al*., 1999; KRZAKAŁA *et al*., 2013). Studies identified the appearance of three peaks with binding energies of 532.7, 531.3 and 529.5 eV that may be associated with Ti-OH.(EKKERT *et al*., 2018; KRZĄKAŁA; KAZEK-KĘSIK; SIMKA, 2013; MAO *et al*., 1999). The binding energy 529.5 and 529.9 of O1s can be associated with the basic Ti-OH state, as this is more active in the chemical reaction. Thus based on the data obtained and the literature consulted it can be said that the surfaces studied are probably forming TiO_2 and sodium titanate. (EKKERT *et al*., 2018; WANG *et al*., 2017). In the XPS analysis it was possible to detect a contaminant element such as carbon, because in this case it was decided to remove the impurities on the surface of the samples with acetone, since the most used method would be the ionic bombardment of Ar+ could change the oxidation state.

CONCLUSION

The results of this study allow us to conclude that the effect of surface activation of the alloy by thermochemical treatment with alkaline NaOH solution depends on the chemical composition and suggests a better biological response, which may induce greater cell adhesion and the growth of calcium phosphates, favoring the bone/bone interaction implant.

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