Materials Research. 2012; 15(3): 355-358
DOI: 10.1590/S1516-14392012005000040

Influence of the Substitutional Solute on the Mechanical Properties of Ti-Nb Binary Alloys for Biomedical Use

Luciano Monteiro da Silva[a], Ana Paula Rosifini Alves Claro[b],

Marília Afonso Rabelo Buzalaf[c], Carlos Roberto Grandini[a*]

[a]*Laboratório de Anelasticidade e Biomateriais, UNESP – Univ. Estadual Paulista, CEP 17033-360, Bauru, SP, Brazil*
[b]*Departamento de Materiais e Tecnologia, Faculdade de Engenharia, UNESP – Univ. Estadual Paulista, CEP 12516-410, Guaratinguetá, SP, Brazil*
[c]*Departamento de Ciências Biológicas, Faculdade de Odontologia, USP – Universidade de São Paulo, CEP 17012-901, Bauru, SP, Brazil*

Received: March 17, 2011; Revised: February 7, 2012

Titanium alloys are widely used in the manufacture of biomedical implants because they possess an excellent combination of physical properties and outstanding biocompatibility. Today, the most widely used alloy is Ti-6Al-4V, but some studies have reported adverse effects with the long-term presence of Al and V in the body, without mentioning that the elasticity modulus value of this alloy is far superior to the bone. Thus, there is a need to develop new Ti-based alloys without Al and V that have a lower modulus, greater biocompatibility, and similar mechanical strength. In this paper, we investigated the effect of Nb as a substitutional solute on the mechanical properties of Ti-Nb alloys, prepared in an arc-melting furnace and characterized by density, X-ray diffraction, optical microscopy, hardness and elasticity modulus measurements. The X-ray and microscopy measurements show a predominance of the α phase. The microhardness values showed a tendency to increase with the concentration of niobium in the alloy. Regarding the elasticity modulus, it was observed a nonlinear behavior with respect to the concentration of niobium. This behavior is associated with the presence of the α phase.

Keywords: *Ti-based alloys, elasticity modulus, biomaterials*

1. Introduction

A systematic search for materials for application in the human body has resulted in the growth of research on so-called biomaterials. Biomaterials for use in implants should exhibit nonaggressive properties and characteristics, such as biocompatibility, biofunctionality, bioadhesion, and corrosion resistance[1-3]. Titanium-based alloys are widely used because they have excellent biocompatibility, good strength-to-weight ratio, and high corrosion resistance[3,4].

Currently, the most widely used metallic biomaterials for biomedical applications are 316L stainless steel and the Ti-6Al-4V alloy[5]. Although the Ti-6Al-4V has a lower modulus of elasticity (112 GPa)[5] than stainless steel 316L (210 GPa)[6], this value is still very high compared with the elastic modulus of bone (cortical bone – 15-30 GPa)[6]. Also, some studies have indicated that long-term cytotoxic effects may arise with vanadium and that aluminum may be associated with neurological disorders. However, other recent analyses have cast doubt on these assertions[3].

Given the uncertainties, there is a need to develop new titanium-based alloys without aluminum or vanadium. Some of the most promising alloying elements are niobium, tantalum, zirconium, and molybdenum[7-10].

*e-mail: betog@fc.unesp.br

From an engineering perspective, the Ti-Nb system exhibits interesting properties for use as a biomaterial. Niobium is nontoxic, nonllergenic, and exhibits high biocompatibility; it also promotes a reduction in the elastic modulus[9,11], increases corrosion resistance, and improves the biological properties of the alloy. Niobium also exerts a high β stabilizing effect[6]. The equilibrium phase diagram of Ti-Nb alloy[12] is isomorphic type, without any reaction or transformation invariant matching. It is observed that the increase in niobium concentration causes a decrease in β-transus temperature alloy indicating the β-stabilizing character of niobium, however, due to the melting point of niobium be greater than titanium, the melting temperature alloy will be larger as increases the concentration of niobium. Futhermore, given that this element is one of Brazil's biggest resources[13], thus the development of technology and applications of this material is interesting both from the standpoint of academic and industrial sectors.

This paper aims to study the effect of niobium as a substitutional solute on the mechanical properties of Ti-Nb alloys.

2. Materials and Methods

It was produced samples of Ti-Nb alloys with a weight percentage of 5 and 10 wt. (%) of niobium. Melting of the alloys was performed at the Laboratório de Anelasticidade e Biomateriais (UNESP/Bauru) using an arc-melting furnace with a nonconsumable tungsten electrode and water-cooled copper crucible in an argon-controlled atmosphere. The precursor materials used were commercially pure titanium (99.7% purity) and niobium (99.8% purity), both supplied by Aldrich Inc. After melting, were obtained two ingots (Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys) with 80 g each one.

Following melting, the obtained ingots were subjected to swaging, yielding samples 4.0 mm in diameter and 40.0 mm in length. The alloys were then subjected to quantitative chemical analysis using the Spectra SpectromaXx model (Molecular Devices, USA). The chemical composition of the samples is presented in Table 1. Homogenization heat treatment was carried out to improve the homogeneity of the alloys and remove internal stresses arising from the swaging. The heating rate used was 10 °C/min to 1000 °C. This temperature was maintained for 24 hours and then cooling down was done slowly with the shutdown of the furnace.

The samples were analyzed using density measurements and X-ray powder diffraction. The density measurements were based on Archimedes's Principle and used the Explorer Analytical Balance (Ohaus, Switzerland). The X-ray diffraction spectra were obtained using a D/Max 2100/PC diffractometer (Rigaku, Japan), with a Cu-Kα radiation of λ = 1.544 Å, 20 mA current, 40 kV potential, and scanning speed of 0.0125°/s. The Vickers microhardness of the samples was determined using the HMV-2 equipment (Shimadzu, Japan), with a load of 1.961N (0.20 kgf) for 60 seconds. The micrographs were obtained using an BX51M microscope (Olympus, Japan). Mechanical spectroscopy was performed to determine the dynamic elasticity modulus of the samples. The mechanical spectroscopy measurements were obtained using a torsion pendulum with a frequency of about 30 Hz in the temperature range from 100 to 700 K, a heating rate of 1 K/min, and a vacuum of 10^{-6} mbar.

3. Results and Discussion

Figure 1 shows the experimental density of Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys. The values are very close to theoretical values (4.62 and 4.73 g.cm^{-3} for Ti-5 wt. (%) Nb and Ti-10 wt (%) Nb, respectively)[10], indicating that the samples exhibit good stoichiometry. The density of the samples increased as the niobium content increased. As the density of the titanium is 4.51 g.cm^{-3} and the density of the niobium is 8.57 g.cm^{-3}, and, the atomic mass of niobium is approximately twice that of titanium and its atomic radius is approximately the same, the density of the material will increase significantly. Thus, there should

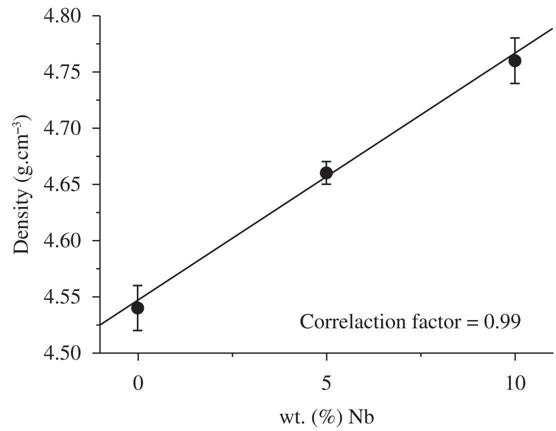

Figure 1. Density of Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb samples.

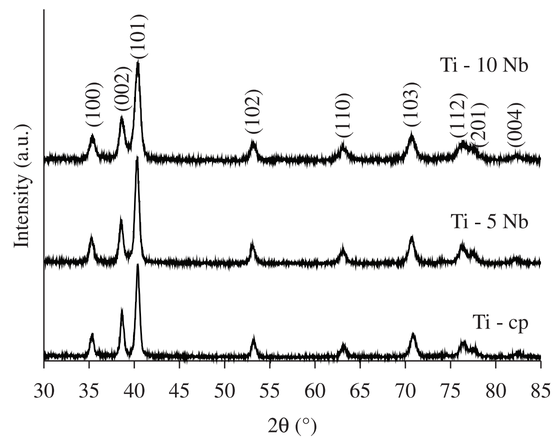

Figure 2. X-ray diffraction for the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys.

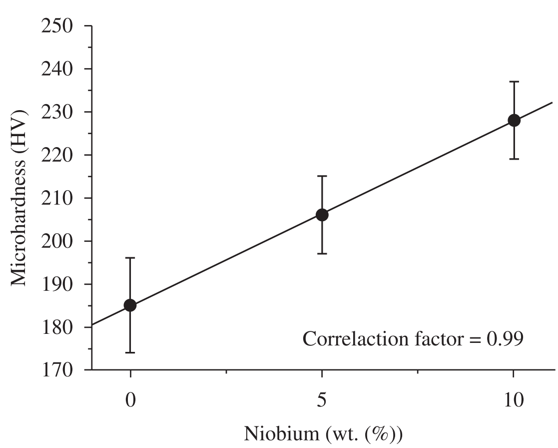

Figure 3. Microhardness of the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys.

Table 1. Chemical composition of the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb samples.

	Nb wt. (%)	Al wt. (%)	Cr wt. (%)	Fe wt. (%)	Mn wt. (%)	Zr wt. (%)	Ti
Ti-5 wt. (%) Nb	5.46	0.0040	0.0026	0.050	0.017	0.045	balance
Ti-10 wt. (%) Nb	8.93	0.012	0.0060	0.064	0.042	0.044	balance

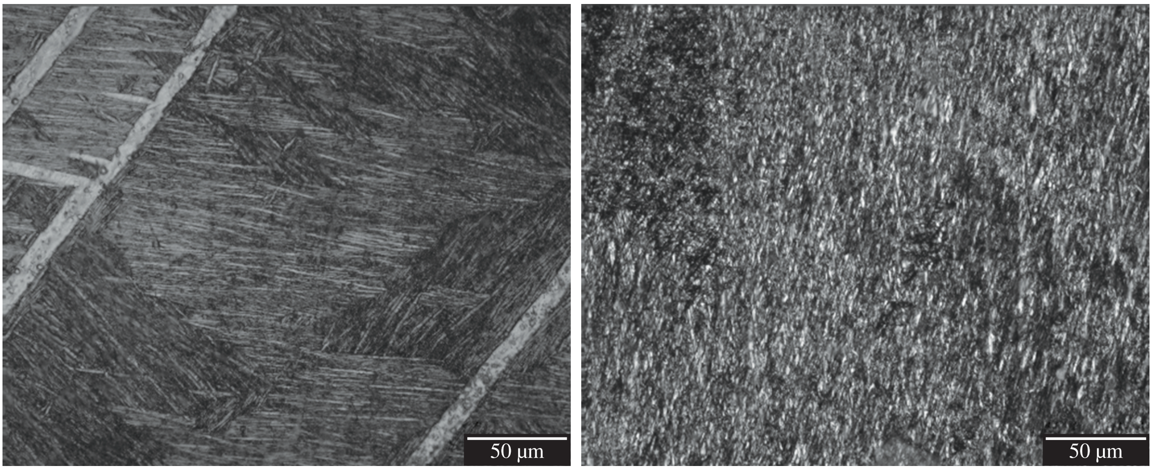

Figure 4. Micrographs of Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb.

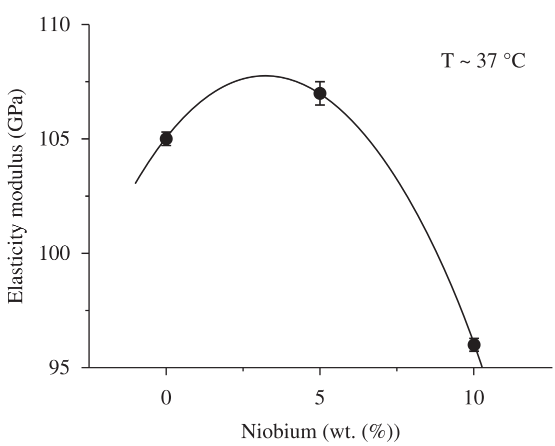

Figure 5. Elasticity Modulus of the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys.

be a strong relationship between the niobium content of the sample and the density, consistent with the obtained results.

Figure 2 shows the X-ray diffractograms of the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb samples. These peaks are related to the α phase of titanium (HCP), as shown in crystallographic data of titanium PDF # 44-1294, obtained using a software PCPDFWIN™. It was also noted that the peaks obtained are in agreement with works previously published[8]. The equilibrium phase diagram shown in Figure 1 shows that the Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb are in the region (α + β), ie, both phases coexist in the alloys, however, the quantities β phase present are not sufficient to reach the detection limit of the diffractometer, then there is the predominance of α phase.

Figure 3 illustrates that there is a strong correlation between the microhardness of the samples and the amount of niobium. Lee et al.[8] reported similar results in their analysis of the same stoichiometries studied in this paper. The authors attribute the increase in the hardness of their samples to the presence of the α phase, which hardens the material, whereas the β phase makes the alloy less hard.

Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb micrographs in Figure 4 showed the presence of needles, which are characteristic of samples that were heated above the phase transition temperature and cooled slowly to the field (α + β)[14]. This morphology is acicular martensite due to the distortion in HCP structure caused by the introduction of small amounts of β stabilizing elements, in this case, niobium[14].

Figure 5 shows the modulus of elasticity of the sample as a function of the niobium concentration. There is an increasing in the value of the modulus of elasticity of Ti-5 wt. (%) Nb alloy followed by a decreasing of this value to the Ti-10 wt. (%) Nb alloy. Although these values are still much higher than the modulus of elasticity of bone, these values are smaller than those presented by the Ti-6Al-4V alloy and stainless steel 316L. Lee et al.[8] obtained similar results and attributed the increase in the elasticity modulus to the presence of the α phase. The same authors observed that when the β phase predominates as a result of the increase in the concentration of niobium, a decrease occurs in the elastic modulus of the alloy.

4. Conclusions

In this paper, it was prepared Ti-5 wt. (%) Nb and Ti-10 wt. (%) Nb alloys, were the samples stoichiometry was respected, within an accuracy of 3%. The X-ray diffraction showed peaks corresponding to a HCP structure with the predominance of α phase. Micrographs showed structures in the form of needles, reinforcing the predominance of the α phase. The microhardness values showed a tendency to increase with the concentration of niobium in the alloy. Regarding the elasticity modulus, we conclude that nonlinear behavior occurs with respect to the concentration of niobium and that this behavior is associated with the presence of the α phase.

Acknowledgements

The authors thank the Brazilian agencies CNPq (Grant # 307471/2007-1), FAPESP (Grants # 2009/16731-9 and 2010/07.593-9) for their financial support.

References

1. Ratner BD, Hiffman AS, Schoen FJ and Lemons JE. *An Introduction to Materials in Medicine*. San Diego: Academic Press; 1996.
2. Geetha M, Singh AK, Muraleedharan K, Gocia AK and Asokamani R. Effect of thermomechanical processing on microstructure of a Ti–13Nb–13Zr alloy. *Journal of Alloys and Compounds*. 2001; 329(1-2):264-271. http://dx.doi.org/10.1016/S0925-8388(01)01604-8
3. Geetha M, Singh AK, Asokamani R and Gocia AK. Ti based biomaterial, the ultimate choice for orthopaedic implants – A review. *Progress in Materials Science*. 2009; 54(3):397-425. http://dx.doi.org/10.1016/j.pmatsci.2008.06.004
4. Silva HM, Schneider SG and Moura Neto C. Study of nontoxic aluminum and vanadium-free titanium alloys for biomedical applications. *Materials Science and Engineering C*. 2004; 24 (5):679-682. http://dx.doi.org/10.1016/j.msec.2004.08.051
5. Soares GDA. *Materiais avançados para saúde médico-odontológica*. In: Assunção FCR, organizadores. *Materiais Avançados 2010-2012*. Centro de Gestão e Estudos Estratégicos; 2010.
6. Yaszemski MJ, Trantolo DJ, Lewandrowski K-U, Hasirci V, Altobelli DE and Wise DL. *Biomaterials in Orthopedics*. New York: Marcel Dekker;2004.
7. Schneider SG. *Obtenção e caracterização da liga Ti-13Nb-13Zr para aplicação como biomaterial*. [Tese]. São Paulo: Instituto de Pesquisas Energéticas e Nucleares, 2001.
8. Almeida LH, Grandini CR and Caram R. Anelastic spectroscopy in a Ti alloy used as biomaterial. *Materials Science and Engineering A*. 2009; 521-522: 59-62. http://dx.doi.org/10.1016/j.msea.2008.09.123
9. Lee CM, Ju CP and Chern Lin JH. Structure-property relationship of cast Ti-Nb alloys. *Journal of Oral Rehabilitation*. 2002; 29(4):314-322. PMid:11966963. http://dx.doi.org/10.1046/j.1365-2842.2002.00825.x
10. Long M and Rack HJ. Titanium alloys in total joint replacement - a materials science perspective. *Biomaterials*. 1998; 19(18): 1621-1639. http://dx.doi.org/10.1016/S0142-9612(97)00146-4
11. Silva LM. *Influência da dopagem com oxigênio nas propriedades anelásticas e biocompatibilidade de ligas Ti-5%pNb e Ti-10%pNb*. [Dissertação]. Bauru: Universidade Estadual Paulista, 2010.
12. Leyens C and Peters M. *Titanium and Titanium Alloys – Fundamentals and Aplications*. Köln: Wiley-VCH; 2003.
13. Brasil. Departamento Nacional de Produção Mineral. Available from: <http://www.dnpm.gov.br>. Access in: 30/04/2011.
14. Linde DR. *Handbook of Chemistry and Physics*. 80th ed. New York: CRC Press; 1999.