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Structural analysis of a Nb–based alloy for biomedical application

JRS. Martins Junior.[1]; CR. Grandini[2],

**Corresponding author: E–mail address: jose.martins@ifsp.edu.br*

Abstract: The purpose of research in the biomaterials field is to produce new materials with physical and chemical properties close to the tissue to be replaced with minimal toxic response to the foreign body. Among the various metallic materials, titanium and its alloys have this great combination of properties. The most promising alloys are those with niobium, molybdenum, tantalum, and zirconium as alloying elements added to titanium. Thus, this kind of alloys integrate a new class of alloys without aluminum and vanadium (which cause cytotoxicity) and have a low modulus of elasticity (below 100 GPa). The objective of this work is to analyze the structure and microstructure of a niobium–based alloy, Ti–50wt%Nb. This alloy was produced in an arc–melting furnace with an inert atmosphere of argon gas. After melting, the samples were characterized by density, X–ray diffraction, scanning electron microscopy, and hardness. The X–ray diffraction data shows the peaks corresponding to the beta phase (with body–centered cubic crystalline structure), corroborated by scanning electron microscopy images. The value of the lattice parameter of the body–centered cubic crystalline structure was 3.2868 Å.

Keywords: Biomaterials, Titanium Alloys, X–ray diffraction, Rietveld´s Analysis.

Introduction

Much research is being developed to characterize the mechanical and biochemical behavior of beta (b) titanium alloys, depending on the processes of obtaining and thermomechanical treatments of these alloys, which greatly influence their properties [1, 2]. Among several Ti–based alloys, a binary composition like Ti–Nb is studied for application in biomaterials [3–6].

The first studies made on the characterization of Ti–Nb alloys were made by Lee et al. (2002) [7], where the authors analyzed the microstructure, mechanical properties, and corrosion resistance of these alloys with Nb content up to 35 wt%. However, Zhang et al. (2001)[8] studied the thermodynamic properties of the Nb–Ti system first. They have been evaluated these properties by using a regular solution model to describe the Gibbs energies of various phases, including both equilibrium and metastable phases. With the thermodynamic parameters obtained in this work, authors discuss the possible occurrence range of w phase. The ω phase is a metastable phase and exhibits hexagonal crystalline structure or depending on the content of alloying elements [9]. Several studies were made to characterize Ti–Nb alloys with the coexistence between a and b phases regarding structure, microstructure, phase composition, mechanical properties, and corrosion resistance. These alloys have Nb content below 40 wt% [4, 10–22]. According to Ozaki et al. [23], above 40 wt% of Nb, only the presence of b phase is observed.

Martins et al.[24] studied Ti–xNb alloys (x = 45 and 50% wt.) produced by mixing powder elementary elements, followed by uniaxial and cold isostatic pressing with subsequent densification by sintering. The phase composition of sintered samples was characterized by X–ray diffraction (XRD) measurements and scanning electron microscopy (SEM). The hardness was obtained by Vickers indentation, specific mass by the Archimedes method, and elastic modulus by resonance ultrasound method. The sintered samples presented only the b phase, higher hardness, and lower elastic modulus compared to Ti6Al4V alloy and experimental specific mass value near theoretical specific mass.

Bonisch et al.[13, 14] studied thermal stability and latent heat of Nb–rich martensitic Ti–Nb alloys. For biomedical applications, alloy compositions with relatively low martensitic transformation (MT) temperatures are more attractive. The latent heat, elastic and irreversible energy contributions of the thermoelastic energy balance are quantified dependent on Nb content in the remaining parts. All energy contributions decrease with increasing Nb content, and the latent heat becomes very small (< 5 J/g) for the Nb–richest martensitic compositions.

Pereira et al.[25] studied Ti–xNb alloys (x = 50, 80, and 90 wt%). This work compared the influence of niobium on the alloys' mechanical properties, corrosion resistance, and cell viability for biomedical application. All studied alloys have body–centered cubic crystalline structures (b phase). The Ti–50Nb alloy showed the best values of elastic modulus among all analyzed alloys. Corrosion resistance, wettability, and cellular viability were analyzed, too. The results of this paper suggest a Ti/Nb ratio close to 1 for Ti–50Nb, showing favorable characteristics to apply in orthopedic devices.

The importance of Nb alloys also occurs from the strategic point of view for Brazil, as it holds more than 95 % of the world resources of this element[26].

Besides the significant number of studies in Ti–Nb alloys, research on the influence of Nb on the structure of Ti–based alloys using Rietveld's Method was not found in the literature.

The Rietveld's Method[27] is a method that allows the refinement of crystalline structures, with X–ray or neutron diffraction data, using the powder method. The determination of the proportion of the phases present in a sample is also exemplarily performed with the Rietveld's Method [28], and no calibration curve is required. Phase quantification is obtained by the relative intensity between the diffraction patterns of each phase. The use of the Rietveld´s Method allows simulating the diffractogram with the present phases.

[1] Instituto Federal de São Paulo, Campus Caraguatatuba, Caraguatatuba (SP), Brazil.
[2] Departamento de Física, Universidade Estadual Paulista, Bauru (SP), Brazil.

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Martins Jr and Grandini[29] applied these two methods to study the influence of the addition of oxygen in the Ti–15Mo alloy, where it was observed that after successive rapid cooling for the introduction of oxygen, there was the formation of the α', which was quantified in percentage by weight in the microstructure by the Rietveld´s Method. In this paper, the size of the lattice parameters and the quantification of crystalline phases were analyzed.

Thus, the objective of this paper was to determine some structural parameters and phase quantification for the Ti–50Nb alloy.

MATERIALS AND METHODS

The samples used in this paper were alloys with 50% in weight of Nb. This alloy was produced in the Laboratório de Anelasticidade e Biomateriais da UNESP/Bauru, using an arc–voltaic furnace. The characterization of the samples was performed through semi–quantitative chemical analysis, density measurements, X–ray diffraction and, scanning electron microscopy. The samples were analyzed in the "as–cast" condition. Further details on chemical, structural and microstructural characterization can be obtained in Martins Jr et al.[30].

After melting were obtained ingot with a mass of 60 g and irregularly shaped (about 8 cm long by 2 cm wide). The mass variation was less than 0.1 g after melting. The chemical composition analysis was obtained by energy dispersive spectroscopy (EDS), using an Oxford, Inca model equipment. Density measurements were carried out with an Ohaus Explorer model analytical balance and a density determination kit, using the Archimedes' Principle. Ten measurements were made in each sample.

The samples were filed to obtain about 3.0 g of powder to fill the sample's support to perform the X–ray diffraction tests. After this step, the powders underwent magnetic separation using an AlNiCo magnet to remove iron fragments from the hand–file. The metallic powder was dispersing over the sample holder with care to avoid preferential orientation, which may cause interference in the quantitative analysis of the diffractogram. It affects the intensity of the peaks. The X–ray diffraction measurements were carried out using a Rigaku D/Max 2100/PC equipment with radiation Cu–Ka of λ = 1.544 Å, a fixed time mode with a step of 0.02, a permanence time of 1.6 s, and a scan of 10 to 100°.

X–ray diffractograms were analyzed by Rietveld´s Method using the General System Analyzer Structure (GSAS) program [31]. The sheets used to obtain crystallographic information were no. 644489–ICSD form for phase from the Inorganic Crystal Structure Database (ICSD) [32].

For the microstructural characterization, it was used a Carl Zeiss microscope, model EVO–LS15. The etching used to reveal the microstructure of the samples was a water solution of 20% HF and 5% HNO_3 [33], with an attack time of 30 seconds.

Microhardness tests were performed on a Shimadzu microdurometer HMV model–2, with a load of 1.96N for 60 s, based on standard technical ASTM–E384[34].

Results and Discussion

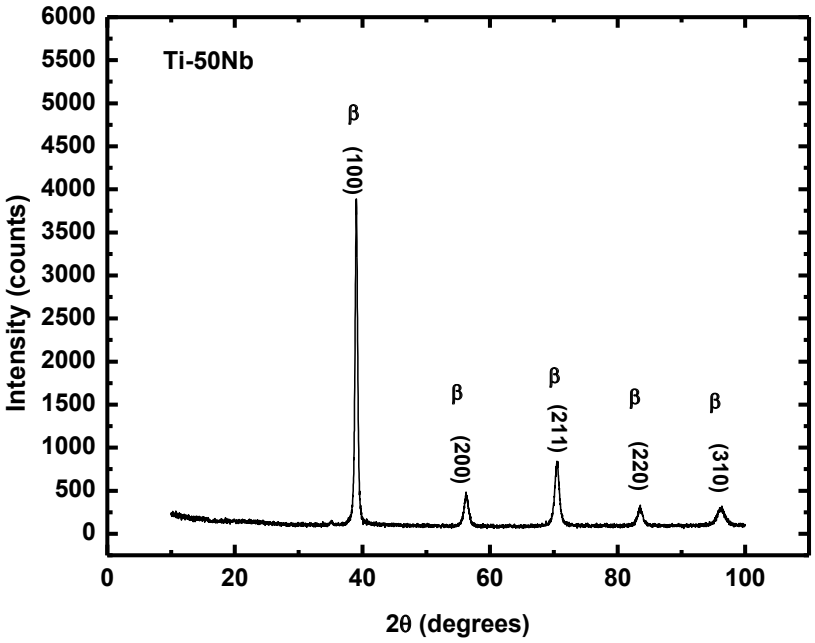
The chemical composition of the Ti–50Nb alloy is presented in Table 1 and shows the main elements found in the semi–quantitative chemical analysis of the samples using the EDS technique. An excellent agreement with the stoichiometric value for the amount of Ti and Nb elements can be observed. This slight difference to the nominal value can be explained by minor variations in Ti and Nb concentration along the sample surface. It is important to remember that the EDS technique is semi–quantitative [35]. Table 1 presents the density values obtained experimentally, using the Archimedes' Principle [36].

The values obtained for the density of the Ti–50Nb alloy are very

Table 1. Semi–quantitative chemical elements obtained by EDS and density results for as–cast Ti–50Nb alloy.

	Ti (wt%)	*Nb (wt%)*	*$\rho_{theoretical}$ ($g.cm^{-3}$)*	*$\rho_{experimental}$ ($g.cm^{-3}$)*
Ti–50Nb	***48.1 ± 0.2***	***51.9 ± 0.2***	***6.55***	***6.544 ± 0.003***

Figure 1 – X–ray diffractogram for the as–cast Ti–50Nb alloy.



close to the theoretical value, which is indicative that the nominal composition of the sample was satisfactorily obtained [37].

The results of X-ray diffraction measures for as-cast Ti50Nb alloy are shown in Figure 1.Similar results were obtained by Martins et al. [24] and Pereira et al. [25]. It can be observed that the diffraction patterns presented peaks typical of the b phase, with body-centered cubic structure [38].

From X-ray diffractograms, a series of information can be obtained. The position of the peaks provides the information on the dimensions of the unit cell, the crystalline system, and identification of the crystalline phases; the intensity of the peaks provides the contents of the unit cell and allows the qualitative analysis of the phases, while the shape and width of the peaks are related to the size of crystallites and defects in the crystalline structure [39]. For Ti-15Mo alloy, in three processing conditions (after melting, after swaging, and after stress relief heat treatment), the variation in peak intensities was observed. It was attributed to the increasing in a' phase concentration and parameters such as temperature and cooling time influenced the formation of this phase [40].

Figure 2 shows the results of X-ray diffraction for as-cast Ti-50Nb alloy, analyzed by the Rietveld´s Method, where it is possible to observe the optimal agreement of the calculated diffraction and that obtained experimentally, showing that refinement was performed in a very satisfactory way [29, 30, 41]. The diffractogram was analyzed only with one crystalline phase (b phase), as it was the best fit using Rietveld's Method. Thus, we indicate that it was impossible to identify the w phase in the studied sample based on the X-ray diffraction analysis.

Table 2 shows the main results of the analysis by the Rietveld

Figure 2 – X-ray diffractogram analyzed by Rietveld´s Method for the as-cast Ti-50Nb alloy.

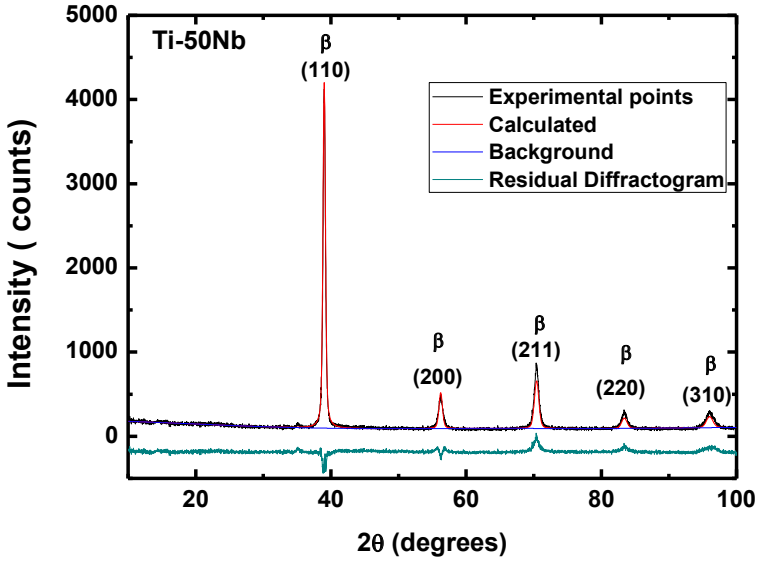
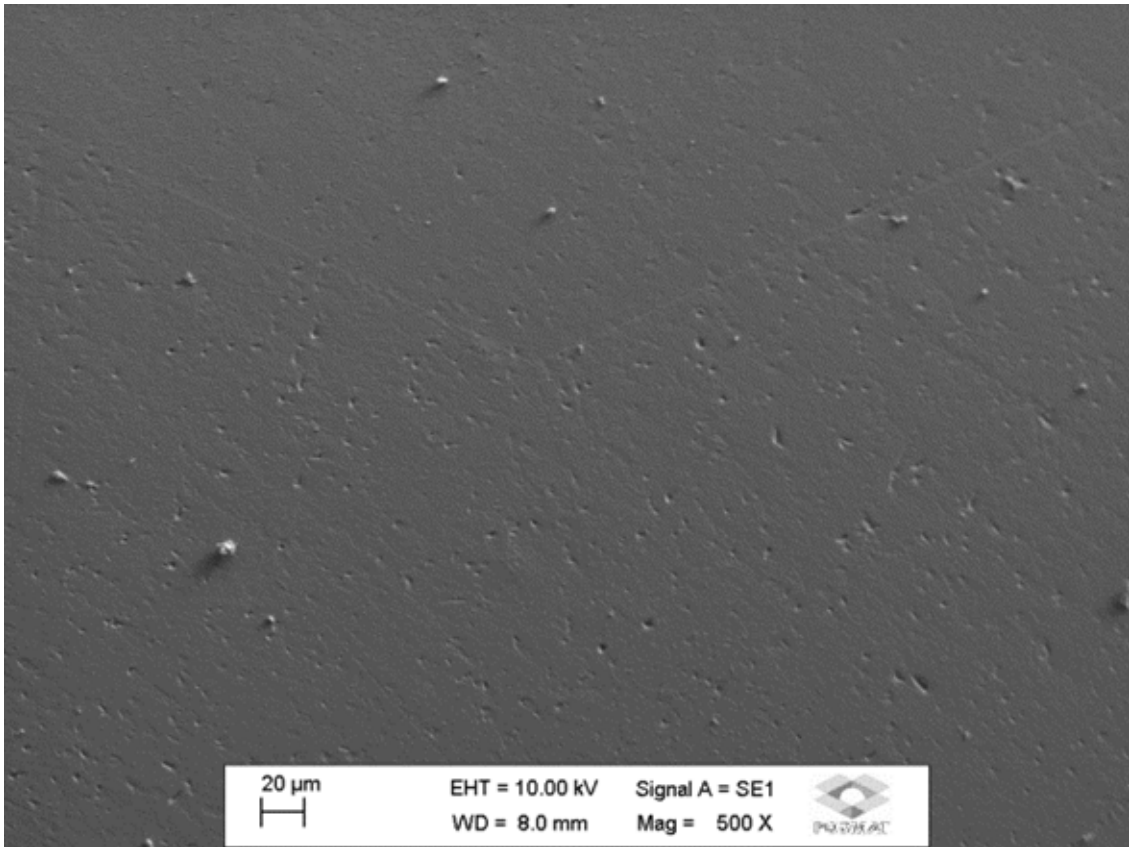


Table 2. Phase quantification and lattice parameter values obtained by Rietveld's Method.

	% β phase	*Lattice parameter (Å)*
Ti-50Nb	100	a=b=c = 3.2868 ± 0.0004

Figure 3 – SEM micrograph for the as–cast Ti–50Nb alloy.



Method. The results presented the only b phase, which is in accordance with Ozaki et al.[23], that establishes that needs more than 40 wt% of Nb for the complete b phase stabilization. As this alloy has 50 wt% of Nb, its crystalline structure is exclusively body–centered cubic (b phase).

Figure 3 shows an SEM micrograph for the as–cast Ti–50Nb alloy, where it is possible to observe only the presence of b phase, as already observed by several authors in the literature [37, 42–46]. In addition, in scanning electron microscopy, small and irregular grains characteristic of alloy can be observed in this condition.

The ω– phase was not observed in the X–ray diffraction measurements [47]. Another critical point is that when the w phase exists, there is a change in mechanical properties[48]. Lin et al.[49] reported metastable w phase and significantly higher hardness than in the samples that did not present w phase. It was also observed in Ti–based alloys that the amount of the w phase is directly proportional to the hardness of the alloy. That is, a decrease in this phase causes a decrease in hardness[50]. In the sample of this study, the hardness value was 195 HV, a low hardness value, compared to alloys that have the presence of w phase[51].

Conclusions

Ti–Nb binary alloy was produced with the Nb proportion of 50% in weight, using an arc–voltaic furnace, for application in the orthopedic field.

X–ray diffraction measurements show that the crystalline structure of the Ti–50Nb alloy is composed only by body–centered cubic (b phase).

The obtained SEM micrographs show only the morphology of the b phase, corroborating the results of X–ray diffraction.

The Ti–50Nb alloy presented a value of hardness around 195 HV, which is very attractive for implants.

Based on the structural, microstructural, and hardness analysis, his alloy is a promising material for use as biomaterials. It presents a crystalline structure and microstructure very interesting for thermomechanical processing. The hardness value found facilitates mechanical conformation in this way facilitating the production of orthopedic prostheses, allowing even production with more complex geometry. In this way the material produced presents new possibilities for the orthopedic area.

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