Development of Ti-13Nb-13Zr implants by powder metallurgy

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Keywords: Titanium alloys, Powder metallurgy, Sintering, Surgical implants

Abstract. The possibility of substituting of functionally damaged hard tissues like bone and teeth for hard tissue devices like artificial bones, artificial hip joints, artificial teeth and dental implants is growing. The goal of the present work is to apply the powder metallurgy technology to titanium implants production. Among the advantages of this approach is the higher dimensional precision and low material loss during parts production. In this work, results of the Ti-13Zr-13Nb microstructural development are presented. This alloy due its high biocompatibility and lower modulus of elasticity is a promising candidate for implants fabrication. Samples were produced by mixing of initial metallic powders followed by uniaxial and cold isostatic pressing with subsequent densification by sintering between 900-1600 °C, in vacuum. Sintering behavior was studied by means of dilatometry. Sintered samples were characterized for phase composition, microstructure and microhardness by X-ray diffraction, scanning electron microscopy and Vickers indentation, respectively. Density was measured by Archimedes method. It was shown that the samples were sintered to high densities and presented homogeneous microstructure. Niobium act as a beta- phase nucleator agent and the Widmanstätten structure grows with the dissolution of the niobium particles by the increase of the sintering temperature. A total homogeneous structure is only obtained after the complete dissolution of all the niobium particles.

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1- Introduction

The metallurgy of titanium and titanium-base alloys has been intensely investigated in the last 50 years. Titanium has unique properties like its high strength-to-weight ratio, good resistance to many corrosives environments, and can be used over a wide range of temperatures. Despite their great potential, the high production costs of titanium-based parts have limited their use, in most of the cases, to some very specific applications in aerospace and chemical industries

Titanium alloys are attractive materials for the manufacture of implants for medical applications due to their superior bicompatibility and outstanding corrosion resistance compared with other conventional metallic materials. Commercially pure titanium and Ti-6Al-4Nb alloy are the most used materials for the manufacture of implants. Due to controversy concerning potential toxic effects of vanadium and aluminum compounds, V-free alloys like Ti-13Nb-13Zr have been recently developed for biomedical applications.

Powder metallurgy (P/M) aims to transform metallic powders, using pressure and heat, by means of a thermal treatment (sintering) that substitutes the classic melting and that is carried out below the melting point of the most important metal [1]. The use of the P/M in the biomedical area is recent and its great advantage is the production of prosthesis near to the final format and possibly less expensive than the conventional processes [2].

For the production of titanium powders, normally, the hydride-dehydride process is used (HDH). This process, that is based on the embrittlement of metals for the hydrogen action, is preferential applicable to the zirconium, titanium and niobium, in reason of these metals to be capable to absorb great amounts of hydrogen in intermediate temperatures. Since that the solubility of hydrogen at 25 °C in these metals is very low, the hydrogen excess precipitates in the form of a fragile hydrate that is easily milled [3].

The titanium possesses great affinity for the hydrogen, carbon, nitrogen and oxygen elements that are formers of interstitial solid solutions. The presence of these elements tends to increase the hardness, the mechanical resistance and to decrease the ductility of the titanium alloys. For applications in implants, the titanium alloys must be in the range of the ELI degree (Extra Low Interstitial) that regulates the application of materials in the biomedical area [4].

The materials most common used in orthopedic prosthesis include stainless steel, cobalt based alloys and titanium alloys. The beginning of the commercial development of titanium in the 1940s was followed by its evolution as implant material. The titanium utilization tried a great growth during the 1970s. Until recently, the mainstream approach taken for the introduction of orthopedic materials has involved adaptation of existing materials, as exemplified by the use of Ti-6Al-4V ELI, an alloy originally designed for aerospace applications [3,4]. The development of specific alloys for applications in implants is due to the concerns by the raised potential citotoxicity of the vanadium and aluminum contained in the Ti-6Al-4V alloy. The vanadium accumulation in the organism results, mainly, in the irritation of the respiratory system. However, the aluminum absorption is also harmful, and its deleterious effects are associates at the neurological disorders, including Alzheimer [5].

Another goal would be the obtainment of alloys with low modulus of elasticity, next to the bone, that could simulate the action of tension distribution of the bone in the adjacent tissue [6]. Long-term experience indicates that insufficient load transfer from the artificial implant to the adjacent remodeling bone may result in bone resorption and eventual loosening of the prosthetic device [7]. These researches had provided a great interest in the production of biomaterials with low modulus of elasticity, having been established that the ideal titanium alloys for orthopedic applications must have low modulus of elasticity, high corrosion resistance and no toxic potential.

The biocompatibility performance of a metallic alloy is closely associated with its corrosion resistance and the biocompatibility of its corrosion products. Electrochemical measurements also confirmed the potency of Ti, Nb and Zr to develop highly protective passive layers, resulting in a much lower potential electrochemical interaction than Ti-6Al-4V. Finally, Nb and Zr exhibit ideal passivity and are not prone to chemical breakdown of the passive layer, exhibiting minimum passive dissolution rates. In fact, Nb and Zr contribute to the formation of a spontaneous highly protective passive film on titanium alloys and are not, as are Al and V, released into the environment as dissolved metal ions, but are rather incorporated into the passive layer [6].

The Ti-13Nb-13Zr alloy was recently developed and is classified as completely biocompatible. This titanium alloy presents low modulus of elasticity allied at the higher values of mechanical resistance [6,8]. This alloy is classified as near-β and its microstructure after water quenching consists of hcp martensite (α'). With subsequent aging, the Ti-13Nb-13Zr alloy consist of hcp martensite (α') and submicroscopic bcc beta precipitates. The dispersed beta precipitates strengthen and harden the material. This alloy in the aged condition present higher tensile strength, a lower modulus and higher toughness than the mill annealed Ti-6Al-4V [8].

In titanium alloys, the niobium stabilize the β-phase. This results in a lower β-phase transus temperature and, upon rapid cooling from β-transus temperature, the presence of a greater proportion of the β-phase titanium in the alloy microstructure. This enhances the ability of the alloy to harden on subsequent aging.

Niobium, when present in contents about 10 - 20 wt. % (preferably 13 wt. %) or in alternative range about 35 - 50 wt. %, produce a low modulus composition when alloyed with titanium. Deviation from theses ranges tends to increase the elastic modulus. Thus, the Ti-13Nb-13Zr alloy is believed to identify an optimal low modulus, titanium alloy composition. Other β-isomorphous stabilizers can be used, however, the niobium is preferred due to its effect in reducing the elastic modulus. Substitution with zirconium can improve strength [9].

The zirconium, considered a neutral element, is capable of stabilizing both α and β-phase titanium alloy, but acts by being in solution in the alloy as a β-stabilizer by slowing the transformation process in the inventive alloy. It is further believed that the larger ionic radius of zirconium (35% larger than that of titanium) help to disrupt ionic bonding forces in the alloy, resulting in some reduction in modulus of elasticity [10].

In ideal terms, an orthopedic prosthesis must satisfactorily function during all the life of the patient. For the majority of the existing prosthesis currently, the useful life varies among 5 to 15 years, indicating that the development of materials and processes that provide a larger useful life at lower cost assumes great importance for the effective rehabilitation of the patients.

Powder metallurgy (P/M) of titanium and Ti-based alloys may lead to the obtainment of components having weak-to-absent textures, uniform grain structure and higher homogeneity compared with conventional wrought products. Also, new P/M-based manufacturing techniques, including near-net-shape consolidation and metal injection molding (MIM) offer an increasing potential for the application of titanium and its alloys. This way, the production of the Ti-13Nb-13Zr alloy by P/M starting from blended elemental (BE) powders might be a cost-effective route considering its lower costs (a necessary prerequisite to expand the use of titanium and its alloys), versatility and also for allowing the manufacture of complex parts [11].

2. Experimental

The blended elemental method (BE) followed by a sequence of cold uniaxial pressing, cold isostatic pressing and vacuum sintering was chosen for the alloys preparation.

The blended elemental method (BE) followed by a sequence of cold uniaxial pressing, cold isostatic pressing and vacuum sintering was chosen for the preparation of the Ti-13Zr-13Nb alloy.

The hydride-dehydride process (HDH) was used for the elemental powders production. To the titanium powders, hydriding was carried out at 500°C in a vertical furnace for 3 hours under a positive pressure. After cooling to room temperature, the friable hydride was milled in a niobium container under vacuum (10^{-2} Torr). Niobium and zirconium powders were obtained using the same route, however, hydriding temperatures were significantly higher (800°C). All the powders were obtained by hydring process and used in the hydrided form, aiming at the reduction of costs and increase of the sintering rate. Tab. 1 shows the powders characteristics and Tab. 2 shows the chemical composition of the powders used in this investigation.

Table 1 - Characteristics of the powders used in the Ti-13Nb-13Zr alloy preparation.

Characteristic	Ti	Nb	Zr
Mean particle size (μm)	5	7	5
Morphology	Angular	Angular	Angular
Melting point (°C)	1670	2468	1850

Table 2 - Chemical composition of the powders used in this investigation.

Elemental powder	Impurity content (%)				
	N	O	C	Si	Fe
Ti	0,872	0,349	0,073	0,025	0,040
Nb	0,038	0,620	0,020	-	0,040
Zr	0,080	0,450	0,028	-	0,030

The starting powders were weighed in batches of about 4g and blended for 15 minutes in a double-cone mixer. After blending, the powders were cold uniaxially pressed under pressure of 60 MPa, in cylindrical 15 mm diameter steel die without lubricants. Afterwards, samples were encapsulated under vacuum (10^{-2} Torr) in flexible rubber molds and cold isostatically pressed at 350 MPa during 30 s in an isostatic press.

Sintering was carried out in niobium crucible in high vacuum condition (10^{-7} Torr), using a Thermal Technology Inc. model Astro 1000 equipment. Sintering temperatures ranged between 900 and 1500 °C and heating rates of 20 °C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 1 h and then furnace cooled to room temperature. Metallographic preparation was carried out using conventional techniques. Specimens were etched with a Kroll solution: 1,5 mL HF: 2,5 mL HNO_3 : 100 mL H_2O to reveal its microstructure. Microhardness measurements were carried out in Micromet 2004 equipment, Buehler, with load of 0.2 kgf. The micrographs were obtained using a SEM LEO model 435VPi. The specific mass of the sintered samples was determined by water immersion method, ASTM-C744-74. The X-ray analyses were carried out in a diffractometer Philips model PW-1837. Particle size distribution was determined by means of a laser-scattering equipment (Cilas model 1064).

3. Results and discussion

The samples have presented high densification, varying between 69 and 71% of the theoretical specific mass, after cold isostatic pressing and, between 93 and 95%, after sintering, with homogeneous microstructure. Ti-13Nb-13Zr alloy was recently developed and is classified as near-β. This titanium alloy presents low modulus of elasticity allied at the higher values of mechanical resistance. The microstructure analysis shows that the Widmanstätten structure grows with the dissolution of the niobium particles, that act as β-phase nucleator agent, by increase of the sintering temperature.

Fig. 1 presents the microstrutural evolution of the samples after sintering with nominal composition BE- Ti-13Nb-13Zr from 900 to 1600 °C. For specimens sintered at 900 °C, the microstructure consists of angular titanium particles (gray contrast) resembling their original morphology and niobium particles (brighter ones). Similar behavior has been also observed during heating of Ti-6Al-4V BE compacts.

At this temperature, the dissolution of niobium particles becomes evident. Niobium and titanium agglomerates (30-40 μm) are observed, indicating that the blending process must be optimized. The former angular-shaped niobium particles become rounded and have their size decreased with time. The boundaries between the angular Ti and Nb particles become diffuse at this temperature. The dissolution of zirconium particles in both α and β areas is fast, spreading with the temperature increase. The first two-phase areas resembling a Widmanstätten structure become distinguishable. These areas consist of a pure niobium core (a strong β-stabilizer in titanium alloys) surrounded by a two-phase microstructure. With increasing sintering temperature, the dissolution of the niobium particles continues with consequent increase in the volume fraction of the two-phase structure.

The dissolution of niobium particles is very fast and at 1000 °C there are few regions without a two-phase microstructure. In the temperature range 900-1300 °C, the most noticeable microstructural features are the spreading of the α+β structure and the chemical homogenization of the alloy. Until 1300 °C, few α phase areas are still present indicating that the homogenization of the alloy is still incomplete. The larger niobium particles present in the initial powder size distribution are found almost dissolved in the core of the Widmanstätten-like structure, whereas the finer ones have vanished in the microstructure. At the higher sintering temperature (> 1500 °C), individual niobium particles are found completely dissolved. The plate-like α structure and intergranular β structure is predominant and chemical composition is reasonably homogeneous throughout the microstructure (at SEM resolution level). It does not exclude the possibility of very fine particles in the nm-range coexist in the microstructure. Further TEM investigation is necessary to clear this point.

The specimens of the Ti-13Nb-13Zr alloy sintered at high temperatures display a fine plate-like α structure and intergranular β, resulting of the slow cooling from the β field. A few remaining pores are still found and density above 90% for specimens sintered in temperatures above 1400 °C.

Above 1500 °C, a homogeneous microstructure, consisting of α plates (Widmanstätten) and hcp-martensite (α') dispersed in intergranular β–matrix is observed. The martensite presence seems to demonstrate that the alloy is more likely an α+β alloy instead of a near-β alloy. The final microstructure is defined by the control of the β phase precipitation in the cooling, that can be retained, to transform into martensitic structures or then allotropicly transform into the α phase. Concerning the alloy microstructure, the dark-contrasting areas are α-phase plates. The β-phase, present among the -phase areas, gives rise to a white contrast.

The samples presented hardness values around 300 HV, next to the observed in samples produced by the conventional methods (melting).

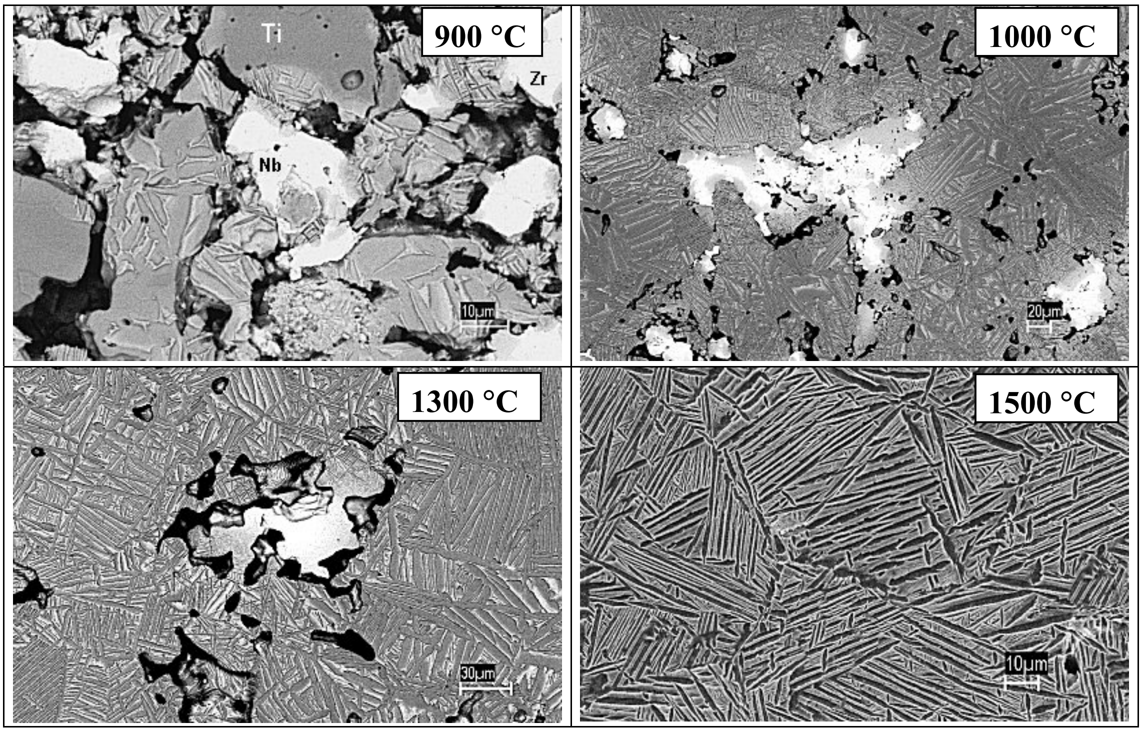

Figure 1- Microstructural evolution of the BE-Ti-13Nb-13Zr during sintering . All samples were sintered at the nominal temperature for 1 h and heating rate equal to 20 °C min^{-1}.

Results of EDS analyses reveal no appreciable changes in terms of Ti, Zr and Nb contents during sintering of this alloy. The nominal composition was kept nearly unchanged even in specimens sintered at 1600 °C for 1 h. A slight decrease in the final Zr content was observed lying close to 12.7 wt.% (12.5-14 % is the range specified in ASTM F1713).

The Fig.2 shows α and β areas (at 1500 °C) where the EDS analyses were carried out. Tab. 3 presents the result of the quantitative analysis of the elements.

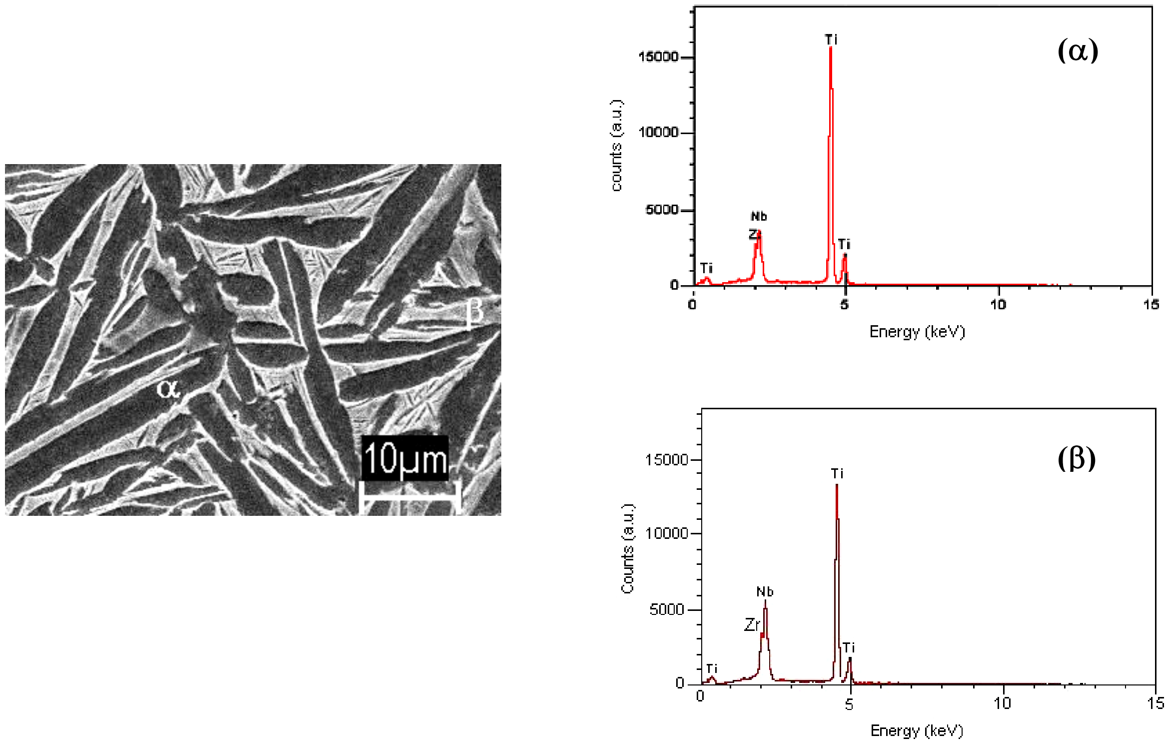

Figure 2- α and β phase areas analyzed for EDS in Ti-13Nb-13Zr alloy.

Table 3- Ti, Nb e Zr contents in α and β areas analyzed (EDS).

Site	Ti (wt. %)	Nb (wt. %)	Zr (wt. %)
(1) β-phase	62.65	22.09	15.26
(2) α-phase	85.27	15.03	9.69

Tab. 2 indicates a superior niobium content in β-phase, due its power of preferential stabilization of this phase. However, although the niobium, in compositional terms, can be considered a neutral element, it strongly acts in the β-phase stabilization, significantly decreasing the β-transus temperature.

X-ray diffraction analysis revealed only peaks of the α and β titanium phases, not being identified peaks related to the hydride, oxide or intermetallics (Fig. 3).

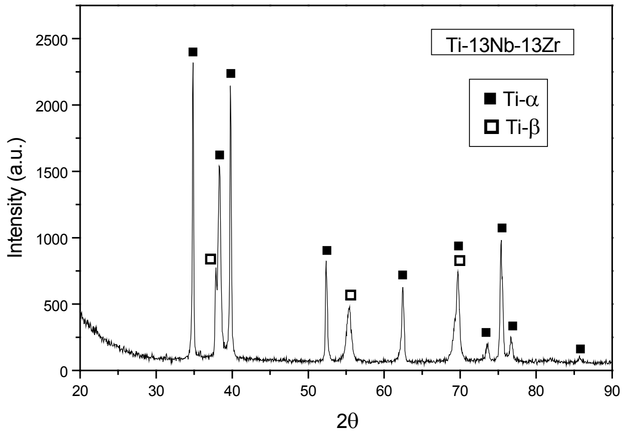

Figure 3- X-ray of Ti-13Nb-13Zr alloy spectra after sintering at 1500 °C.

The expansion/contraction behavior of a Ti-13Nb-13Zr compact during sintering was examined by a dilatometer. The result is shown in fig. 4. Up to 400 °C, the compact expanded slightly as temperature increased. The contraction begins from 500 ºC. Densification continued up to 1200°C and overall contraction exceeding 11% was achieved. The contraction starts in a low temperature when compared with others titanium alloys sintered from dehydrided powders [12]. This fact indicates the influence of hydrogen atoms in the sintering mechanisms providing a contraction even in low temperatures when hydrided powders are used.

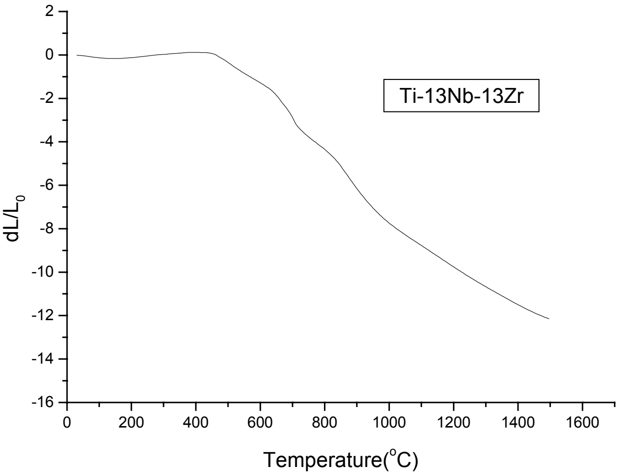

Figure 4- Expansion/contraction behavior of a Ti-13Nb-13Zr compact heated until 1400 °C.

4. Conclusions

1- The blended elemental P/M process demonstrated to be efficient for the production of the Ti-13Nb-13Zr Alloy. The samples had presented high densification and adequate microstructure. Due the complete dissolution of the alloys elements in the titanium matrix, a good combination of microstructure, mechanical properties and densification could be reached. The sintering parameters provided a homogeneous microstructure, with low porosity and contamination. Higher sintering temperatures or longer holding times can lead to intensive grain growth. The first two phase areas ($\alpha+\beta$) are formed at 900 °C, with the dissolution of the smaller niobium particles. Niobium act as a β-phase nucleation agent, consequently, the Widmanstätten structure grows with the dissolution of the Nb particles by the increase of the sintering temperature. A total homogeneous structure is only obtained after the complete dissolution of all the Nb particles at 1500 °C. The presence of martensite in as-sintered Ti-13Nb-13Zr alloy indicates that the alloy is more likely an $\alpha+\beta$ alloy instead of a near-β alloy. The hydrogen removal during sintering provides shrinkage from low temperatures promoting low porosity in the samples sintered at 1500 °C. The high densification reached demonstrates not to be essential a hot pressing stage for the parts production in applications where it is not necessary high mechanical properties and performance. The hardness values observed in the samples are within the range used in commercially manufactured parts produced by powder metallurgy techniques.

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