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Production of a Low Young Modulus Titanium Alloy by Powder Metallurgy

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Titanium alloys have several advantages over ferrous and non-ferrous metallic materials, such as high strength-to-weight ratio and excellent corrosion resistance. A blended elemental titanium powder metallurgy process has been developed to offer low cost commercial products. The process employs hydride-dehydride (HDH) powders as raw material. In this work, results of the Ti-35Nb alloy sintering are presented. This alloy due to its lower modulus of elasticity and high biocompatibility is a promising candidate for aerospace and medical use. Samples were produced by mixing of initial metallic powders followed by uniaxial and cold isostatic pressing with subsequent densification by isochronal sintering between 900 up to 1600 °C, in vacuum. Sintering behavior was studied by means of microscopy and density. Sintered samples were characterized for phase composition, microstructure and microhardness by X-ray diffraction, scanning electron microscopy and Vickers indentation, respectively. Samples sintered at high temperatures display a fine plate-like α structure and intergranular β. A few remaining pores are still found and density above 90% for specimens sintered in temperatures over 1500 °C is reached.

Keywords: *powder metallurgy, titanium alloys, modulus of elasticity, near-net-shape*

1. Introduction

Titanium and its alloys provide high strength-to-weight ratios, good fatigue strength and increased corrosion resistance compared with others materials. Its acceptance in aerospace and medical application has been limited by costs considerations such as high cost of raw material, high buy-to-fly ratios (as high at 15:1), and expensive machining operations[1]. Significant cost reductions can be obtained by vacuum hot pressing (VHP) and powder metallurgy (P/M) techniques by producing near net shapes and consequently minimizing material waste and machining time[2-4].

Titanium alloys exhibit a low modulus of elasticity which is roughly half that of steels and nickel alloys. Materials with high flexibility (i.e. low elastic modulus) present reduced bending and cyclic stresses in deflection-controlled applications, making it ideal for springs, bellows, body implants, dental fixtures, dynamic offshore risers, drill pipe and various sports equipment[5-6]. Titanium's inherent nonreactivity (nontoxic, nonalergic and fully biocompatible) with the body and tissues has driven its wide use in body implants, prosthetics devices and jewelry, and in food processing. Stemming from the unique combination of high strength, low modulus of elasticity and low density, titanium alloys are intrinsically more resistant to shock and explosion damages (military applications) than most other engineering materials[7-8].

P/M techniques offer the advantage of manufacturing near net shapes products with a considerable increase in the materials utilization factor in the case of titanium alloys. The P/M blended elemental technique (BE) can attain high relative density, over 99.5%, making use of high diffusivity of titanium powder during sintering, resulting in excellent mechanical properties. Its main advantage over others powder metallurgy methods is the elimination of the high production costs from expensive techniques (such as hot isostatic pressing) for the obtainment of high densification level[9-10].

The Ti-35Nb alloy is being evaluated for aerospace and implant applications by Centro Técnico Aeroespacial (CTA)[11]. Ti-35Nb (β-titanium alloy) can retain a fine beta grain structure after solution annealing at 800 °C with rapid quenching. Ti-35Nb has excellent corrosion resistance, however, its tensile strength (in annealed condition) is lower than that of the Ti-6Al-4V alloy but comparable of C.P. (commercial purity) titanium, grade 4. Furthermore, the mechanical properties of the alloy can be increased by heat treatments[12].

This work presents results about the Ti-35Nb development by P/M aiming its effective utilization in aerospace aplications and orthopedic implants. The main contribution is on the microstructural development searching the establishment of an optimized microstructure, adequate for the mechanical requirements. The P/M technique allows the production of porous implants, an interesting characteristic when optimized osteointegration conditions is required.

2. Experimental

The blended elemental method (BE) followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering was chosen for the preparation of the alloy.

Titanium powder was obtained by the hydride-dehydride technique (HDH). 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 without protecting atmosphere. The dehydriding stage was carried out at 500 °C in dynamic vacuum conditions. Nb powder was obtained using the same route, however, hydriding-dehydriding temperatures were significantly higher (800 °C). Table 1 shows the characteristics of the elemental powders used in the production of Ti-35Nb samples.

The starting powders were weighed (5 grams) and blended for 15 minutes in a double-cone mixer. After blending, powders were cold uniaxially pressed (80 MPa), in cylindrical 15 mm diameters steel dies. Afterwards, samples were encapsulated, under vacuum, in flexible rubber molds and cold isostatically pressed (CIP) at 300 MPa during 30 seconds in an isostatic press.

Sintering was carried out in titanium crucible in high vacuum condition (10^{-6} Torr), using a Thermal Technology Inc. model Astro 1000 equipment. Sintering temperatures ranged between 900 up to

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1600 °C and heating rates of 20 °C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 1 hour and then furnace cooled to room temperature. Metallographic preparation was carried out using conventional techniques. Specimens were etched with a Kroll solution: (3 mL HF: 6 mL HNO_3: 100 mL H_2O) to reveal its microstructure. Microhardness measurements were carried out in a Micromet 2004 equipment, Buehler, with load of 0.2 kgf. The photomicrographs were obtained using a SEM LEO model 435 VPi. The density of the sintered samples was determined by the Archimedes method.

3. Results and Discussion

The Ti-35Nb samples presented high densification, around 70% of the theoretical density, after cold isostatic pressing and, among 93 and 95%, after sintering above 1600 °C, with homogeneous microstructure.

Ti-35Nb alloy was recently developed and is classified as β-rich titanium phase[12]. This titanium alloy presents low modulus of elasticity with high values of mechanical resistance after heat treatment (solubilizing and aging). The microstructure analysis shows a microstructure typically Widmanstätten (α + β) growing with the dissolution of the niobium Nb particles that act as β-phase nucleator agent, by increase of the sintering temperature.

Figure 1 presents the microstructural evolution of the samples after isochronal sintering with nominal composition BE-/Ti-35Nb from 900 up to 1600 °C. Concerning the alloy microstructure, the dark-contrasting areas are α-phase plates. The β-phase, present among the α-phase areas, gives rise to a white contrast.

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 1000 °C, the dissolution of niobium particles is evident, since the former angular-shaped niobium particles become rounded and their sizes decrease with time. The boundaries between the angular Ti and Nb particles become diffuse at this temperature. 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.

At 1100 °C, there are few regions without a two-phase microstructure indicating a high dissolution of niobium particles. 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. 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 (> 1600 °C), individual niobium particles are found completely dissolved. The homogenous microstructure resulting of the slow cooling from the β field is constituted of fine plate-like α structure dispersed in a β-matrix and the chemical composition is reasonably homogeneous throughout the microstructure (at SEM resolution level). 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 into the α phase, in an allotropic way. A few remaining pores are still found and density above 95% of theoretical is obtained.

The hardness values of the samples sintered between 900 up to 1600 °C is increased in function of the sintering temperature, staying in the range from 100 to 300 HV. Samples sintered at 1600 °C presented hardness values around (300 ± 10) HV, next to the observed in samples produced by the conventional methods[12]. In general, the density and microhardness of sintered materials increase when the sintering temperature is raised, because the sintering at higher temperatures promotes additional particle-to-particle bonding and more complete alloying due to the higher diffusion rates and mass transport[9].

Results of EDS analyses reveal no appreciable changes in terms of Ti and Nb contents during sintering of this alloy. The nominal composition was kept nearly unchanged even in specimens sintered at 1600 °C for 1 hour. The Figure 2 shows stabilized β areas (in samples after sintering at 1300 °C and 1600 °C) where the analyses for EDS were carried out. Table 2 presents the result of the semi-quantitative analysis of the elements.

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 (Figure 3). It does not exclude the possibility of very fine Nb particles in the nm-range coexist in the microstructure. Further TEM investigation is necessary to clear this point.

4. Conclusions

- The results show that the blended elemental P/M process leads to the obtainment of low porosity specimens (95% of theoretical density). The predominant microstructure found in specimens sintered above 1500 °C is Widmanstätten-like consisting of fine plate-like α with intergranular β;
- The microstructural evolution observed during isochronal sintering indicates an combination of densification and optimization microstructure reached because the complete dissolution of the β stabilizer (Nb) in the titanium matrix;
- The formation of two phase areas (α + β) begins at 900 °C, with the dissolution of the smaller niobium particles. Niobium act as a β-phase nucleator 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;
- 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;
- Since the mechanical properties is influenced by the porosity, the high densification reached in the Ti-35Nb specimens demonstrates not to be essential a hot pressing stage to the parts production with densification bellow 95% of theoretical

Table 1. Characteristics of the powders used in the Ti-35Nb alloy preparation.

Characteristic	Ti	Nb
Mean particle size (μm)	15	20
Particle morphology	Angular	Angular
Melting point (°C)	1670	2468

Table 2. Ti and Nb contents in α and β areas analyzed in the Figure 2 (EDS).

	Ti (wt. (%))	Nb (wt. (%))
(1) 1300 °C	64.93	35.07
(2) 1600 °C	62.00	37.98

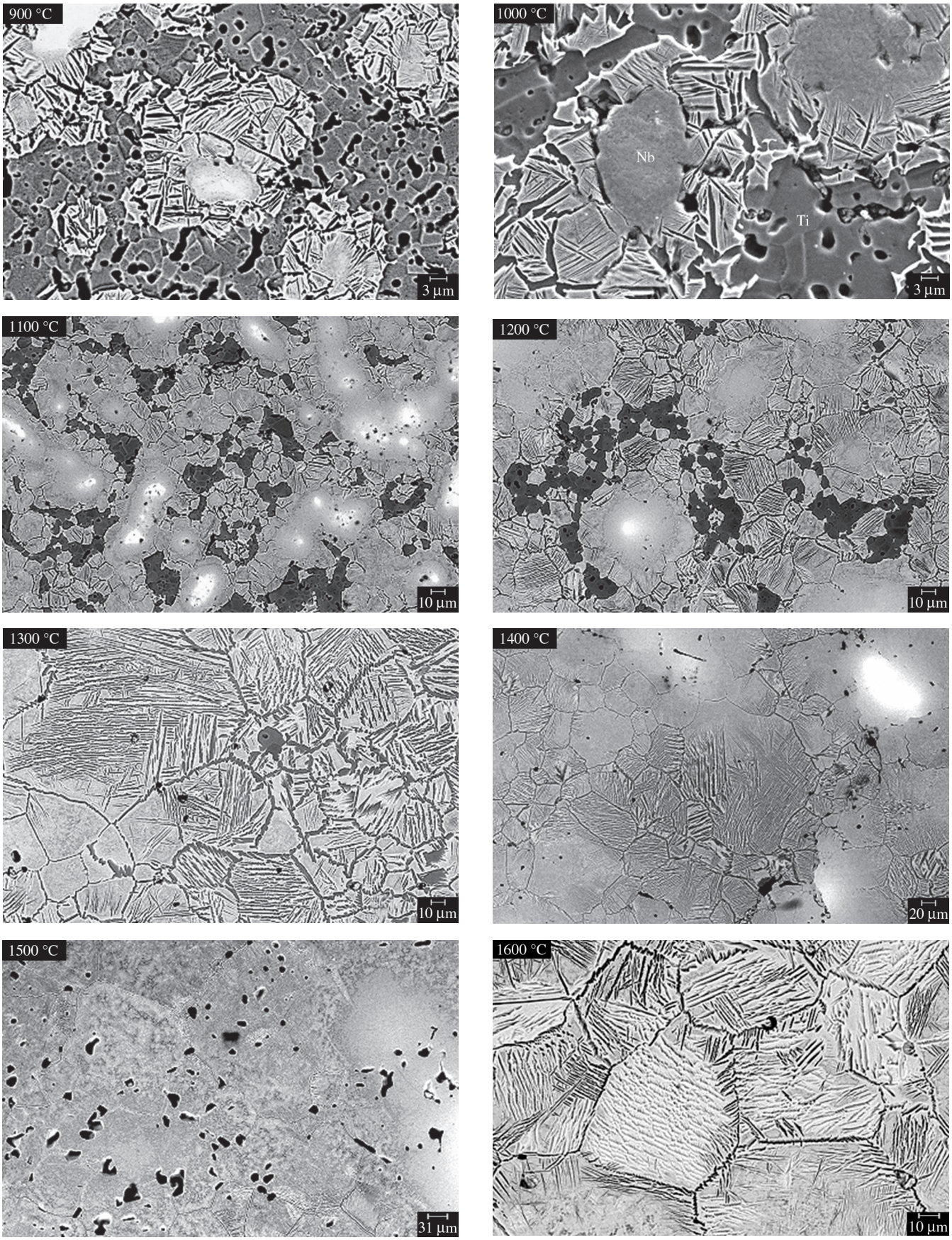
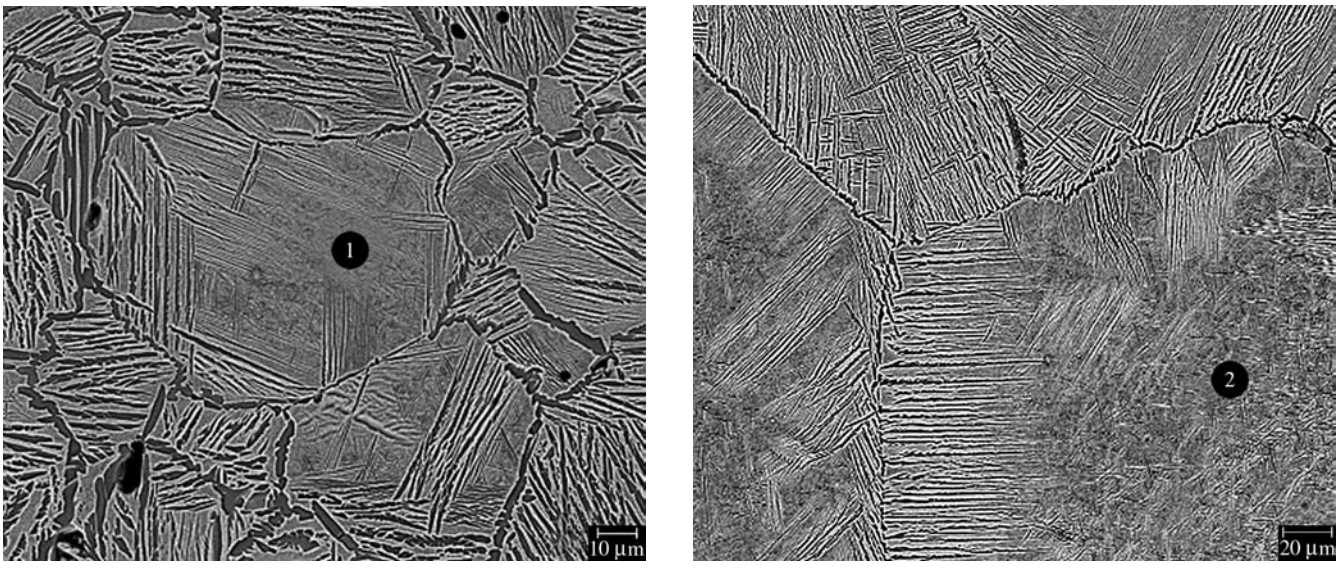


Figure 1. Microstructural evolution of the BE-Ti-35Nb during sintering. All samples were sintered at the nominal temperature for 1 hour and heating rate equal to 20 °C/min^{-1}.



(a) 1300 °C (b) 1600 °C

Figure 2. β-phase areas analyzed for EDS in the samples of Ti-35Nb alloy sintered at 1300 °C and 1600 °C.

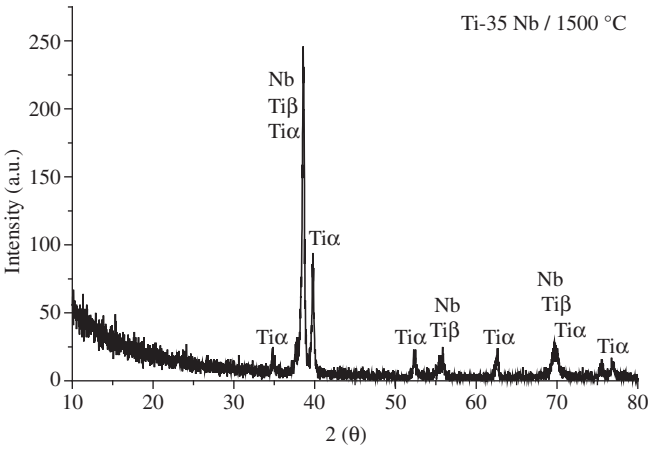


Figure 3. X-ray diffraction pattern of Ti-35Nb alloy spectra after sintering at 1500 °C.

density; and

- Due to the additional particle-to-particle bonding and high diffusion rates and mass transport, the hardness values of the samples increase in function of the sintering temperature. Samples sintered above 1600 °C presented hardness values near the range observed in samples produced by conventional methods.

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