PRODUCTION OF TI-13Nb-13Zr FROM HYDRIDED POWDERS

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Keywords: powder metallurgy, titanium alloys, near-net-shape.

Abstract Titanium alloys parts are ideally suited for advanced aerospace systems and surgical implants because of their unique combination of high specific strength at both room temperature and moderately elevated temperature, in addition to excellent corrosion resistance. Despite these features, use of titanium alloys is limited by cost. The alloys processing by powder metallurgy eases the obtainment of parts with complex geometry. In this work, results of theTi-13Nb-13Zr alloys production are presented. Samples were produced by mixing of initial metallic powders followed by uniaxial and cold isostatic pressing with subsequent densification by sintering between 900 up to 1500 °C, in vacuum. Furthermore, a comparative study involving the utilization of hydride and dehydrided powders and hot pressing was investigated. The samples were characterized for phase composition, microstructure and microhardness by X-ray diffraction, scanning electron microscopy and Vickers indentation, respectively. It was shown that the samples sintered with hydrided powders presented the best microstructural and densification resultys.

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1. Introduction

As far as structural or mechanical compatibility is concerned, metals and alloys are suitable for applications to hard tissues such as artificial hip joints because of their good mechanical properties. Among various metallic biomaterials, Ti and its alloys are most widely used because of its excellent corrosion resistance, biocompatibility and high strength-to-weight ratio. However, one of the major problems concerning metallic implants in orthopedic surgery is the mismatch of Young's modulus between the bone (10–30 GPa) and metallic implants (110 GPa for Ti). Bone is insufficiently loaded due to the mismatch, as called "stress-shielding". In general, Young's modulus of most metals is at least 10–20 times higher than those of hard tissues. Many investigators have shown that the stress-shielding retards bone remodeling and healing, which results in increased bone porosity [1]. One way to alleviate the problem is, therefore, to reduce Young's modulus of metallic materials by the use of new low modulus materials or/and introducing pores, thereby minimizing damages to tissues adjacent to the implant and eventually prolong device life time. In addition, bone/implant fixation is achieved by interdigitation between bone and porous implant matrix. The roughened surface geometry of porous implant promotes bone ingrowth into the pores and provides not only anchorage for the fixation but also a system which enables stresses to be transferred from the implant to the bone [2].

The use of titanium and its alloy as biomaterial is increasing due to their low modulus, superior biocompatibility and enhanced corrosion resistance when compared to more conventional stainless steel and cobalt-based alloys. These attractive properties have been a driving force for the early introduction of commercially pure titanium and Ti–6Al–4V alloy. However, in recent years, vanadium has been found to cause cytotoxic effects and adverse tissue reactions, while aluminium has been associated with potential neurological disorders [2].

Hence, new alloys that do not contain these elements are receiving a great deal of attention. Alloys containing elements such as Nb, Zr, Ta, Pt and Ti are being evaluated extensively since these are the only five elements which have been identified as producing no adverse tissue reaction [2,3]. Ti–13Nb–13Zr is one such alloy which has shown great promise [3]. It possesses low modulus, improved biocompatibility, improved corrosion and wear resistance. Apart from the composition, performance of the alloys is greatly influenced by the microstructure. The microstructure in titanium alloys can be controlled by thermomechanical treatment. In the present work, the effect of hydrided and dehydrided powders in the Ti-13Nb-13Zr sintering was investgated. Furthermore, the densification and microstructural features between hot pressing and pressureles sintering were compared aiming optimized final properties.

Ti-13Nb-13Zr is a high strength, low modulus and biocompatible alloy. Implants of this alloy have a modulus of elasticity closer to that of bone than other typically-used metal alloys and do not include any elements which have been shown or suggest as having short term potential adverse effect. Ti-13Nb-13Zr is classified as a near-β titanium alloy [4].

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. 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 [4].

2. Experimental

Ti-13Nb-13Zr samples were produced blended elemental method followed by a sequence of uniaxial and cold isostatic pressing with subsequent densification by sintering or hot uniaxial pressing.

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). During the process contents of hydrided and dehydride were collected for the experiments.Table 1 shows the principal characteristics of those powders.

Table 1 - Characteristics of the powders used in the alloys preparation.

Characteristic	Ti	Nb	Zr
Mean particle size (μm)	5	7	5
Morphology	Angular	Angular	Angular

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 dia.-dies. Afterwards, samples were encapsulated under vacuum in flexible rubber molds and cold isostatically pressed (CIP) at 300 MPa during 30 s in an isostatic press.

Sintering was carried out in titanium crucible in high vacuum condition (10^{-7} Torr), using a Thermal Technology Inc. model Astro 1000 equipment. Sintering temperatures ranged between 900 and 1600 °C and heating rates of 20 °C/min. Hot pressing was carried out with 20 MPa of compaction pressure in graphite dies. 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: (3mL HF: 6mL 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 micrographs were obtained using a SEM LEO model 435 VPi. The density of the sintered samples was determined by the Archimedes method. The expansion/contraction behavior of a Ti-13Nb-13Zr compact during sintering was examined by a dilatometer, where a green compact with a 6 mm diameter and a 15 mm length was heated in vacuum of the 10^{-3} Torr from room temperature to 1400 °C at a rate of 20 °C.

3. Results and Discussion

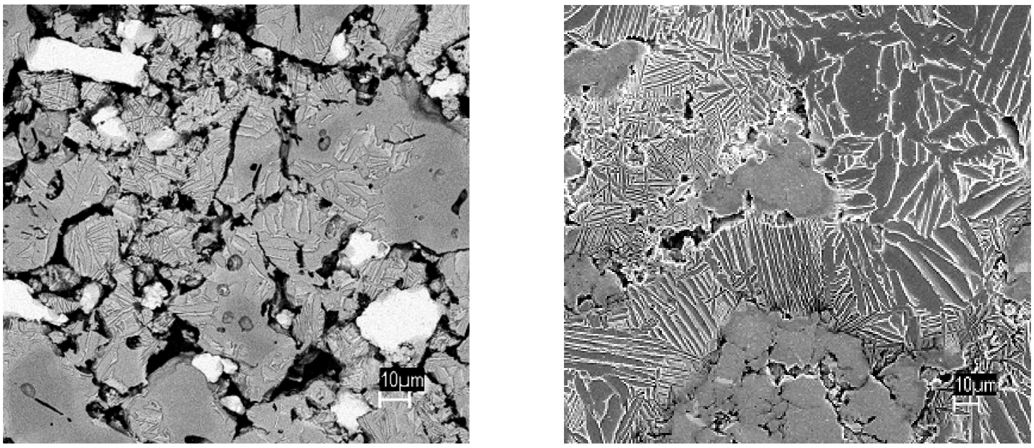
The samples presented densification around 70% of the theoretical specific mass, after cold isostatic pressing, around 95%, after sintering and above 97% after hot pressing, with homogeneous microstructure.

Fig. 1 presents the microstrutural evolution of the samples after sintering with nominal composition Ti-13Nb-13Zr from 900 to 1500 °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). At this temperature, the dissolution of niobium particles becomes evident. The former angular-shaped niobium particles become rounded and have their size decreased with time. 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.

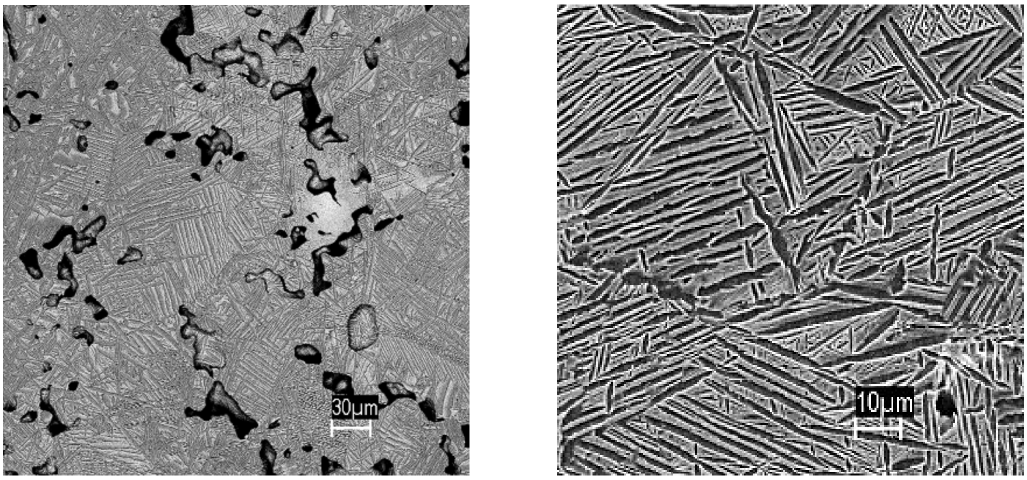
In the temperature range 900-1300 °C, the most noticeable microstructural features are the spreading of the $\alpha+\beta$ structure and the chemical homogenization of the alloy. Until 1300 °C, few α phase areas are still present indicating that the homogenization of the alloy is still incomplete. The 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.

Fig.2 presents the microstrutural evolution of the samples of Ti-13Nb-13Zr alloy after uniaxial hot pressing at 900, 1100 and 1300 °C. The microstructural development follows the same mechanism descripted for the samples obtained by sintering. The most noticeable microstructural features are the faster spreading of the $\alpha+\beta$ structure and the chemical homogenization of the alloy; and pore elimination compared to the sintering process. These characteristics were obtained by the combination of high pressure and temperature, improving the transport mechanisms and pore elimination. The drawback of the process is the presence of titanium carbides from the graphite dies contamination due the titanium high reactivity.

Sintered samples presented hardness values around 300 HV, next to the observed in samples produced by the conventional methods (melting). The hardness values of hot pressed samples were around 350 HV, probably due to the carbon contamination.



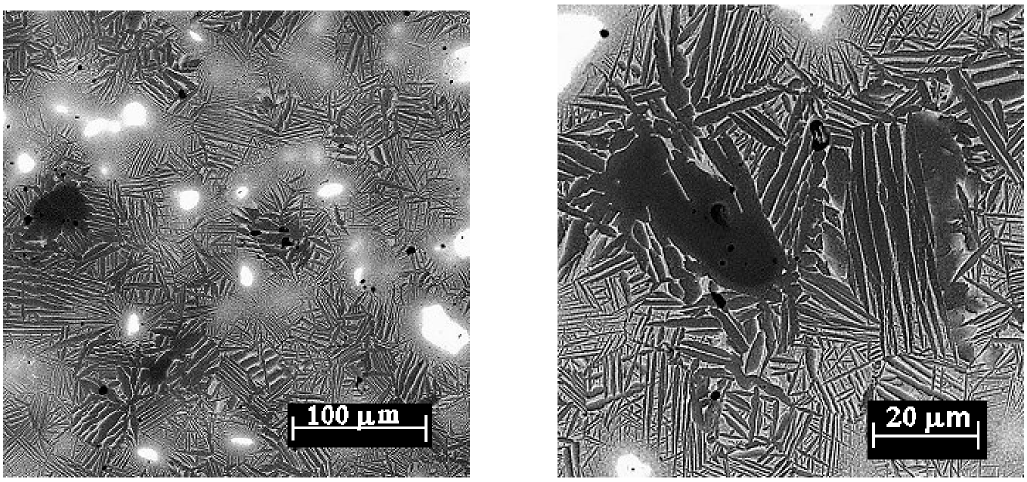
(a) 900 °C (b) 1100 °C



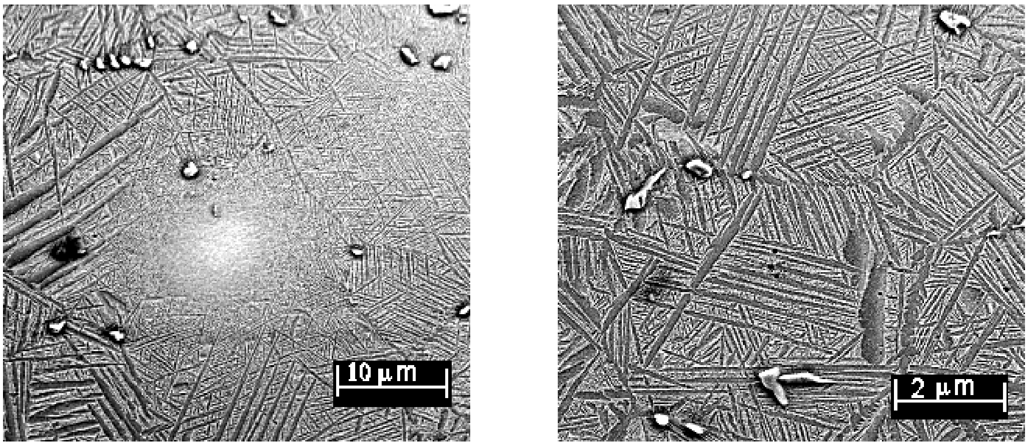
(a) 1300 °C (b) 1500 °C

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}.

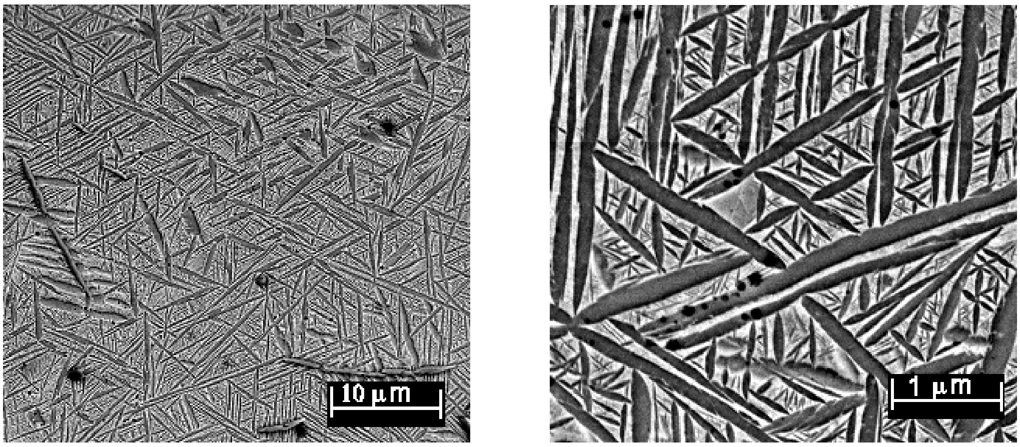
X-ray diffraction analysis revealed only peaks of the α and β titanium phases, not being identified peaks related to the hydride, oxide or intermetallics (Fig. 3a). The expansion/contraction behavior during sintering of a Ti-13Nb-13Zr compact using hydrided and dehydrided powders were investigated by a dilatometer. The results are shown in Fig. 3b. In the Ti-13Nb-13Zr sample produced with dehydrided powders, the compact expanded slightly as temperature increased. At 800 °C, contraction owing to densification started. This temperature is close to the β transus temperature of titanium powders. Since the diffusivity of β titanium is much higher than that of α titanium, it is speculated that mutual diffusion between titanium and the other elemental powders is activated through the range of temperatures at which titanium is β phase. Densification continued up to 1200°C and overall contraction exceeding 6% was achieved. In the a slightTi-13Nb-13Zr sample produced with hydrided powders after expansion, The contraction begins from 440 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 [15]. This fact indicates the influence of hydrogen atoms in the sintering mechanisms providing a contraction even in low temperatures.



(a) 900 °C

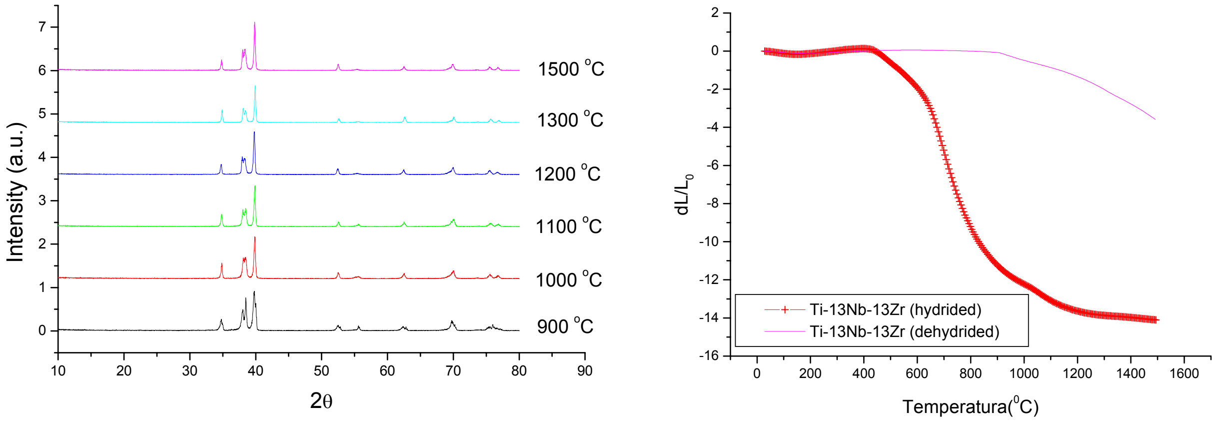


(b) 1100 °



(c) 1300 °C

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



(a) (b)

Figure 3- (a) X-ray of Ti-13Nb-13Zr alloy spectra after sintering between 900 to 1500 °C and (b) Expansion/contraction behavior of a Ti-13Nb-13Zr compact heated up to 1500 °C using hydrided and dehydrided powders.

CONCLUSIONS

The Ti-13Nb-13Zr processing by sintering (above 1500 °C) results in the obtainment of a Widmanstätten microstructure throughout the samples with chemical homogeneity. The samples present a low volume fraction of coarse spherical pores. Due to the combination of high pressure and temperature, samples processed by uniaxial hot pressing presented a faster spreading of the α+β structure, desification and chemical homogenization (at 1300 °C), however, a carbon contamination was observed. For both process, niobium act as a β-phase initiator agent, consequently, the Widmanstätten structure grows with the dissolution of the Nb particles by the increase of the sintering temperature. The dilatometric analysis showed that the alloy processing from hydrided powders is more efficient due to acceleration in the sintering mechanisms by the influence of hydrogen atoms movement with high densification rate at low temperatures (400 up to 1000°C).

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