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MICROSTRUCTURAL EVOLUTION OF Ti-13Nb-13Zr ALLOY DURING SINTERING

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

Abstract With the prolonged average duration of life, there is an increase concern for repair of bone, joints and teeth which deteriorated and lose their functions. Thus, research of artificial materials for implants has assumed an important role in the implants development. The trend of the current research in orthopedic implants is based in the development of titanium alloys with low modulus of elasticity, next to the bone, and toxic elements free. In this work, results of the Ti-13Zr-13Nb alloy sintering 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 800 at 1500 °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 from the elements dissolution. Processing parameters were optimized in order to reduce the interstitial pick-up (O, C, N and H) and to minimize grain growth during sintering.

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

1. Introduction

Titanium-based alloys are widely used as load-bearing orthopedic implants, due to their relatively good fatigue resistance and biological passivity. One of the examples is the application of Ti–6Al–4V as femoral stems in total hip replacements. However, these materials still suffer from a large degree of biomechanical incompatibility, due to their relatively high elastic modulus (about 120 GPa), compared with that of the bone (max. 30 GPa) [1].

When used as a hip implant, titanium overtakes a considerable part of the body loading, which shields the bone from the necessary stressing required to maintain its strength, density, and healthy structure. Such an effect, usually termed as “stress shielding”, eventually causes bone loss, implant loosening, and premature failure of the artificial hip [2]. Moreover, the existing alloys can also release toxic ions (e.g. V and Al) into the body, leading to undesirable long-term effects. These result in the current implant life being around 10–15 years in vivo, whereas a desirable implant should last as long as the patient’s life span, without causing any discomfort to the patient. The ideal material should possess good strength, high fatigue resistance, and a low elastic modulus [3].

Considerable efforts have been devoted by materials engineers to enhance the yield strength and to reduce the modulus. Any reduction in the stiffness of the implant, for example, through substitution of present orthopedic alloys with newer, lower modulus materials, is expected to enhance stress redistribution to the adjacent bone tissues, therefore minimizing stress shielding and eventually prolonging device lifetime. Up to now, some new β and (α+β) type titanium alloys, such as Ti 15Mo–5Zr–3Al, Ti–5Al–2.5Fe, Ti–6Al-7Nb [4,5] and Ti–13Nb–13Zr [6], have been developed for applications as medical implants.

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 [7].

Studies of the biological behavior of metallic elements have shown that the composition of biomaterials should be carefully developed to minimize adverse body reactions. Local adverse tissue reactions or elicit allergy reactions caused by metallic implants originate from the release of metal ions from the implant. Response to these observations initially resulted in the development of two alloys, Ti–6Al–7Nb and Ti–5Al–2.5Fe, where Nb and Fe were substituted for V in Ti–6Al–4V, V having been reported to be toxic and to show adverse tissue effects. These alloys still, however, contained Al which has been suggested to be causal in osteolysis and neural disorders [8]. Subsequent β-titanium alloys based on the Ti–Mo system were then developed, although the large percentage of Mo may still be potentially detrimental, Mo having been associated with severe tissue reactions in animal studies [2]. Ultimately, development of Ti–13Nb–13Zr may have answered the issue of biocompatibility with the exclusive addition of biocompatible elements, i.e. Zr and Nb [7].

The biocompatibility performance of a metallic alloy is closely associated with its corrosion resistance and the biocompatibility of its corrosion products. Corrosion data show excellent resistance for titanium and its alloys though some precautions should be taken in order to optimize their composition [9]. β-titanium alloys generally show attractive corrosion behavior, their corrosion resistance again depending on alloy composition and environment. Electrochemical measurements of Ti–13Nb–13Zr also confirmed the potential of Ti, Nb, and Zr to develop highly protective passive layers, resulting in a much lower potential electrochemical interaction than Ti–6Al–4V [10]. 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.

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, 12].

2. Experimental

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

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 principal characteristics of those powders.

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

Characteristic	Ti	Nb	Zr
Mean particle size (μm)	10	9	10
Morphology	Angular	Angular	Angular
Melting point (°C)	1670	2468	1850
Oxygen content (wt ppm)	3490	6200	4500

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. 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 has 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, Fig. 1.

Figure 1- Shrinkage after cold isostatic pressing and sintering.

3.1. Microstructural evolution

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. 2 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 α-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).

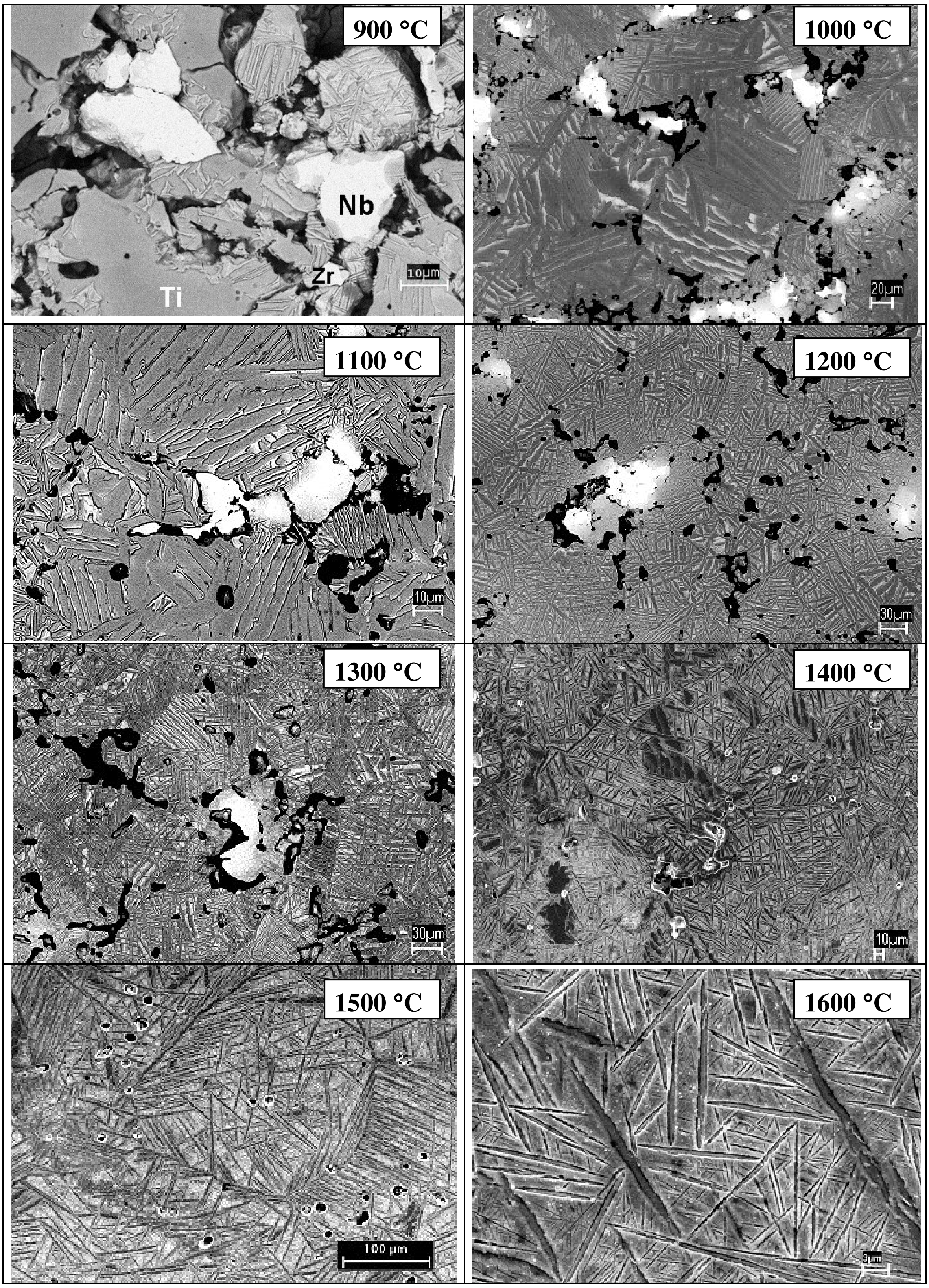


Figure 2- Microstructural evolution of the BE-Ti-13Nb-13Zr during sintering . All samples were sintered at the nominal temperature for 1 h and heating rate equal to 20 C min^{-1}.

An interesting feature is the presence of α’ needles inside the β phase. Fig. 3, shows the difference between α (Widmanstätten) e martensite α' (hc) areas. The region 1 consists of plates formed parallel to one specific plane of β phase. Region 2 consists of α’ needles disperse in β-phase matrix, originate from martensitic transformation.

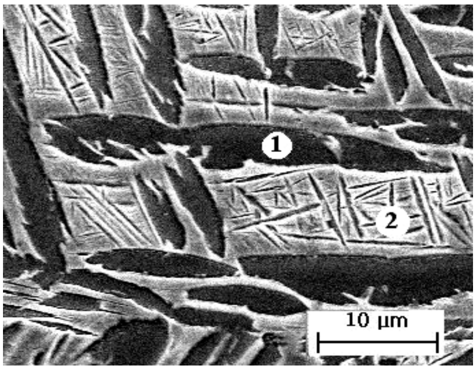


Figure 3- Micrograph showing the difference between (1) Widmanstätten and (2) martensitic α’-areas.

3.2. Chemical composition of BE- Ti-13Nb-13Zr alloys

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 1500 °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).

Fig. 4 shows the α and β areas (at 1500 °C) where the analyses for EDS were carried out. Table 2 presents the result of the quantitative analysis of the elements.

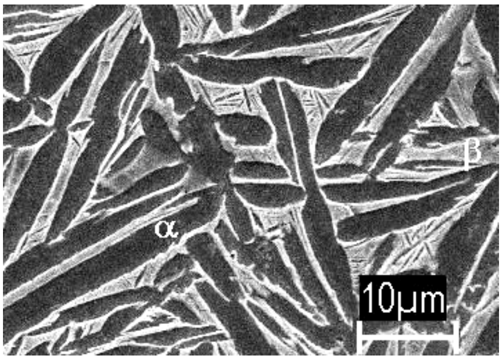


Figure 4- α and β phase areas analyzed for EDS in Ti-13Nb-13Zr alloy.

Table 2- 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

Table 2 indicates a higher niobium content in β-phase, since Nb promotes a strong stabilization of this phase. However, although 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. 5).

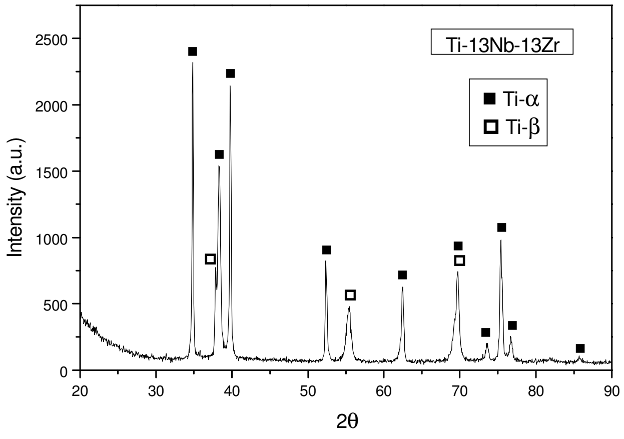


Figure 5- X-ray of Ti-13Nb-13Zr alloy spectra after sintering at 1500 °C.

The expansion/contraction behavior of a Ti-13Nb-13Zr compact during sintering was examined by a dilatometer. The result is shown in Fig. 6. Up to 700 °C, 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.

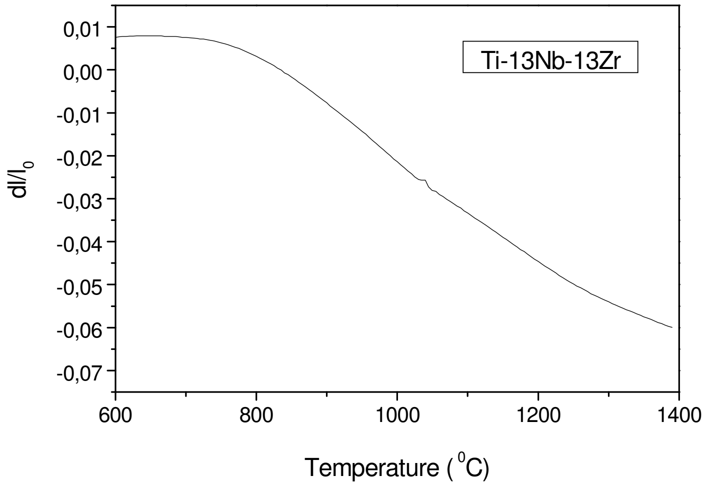
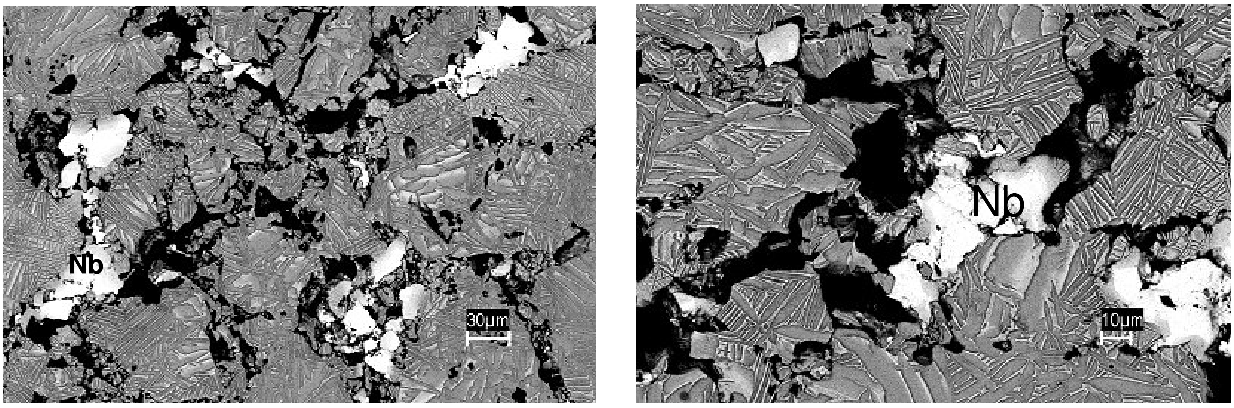


Figure 6- Expansion/contraction behavior of a Ti-13Nb-13Zr compact heated up to 1400 °C.

Since the sintering begin next to the β transus temperature of titanium (800 °C), the possibility of the Ti-13Nb-13Zr production via P/M at lower temperatures (below 1500 °C) with longer holding times seems possible. Therefore, a sample was cold uniaxially pressed and sintered at 1000 °C for 5 h at 20 °C/min, aiming to evaluate the microstructural development in low temperature and long holding time conditions. The results are shown in Fig. 7, where an almost completely homogenous microstructure is obtained. The larger niobium particles and agglomerates present in the initial powder size distribution are found not completely dissolved in the core of the Widmanstätten-like structure. The residual porosity is intentional and it is convenient for the implant osteointegration.



(a) (b)

Figure 7- Microstructure of Ti-13Nb-13Zr sample sintered at 1000 C for 5 h, 20°C/min. (a) microstructural distribution (b) porosity details. White areas are agglomerates of niobium particles.

CONCLUSIONS

1- A blended elemental P/M process has been developed to offer cost effective products in a mass production scale. The results show that the process can produce as-sintered high density titanium alloys with adequate microstructure. Ti-13Nb-13Zr is found to be a promising alloy for the production via P/M.

2- Due to complete dissolution of the alloy elements in the titanium matrix, a good combination of microstructure, mechanical properties and densification could be reached.

3- The formation of two phase areas ($\alpha+\beta$) begin 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.

4- An important feature is the presence of α' needles inside the β phase. 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.

5- 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.

6- The high densification reached demonstrates not to be essential a hot pressing stage to the parts production in applications that demand intermediates performance with good mechanical properties.

7- The dilatometric analysis showed that sintering can occur at lower temperatures, with longer holding times. The sample sintered at 1000 °C presented an almost completely homogenous microstructure. Therefore, for implants where an excellent osteointegration condition is necessary, can be used a combination of both low sintering temperatures and longer holding times.

8- The hardness values in the samples (300 HV) are near the range used in commercially manufactured parts produced by conventional techniques.

9- The combination of relatively low-cost powders, compaction techniques with high productivity, good sintering conditions, minimal machining and adequate hardness values can provide titanium parts more attractive in medical applications.

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