DEVELOPMENT OF BLENDED ELEMENTAL TI-35NB-7ZR-5TA ALLOY BY ISOCHRONAL SINTERING FOR SURGICAL IMPLANTS[1]

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Abstract

The processability of Ti alloys has always been an important concern as a result of its high reactivity at elevated temperatures and cost. Ti-35Nb-7Zr-5Ta is an important new titanium alloy developed for surgical implants. The titanium alloys processing by powder metallurgy eases the obtainment of parts with complex geometry and probably, cheaper. The present work was aim to investigate the properties of Ti-35Nb-7Zr-5Ta produced from blended elemental techniques. Samples were densification by sintering at 800-1500 °C. Sintering behavior was studied by means of dilatometry. Sintered samples were characterized for phase composition, microstructure and microhardness. The mechanical properties were measured using a four points bending tests. Density was measured by Archimedes method. The samples presented a good densification and a totally β-type microstructure, with complete dissolution of alloying elements in the titanium matrix with the temperature increase and low pore content.

Key words: Powder metallurgy; Titanium alloys; Sintering.

DESENVOLVIMENTO DA LIGA TI-35NB-7ZR-5TA A PARTIR DA MISTURA DE PÓS ELEMENTARES PARA IMPLANTES CIRÚRGICOS

Resumo

Os altos custos de fabricação dos componentes à base de titânio e a sua alta reatividade a altas temperaturas causam um maior interesse na sua processabilidade. A liga Ti-35Nb-7Zr-5Ta tem sido desenvolvida para uso em implantes cirúrgicos. As ligas de titânio produzidas a partir da metalurgia do pó facilitam a obtenção das partes com geometria complexa e provavelmente, mais barato. As amostras da liga Ti-35Nb-7Zr-5Ta foram obtidas a partir da sinterização entre 800 e 1500°C. Estas foram caracterizadas por meio de microscopia eletrônica de varredura, difração de raios x, medida de microdureza vickers, e determinação da densidade. As amostras apresentaram elevada densificação e microestrutura β homogênea, com uma completa dissolução dos elementos na matriz de titânio com o aumento da temperatura e baixa porosidade.

Palavras-chave: Metalurgia do pó; Ligas de titânio; Sinterização.

1 *Technical contibution to 62nd ABM - International Annual Congress, July 23rd to 27th, 2007, Vitória - ES – Brazil*
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1 INTRODUCTION

Bone injuries and failures often require the inception of implant biomaterials. Research in this area is receiving increasing attention worldwide. A variety of artificial bone materials, such as metals, polymeric materials, composites and ceramics, are being explored to replace diseased bones.(1)

The researches in this area aim material which shows integrated advantages such as satisfactory mechanical properties, good biocompatibility, and sufficient bioactivity. Titanium and its alloys are also widely used in biomedical applications as artificial hip, orthopaedic, or dental implants because of their acceptable biocompatibility and low density, coupled with good balance of mechanical properties and corrosion resistance.(2,3)

Most titanium alloys traditionally used for biomedical applications were originally developed for aerospace applications. In contrast, recently introduced low-modulus metastable β-Ti alloys were developed specifically for orthopedic applications, aiming to decrease the elastic modulus difference between natural bone (10–30 GPa) and the implant material, thereby promoting load sharing between bone and implant. This effort was undertaken in recognition of the fact that when insufficient load sharing occurs, for example as a result of either Ti-6Al-4V or cobalt implants being employed, natural bone resorption and loosening of the joint occur. Indeed, this phenomenon, termed “stress-shielding induced bone resorption,” is one of the main factors necessitating total hip replacement revision surgery.(4)

Ti–Nb–Ta–Zr system (β-type alloys), which comprise non-toxic elements, have been developed for biomedical applications. The Nb present in these alloys, a known β stabilizer, reduces the modulus of the alloy. Further, the presence of β phase in the microstructure enhances the ability of the alloy to harden on subsequent aging. The addition of Zr results in high level of blood compatibility when used in cardiovascular implants and leads to better corrosion resistance due to the formation of stable oxide layer.(5)

Ti–35Nb–7Zr-5Ta, has been reported to possess excellent properties required for biomaterials, such as excellent tensile properties, excellent fatigue properties, excellent frictional wear properties, low elastic modulus, excellent remodeling of bone, low cytotoxicity, and so on Qazi, Marquardt e Rack.(6)

Ti-35Nb-7Zr-5Ta in the solution-treated condition has an elastic modulus of 55 GPa, a yield strength of 530 MPa, and an elongation of 20%. However, the strength of these alloys can be improved, albeit at some increase in elastic modulus, by increasing their oxygen content and/or by artificial aging. These increases make them attractive candidates for other biomedical applications.(6)

However, the use of titanium alloys in industrial area, compared with that of other light metals such as aluminum and magnesium, is still limited due to high manufacturing costs associated with expensive raw materials and processing difficulties. To reduce the costs, several near net shape manufacturing techniques such as superplastic forming, isothermal forging, diffusion bonding, investment casting, and powder metallurgy (P/M) have been developed. Of these, the blended elemental (BE) P/M approach appears to be one of the most promising for producing titanium parts at reduced cost.[7,8]

The powder metallurgy (P/M) process is already an established method for the manufacture engineering components with precision quality. The main characteristic of the P/M process is its ability to manufacture parts or components in a wide range of sizes, having a good surface finish, with little or no subsequent machining.[9] Generally, P/M technique consists of the production of a controlled blend of metal powders, pressing the mixture in suitable dies, and subsequent heating (sintering) the compacted powder in a controlled atmosphere and temperature to obtain the required density and strength.[10] The hydriding process was the used method to produce the powders in this work. Among the reasons to justify this choice, low production costs and low oxygen content are the most striking.

Porous components based on biocompatible metallic materials such as Ti-35Nb-7Zr-5Ta are expected to provide better interaction with bones. This is due to the higher degree of bone growth into porous surfaces and the higher degree of body fluid transport through three-dimensional interconnected array of pores, leading to improved implant fixation. Furthermore, the relatively low elastic moduli of porous metals as compared with those of bulk metals are expected to reduce the extent of stress shielding.[11] Thus, the purpose of this study was to evaluate the properties of Ti-35Nb-7Zr-5Ta alloy obtained via powder metallurgy (P/M) aiming a future application in the surgical implants area.

2 MATERIAL AND METHODS

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

All the powders were obtained by hydriding method and sintered in hydrided state. For the titanium hydrided powder production, the hydriding was carried out at 500 °C, in a high vacuum furnace. After reaching the nominal temperature, the material was hold for 3 hours, under a positive hydrogen pressure. After cooling to room temperature, the friable hydride was milled in a titanium container in vacuum (10^{-2} Torr). Nb, Zr and Ta hydride powders were obtained using the same route; however, hydriding temperatures were significantly higher (800 °C). Table 1 presents the content of intersticial elements these powders.

The starting powders were weighed (30 grams) and dried for one hour in stove and blended for 30 minutes in a planetary mill with six drips of alcohol. After blending, the powders were cold uniaxially pressed under pressure of 60 MPa, in cylindrical 15 mm dia.-dies. Afterwards, samples were encapsulated under vacuum in flexible rubber molds and cold isostatically pressed (CIP) at 350 MPa during 30 s in an isostatic press.

Sintering was carried out in niobium crucible in high vacuum condition (10^{-7} torr), between 800-1500 °C with heating rates of 20 °C/min. After reaching the nominal temperature, samples were hold at the chosen temperature for 2 h and then furnace-cooled to room temperature. Metallographic preparation was carried out using conventional techniques. Specimens were etched with a Kroll solution:

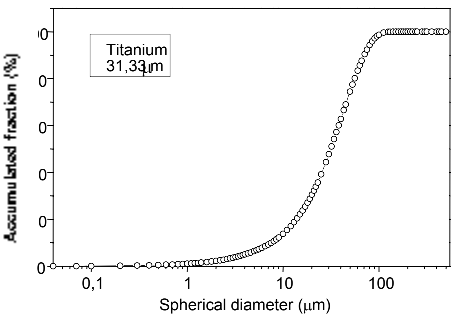
1,5mL HF: 2,5mL HNO_3: 100 mL H_2O to reveal its microstructure. Microhardness measurements were carried out in a Micromet 2004 equipment (Buehler) with a load of 0.2 kgf. The micrographs were obtained using a SEM LEO model 435VPi. The micrographs were obtained using a SEM LEO model 435VPi. The specific mass of the sintered samples was determined by Archimedes method, ASTM-C744-74. Particle size distribution was determined by means of laser-scattering equipment (Cilas model 1064). The mechanical properties were measured using a four points bending tests, performed on an Instron 4301 servo-hydraulic universal testing machine, of 0.5 mm/min and load–displacement data were acquired electronically during the test. Samples have a 44 mm length and a 4, 6 mm×4, 1 mm cross-section.The expansion/contraction behavior during sintering was examined by a dilatometer Netzsch-Dil 402C (DEMA-UFSCar).

Table 1. Content of intersticial elements of the powders used in this investigation.

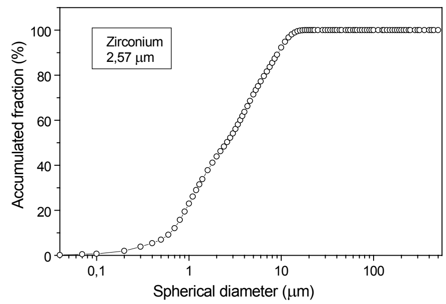
Elemental powder	Impurity content (%)				
	N	O	C	Si	Fe
Ti	0,872	0,349	0,073	0,025	0,040
Nb	0,038	0,620	0,020	-	0,040
Zr	0,080	0,450	0,028	-	0,030
Ta	0,150	0,550	0,033	0,030	0,030

3 RESULTS

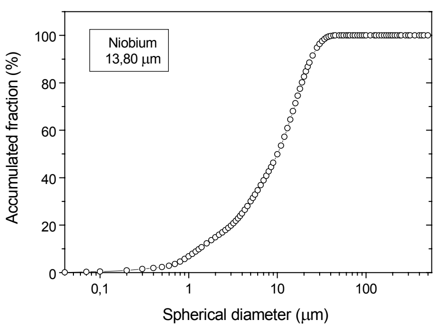
The Figure 1 shows the particle size distribution of the elemental powders obtained after hydriding. A large variation of the mean particle sizes between zirconium powders (~3μm) and niobium, titanium and tantalum powders (~14, ~31 and ~100 μm) was observed. This fact has influence on the sintering mechanisms involving the dissolution of the particles, phases stabilization and it is responsible for the final porosity in the samples.



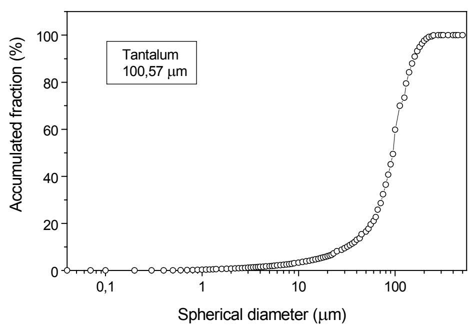
(a) TiH_2



(b) ZrH_2



(c) NbH_2



(d) TaH_2

Figure 1– Particle size distribution of the elemental powders used.

The microstructural analyses show the development of a β metastable microstructure with the increase the temperature from the dissolution of β-phase stablizers (Nb and Ta). The comprehension of the microstructure development of the alloy is well know and presented in former papers.(12)

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 EDS analysis confirmed that the Nb is present in larger amount in β-areas.

The specimens processed at lower temperatures (below 1500 °C) did not develop a β-like microstructure distributed throughout the samples. These results indicate that there was not enough time for mutual diffusion (homogenization) and further formation of a β microstructure throughout the specimens (Figure 2).

The specimen sintered at 1500°C presented the best results when compared to the microstructure found in commercial samples, with a β-homogeneous microstructure and low porosity obtained after the dissolution of the accumulation of particles agglomerates (of a same metal) (Figure 3).

The presence of porosity related with these areas occurs because the low velocity of the mass transports process. This fact is caused by the particles agglomerates accumulation (same metal), indicating that the alloy preparation stage must to be optimized.

The values of hardness stayed in 345 HV, while the hardness commonly reported for hot wrought alloys is about 350 HV.(13) For samples sintered at 1500 ºC presented high densification (5, 68 g/cm^3), 98 % of the theoretical density (5, 72 g/cm^3).(13)

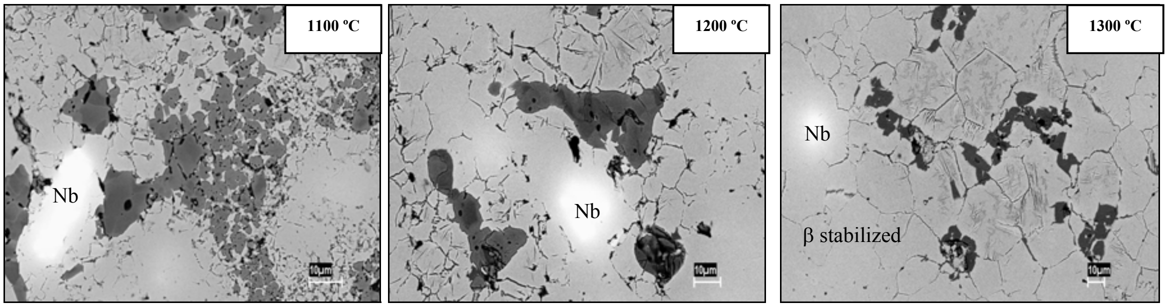


Figure 2- Microstructural development of T135Nb-7Zr-5Ta alloy from β stabilizer dissolution (Nb and Ta) in samples sintered at 1100, 1200 and 1300 ºC.

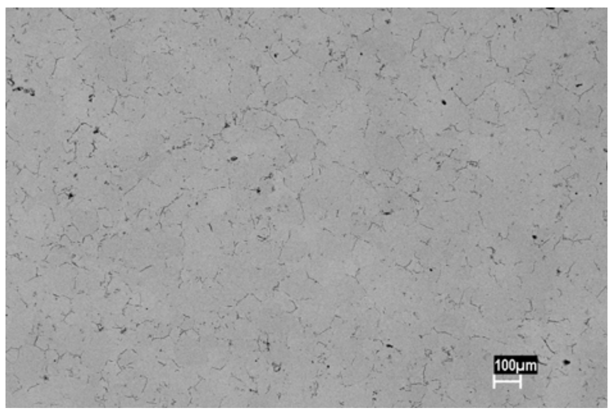


Figure 3 - Microstructure Ti-35Nb-7Zr-5Ta alloy during sintering at 1500 ºC (heating rate equal 20 ºC·min^{-1}).

Representative stress–displacement curves obtained from the full-scale four point bending test specimen is represented in Figure 4. The Ti-35Nb-7Zr-5Ta alloy sintered at 1500 ºC exhibited bending strength around 471, 87 MPa and the modulus of elasticity around 72 GPa, while literature values obtained by tensile tests are 596, 7 MPa and 55 GPa, respectively.(14)

Figure 5 shows the expansion/contraction behavior of Ti-35Nb-7Zr-5Ta from 200 to 1500 ºC. The curve is smooth up to 440 ºC. 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.

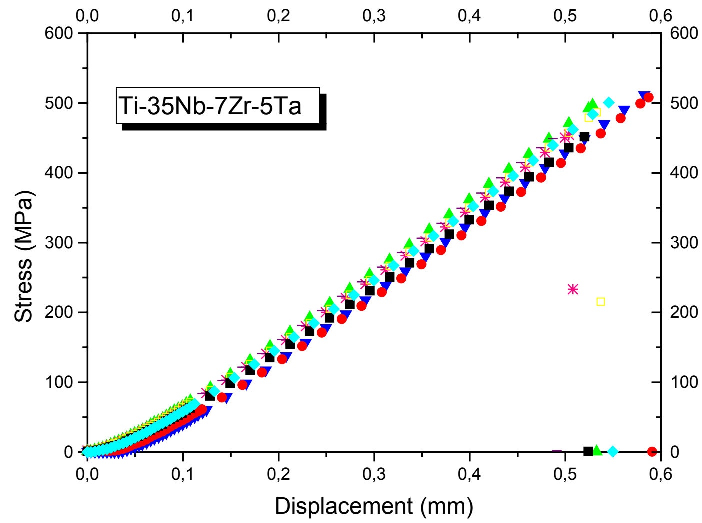


Figure 4- Stress-displacement curves from the four-point bending tests of Ti-35Nb-7Zr-5Ta samplessintered at 1500 ºC.

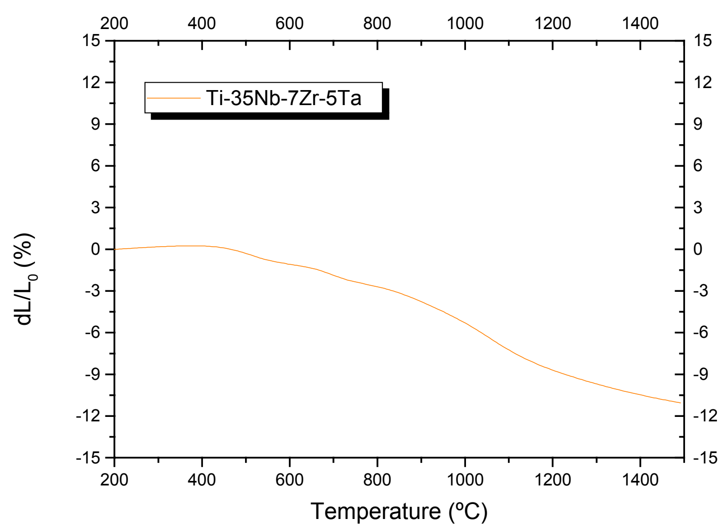


Figure 5- Expansion/contraction behavior of Ti-35Nb-7Zr-5Ta sintered until 1500ºC.

4 CONCLUSIONS

Blended elemental powder metallurgy method proved to be successful in manufacturing Ti-35Nb-7Zr-5Ta alloy. This involved cold compaction and sintering at temperature of 1500 °C after the total dissolution of the elements in the titanium matriz. The results show that a β-homogeneous microstructure is obtained in the whole sample extension. The samples presented a good densification and adequate microstructure. The hydrided powders provided activation in the sintering mechanism promoting contraction in low temperature (400 °C). The hardness values observed in the samples are within the range used in parts produced by conventional techniques (350 HV). The bend strength and elastic modulus of the alloy provide good conditions for surgical implants utilization.

Acknowledgment

The authors would like to thank FAPESP for the financial arrangements and DEMAR-FAENQUIL for the Nb and Ta supplying.

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