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Characterization of Ti-27Nb-13Zr Alloy Produced by Powder Metallurgy.

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Abstract. Titanium alloy are widely used in biomedical applications due to their excellent properties such as high strength, good corrosion resistance and excellent biocompatibility. Researches are being developed with elements such as Nb and Zr that reach all criterions for excellent biocompatibility and provide titanium alloys with Young’s modulus close to human bone. The aim of this work was to produce Ti-27Nb-13Zr alloy with different milling times by powder metallurgy process. The mixtures were performed by high energy milling and sintering in high vacuum furnace with temperature of 1300 °C / 3 h. The microstructures of samples were analyzed by SEM and XRD, while the mechanical behavior was evaluated by elastic modulus and Vickers hardness test. The diffraction results of sintering treatment indicate that the alloys are composed of α and β phases. Images obtained by SEM indicate the formation of equiaxial structures. Vickers hardness measurements from sintered samples with 1300 °C / 3 h indicate mean values around 413, 473 and 609 HV for 2, 6 and 10 hours of milling, respectively. The values of elastic modulus enable use the alloy as biomaterial.

Introduction

New metallic alloys for implants with good biocompatibility, Young’s modulus compatible with modulus human bone, 10 – 30 GPa [1], have been developed with elements as Nb and Zr in replacement of Al and V that may lead toxic effect and neurological disorders [2-6]. On titanium alloys are desirable low elastic modulus and high mechanical strenght. The first property in order to avoid stress shielding occurring at interfaces due to a large difference in modulus between implant and natural human bone, and the second to resist the efforts of the body.

One way for production of metallic alloys is powder metallurgy (PM) that is an excellent tool for the near net-shape fabrication of surgical implants due to some inherent advantages, including the capability of precisely adjusting chemical compositions, feasibility, modulus reduction through the inclusion of pores and also and reduction of costs [1]. Commonly the powders used involve hydrogenation – dehydrogenation (HDH) process on metals scraps. The introduction of hydrogen atoms in metal´s interstitial sites promotes the metal embrittlement and through a mechanical grinding process the hydrogenated material is reduced to fine powder. After the hydrogen is then removed by heating the material under a vacuum [7,8].

The aim of this study is characterize Ti-27Nb-13Zr alloy produced by PM, verify the influence of milling time in sintering process, analyze the mechanical properties (elastic modulus and hardness) and microstructure of alloy.

Materials and methods

The Ti-13Zr-27Nb alloy was produced from the powder mixture of Ti, Nb and Zr. The zirconium and niobium powders were obtained from the hydrogenation of scraps and small metal plates, respectively. Ti powder was purchased from Brats Sintered Filters & Metallic Powders.

The hydrogenation temperature applied to zirconium 650 °C for 30 minutes, with ramp 20 °C for minute and hydrogen gas pressure of 9.5 bar. The scrap niobium also was hydrogenated in temperature of 700 °C for 30 minutes. There was no need to hydrogenate Ti powder, because it has already been provided as a hydride. The powders were characterized and weighed in proportions indicated by league and ground in high-energy mill Pulverisette 7 Premium produced by Fritsh

GmbH for 2, 6 and 10 h with speed of 300 rpm and ratio ball to powder of 10:1. The milling crucible posses sheathing of zirconium oxide, the balls, with diameter 5 mm, are also produced by same material. At the end the powders were dried by reducing pressure of the crucible with a mechanical pump vacuum.

Before mixing the powders pickling solutions were utilized to remove impurities of hydrides, the solution applied on ZrH was 100 ml distilled water to 10 ml HNO3 and for NbH was employed 50 ml H2SO4, 20 ml HNO3, 20 ml HF and 10 ml distilled water. It wasn't necessary clean up titanium powder with pickling acids because he isn´t derived from scraps. Afterwards portions with 0.5 g mass were uniaxially compacted in matrix of 6.5 mm diameter followed by cold isostatic pressing with pressure of 206 MPa. For the elastic modulus measures were used rectangular specimens of size 40 x 5 x 2 mm compacted in rectangular matrix with pressure of 8.45 MPa. The temperature of sintering in a high vacuum furnace was of 1300 °C for periods of 1, 2 and 3 hours and then furnace cooled. For analyses in scanning electron microscope (SEM), Philips XL-30 model, the sintered samples were inserted in epoxy resin and subjected to conventional metallographic preparation, including sanding with SiC sandpaper 220, 400, 600, 1000 and 1200. Hereafter they were polished with colloidal silica (0.06 microns). The Kroll solution was used for metallographic etching. The hardness measures were performed in the equipment Macrovickers 5112, produced by Buehler, with load of 300g in the time of 15s with the polished samples. The measures of X rays were executed in Rigaku DMAX 2200 equipment, operating at 40 kV, 20 mA and copper radiation (λ = 1.5418 Å). The range applied was 20º to 90º and scan speed of 2° / min. The XRD patterns were compared with the database PDF-2 of the International Centre for Diffraction Data (ICDD). The elastic modulus of the alloy was determined by dynamic method based on impulse excitation of vibration using Grindosonic apparatus, and the measures were performed by means of international standarts set by ASTM.

Results and discussion

The hydrides powders in Fig. 1 exhibit angular morphology and particle size (D50%) of 98.5 µm for ZrH and 92.5 µm for TiH. The NbH powder used are the particle that passed through sieve of 40 mesh, therefore less 425 µm. As show Fig. 2(c), the hydride of niobium had larger particle size, hindering the analysis by laser granulometry.

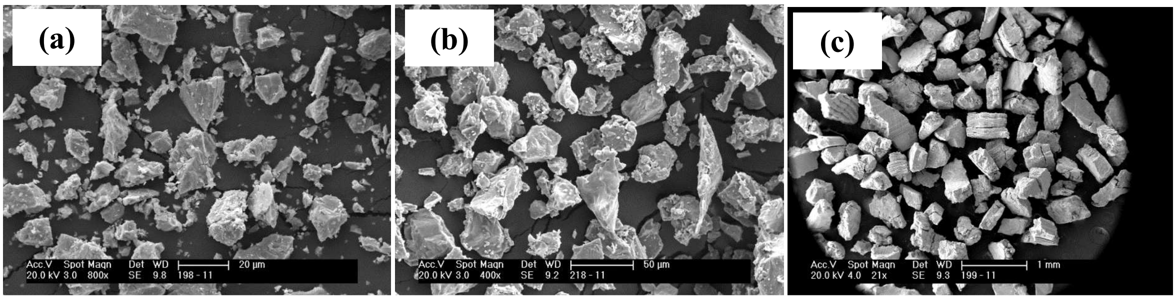

Fig. 1 – SEM powders hydrides of zirconium (a), titanium (b) and niobium (c).

The present phases at the mixtures before sintering, Fig. 2, are hydrides (TiH, NbH and ZrH), Ti-α and Nb. The formation of niobium is probably due to incomplete hydrogenation of scrap which suggest the time of 30 minutes in furnace with H_2 atmosphere is not enough for complete formation of NbH.

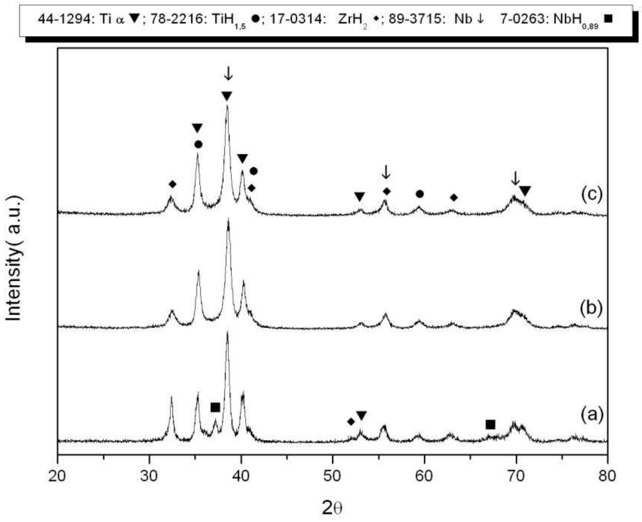

Fig. 2 – XRD of Ti-27Nb-13Zr before sintering, 2 hours milling (a), 6 hours milling s (b) and 10 hours milling (c).

Table 1 shows the cumulative distribution of Ti-27Nb-13Zr with 2, 6 and 10 hours of milling (hm). The significant reduction in D50% is due increased milling time and consequently greater number of collisions (impact) between the balls of crucible and the alloy particles promoting the breakage of larger particles by processes as microforging, fracture, agglomeration and deagglomeration [9].

Table 1 – Cumulative distribution of Ti-27Nb-13Zr alloy.

milling Time [h]	D10% [μm]	D50% [μm]	D90% [μm]
2	10.60	39.7	94.10
6	3.20	9.0	15.9
10	1.4	4.6	9.10

The variation green density of samples is in Fig. 3, as seen there is decrease on density due the reduction on particle size. The wider particle-size distribution including large and small particles, in powders with 2 hm, might favour stacking and higher green density where smaller particles would fit into the interstices between the large particles. Furthermore, small particles give a greater number of contacts, causing increased resistance to compaction, therefore, the interparticle friction increases with decreasing particle size, resulting in increased agglomeration and lower green density, powders with 6 and 10 hm [10].

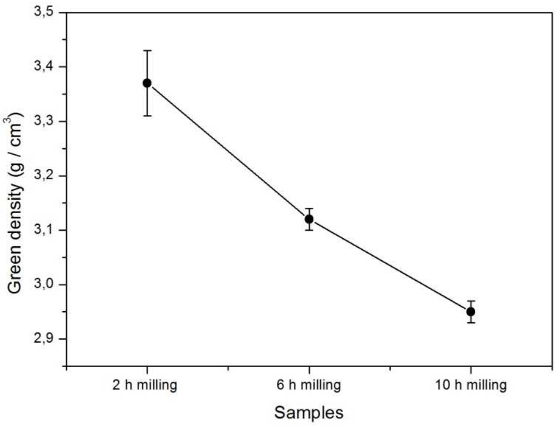

Fig. 3 – Variation on green density in samples with different time of milling.

The theoretical density of Ti-27Nb-13Zr alloy is 5,86 g cm^{-3}. After sintering in 1300 °C by 3 h the densities for alloy were 4.85 g cm^{-3} (82.7%), 5.2 g cm^{-3} (88.73%) and 5.3 g cm^{-3} (90.44%) respectively for 2, 6 and 10 hm. Consequently, the values for average porosity are 17.3%, 11.27% and 9,56% for 2, 6 and 10 hm. Powders with smaller particle size have bigger shrinkage and lower porosity, consequently higher density, in addition, is easier sintering fine powders due the superior surface area.

The Fig. 4 shows SEM of samples treated with 1300 °C by 3 h and different milling time. In (a) and (b) occurs the formation of large pores, undissolved regions of niobium and formation of structure Ti-β with portions of Ti-α. In (c) and (d) the porosity is smaller than (a), the Nb still continues undissolved and begins the nucleation Ti-α in the microstructure of alloy. In (e) and (f) are observed small portions of niobium and uniform distribution of Ti-α on Ti-β matrix. The structure present in (c) and (f) is called equiaxial microstructure, α-particles scattered in β-matrix.

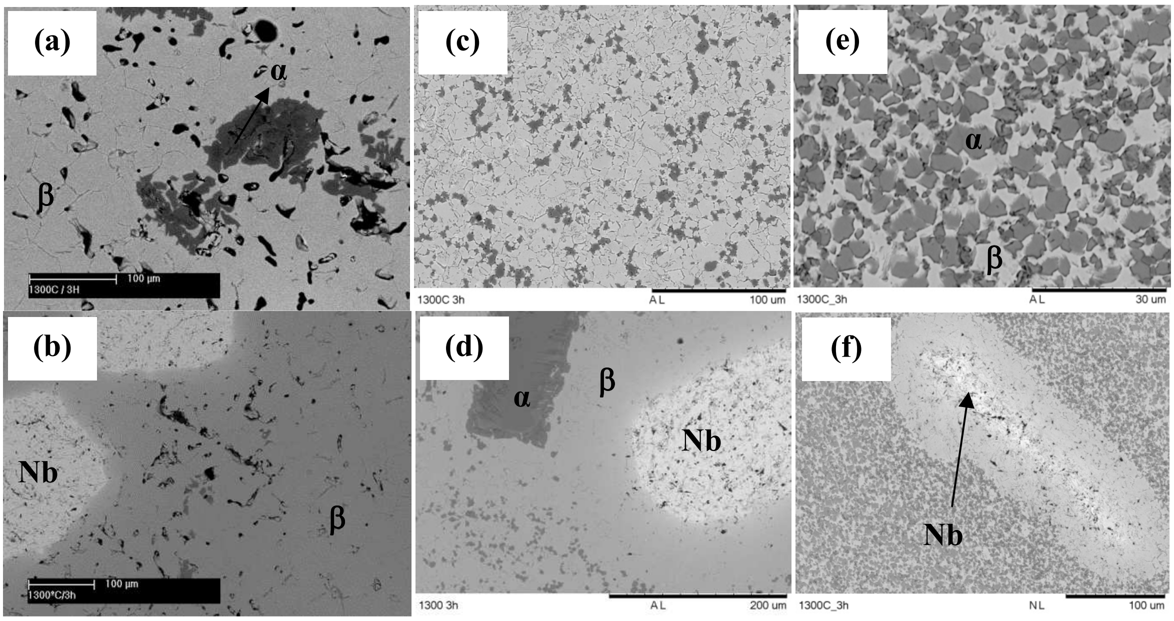

Fig. 4 – SEM of Ti-27Nb-13Zr treated 1300 °C by 3 h, milling time of 2 hours for (a) and (b), 6 hours for (c) and (d), 10 hours for (e) and (f).

The increase in milling time of the mixture powders augments the amount Ti-α colonies, due the lower particle size, consequently greater surface area that implying on higher diffusion mechanism.

The alloy is study is mainly formed by Ti-α and Ti-β phases, Fig. 5. The presence phase orthorhombic martensite, α'', which a transition between phase the hexagonal structure, α', and body centered cubic, β, is due the amount of Nb (> 20 %) involved in alloy composition allied cooling rate applied to treatment [6,11,12]. The increase in hours of milling provides peaks more intense of Ti-α, Fig. 5(c).

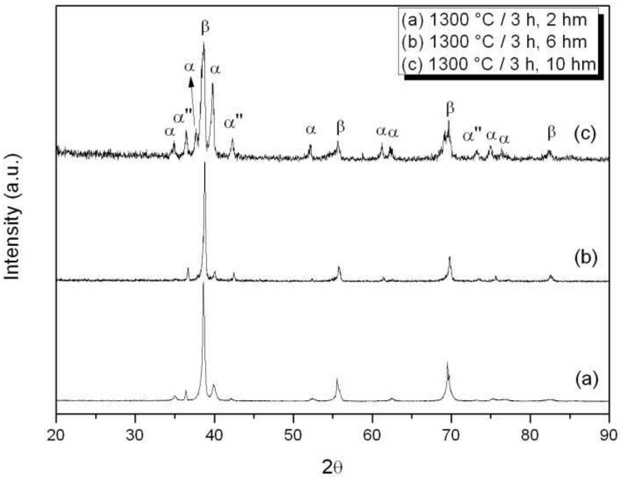

Fig. 5 – XRD of Ti-27Nb-13Zr after sintering.

The elastic modulus and hardness of alloy sintered 1300 °C / 3h are in Fig. 6. These mechanical properties increase with milling time. Samples with 2 milling hours show small values for modulus (50 GPa), more close to human bone, but the hardness is less than the other specimens leading larger wear. These specimens exhibit portions large niobium undissolved.

The condition 1300 °C by 3 h with 10 milling hour exhibit value modulus close to Ti-13Nb-13Zr alloy [13,14], and high hardness which could meet the requirement of a long service life (over 20 years) and implantation in young patients[15].

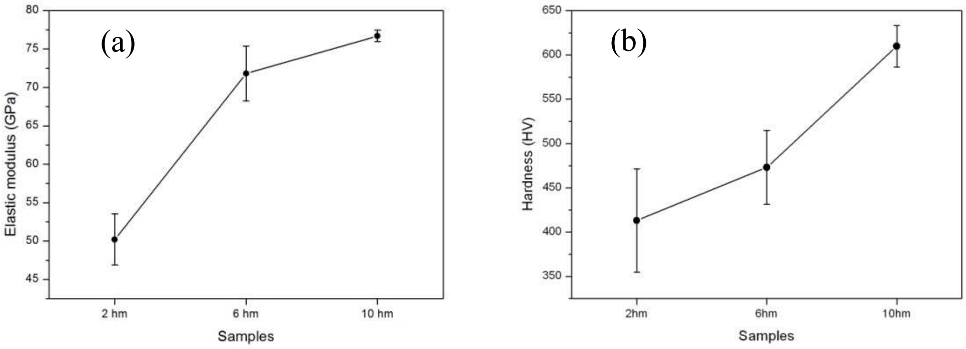

Fig. 6 – Elastic modulus (a) and hardness (b) for specimens treated with 1300 °C by 3 hours.

Conclusions

With the analysis of the obtained results, it can be concluded that the time of 30 minutes in furnace with H_2 atmosphere is not enough for complete formation of NbH and this result interfered in portions undissolved of niobium in sintering. The alloy is classified as α + β and cooling rate with large amount Nb produced α'' phase. Superior milling time presented equiaxed structure and smaller portion undissolved of Nb. The treatment applied in samples with 10 milling hours exhibit modulus and hardness according data of ti-13Nb-13-Zr alloy, density of 90.44 % of theoretical density and smaller porosity.

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