*Materials Science Forum Vols. 727-728 (2012) pp 102-107*
*Online available since 2012/Aug/24 at www.scientific.net*
*© (2012) Trans Tech Publications, Switzerland*
*doi:10.4028/www.scientific.net/MSF.727-728.102*

# PRODUCTION OF Ti-13Nb-13Zr ALLOY BY PM FOR BIOMEDICAL APPLICATIONS USING ZIRCONIUM OXIDE GRINDING BOWL AND BALLS

J. H. Duvaizem[1a], A. M. Fajardo[1], L. P. Barbosa[1b], A. H. Bressiani[1c], H. Takiishi[1d]

[1] Energetic and Nuclear Research Institute - Av. Lineu Prestes, 2242, 05508-000 - São Paulo - SP

[a] jduvaizem@ipen.br, [b] luzinete@ipen.br, [c] abressia@ipen.br, [d] takiishi@ipen.br

**Keywords:** biomaterial, Ti-Nb-Zr alloys, Ti alloys, powder metallurgy, HD.

**Abstract:** In this present work Ti-13Nb-13Zr alloy was produced by PM using planetary ball mill with zirconium oxide grinding bowl and balls to reduce contamination. The effect of milling time upon microstructure and microhardness was studied. Powders have been produced by hydrogenation of Ti, Nb and Zr at 1MPa. Milling speed was 200 rpm during 90 to 360 min. Sintering was carried out at 1150°C during 10h. Powder size distribution was analyzed using CILAS equipment and chemically characterized by X-Ray Fluorescence (XRF). Microhardness was determined by means of a Vickers microhardness tester. Microstructure and phases were analyzed employing scanning electron microscopy (SEM) and X-Ray diffraction.

## Introduction

Metallic implants and osseointegrated prosthesis are currently made from cobalt-chromium (Co-Cr) alloys, stainless steels and conventional $\alpha+\beta$ titanium alloys such as Ti-6Al-4V. Ti and its alloys are commonly used due to their low density, superior biocompatibility and corrosion resistance, good mechanical properties and low elastic modulus. However, the potential toxic effect of elements such as vanadium and aluminum led to the development of new alloys composed only of elements with no cytotoxicity, improving the biocompatibility [1,2]. A low modulus of elasticity is required to reduce the stress-shielding effect, which leads to bone resorption and implant loosening [3]. Increasing the hardness of the material surface is an effective method of improving wear resistance, reducing metallic ion release [4]. In the milling stage, a considerable ammount of impurities are introduced in the material [5], therefore in this work zirconium oxide grinding bowl and balls were used in order to reduce contamination.

## Experimental

Commercially pure (CP) titanium, niobium and zirconium were heat treated under hydrogen atmosphere of 1 MPa at 700, 600 and 500°C, respectively, and then mechanically broken in particles (<425 μm). The hydride powder was weighted, Ti - 74, Nb - 13, Zr - 13 (%wt) and milled in planetary ball milling (PBM) using 200 rpm speed during 90, 180, 270 and 360 minutes. The milled powders were isostatically pressed at 200 MPa and sintered at 1150°C for 10 hours under high vacuum ($10^{-3}$ Pa), followed by air cooling. Zirconium oxide grinding bowl and balls were used aiming the reduction of contaminant levels introduced during milling stage. Proportion used between grinding balls and material was 10:1 (in mass), and cyclohexane was used as organic additive.

Microstructures and phases were characterized using scanning electron microscopy (SEM). Microhardness was determined using a Vickers microhardness tester. Particle size distribution was determined utilizing CILAS 1064 equipment. Samples were chemically characterized via X-Ray Fluorescence (XRF) in initial stage, after hydrogenation process and milling stage.

## Results

Elements on starting materials, after hydrogenation and milling stages were chemically characterized via X-Ray Fluorescence, and presented in Table 1, 2 and 3.

**Table 1** – Chemical composition of starting materials obtained via XRF.

| Titanium | | Niobium | | Zirconium | |
|---|---|---|---|---|---|
| Element | Content [%] | Element | Content [%] | Element | Content [%] |
| Ti | 99,6 ± 0,5 | Nb | 99,9 ± 0,5 | Zr | 96,6 ± 0,5 |
| Fe | 0,12 ± 0,01 | Others | 0,10 ± 0,01 | Mg | 0,03 ± 0,01 |
| Others | 0,28 ± 0,01 | | | Cl | 0,11 ± 0,01 |
| | | | | Others | 3,20 ± 0,01 |

**Table 2** – Chemical composition of materials after hydrogenation obtained via XRF.

| Titanium | | Niobium | | Zirconium | |
|---|---|---|---|---|---|
| Element | Content [%] | Element | Content [%] | Element | Content [%] |
| Ti | 99,0 ± 0,5 | Nb | 99,0 ± 0,5 | Zr | 97,3 ± 0,5 |
| Fe | 0,38 ± 0,01 | Fe | 0,23 ± 0,01 | Mg | 0,21 ± 0,01 |
| Others | 0,65 ± 0,01 | Others | 0,77 ± 0,01 | Cl | 0,68 ± 0,01 |
| | | | | Fe | 0,12 ± 0,01 |
| | | | | Others | 1,70 ± 0,01 |

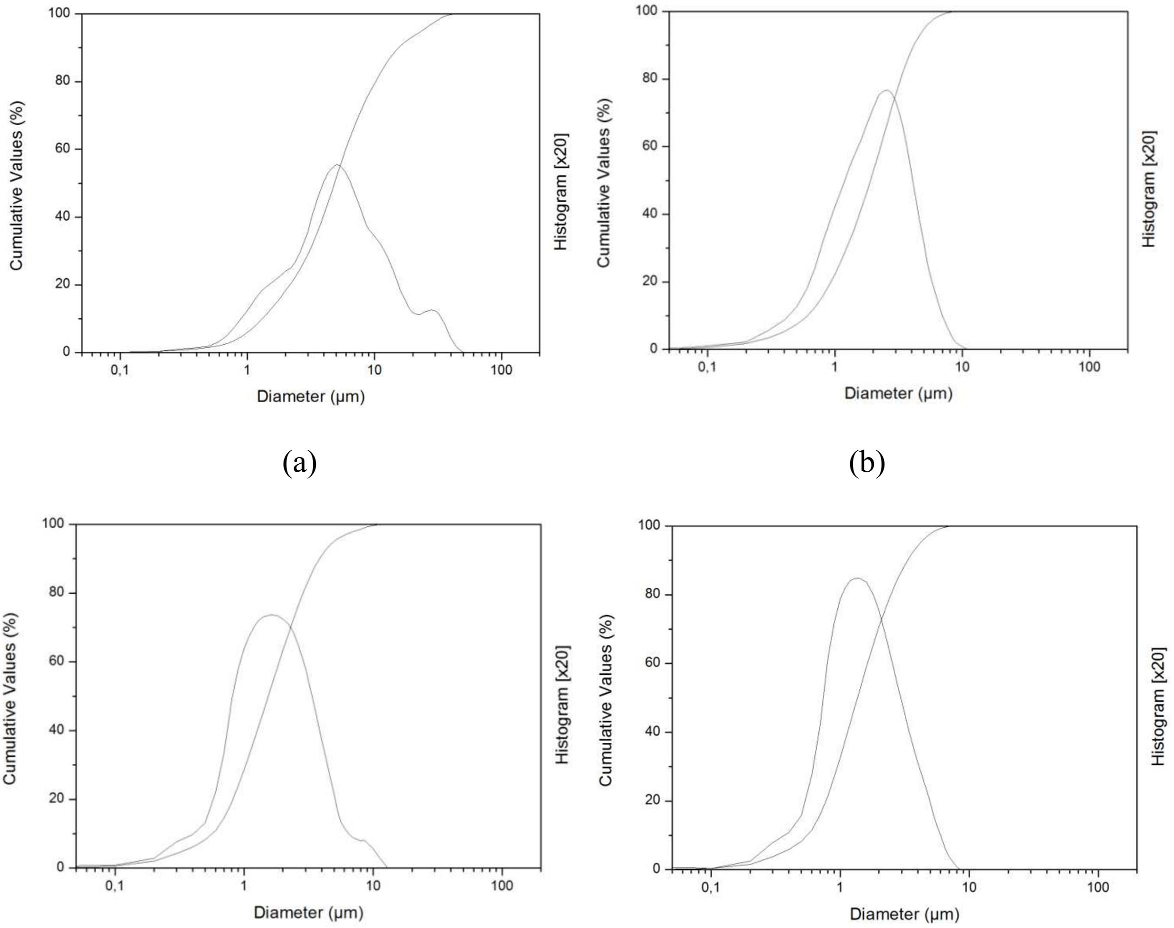
After hydrogenation powders are submitted to a pickling process to remove existing contaminants. Pickling was realized in solution 10:1 of distilled water and nitric acid, followed by immersion in acetone to remove residues of acid, and drying at 40ºC.

**Table 3** – Chemical composition of particulates after high speed milling using PBM with zirconium oxide bowl and balls during 180 and 360 min obtained via XRF.

| 200rpm-180min | | 200rpm-360min | |
|---|---|---|---|
| Element | Content [%] | Element | Content [%] |
| Ti | 75,1 ± 0,4 | Ti | 73,7 ± 0,4 |
| Nb | 12,5 ± 0,1 | Nb | 13,5 ± 0,1 |
| Zr | 11,9 ± 0,1 | Zr | 12,3 ± 0,1 |
| Fe | 0,40 ± 0,01 | Fe | 0,43 ± 0,01 |
| Others | 0,10 ± 0,01 | Others | 0,10 ± 0,01 |

Using zirconium oxide grinding bowl and bowls the level of contamination introduced during milling stage was reduced, i.e. Fe content obtained by Duvaizem [5] was approximately 2%, using stainless steel bowl and hard steel balls with milling time of 90 min. Using zirconium oxide bowl and balls with milling time of 360 min Fe contamination reduced to 0,4%.

Fig. 1 shows the particle size distribution of milled powder obtained via CILAS. Mostly due to the difference in densities and hardness between balls made of zirconium oxide (5,7 g/cm³) and hard steel (7,9 g/cm³), the particle size distribution of the powder produced using zirconium oxide exhibited higher values of medium particle size and greater enlargement than obtained by Duvaizem [5], for same conditions of milling speed and time (200rpm during 90min). The increase in milling time reduced medium particle size and the enlargement of particle size distribution, improving homogeneity.

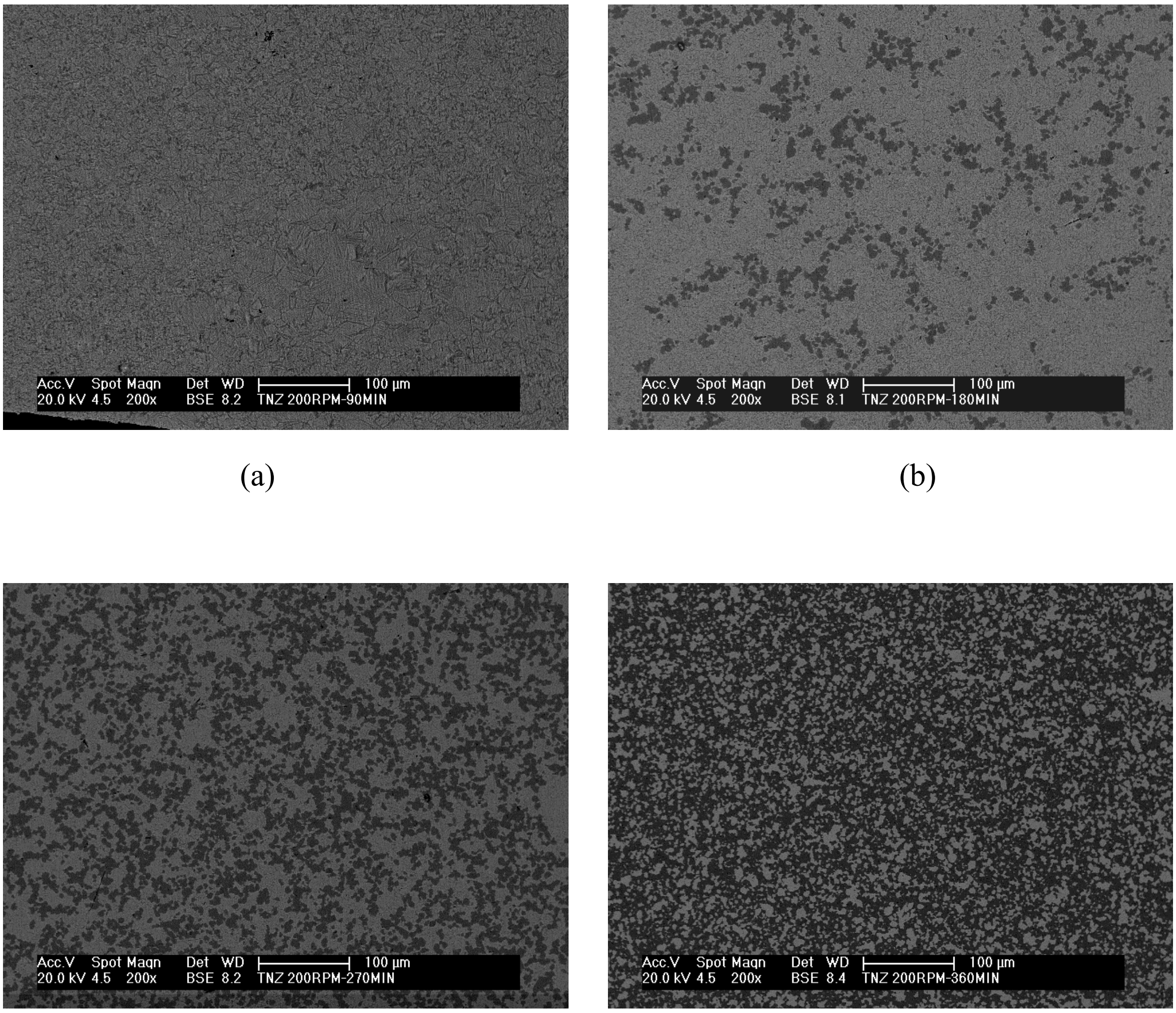


(a) (b)

(c) (d)

Fig. 1 – Particle size distribution obtained via CILAS of Ti-13Nb-13Zr alloy produced using PBM, zirconium oxide grinding bowl and balls with speed of 200 rpm during (a) 90, (b) 180, (c) 270, (d) 360 min.

Fig. 2 (a-d) shows SEM micrographs of Ti-13Nb-13Zr alloy produced using different milling times. Samples produced using 200rpm for 90min presented areas containing free Ti and Nb, caused essentially by the less homogeneous particle size distribution and higher medium particle size, characteristics of great influence in the sintering process. The increase in milling time enhanced particle size distribution homogeneity and reduced medium particle size improving sintering mechanisms, leading to a better microstructural homogeneity. Areas containing free Ti and Nb were no longer observed, grain size reduced and precipitation of α phase increased.



(a) (b)

(c) (d)

Fig. 2 – SEM images of Ti-13Nb-13Zr alloy produced by PM, sintered at 1150° C for 10h, using PBM with 200 rpm speed during: (a) 90, (b) 180, (c) 270, (d) 360 min.

The increase in milling speed headed to the gradual disappearance of Widmanstätten pattern as seen on Fig. 2. a and b, and not observed on Fig. 2. c and d. Formation of grains containing α and β phases individually was observed for milling time of 360 min (Fig. 2.d), as opposed to commonly observed precipitation of α phase in β grains interior and boundaries.

Fig. 3 shows X-Ray diffraction patterns of Ti-13Nb-13Zr alloy produced using different milling times. Nb and Zr are in solid solution on Ti lattice, and only peaks related to α and β phases of titanium were observed. The elements in solid solution increase cell parameters values, leading to expansion of titanium lattice and dislocation of peaks to lower angles.

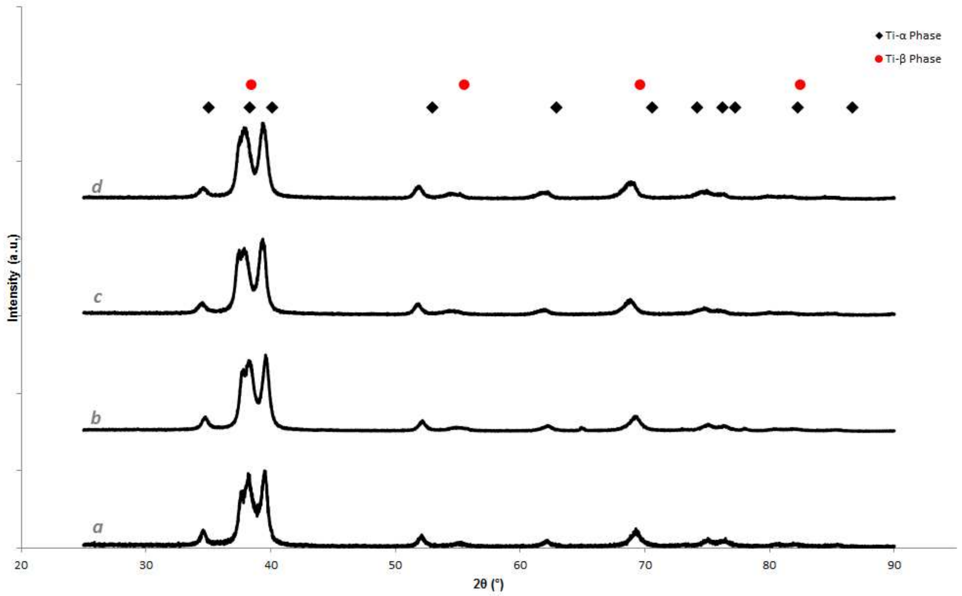


Fig. 3 – X-Ray diffraction patterns of Ti-13Nb-13Zr alloy produced by PM, sintered at 1150° C for 10h, using PBM with 200 rpm speed during: (a) 90, (b) 180, (c) 270, (d) 360 min.

Fig. 4 shows Vickers microhardness values obtained for the Ti-13Nb-13Zr alloy produced using different milling times. As observed on SEM images, both the refinement of microstructure via decrease of grain size and precipitation of larger amounts of α phase contributed to an increase of microhardness.

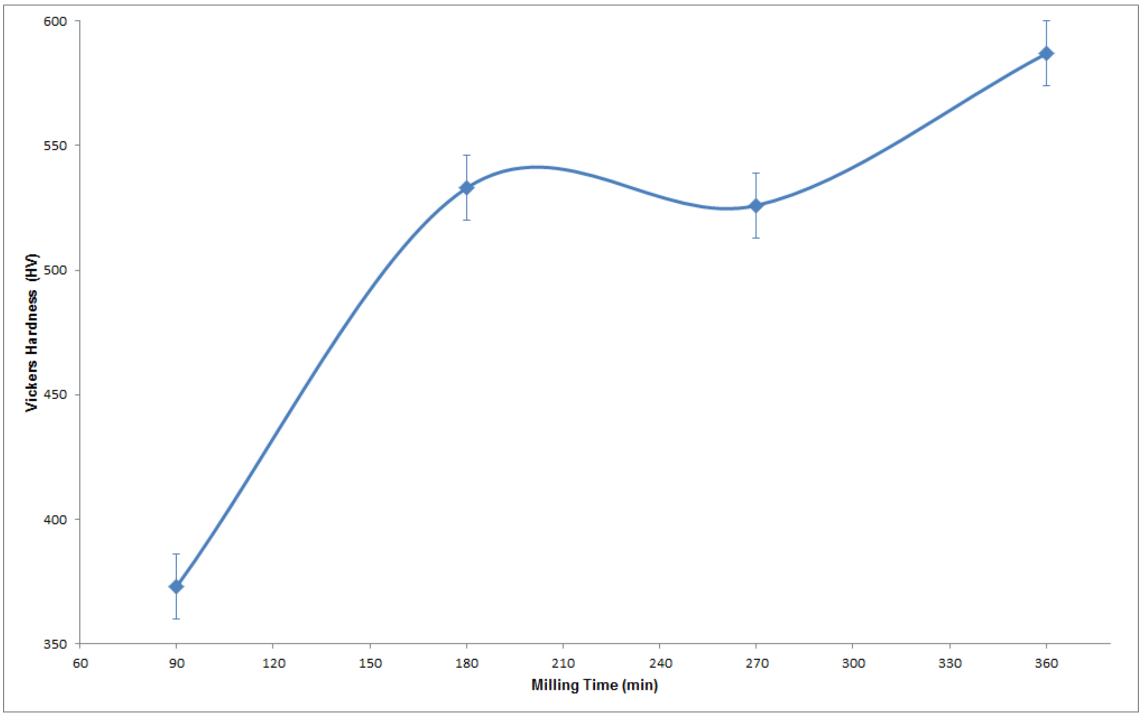


Fig. 4 – Vickers microhardness values of Ti-13Nb-13Zr alloy produced by PM, sintered at 1150° C for 10h, using PBM with 200 rpm speed during 90 to 360 min.

## Conclusion

Using zirconium oxide grinding bowl and balls reduced contamination upon milling stage, however an increase in milling time was necessary to improve particle size distribution homogeneity, with minor contamination introduction.

Better particle size distribution homogeneity in combination with medium particle size decrease obtained with the increase of milling time contributed in acceleration of sintering mechanisms, improving microstructural homogeneity after sintering. Wider areas containing α phase were observed, and grain size was refined, increasing microhardness.

Samples produced using PBM with 200 rpm speed and 180 min presented good microstructural homogeneity and appropriate mechanical properties when sintered under high vacuum at 1150°C during 10 h.

## Acknowledgements

Many thanks are due to CNPQ, FAPESP and IPEN-CNEN/SP for supporting this investigation. Thanks are due to J.R. Martinelli, V.L.R. Salvador, M.A. Scapin and N.B. Lima for CILAS, XRF and X-Ray analyses.

## References

[1] P. Laheurte, F. Prima, A. Eberhardt, T. Gloriant, M. Wary and E. Patoor: Journal of the Mechanical Behaviour of Biomedical Materials Vol. 3 (2010), p. 565.
[2] P. Majumdar, S. Singh and M. Chakraborty: Wear Vol. 264 (2008), p. 1015.
[3] M. Geetha, A. Singh, R. Asokamani and A. Gogia: Progress in Materials Science Vol. 54 (2009), p. 397.
[4] M. Niinomi: Journal of the Mechanical Behavior of Biomedical Materials Vol. 1 (2008), p. 30.
[5] J.H. Duvaizem: Estudo das Propriedades Mecânicas e Microestruturais de Ligas à Base de Titânio-Nióbio-Zircônio Processados com Hidrogênio e Metalurgia do Pó Para Utilização em Implantes Dentários. Mestrado (Dissertação). São Paulo, (2009). Intituto de Pesquisas Energéticas e Nucleares (IPEN/USP). (SP)

**Advanced Powder Technology VIII**
10.4028/www.scientific.net/MSF.727-728

**Production of Ti-13Nb-13Zr Alloy by PM for Biomedical Applications Using Zirconium Oxide Grinding Bowl and Balls**

10.4028/www.scientific.net/MSF.727-728.102