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Effect of NbH Particle Size and Cooling Type on the Microstructure, Phase Composition and Microhardness of Ti-20Nb-20Zr Alloy

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Abstract. Titanium alloys are widely used as implants in orthopedics and dentistry due to their properties such as high strength, corrosion resistance, biocompatibility and good fatigue resistance. Alloys composed of non-toxic elements, like Nb and Zr, provide lowest Young's modulus with values near to human bone modulus. The goal of this work was to study the effect of NbH particle size and cooling type on the microstructure, phase composition and microhardness of Ti-20Nb-20Zr alloy. The powders were produced by hydrogenation method. Two different powders of NbH were prepared: powders comminuted (C) and comminuted followed by milling (C+M). After, the alloy powders were milling and homogenizated for 6 h / 300 rpm and sintered at 1300 °C / 3h followed furnace cooling. Afterward, the specimens were treated at 1000 °C / 1 h and cooling in air and water. The samples were characterized by XRD, SEM and Vickers microhardness. The results showed that the alloy is classified as α + β. Vickers microhardness of Ti-20Nb-20Zr ranged between 680-700 and 540-600 HV from alloys prepared with NbH-comminuted and NbH comminuted + milled, respectively. Results indicated that NbH agglomerate behave as barriers for the sintering process of the alloy.

Introduction

Titanium and its alloys have been widely used in biomaterials due to their superior biocompatibility and excellent corrosion resistance in conjunction with low density and elastic modulus when compared with the Co-Cr alloy and stainless steel 316L [1]. The addition of Nb and Zr in the composition of titanium alloy enhances the biocompatibility, strength, corrosion resistance and reduces Young's modulus [2]. Niobium is added because is a β-phase stabilizer and highly biocompatible [3] whereas Zr is a neutral element in terms of phase stabilization, even though some research work suggests that zirconium stabilizes the β-phase, over the wide range (6 - 30 at.%), in the Ti-Nb-Zr system [4,5].

The powder metallurgy (PM) technique aims to transform metallic powders, using pressure and heat, by means of a thermal treatment called sintering that is carried out below the melting point of the major constituent of the alloy [6]. It is an excellent method for near net-shape production of surgical implants due to some inherent advantages such as the capability of precisely adjusting the chemical composition, feasibility, reduced cost and reduction of modulus by introducing pores [7].

The powders used in PM can be prepared by the hydrogenation – dehydrogenation (HDH) process using metal scrap. This process introduces hydrogen atoms into the metal´s interstitial sites to promote embrittlement of the metal. The hydrogenated metal is then mechanically ground to obtain a fine powder that is heated under vacuum to remove the hydrogen [8,9]. The advantages of HDH process are: It's low cost, possibility of obtaining better green density values and improvement in densification during sintering, possibility of controlling both content in sintered samples and the hydrogen emitted from the hydrogenated powders which might become a protective atmosphere during powder sintering [8,10].

The powder obtained by HDH is characterized by angular morphology which is ideal for processing using powder metallurgy [11]. The angularity on particles increases compressibility, can assist packing and sintering [12, 13]. In terms of stages of sintering, decreasing particle size leads to increasing sintering, thus, in PM, it is crucial to use lower particle size [14].

The aim of this work is to study the effect of particle size NbH and cooling type on the microstructure, phase composition and microhardness of Ti-20Nb-20Zr alloy prepared by powder metallurgy for biomedical applications.

Materials and methods

The Ti-20Nb-20Zr alloy was produced by high energy milling of TiH, NbH and ZrH. The zirconium and niobium powders were obtained from the hydrogenation of sponges and small metal plates, respectively. TiH powder was purchased from Brats Sintered Filters & Metallic Powders. The hydrogenation was performed in furnace EDG10P–S. The temperature applied to zirconium was 650 °C for 30 minutes, with a heating rate of 20 °C per minute and hydrogen gas pressure of 9.5 bar. The scrap niobium was hydrogenated at a temperature of 700 °C for 90 minutes. In this study, two different types of NbH were used: comminuted (C) and comminuted followed by milling for 1 h / 300 rpm – (C+M). The alloy was obtained by wet milling (cyclohexane) for 6 h / 300 rpm. Afterwards, were uniaxially compacted in a 6.5 mm diameter matrix followed by cold isostatic pressing with pressure of 200 MPa. The sintering temperature in a high vacuum furnace was of 1300 °C and the specimens were heated to this temperature at 5 °C / min until 500 °C / 1 h and 730 °C / 0.5 h for dehydrogenation. Then at 7 °C / min up to 1300 °C and held for 3 hours and furnace cooled - FC. After, samples were treated at 1000 °C / 1 h followed by two types of cooling: air, with tube under vacuum – AC, and water cooling – WC. For scanning electron microscope analyses (SEM), Philips XL-30 model, the sintered samples were subjected to conventional metallographic preparation with epoxy resin, SiC sandpaper 220 to 1200, polishing with colloidal silica (0.06 microns) and etched in Kroll solution for 10 seconds. The grain size distribution was studied using laser scattering technique (Cilas 1064). The microhardness measures were carried out in Macrovickers 5112 equipment, Buehler, using load of 300 g / 15 s and standard ASTM E384-11. The X ray diffraction analyses were performed in Rigaku DMAX 2200 equipment, operating at 40 kV, 20 mA, step 0,02° / 6 s and copper radiation (λ = 1,5418 Å). The applied 2θ range was from 20 to 80°. The XRD patterns were compared to the PDF-2 database of the International Centre for Diffraction Data (ICDD).

Results and discussion

Table 1 presents the characteristics – cumulative values and morphology – of starting powders and alloy powders. The milling time and the use of NbH (C) and NbH (C+M) did not present significant influence on the difference of alloy particulates – D50% – of alloy 1 and 2. The angular morphology is due comminution of powders obtained by HDH process [15].

Table 1 – Cumulative values and morphology of powders and alloy powders.

	D10% (μm)	D50% (μm)	D90% (μm)	Morphology
TiH	33.5	92.5	337.2	Angular
NbH (C)*	-	-	-	Angular
NbH (C + M)	2.2	6.4	13.8	Angular
ZrH	6.3	64.1	394.4	Angular
Alloy 1(C)	2.2	7.5	14.5	Angular
Alloy 2(C+M)	2.5	7.2	14.2	Angular

*NbH (C) < 425 μm; Alloy 1(C) using NbH comminuted; Alloy 2 (C+M) using NbH comminuted and milled.

In Fig.1, general aspects of sintered sample surfaces are shown. There were niobium portions undissolved – white points – on the surfaces – Fig. 1 (a), (b), (c) and (f). However, in the Fig.1 (d) and (e) Nb portions were not present, therefore, in these samples the milling process and sintering were more effective. During high energy milling the NbH and ZrH powders are fragmented and inserted in TiH. But the dispersion of NbH particles in the mixture was not homogeneous. Thus, when the powder mixtures were pressed, NbH agglomerated made the dissolution process more difficult. In addition, the diffusion coefficient of Nb is lower than α-Ti in the β-Ti matrix [3].

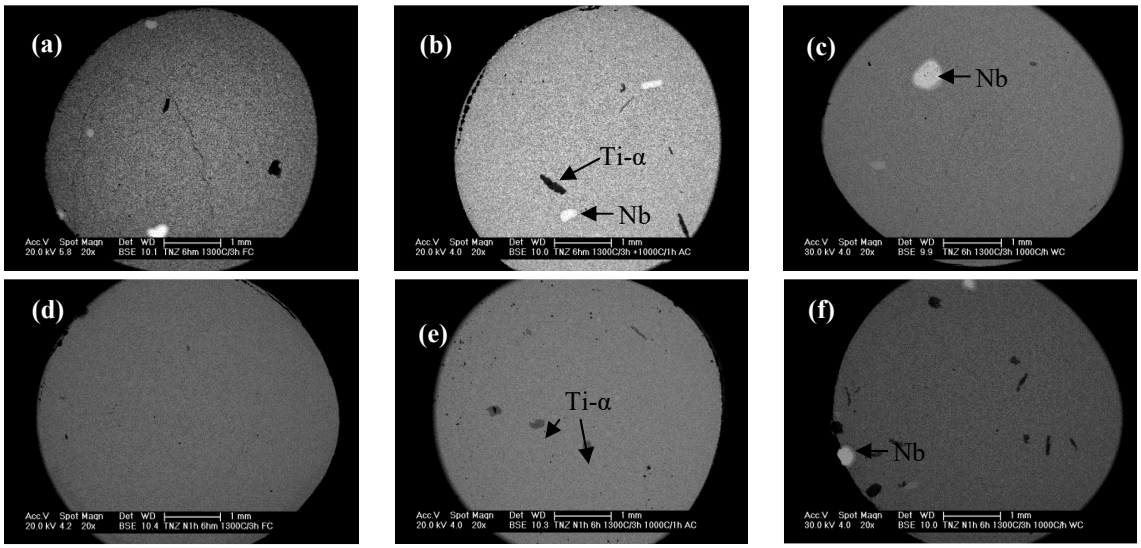

Fig. 1 – SEM micrographs of general aspect of Ti-20Nb-20Zr – (a) FC, (b) AC and (c) WC produced with NbH(C); (d) FC, (e) AC and (f) WC prepared with NbH(C+M).

The microstructures of alloys are observed in Fig.2. Two morphologies are presents: α-Ti (dark gray) appears in form of colonies and lamellae inward of β-Ti (light gray). EDS analysis revealed that β-phases are regions rich in Nb. The thermal treatment followed by cooling in air or water promoted decreasing of α phase and increase of β phase. The reduction is more evident in the alloy prepared with NbH (C+M), Fig. 2 (e) and (f), since this alloy presents smaller size particle than alloy produced with NbH (C). Furthermore, the higher surface area of the smaller particles, for alloy prepared with NbH (C+M), increases the number of bonds among the particles and promotes more efficient solid-state diffusion processes [15]. The α phase retention at the β phase is due to lower diffusion coefficient of α-Ti when compared with β-Ti during sintering.

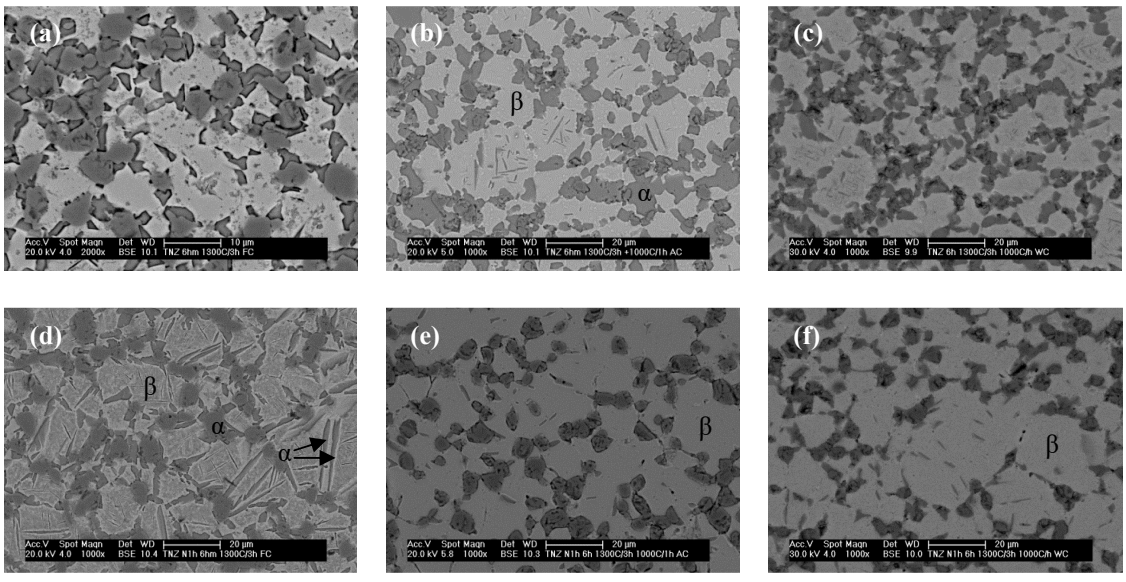

Fig. 2 – SEM micrographs of sintered Ti-20Nb-20Zr – (a) FC, (b) AC and (c) WC, alloy produced with NbH(C); (d) FC, (e) AC and (f) WC prepared with NbH(C + M).

The presence of both α (hcp) and β (bcc) phases is evident in all X-ray diffractograms of sintered samples in Fig. 3. The intensity of the principal peaks, indicated by arrow, corresponding to the β-Ti phase gradually increased with increasing on the rate cooling ($T_{cooling\ in\ water} > T_{cooling\ in\ air} > T_{cooling\ in\ furnace}$), unlike α-Ti behavior.

The better solubility of Nb particle, in the alloy with NbH (C+M), suppressed the β→α during cooling and leads to the content increase of β phase [10].

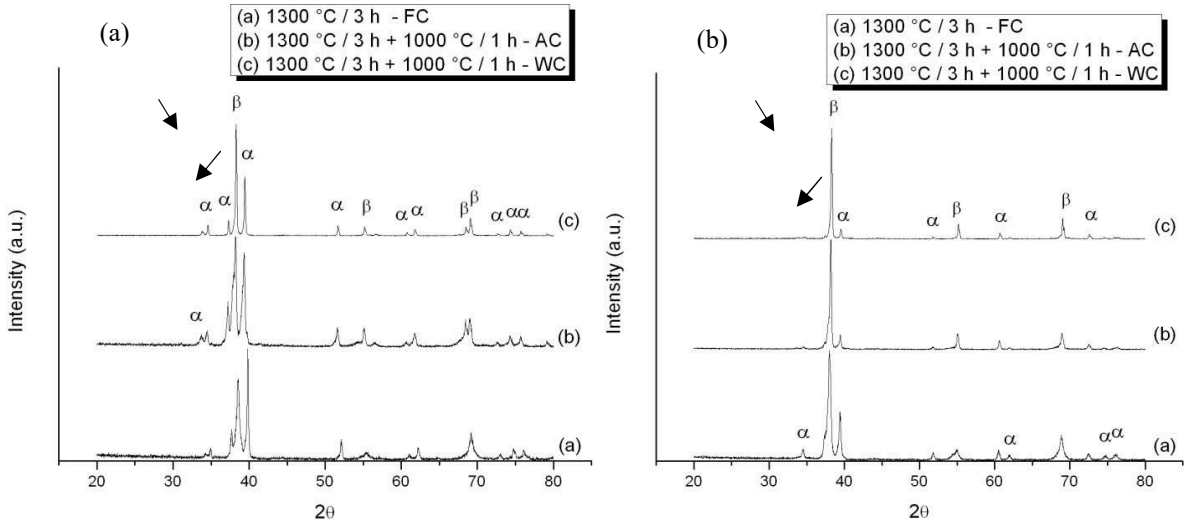

Fig. 3 – X-ray diffractograms of alloy Ti-20Nb-20Zr sintered and cooled under FC, AC and WC, (a) Ti-20Nb-20Zr with NbH (C); (b) Ti-20Nb-20Zr with NbH (C+M).

The effect of heat treatment (FC, AC and WC) on microhardness of Ti-20Nb-20Zr alloy is presented in Fig. 4. The variation of this property with respect to the cooling rate was similar, air cooled (AC) samples showed higher microhardness than samples cooled in furnace and water cooling. In this case, the distribution of volume α phase in form of colonies in the matrix increased the hardness due to higher hcp packing factor in compared to bcc, 0.74 and 0.68, respectively.

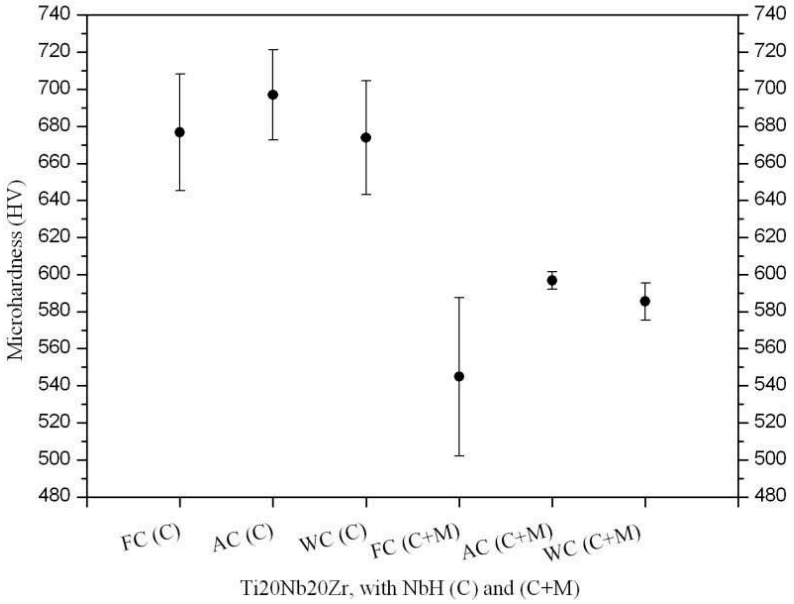

Fig 4 – Microhardness of Ti-20Nb-20Zr alloy.

Conclusions

The use of NbH (C+M), as alloying element in the Ti-20Nb-20Zr alloy, combined with heat treatment produced samples with more homogeneous microstructure and had fundamental role in the Vicker microhardness. Agglomerated NbH slowed down the sintering process of the alloy and

influenced the final microstructure. The cooling type had influence on the β-Ti phase formation. The Ti-20Nb-20Zr alloy produced with NbH(C+M) is the more indicated for biomedical applications, since the microstructure is more homogeneous for both FC and AC cooling types, besides, from XRD results, it is mainly composed of β phase.

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