Amigó Mata, A.; Zambrano, JC.; Martínez, S.; Amigó Borrás, V. (2014). Microstructural characterisation of Ti-Nb-(Fe-Cr) alloys obtained by powder metallurgy. Powder Metallurgy. 57(5):316-319. doi:10.1179/0032589914Z.000000000210.

# Microstructural characterization of Ti-Nb-(Fe-Cr) alloys obtained by powder metallurgy

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**Abstract:**
Ti β-alloys based on the Ti-Nb alloy system exhibit growing interest in the biomaterial community. The addition of small amounts of Fe and Cr further increases β-phase stability, improving the properties of Ti-Nb alloy. Production of such alloys by powder metallurgy (PM) starting from elemental powders has the problem of lacking homogeneity due to restricted solid state diffusion. To improve mixing and diffusion of the elements mechanical alloying is used. This paper studies the microstructural characterization and mechanical properties obtained by bending tests of Ti-Nb-(Fe-Cr) alloys obtained by conventional PM with elemental powder mixture and mechanical alloying. The mechanical alloying allows a much more homogeneous composition and particle morphology, characterized by rounded and significantly enlarged powder particles. In the sintered samples two phases appear, namely alpha and beta phase. The α phase appears at the grain boundaries and in lamellae growing from the edge inward, formed mainly by Ti and lower Nb content than nominal. The beta phase is enriched with Nb, Fe and Cr. The addition of the both latter elements increases considerably mechanical properties of Ti-Nb alloys, providing increased ductility.

**Keywords**: beta Ti, Ti-Nb alloys, powder metallurgy, Fe and Cr additions

## Introduction:

Titanium alloys have demonstrated properties attractive for biomedical applications due to their lower modulus, superior biocompatibility and excellent corrosion resistance compared to stainless steels and Co-Cr alloys. Ti6Al4V has been become the most used implant materials, but it is known that V and Al are toxic for the human body [1, 2]. β type titanium alloys with lower modulus of elasticity and greater strength have been developed recently and it has been reported that Ti–Nb alloys exhibit complete biocompatibility. The presence of titanium body centered cubic crystal structure (β phase) at room temperature cause a decreasing of elastic modulus, improving the stress shielding problem. Therefore, β titanium alloys are promising materials for bio-applications [3-5].
Multicomponent titanium alloys can be divided into α, α+β and β-Ti, and usually the equation of Aluminum equivalent ($Al_{eq}$ ) and Molybdenum equivalent ($Mo_{eq}$) are applied to define the type of alloy. The effect of $Al_{eq}$ and $Mo_{eq}$ on the strength and fracture toughness of titanium alloys has been studied and the result shows that the tensile strength of the alloy increases with increasing of aluminum equivalent and molybdenum equivalent and the fracture toughness decreases gradually [6, 7]. The addition of small amounts of Fe and Cr increase β phase stability, therefore further improving the properties of theTi-Nb alloy. The Molybdenum equivalent can be calculated for Ti-Nb-Fe-Cr alloys in the simplified form:

$$[Mo]_{eq}=[Nb]/3.6+1.25[Cr]+2.5[Fe] \qquad \text{Equation 1}$$

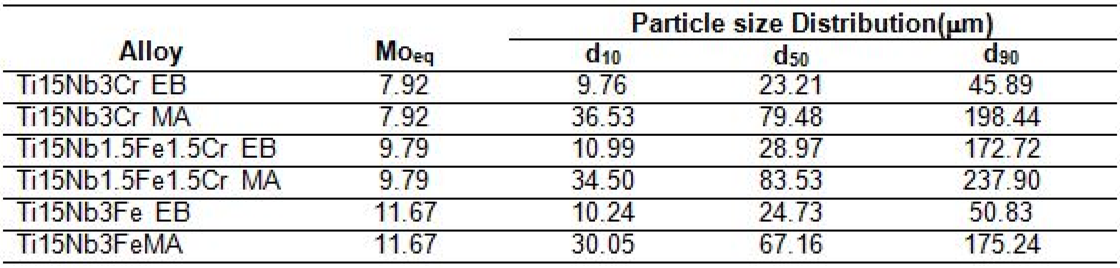
Powder metallurgy (PM) has been taken into account for lowering the cost of titanium alloy parts since 1970s. The PM process is a promising method for the production of near-net shape parts. Up to now, there are few reports on the fabrication of Ti–Nb based alloys by the PM process [8, 9]. Mechanical alloying (MA) is a potential powder processing technique that allows production of homogeneous materials starting from blended elemental powder. It is a solid-state powder processing technique using a high-energy ball mill to favor plastic deformation for cold welding and reduce the process time. This process involving repeated welding, fracturing, and rewelding of powder particles in a high-energy ball mill [10]. It has been recognized that powder mixtures can be mechanically activated to induce chemicals reactions at low temperatures, extending the solid state solubility limits, developing amorphous phases and enabling alloy of elements. The potential of this technology for manufacturing homogeneous Ti-Nb-Fe-Cr alloys is investigated in the present work. During MA, heavy plastic deformation is introduced into the particles. This is manifested by the presence of a variety of crystal defects such as dislocations, vacancies and stacking faults. The presence of this structure defect enhances the diffusivity of solute elements into the matrix. Further, the temperature rise during milling further aids the diffusion behavior. Improving chemical homogeneity obtained in PM samples during sintering. Great number of variables can affect the MA results. Compare elemental blended samples with mechanical alloying results is necessary. In this study, the Ti-Nb based alloys were obtained by the PM process using elemental blended and subsequently mechanically alloyed Ti, Nb, Fe and Cr powder mixtures. The Molybdenum equivalent was varied to improve the mechanical properties of Ti-Nb alloy with a view to its use as a biomedical material.

## 2. Experimental Procedure

### 2.1. Materials and processing techniques

The nominal compositions of powders were as follows: Ti15Nb3Cr, Ti15Nb1.5Fe1.5Cr and Ti15Nb3Fe (all compositions in wt. %). The powders of commercial Ti (99.7%, -325 mesh), Nb (99.8%, -325 mesh) and Cr (99%,-325 mesh) were supplied by Alfa Aesar and Fe (-230 mesh) by Hogänas. The blend of elemental powders was conducted in a closed vial in a blender model Bioengineering Inversin for 20 min. The choices of compositions were based on the molybdenum equivalent as calculated and presented in Table 1. The $d_{10}$, $d_{50}$ and $d_{90}$ values represent the particle diameters, where 10, 50 and 90 mass % of the powder particles have a smaller equivalent diameter and significant increase of particle size distribution after the mechanical alloying was observed.

Table1. Characteristic properties of elementally blended (EB) and mechanically alloyed (MA) samples: molybdenum equivalent and particle size distribution.



| Alloy | $Mo_{eq}$ | Particle size Distribution(µm) | | |
|---|---|---|---|---|
| | | $d_{10}$ | $d_{50}$ | $d_{90}$ |
| Ti15Nb3Cr EB | 7.92 | 9.76 | 23.21 | 45.89 |
| Ti15Nb3Cr MA | 7.92 | 36.53 | 79.48 | 198.44 |
| Ti15Nb1.5Fe1.5Cr EB | 9.79 | 10.99 | 28.97 | 172.72 |
| Ti15Nb1.5Fe1.5Cr MA | 9.79 | 34.50 | 83.53 | 237.90 |
| Ti15Nb3Fe EB | 11.67 | 10.24 | 24.73 | 50.83 |
| Ti15Nb3FeMA | 11.67 | 30.05 | 67.16 | 175.24 |

Mechanical alloying was performed in a planetary ball mill model PM 400/2 Retsch using a rotation speed of 300 rpm, vial and balls of FeCr steel were used. The ball to powder weight ratio was 10:1. The milling batch had a mass of 20 g for each run. To prevent an excessive temperature rise of the powder during milling, milling was stopped at 45 min, and then the grinding bowl was allowed to cool for 20 min. To minimize powder oxidation, milling was carried out under an argon atmosphere.

The powders of elemental blend and mechanical alloying were compacted in a universal testing machine Instron 432 Model with a load cell of 500 kN, with a compaction pressure of 600 MPa. The matrix used was rectangular with dimensions of 30 × 12 mm, the powder mass required to obtain a sample height of 5 mm was about 7 g. The specimens were sintered under high vacuum (approximately $10^{-4}$ to $10^{-5}$ mbar) in a tubular furnace carbolite HVT 15/75/450 model, at 1280 °C, After a dwell time of 2 h, the samples were furnace cooled at 10 °C/min.

### 2.2. Powder characterization and microstructure

To characterize the morphology and chemical composition of the powder, SEM and EDS and the particle size distribution has been used. To measure the particle size, the method of diffracted light scattering of the laser beam on particles suspended in distilled water has been used in a Mastersizer 2000 laser diffractometer. For microstructural characterization a transversal section of the sintered samples was cut and metallographically prepared. The microstructure was observed using an optical microscope Nikon LV100. To quantify phases and internal porosity, NIS-Elements® image analysis software was used. Backscattered electron images (BSE) of the microstructure at different magnifications were obtained in a scanning electron microscope Jeol JSM6300. Microanalysis was performed by energy dispersive spectroscopy (EDS) for quantification of chemical composition, using an Oxford Instruments X-ray detector installed in microscope.

### 2.3. Mechanical properties

The mechanical properties have been investigated by various tests. For hardness measurement automatic Centaur Model HD-9-45 hardness tester was used. The measurements were performed with application load of 10 Kg. In order to obtain the elastic modulus ultrasonic methods were used with a Karl Deutsch digital Echograph. To determine the mechanical properties bending test were done. A universal testing machine Instron 4204 Model, with 50 kN load cell was used. Tests were carried out according to standard EN ISO-3325 [11].

## 3. Results and discussion

### 3.1. Structure evolution of powder blends during mechanical alloying

The surface morphologies and the change of particle size of Ti, Nb, Fe and Cr powders before and after milling are shown in Fig 1.a and 1.b. After ball milling, an increase of particle size and agglomeration of particles to large aggregates can be observed. This result indicates that the mechanically alloyed powders are still in the early stages of milling; the force of the impact plastically deforms the powder particles leading to beginning work hardening and fracture. The new surfaces created enable the particles to weld together leading to an increase of particle size. As we can see in Fig 1.c, the ductile alloying elements get flattened to platelet shapes by a micro-forging process [10].

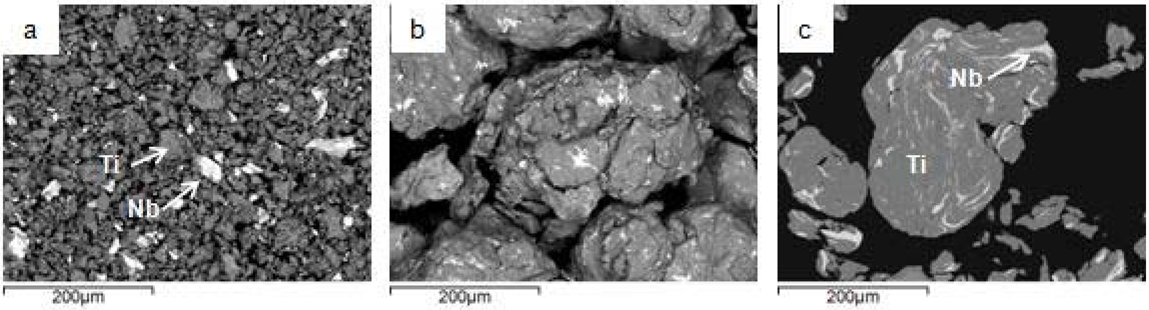


Figure 1: SEM image of Ti15Nb1.5Fe1.5Cr. a) Elemental blend. b) Mechanical alloying 45 min. c) Transversal section of mechanical alloying. Particles identified by using EDS and SEM.

### 3.2. Microstructure

Figure 2 shows SEM images of the as-sintered elementally blended (EB) and mechanically alloyed (MA) samples in the backscattered modus. In average, the microstructure is mainly composed by $\alpha$+$\beta$ colonies. In the case of EB, the microstructure contains very fine and almost continuous grain boundary $\alpha$ (GB$\alpha$) and lamellae $\alpha$ plates, which grew from GB$\alpha$ into the direction of the adjacent $\beta$ matrix (Fig 1.a, 1.c and 1.e). For MA samples, there is a duplex $\alpha$+$\beta$ microstructure with lamellae $\alpha$ plates decreasing with increasing of Molybdenum equivalent (Fig 1.b, 1.d and 1.f) [12, 13].

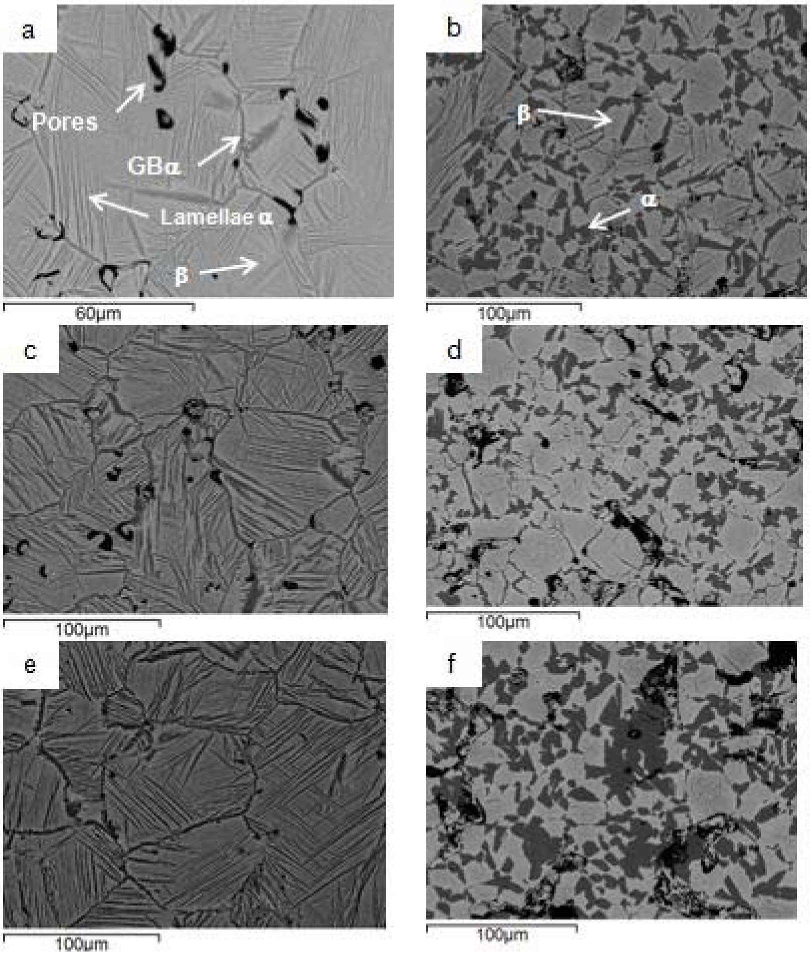


Figure 2: SEM micrographs showing the as-sintered microstructure of elemental blend and mechanical alloying. a) Ti15Nb3Cr EB. b) Ti15Nb3Cr MA. c) Ti15Nb1.5Fe1.5Cr EB. d) Ti15Nb1.5Fe1.5Cr MA. e) Ti15Nb3Fe EB. f) Ti15Nb3Fe MA

The porosity of the samples and the percentage of phases were obtained from images taken by optical microscopy using an image analysis program (See Table 2). EB samples show less porosity than MA samples. The gain of porosity percentage can be explained with the increase of the particle size distribution (between 3 or 4 times) and the increased of particle hardness due to plastic deformation during the MA process. Particle hardening results in aggravated powder compaction. The formation of bonding necks decrease, and therefore complete elimination pores becomes difficult [14].

Table 2: Internal porosity and phase distribution of Elemental Blend (EB) and Mechanical alloying (MA) samples.

| Process | Alloy | %Internal Porosity | Phases Distribution (%) | |
|---|---|---|---|---|
| | | | % Alpha | % Beta |
| EB | Ti15Nb3Cr | 4.3±0.2 | 24.1±2.5 | 75.9±2.5 |
| | Ti15Nb1.5Fe1.5Cr | 3.3±0.5 | 36.7±1.5 | 63.3±1.5 |
| | Ti15Nb3Fe | 4.1 ± 0.4 | 29.4±0.5 | 70.6±0.5 |
| MA | Ti15Nb3Cr | 8±0.3 | 32.6±3.9 | 67.4±3.9 |
| | Ti15Nb1.5Fe1.5Cr | 8.4±0.4 | 33.4±4.8 | 66.6±4.8 |
| | Ti15Nb3Fe | 10.8±1.7 | 42.2±4.5 | 57.8±4.5 |

### 3.3 Mechanical Properties:

The bending tests show relatively high values of ultimate strength for EB samples, which are almost competitive to cast Ti-Nb alloys: For comparison, C.M. Lee et al reported a bending strength of 1550 MPa for cast Ti15Nb [15]. Mechanical alloying process leads to a hardening of powder particles due to the severe plastic deformation, which is characteristic for the process. This behaviour results in insufficient densification when using conventional pressing and sintering. Obviously, the remaining porosity is the most important factor significantly influencing the mechanical properties and therefore leading to the big difference of bending strength observed in Figure 3. It would be more convenient to use compaction processes like Hot Isostatic Press or Spark Plasma Sintering (SPS) characterized by superposing temperature and pressure. The use of fast densification processes as SPS can improve the mechanical properties for the MA, but for EB causes greater lack of element diffusion [16]. In all cases a decrease in the bending strength is observed with increasing of [Mo]eq (Fig 3) where a larger amount of beta phase is observable.

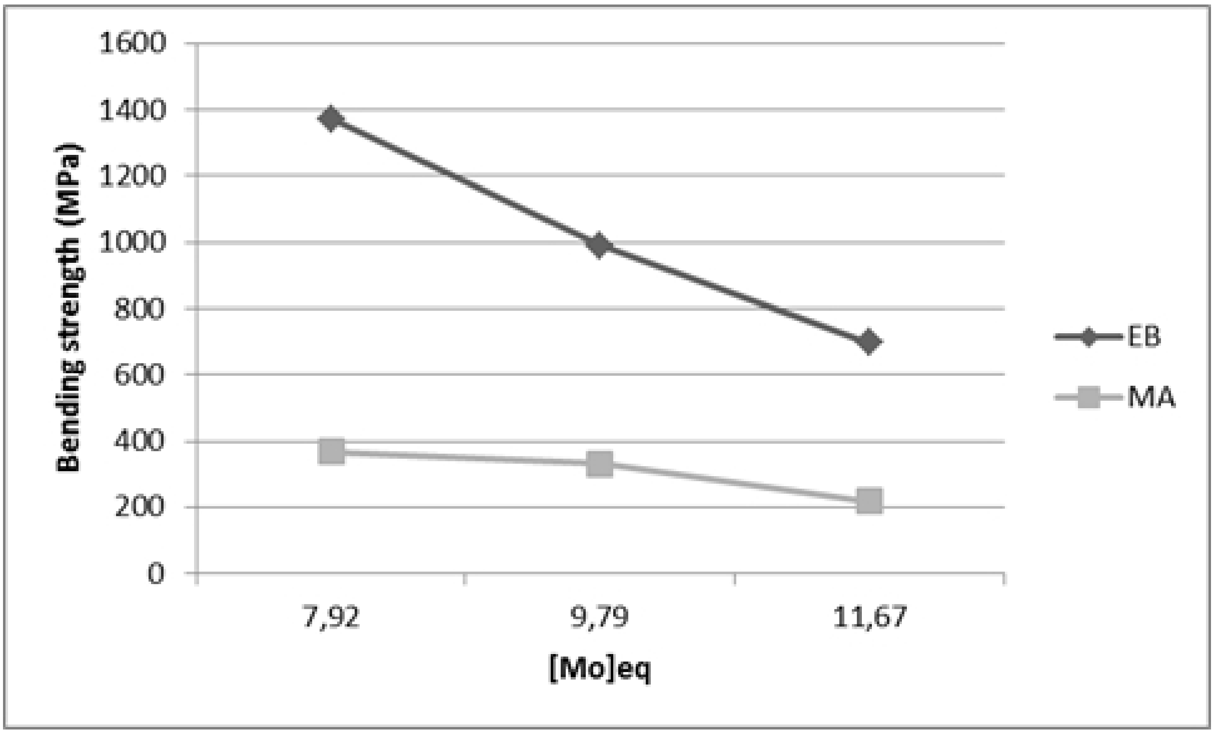


Figure 3: Bending strength of Ti15Nb-X(Cr,Fe) alloys

Usually the elastic modulus of CP-Ti is around 120 GPa [17]. The appearance of beta phase cause a decrease in elastic modulus, obtaining values between 75-83 GPa for EB and 50-59 GPa for MA, if measured by ultrasonic methods. Lower values are obtained in the case of MA because these samples show higher porosity levels (Table 2). Other authors report values between 68-50 GPa for cast Ti-Nb-Si alloys [18].

Hardness tests exhibit higher values for EB (around 370 $HV_{10}$) than for MA (around 220 $HV_{10}$ except for MA of Ti15Nb3Fe alloy which has a significantly higher value (322 $HV_{10}$) than other MA samples). This increase reflects the distribution of the alpha + beta phases in the duplex microstructure that appears for the MA with Fe. Other authors reported hardness values about 320HV for Ti30Nb(0-7.5)Ta cast alloys [19].

## 4. Conclusions:

In the present study, manufacturing of Ti-Nb-Fe-Cr alloys by mechanically alloying provided a higher level of porosity than elementally blended powder compacted and sintered with the same parameter set. This porosity may be caused by plastic deformation gained from the process. MA might lead to an enhanced uptake of oxygen that stabilizes the alpha phase, this possibility should be studied deeper in other works.

A microstructural change occurs if MA samples were compared with EB samples. EB samples presented a lamellar microstructure while MA samples have a duplex microstructure.

This microstructural changes and the residual porosity values justify the mechanical properties obtained in the bending test and hardness.

As expected, the elastic modulus decreases with increasing porosity. Obviously, the Molybdenum equivalent influences bending strength but does not have a significant influence on the elastic modulus. Nevertheless, clarification of these observations requires a more thorough study.

## Acknowledgements

This paper is based on a presentation at Euro PM 2014, organised by EPMA in Salzburg, Austria on 21–24 September 2014. This work was funded by UPV by the Staff Training Program for Predoctoral Researchers dated 28 February2014. The Ministry of Science and Innovation of Spain by project research MAT2011–28492–C03 and Generalitat Valenciana by ACOMP / 2014/151.

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