MICROSTRUCTURE OF Ti-Cu AND Ti-Nb CAST ALLOYS FOR MEDICAL AND DENTAL IMPLANTS

Protásio Nery Andrade
UNICAMP/FEM/DEMA - CP 6122, CEP 13083-970, Campinas SP - Brazil
protasio@fem.unicamp.br

Rodrigo José Contieri
UNICAMP/FEM/DEMA - CP 6122, CEP 13083-970, Campinas SP - Brazil
rodcont@operamail.com

Adelino de Aguiar Coelho
UNICAMP/IFGW/DEA - CP 6122, CEP 13083-970, Campinas SP - Brazil
coelho@ifi.unicamp.br

Conrado Ramos Moreira Afonso
UNICAMP/FEM/DEMA - CP 6122, CEP 13083-970, Campinas SP - Brazil
croma@fem.unicamp.br

Peterson Luiz Ferrandini
UNICAMP/FEM/DEMA - CP 6122, CEP 13083-970, Campinas SP - Brazil
peterson@fem.unicamp.br

Rubens Caram
UNICAMP/FEM/DEMA - CP 6122, CEP 13083-970, Campinas SP - Brazil
rcaram@fem.unicamp.br

Abstract*. Titanium and its alloys are widely applied in several fields, like medical, chemical and aerospace industries, mainly due to their properties, including its excellent high strength-to-weight ratio and superior corrosion behavior. Processing titanium alloys is very expensive and it is a barrier in increasing its application in a number of industries, including the manufacturing of medical and dental devices. An approach to overcome such difficulties is applying precision casting. The purpose of this work is to study the development of Nb and Cu alloyed titanium to be used in the fabrication of implants and processed in a centrifugal casting equipment, using copper mold. Firstly, samples with different compositions were arc melted using a non-consumable tungsten electrode and water-cooled copper hearth under high purity argon atmosphere. The ingots were recast in a cooper mold and finaly the effect of the composition on the microstrucutre was evaluated.*

Keywords*: Beta Ti Alloys, Phase Transformation, Mechanical Properties, Dental Implants.*

1. Introduction

Titanium may be considered a relative new option as a structural material since it became commercially available not until the 50´s, when the Kroll process was developed. The Kroll process is still the most employed in the production of titanium metal. Pure titanium does not present high mechanical strength but when alloyed with elements like Al, V, Ta, Fe, Mo, Nb and Cu its mechanical properties can be remarkably improved.

Pure titanium shows an allotropic transformation at 882.5°C, when the α phase (HCP), stable at low temperatures, turns into β (BCC), which remains stable up to the melting point at 1670°C. This solid transformation allows for the possibility of mechanical behaviour improvement by alloying and thermomechanical treatment. Titanium is a transition metal and its electronic structure permits it to form solid solution with a considerable number of other elements. The titanium alloying elements may be defined as α stabilizer, β stabilizer or neutral and its alloys may be classified, according to the phases present, as α, near-α, α+β, metastable β and stable β. Figure 1 shows the effect of α and β stabilizers on the phase precipitation in titanium alloys.

As a biomaterial, the use of titanium has been rapidly growing in the last two decades and its use as implant material in the orthopedic field begun in the 60's. Since then, Ti-6Al-4V ELI, an α+β type alloy has been the most widely used as an implant material, due to its biocompatibility, corrosion resistance and mechanical properties. However, due to being toxic, vanadium has been substituted, which lead to the development of other alloys, the most promising Ti-6Al-7Nb and Ti-5Al-2.5Fe. Like other metallic alloys, mechanical properties of the titanium alloys depend not only on composition but also on microstructure, which is heavily influenced by thermo mechanical processing. The α+β alloys show a much better mechanical behaviour when compared to the α alloys, due to the combination of the α and β phases, and this behaviour depends on the relative amounts of each phase. The interesting mechanical behaviour, the good formability and the highly interesting low elastic modulus make the β titanium alloys the most promising metallic materials to be used in the fabrication of medical and dental implants. Low elastic modulus allows load transfer from the implant to the adjacent bone, which prevents bone resorption.

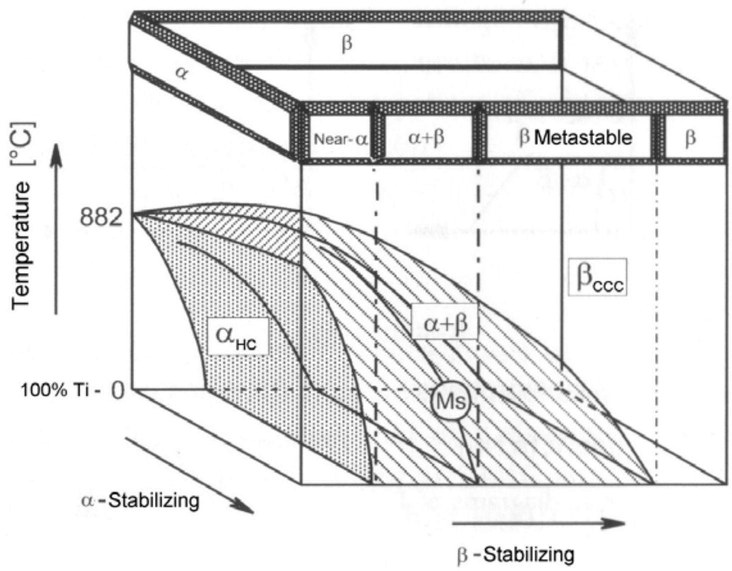

Figure 1. Partial phase diagram of titanium and possible alloys found (Lütjering, 2003)

When compared to aluminum and iron, titanium alloys are expensive, which considerably hinders an increase in its application. The high cost is not only due to the price of titanium raw material but mainly due to the process fabrication, especially when machining is required. An approach in order to overcome these difficulties is applying precision casting. Casting tends to be a way to overcome complexities found in titanium goods fabrication, but on the other hand, it also faces some difficulties, such as the titanium high melting point, reactivity with the mold and affinity with interstitial elements, which requires melting under controlled atmosphere. Besides, composition and cooling rates are quite important in determining the final microstructure.

A recent number of studies have reported results on titanium casting, including studies on the Ti-Cu and Ti-Nb systems. While the Cu alloying leads to a decrease in titanium melting point, making the casting easier and improving mechanical properties, Nb additions stabilize β, resulting in low elastic modulus (Aoki, 2004). The Ti-Cu and Ti-Nb phase diagrams are seen in figures 2 and 3. Thus, the purpose of this study is to evaluate the microstructure of Cu and Nb alloyed Ti, cast in a centrifugal equipment.

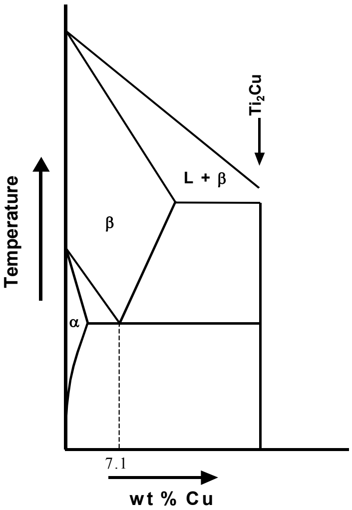

Figure 2. Ti-Cu partial phase diagram.

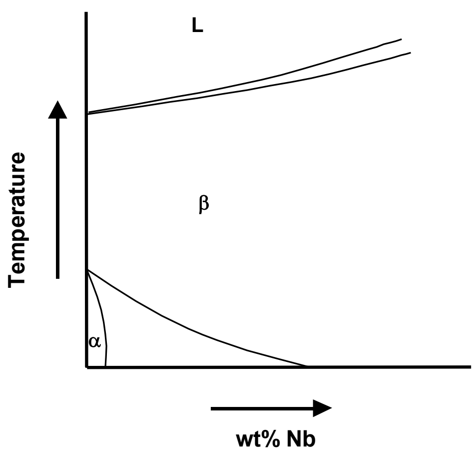

Figure 3. Ti-Nb partial phase diagram.

2. Experimental Procedure

High chemical purity Ti, Nb and Cu were arc melted using a non-consumable tungsten electrode and a water-cooled cooper hearth under high purity argon atmosphere. 30 g ingots were produced. In order to enhance homogeneity the ingots were flipped and remelted 5 times. The loss of mass during melting was evaluated to be less than 0.1 wt%. The four compositions chosen were Ti-5.0%Cu, Ti-15%, Ti-10%Nb and Ti-25%Nb (wt%), that were selected based on the eutectoid transformation in the Ti-Cu system and in the Nb necessary amount to partially stabilize β under slow cooling. Afterwards, the samples were centrifugally cast (Watanabe, 2003) in copper molds at room temperature and applying a maximum rotation of 1000 m^{-1}. The final cast ingot is seen in figure 4.

The samples were conventionally prepared for metalographic analysis and etched with: water (50 ml); HF (40 ml); HCl (20 ml). It was performed optical microscopy (OM), scanning electron microscopy (SEM) and X-ray diffraction (XRD) using CuK_α radiation. Vickers hardness was determined using a load of 200 gf, applied for 20s and the results are 10 measurement average.

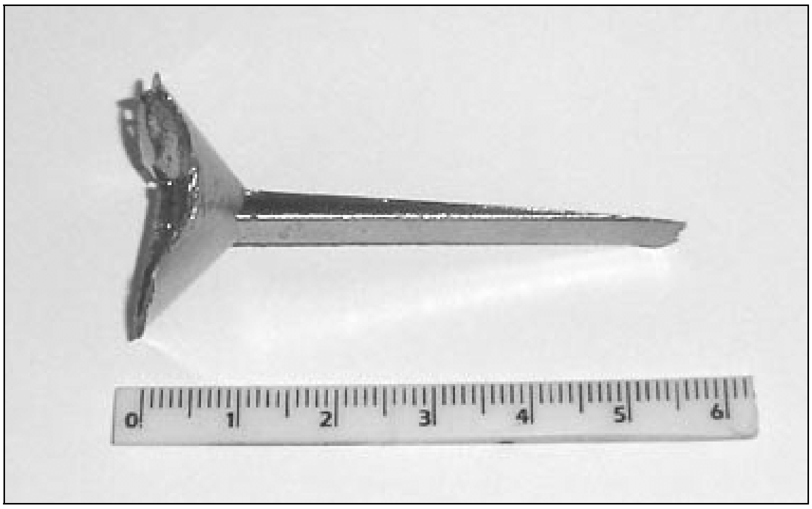

Figure 4. Final cast ingot.

3. Results and Discussion

According to Long and Rack (Long, 1998), the microstructure of a titanium alloy depends on its composition and mostly, the heat treatment applied. Alloys with low β stabilizers content tend to present α phase and the amount presented decreases as the content of the β stabilizers increases. The cooling rate from high temperature is an important parameter in determining the final microstructure. Low cooling rates favor α precipitation as well as higher rates limit such a precipitation, resulting in a combination of α and β. However, martensitic structures may be formed depending on the final temperature the sample is cooled to. Alloys presenting high β stabilizer content will show only β at room temperature.

3.1. Ti-Cu Alloys

Based on the Ti-Cu phase diagram, Cu is considered a β stabilizer. This phase diagram shows a eutectoid transformation close to 7.1% Cu and accordingly, samples processed under low cooling rates would produce microstructures formed by a mixture of Ti_2Cu and α-titanium, the volume fraction of each phase depending on composition (Kikuchi, 2003). On the other hand, a rapid cooling from high temperature may result in a martensitic microstructure. Figure 5.a presents the microstructure of a 5.0 % Cu (hypoeutectoid) sample cast in a cooper mold. It seems that the resulting cooling rate was high enough to promote martensitic transformation all over the ingot and suppress Ti_2Cu formation.

As the Cu content was raised to 15 % (hypereutectoid composition) it was expected to form Ti_2Cu and change martensite formation. The results obtained corroborated this hypothesis, as shown in Figure 5.b, where the obtained dendritic and eutectoid morphologies are seen. The eutectoid structure seen in figure 6.a of the 15 % Cu sample shows dendritic morphology, where the dendrite arms are formed by martensite and Ti_2Cu is precipitated in the interdendritic regions, as shown in figure 6.b. As already said, the precipitated phase is Ti_2Cu and the matrix is formed by α′ martensite. The dendrite arms solidified as β and due to segregation during solidification, the dendrite cores had its Cu content reduced, while in the interdendritic regions the Cu amount of Cu increased (dark gray region) (fig. 6.b.). According to the phase diagram (Figure 2), in the Cu rich region the possibility of forming Ti_2Cu is higher. This suggests that the interdendritic region has a high volume fraction of Ti_2Cu. During rapid cooling, the β phase is transformed into α′ martensite, being finely dispersed within the dendrite core. The Cu amount in the alloy is not high enough to lower the martensitic transformation start to below the room temperature, so martensite is formed. Ti and Cu distribution in the interdendritic regions was mapped by X-ray image, which is seen in figure 6.b.

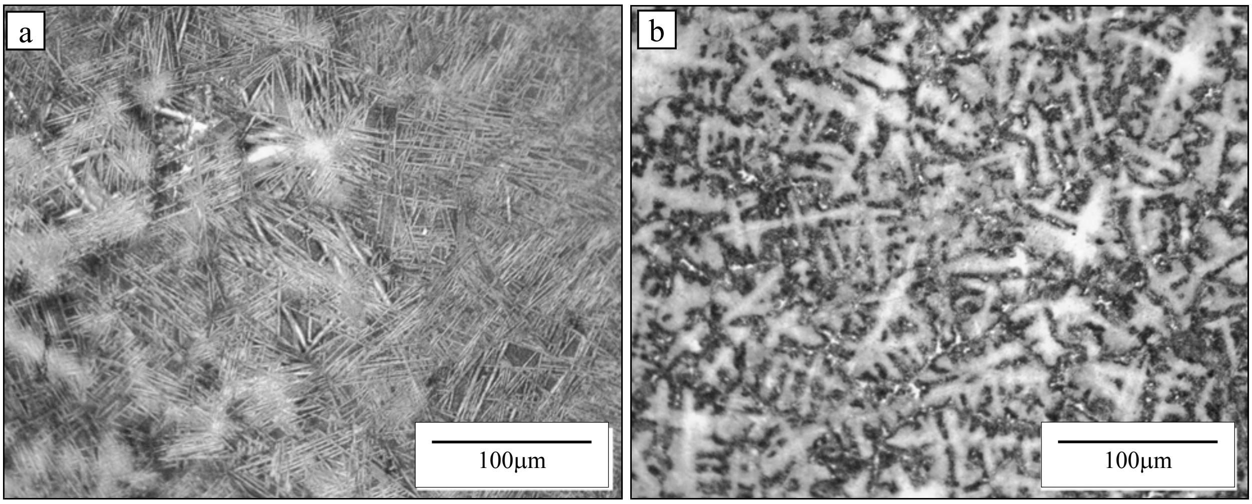

Figure 5. Optical micrograph of 5% Cu sample showing a martensite structure and (b) 15% Cu sample showing dendritic structure in a martensitic matrix.

Figure 7 presents X-ray diffractograms of the Ti-5.0Cu and Ti-15Cu alloys. According to XRD the hypoeutectic Ti-5.0Cu alloy presents only α′ martensite. This is in agreement with the microstructure seen in fig. 5.a. Due to the high cooling rate imposed during cooper wedge mold casting the phase identified through XRD analysis is not the equilibrium phase expected in the binary phase diagram of Ti-Nb. XRD showed that the Ti-15Cu hypereutectic alloy presents α′ martensite and Ti_2Cu. Instead of forming the equilibrium phases, α and Ti_2Cu, a metastable microstructure was formed during the rapid cooling, as can be seen in figure 5.b, resulting from the transformation of β into α′ martensite.

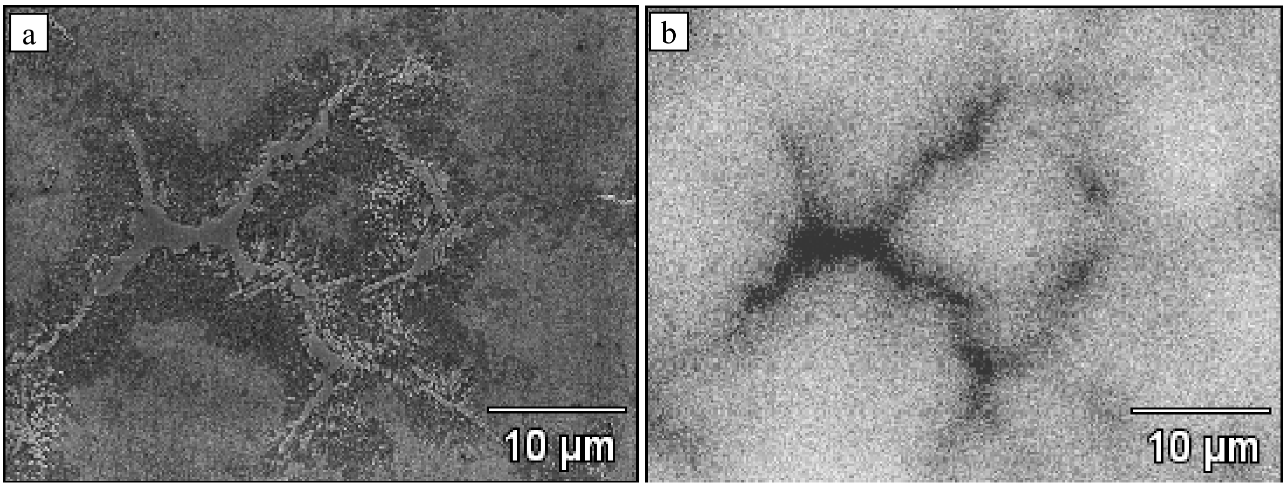

Figure 6. (a) SEM micrograph of 15% Cu sample showing a dendrite arm and respective (b) X-ray mapping of copper.

The influence of Cu on the mechanical behavior of Ti was estimated by Vickers hardness. Table 1 shows hardness variation as a function of Cu content. Hardness increases with increasing Cu content, which is related to changing from hypoeutectic to hypereutectic composition. It agrees with the fact that a hypereutectic composition favors the formation of Ti_2Cu besides the formation of α′ martensite, which increases the hardness of the alloy.

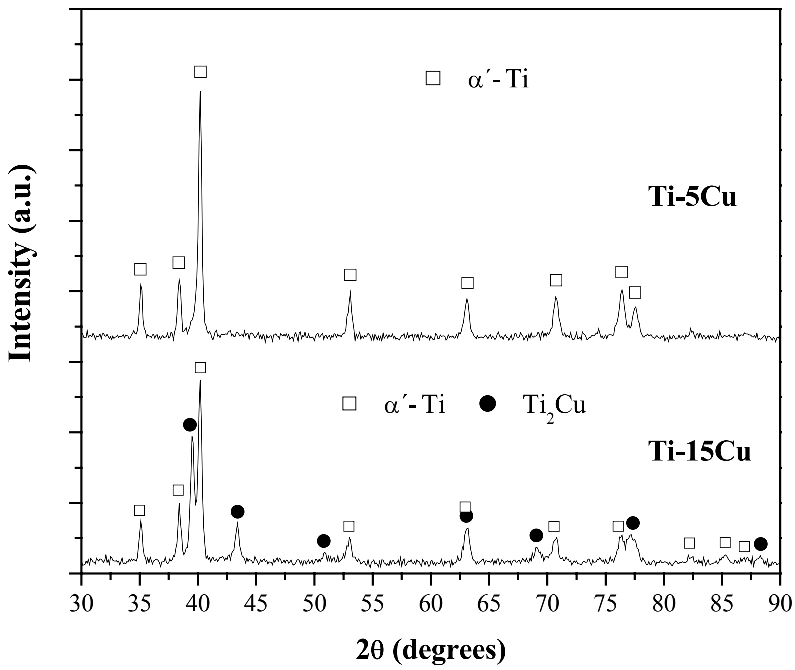

Figure 7. X-Ray diffraction of the Ti-Cu alloys

Table 1. Composition (wt%Nb) of the Ti-Cu alloys and Vickers Hardness (HV) of copper wedge mold cast samples.

Composition (wt%)	Ti-5.0%Cu	Ti-15%Cu
Hardness (HV)	294 ± 25	384 ± 34

3.2. Ti-Nb Alloys

The Ti-Nb phase diagram is considered an isomorphous type diagram, while Nb is considered a β stabilizer element. A β isomorphous type occurs when the content of β stabilizer element is high enough to stabilize the β phase at room temperature (Lütjering, 2003). The partition coefficient of the Ti-Nb system is greater than one, which means that there is a solute retention during solidification, resulting in a higher solute concentration in the primary phase, the β matrix. Figure 8.a shows an optical micrograph of the Ti-10Nb alloy, constituted by α' martensite and small grains of about 200 µm, that are attributed to the rapid cooling imposed by the copper wedge mold casting. Figure 8.b shows the microstructure obtained when the Nb content was increased to Ti-25Nb and the structure is dendritic and refined. On cooling, one sees the formation of the martensitic matrix. The microstructure vary significantly when compared to the α + β equilibrium microstructure due to the high cooling rate imposed by the wedge mold casting, which increases the metastable β phase volume fraction and favors the formation of martensite α". Figure 9 shows a micrograph of the Ti-25Nb sample exhibiting a clear separation between a portion of dendritic structure, in the inner region of the wedge and a portion of directional columnar structure perpendicular to the mold wall (parallel to the heat extraction direction). Figure 10.a presents a transversal section of the Ti-25Nb alloy where one can see dendritic arms, α" martensite finely dispersed along interdendritic regions and a β matrix. X-ray image of titanium is seen in Fig. 10.b where the dark gray region corresponds to the Ti high content areas. It confirms that there is a higher Ti content within the interdendritic regions and a higher Nb content within the dendrite arms, which agrees with the higher than one partition coefficient of the Ti-Nb binary phase diagram. Figure 11 shows X-ray diffractograms of the Ti-10Nb and Ti-25Nb alloys, quenched due to the rapid cooling rates imposed by the casting. XRD analysis of alloys presenting lower Nb contents than 10% shows α' martensite formed by β transformation. When the Nb percentage was increased to Ti-25Nb, the phases found changed to α" martensite and β. The higher Nb content hinders α' martensite formation and favors β stabilization. These results, obtained under copper wedge mold casting, were considered coherent, since Lee et al. (2002) used furnace cooling, and Hon et al. (2003) used graphite mold, both leading to considerably lower heat extraction rates. Using the XRD analysis Lee (2002) found a microstructure composed of α + β and Hon (2003) found α" martensite.

Vickers hardness was determined and the values were found to decrease with increasing Nb content, going from 248 ± 5 for the alloy Ti-10Nb to 216 ± 8 for the alloy Ti-25Nb, which was attributed to β retention, that is softer than α' and α" martensites.

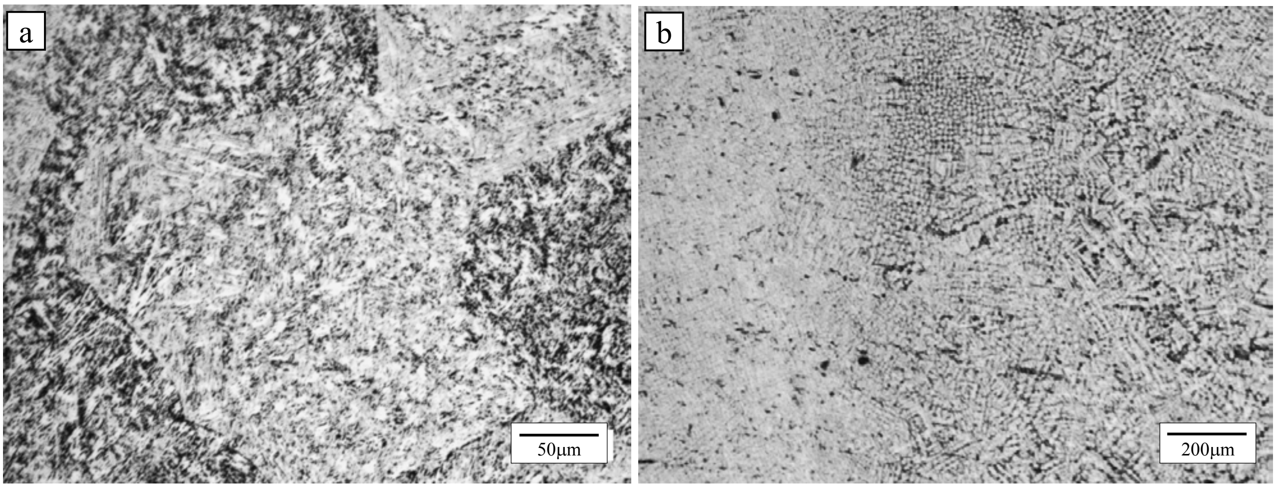

Figure 8. Optical micrographs, showing the (a) martensitic structure of the Ti-10Nb alloy and (b) the dendritic structure within the martensitic matrix of the Ti-25Nb alloy.

Table 2. Composition (Nb wt%) of Ti-Nb alloys and Vickers hardness (HV) of copper wedge mold cast samples.

Composition (%wt)	Ti-10%Nb	Ti-25%Nb
hardness (HV)	248 ± 5	216 ± 8

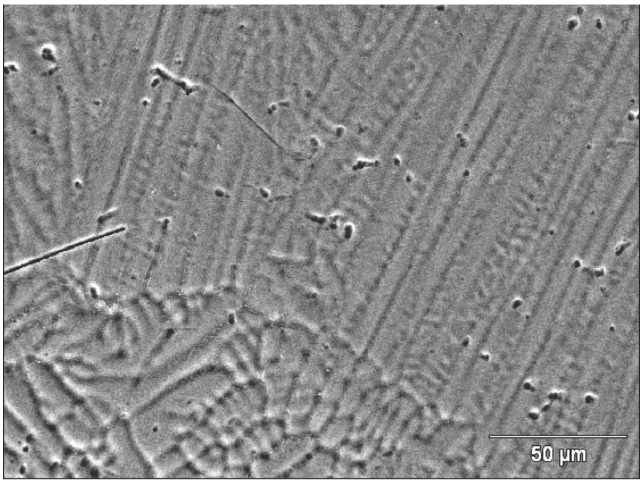

Figure 9. SEM micrograph of the Ti-25Nb alloy near the wedge tip.

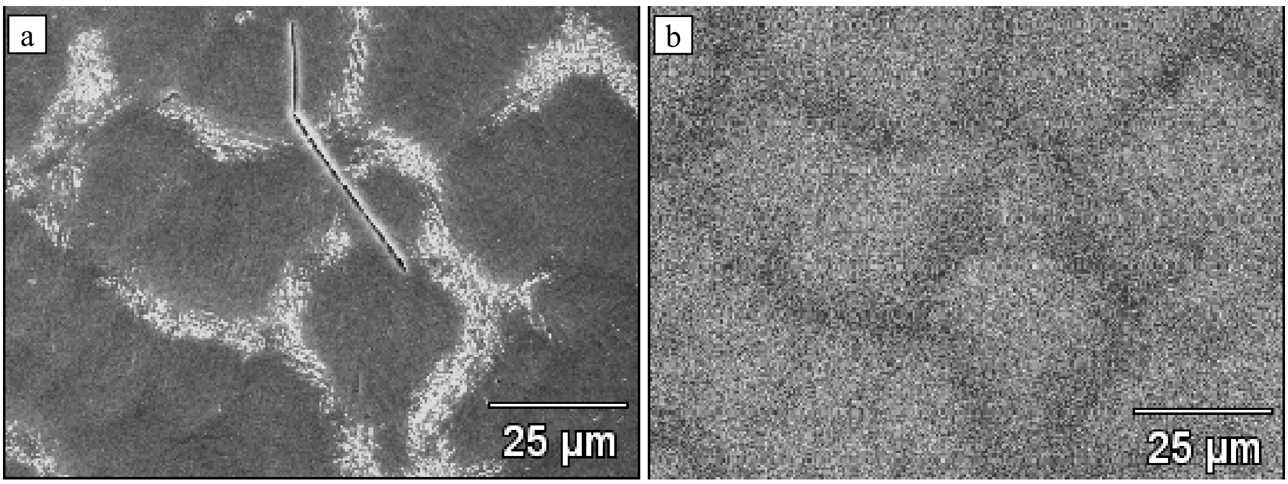

Figure 10. (a) SEM micrograph of the Ti-25Nb sample showing a dendrite arm (b) X-ray image of titanium.

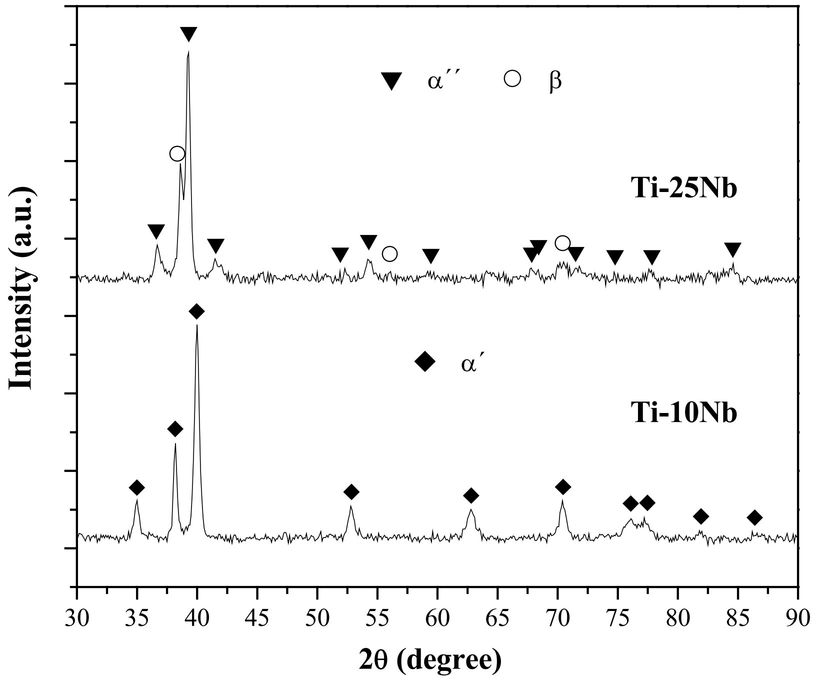

Figure 11 – X-Ray diffraction patterns of the Ti-10Nb and Ti-25Nb alloys

4. Conclusions

Ti-Cu and Ti-Nb alloys were cast under high cooling rates. It was concluded that the microstructure of Ti-Cu alloys depends on the composition. Hypoeutectoid alloys result in martensitic structures, without any formation of Ti_2Cu. As the Cu content increases from Ti-5.0Cu to Ti-15Cu and the hypereutectoid composition is reached, a microstructure formed by Ti_2Cu and α' martensite takes place. Hardness increases with increasing the Cu content, as it favors the formation of the intermetallic phase. For the Ti-Nb alloys, similar results were obtained. The samples of Ti-10Nb show microstructure formed by α' martensite. As the Nb content is increased, the microstructure is substituted by a combination of α" martensite and β phase. As the Nb content increases, the Vickers hardness decreases due to β retention.

4. Acknowledgements

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5. References

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