# THE EFFECT OF INTERSTITIAL ELEMENTS O AND B ON TRANSITION TEMPERATURE (A-B) OF Ti-35Nb-6Ta BIOMEDICAL ALLOY

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## Abstract

The beta-transus temperature is very important for all beta-titanium alloys during their processing. This temperature is influenced by the chemical composition of the alloy. Interstitial elements (O, N, B) can strongly influence beta-transus temperature even in very low concentration. In this work the influence of O and B elements on transition temperature of Ti-35Nb-6Ta has been studied. Specimens with various additions of O or B were prepared. These specimens were aged at 500 °C for 24 hours in order to obtain equilibrium α+β microstructure. Subsequently the specimens were annealed at various temperatures (with 50°C or 10°C increment) and water quenched. The microstructure was then studied. At lower temperature α-precipitates coarsening has been observed and at higher temperatures precipitates dissolution took place. It was find out that oxygen addition strongly influences the transition temperature (increase approximately 410°C/wt. %), but the effect of boron is weak (addition of 0.5 wt. % caused increase of 15 °C).

**Keywords:** Beta-titanium alloy, transition temperature, interstitial elements, biomedical materials

## 1. INTRODUCTION

Beta-titanium alloys are perspective materials for bioapplications due to their high strength to weight ratio, corrosion resistance, biocompatibility or low Young's modulus [1,2]. Low Young's modulus is very important to avoid the so called "stress-shielding effect" during long term use [3]. Beta-titanium alloys should contain only elements that would cause no problems to human body (non-toxic elements) [4]. Previously used materials (stainless steel, Co-Cr alloys, Ti-6Al-4V...) contain certain fraction of potentially harmful elements (e.g. Al, V, Cr...) and have significantly higher Young's modulus than the human bone (10-40 GPa). Because of that the development of new beta-titanium alloys dedicated for medical use is on the way.

Mechanical properties of beta-titanium alloys are influenced by the chemical composition and thermo-mechanical processing. The modification of these alloys by adding interstitial elements (O, B, N) seems to be perspective to improve mechanical properties, because oxygen and nitrogen can increase the tensile strength significantly without excessive modulus increase [5-7]. Boron can be added in small amounts in order to grain refinement [8,9]. Oxygen and nitrogen are always present in a certain amount in alloys due to contamination during preparation (either arc melting or powder metallurgy).

Beta-transus temperature is essential characteristic temperature that determine the transition from stable alfa-phase to beta-phase region. The knowledge of this temperature is important during thermo-mechanical processing of the alloy so that we can process the alloy in stable β or α+β region [10]. It has been reported that the presence of only very small fraction of interstitial elements can strongly influence the beta transus temperature of the alloy, however significant differences between the influence reported by various authors can be found [11,12]. Other works were dedicated to study of oxygen and nitrogen influence on martensite start ($M_S$) temperature [13-15]. In this paper the influence of oxygen and boron on beta-transus temperature in Ti-35Nb-6Ta beta-titanium alloy has been studied.

## 2. METHODS

Alloy with nominal chemical composition Ti-35Nb-6Ta (all compositions in this work are in wt. % unless it said different) has been prepared in a vacuum arc melting furnace LAYBOLD HERAEUS L200h with a water cooled copper crucible. The oxygen content was measured to be 0.05 % (marked 0O). These measurements were performed by melt extraction method on Bruker G8 Galileo analyzer. Another specimens were melted with various addition of $TiO_2$ powder and the resulting oxygen content was then measured to be 0.25; 0.45; 0.65 and 0.85 % (specimens marked as 02O; 04O; 06O and 08O respectively). These specimens were machined and subsequently hot forged at 900-1100 °C into cylindrical rods with 40 % section reduction. Hot forged specimens were annealed at 950 °C for 0.5 h and water quenched. The rods were machined in order to remove the oxidized surface and defects. Cold swaging was performed on specimens with section reduction 90 %. These wires were aged 500 °C / 24 h / furnace cooled. Subsequently annealing at temperatures from 600 to 1100 °C with 50 °C for 2 hours has been performed. Subsequently additional annealing with 10 °C between temperatures where beta-transus temperature has been determined was performed. Specimens were water quenched after annealing. The same preparation was also performed on specimens with 0.5 % B addition (marked as 05B). In this specimen and in Ti35Nb6Ta specimen additional annealing with 5°C increment has been done. The beta-transus temperature has been determined as the temperature where significant decrease in precipitates volume fraction has been observed.

The microstructure has been studied by using light microscopy (LM). Specimens were prepared via standard metallographic route. Specimens were grinded up to #4000 with SiC papers and polished with Struers OP-S emulsion with addition of 0.6 ml OP-S, 2 ml $H_2O$ and 2 ml $NH_3$. For etching 3 ml HF + 8 ml $HNO_3$ + 100 ml $H_2O$ etchant was used. Nikon EPIPHOT 300 was used for light microscopy observation. The evaluation of precipitates volume fraction was done through image analysis. Additional microscopy evaluation of fine precipitates has been done by using transmission electron microscopy (TEM). Specimens were prepared by grinding up to 100 µm thickness. Specimens were then electropolished by using a Struers TENUPOL 5 machine. Electropolishing has been done in 10 % perchloric acid + 20 % glycerol + 70 % methanol electrolyte at -20 °C and 20 V. Observations were done on JEOL 2000EX transmission electron microscope at 200 kV. Phase identification has been done from selected area diffraction pattern (SADP). Vickers hardness tests (HV10) were performed on hot forged and solution treated specimens on Zwick Roell ZHU 250 Top testing machine.

## 3. RESULTS AND DISCUSSION

The beta-transus temperature was determined in all studied specimens with various oxygen or boron addition. Firstly cold swaged specimens were aged in order to obtain microstructure with high fraction of α-phase precipitates. The microstructure has a wave like morphology (in a cross section) due to intensive cold deformation. In 05B specimen coarser lath-like particles can be observed. These particles are TiB particles as Majumdar et al. reported [16]. Two types of α-precipitates can be observed in deformed microstructure after aging (in **Figs. 1, 2**). Coarser precipitates can be observed on grain boundaries of all specimens. It was confirmed by TEM analysis that these precipitates are α-phase precipitates. In addition to these precipitates gray areas can be observed in light micrographs (**Fig.1**). These areas contain high fraction of fine needle-like α-precipitates as can be seen in **Figs. 2, 3** obtained by TEM. These precipitates cannot be distinguished by using light microscope, but due to etching effects they appear as grey areas.

During subsequent annealing fine precipitates became coarser. When the specimens are annealed at temperatures below the beta-transus temperature precipitates coarsening has occurred, but their volume fraction remains the same. During annealing at temperatures above the beta-transus temperature precipitates coarsening also takes place, but also dissolution can be observed and therefore the precipitates volume fraction decrease. After certain annealing period above beta-transus temperature all precipitates are dissolved. This process is accelerated by increasing annealing temperature. Fine precipitates in grain interiors can be distinguished in micrographs of annealed specimens (e.g. in **Fig. 2**). These precipitates originate from needle like precipitates. The dependence volume fraction of α-precipitates (measured by using the image analysis) vs. annealing temperature is shown in **Fig. 5**. It can be seen that the volume fraction of α-precipitates remains the same at lower annealing temperatures. From certain temperature the volume fraction started to decrease. At this temperature dissolution takes place instead of precipitate coarsening and it is supposed that after enough long annealing period at this temperature all α-precipitates would be dissolved. When the temperature is further increased, precipitates disappeared even after 2 h annealing period as can be seen in **Fig. 6** where no α-precipitates have been observed. Moreover the microstructure consists of fine recrystallized grains. So this indicates that recrystallization took place during annealing. The TiB particles still remains in microstructure of 05B specimen.

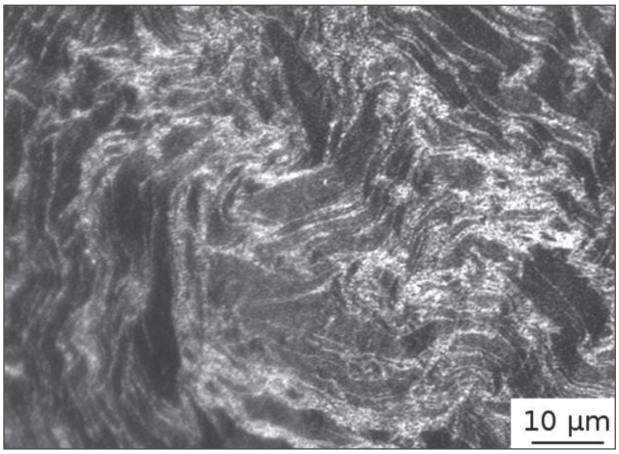


**Fig.1** Light micrograph of 0O specimen aged 500 °C / 24 h

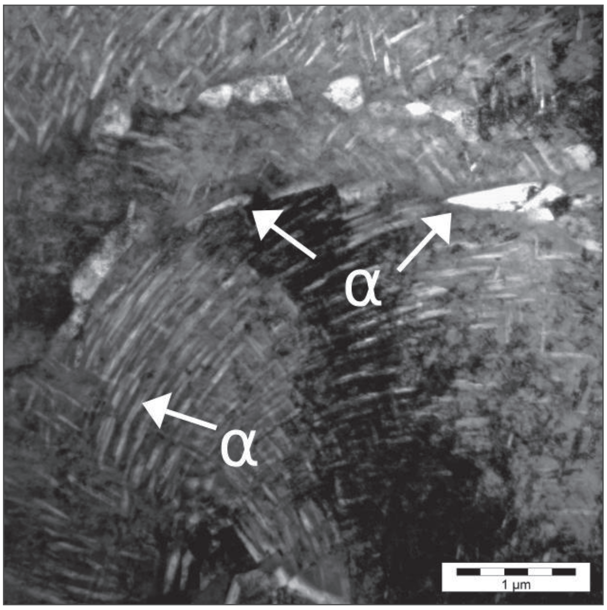


**Fig. 2** TEM micrograph of 0O specimen aged 500 °C / 24 h

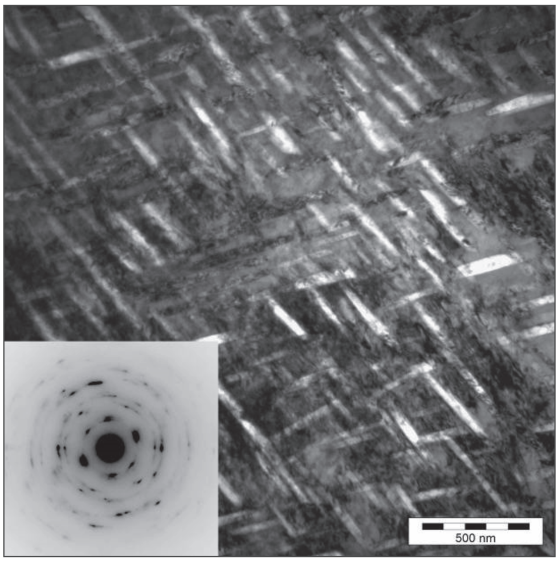


**Fig. 3** Precipitates in grain interiors of 0O specimen aged 500 °C / 24 h (inset-selected area diffraction pattern with α-phase spots)

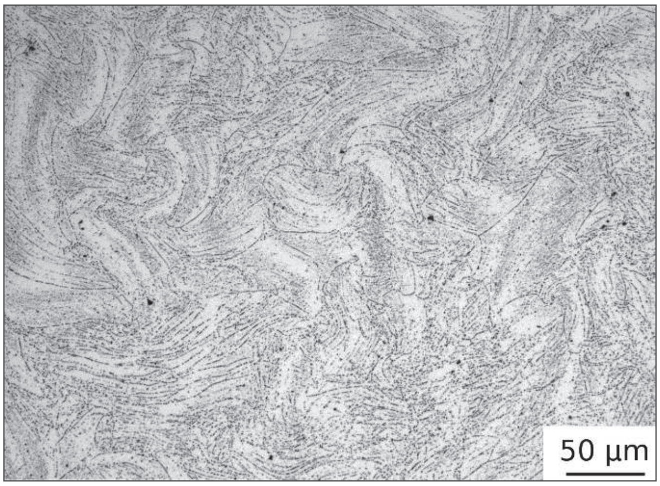
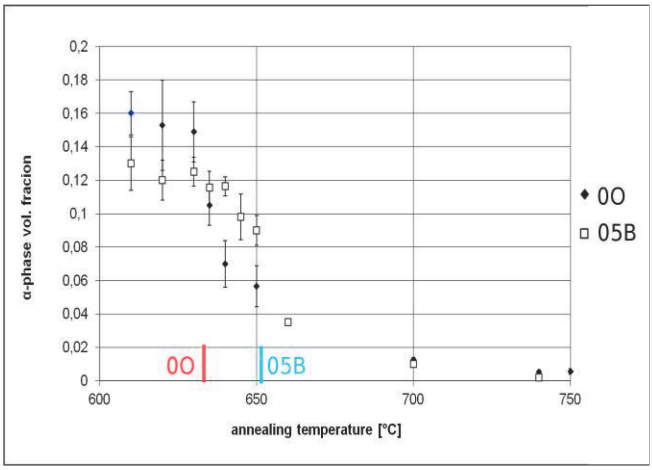


**Fig.4** Light micrograph of 04O specimen annealed 800 °C / 2 h



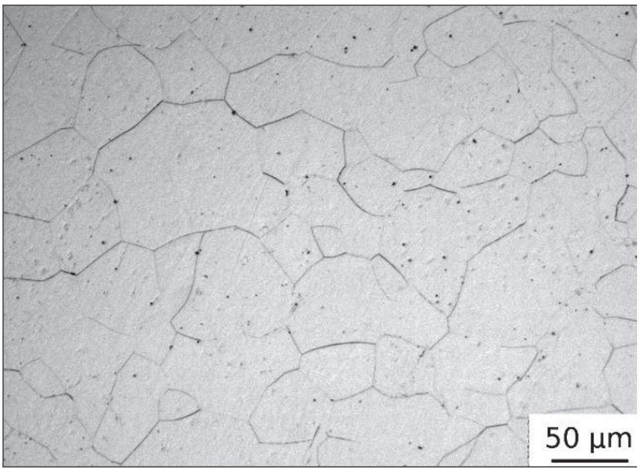
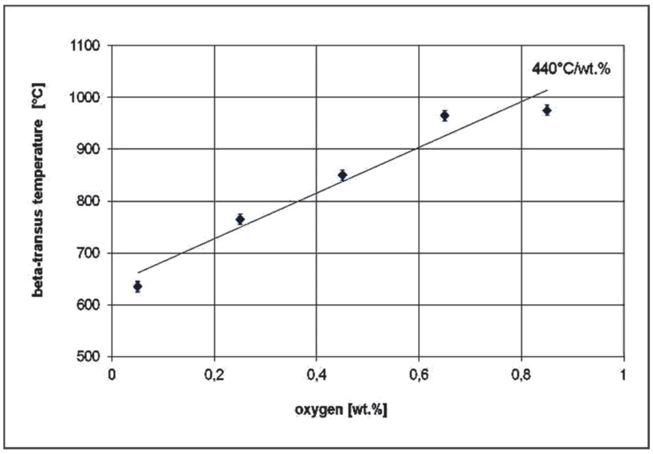


**Fig. 5** Dependence α-precipitates volume fraction vs. annealing temperature for 0O and 05B specimens with highlighted beta-transus temperature

**Fig. 6** Light micrograph of 04O specimen annealed 950 °C / 2 h

The dependence of determined beta-transus temperature vs. oxygen amount is plotted in **Fig. 7**.

It can be seen that the beta-transus temperature increases with increasing oxygen amount. This is consistent with the fact that oxygen is known as α-stabilizer in titanium. The increase seems to be approximately linear within studied oxygen addition range. It can be calculated that the increase of beta-transus temperature is approximately 440°C per 1 wt. %. This is similar to the value that Geng et al. [12] reported (429 °C / wt. %) in Ti-29Nb-13Ta-4.6Zr alloy. On the other hand other authors [11] obtained value about 200 °C / at.% (equal to 710°C/wt. %) in Ti-35Nb alloy. So it is supposed that there can be significant difference in the influence of oxygen on beta-transus temperature in various types of alloys, but further study on various alloys should be performed to ascertain this hypothesis.



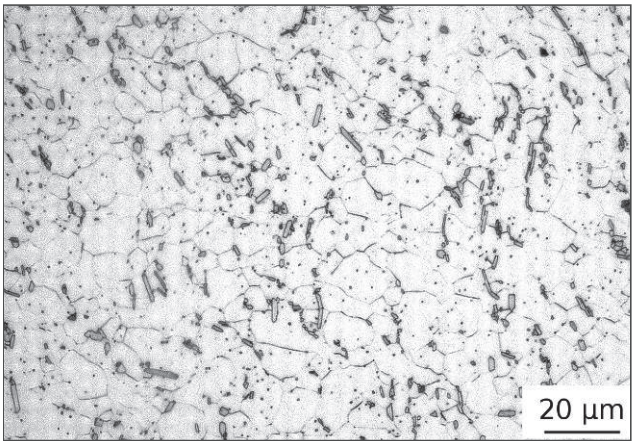


**Fig. 7** Dependence determined β-transus temperature vs. oxygen amount in Ti35Nb6Ta alloy

**Fig. 8** Light micrograph of 05B specimen annealed 700 °C / 2 h

The effect of boron addition is much less significant. As can be seen in **Fig. 5**, where the volume fraction of precipitates in 0O and 05B specimens are plotted the difference in beta-transus temperature is approximately 15 °C. This doesn't mean that the effect of boron is 30 °C / 1 wt. %. The effect of boron is very limited due to its very low solubility in beta-titanium. The solubility was reported to be approximately 0.02 wt. %. In higher amount the boron is than present in form of TiB particles and these particles are stable even above the beta-transus temperature (see **Fig. 8**). TiB particles have probably no effect on beta-transus temperature and although it seems that boron effect is very high (we can conclude about 750 °C / wt. % = 15/0.02) the beta-transus temperature is influenced only up to boron solubility in beta matrix. Higher values (~ 60 °C) were reported by Tamirasikandala et al. where β-matrix supersaturated with boron has been studied. Other authors reported values corresponding to the above mentioned idea.

## CONCLUSIONS

The influence of oxygen and boron addition on Ti35Nb6Ta transition temperature (beta-transus temperature) has been studied. On the basis of obtained results it can be concluded that:

1) High fraction of fine needle-like α-precipitates is present after aging at 500°C. These precipitates coarsened and subsequently are dissoluted during annealing at temperatures above beta-ransus temperature.
2) Oxygen addition to Ti35Nb6Ta alloy increases the beta-transus temperature of approximately 440°C/wt. %. In studied oxygen addition range the increase in beta-transus is linear with oxygen addition increase.
3) The increase of beta-transus temperature caused by boron addition is significantly lower due its limited solid solubility in beta-titanium matrix.

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