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THE EFFECT OF DIFFERENT FORMS OF OXYGEN ON PROPERTIES OF BETA TITANIUM ALLOYS

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Abstract. The beta-titanium alloys are widely used in many applications (medicine, aerospace industry etc.) due to their superior properties, such as corrosion resistance, biocompatibility and high strength to weight ratio. One of the ways how to increase the strength of those alloys is the addition of oxygen. The oxygen can be present in various forms in the alloy – in a solid solution or in the form of oxides. In this work, the effect of two forms of oxygen (i.e., solid solution and dispersion particles) was studied. Two alloys, one arc melted with different oxygen additions and one prepared via powder metallurgy where the titanium powder was oxidized, were prepared. The microstructure and mechanical properties were studied. A significant increase in strength with increasing the oxygen content in the solid solution has been observed. However, the powder oxidation has almost no effect on a tensile strength probably due to quite large interparticle distances between titanium oxide particles.

Keywords: beta-titanium alloys; oxygen; microscopy; mechanical properties.

1. Introduction

The beta-titanium alloys are materials with a high potential of use in biomedical applications (e.g., artificial joints, implants, screws etc.) [1]. This is thanks to their suitable properties for such purpose. They exhibit excellent corrosion resistance, high strength to weight ratio and low Young's modulus (in comparison with other metallic materials used for bioapplications). The Young's modulus of an implant material should be close to that of the replaced bone to limit the so called stress shielding effect [2]. The modulus of a bone is reported to be between 10 and 40 GPa [3], which is significantly lower than the modulus of most metallic materials (stainless steel 210 GPa, or CoCrMo alloy 230 GPa). Moreover, the beta-titanium alloys are frequently composed of fully biocompatible elements that represent minimal risk for human body during a long term use [4]. Nevertheless, the tensile strength is desired to be further improved, maintaining the Young's modulus as low as possible. There are many ways how to increase the tensile strength (precipitation strengthening, deformation strengthening, dispersion strengthening, solid solution strengthening) [5–8]. It was reported that the addition of oxygen could significantly improve the tensile strength of the alloy [9, 10]. The oxygen could be present in various forms (i.e., oxides, soluted in the matrix). In this work, the oxygen addition has been carried out via two different ways and the effect on mechanical properties has been studied.

2. Experimental

The beta-titanium alloys with the nominal chemical composition Ti-25Nb-4Ta-8Sn-XO was prepared by arc melting in an electrical arc melting furnace with a non-consumable tungsten electrode and water cooled copper crucible under Ar atmosphere. Pure elemental metals were used for the arc melting (Ti – grade 2) and (Ta, Nb, Sn – minimum purity 99.9 %). The oxygen addition was carried out by TiO_2 powder addition in different amounts into the batch. By this way, alloys with 0.1 (no addtion); 0.3; 0.5; 0.7 and 0.9 wt% of oxygen were obtained. Alloys were remelted at least six times to ensure a good chemical homogeneity. The second type of the alloy synthesis was via blending elemental powders with a particle size of −325 mesh supplied by ALFA Aesar Gmbh. The titanium powder was oxidized on air at 200 °C for 0.5, 1, 2 or 4 hours prior to the powder mixing Elemental powders were weighted, mixed (in TURBULA 2F device for 10 h) and subsequently cold isostatically pressed (CIP) at 400 MPa. After the CIP, the alloy was sintered (1400 °C/10 h). All alloys were (after both arc melting and the CIP) hot forged with a minimal section reduction by 40 % and solution treated 1000 °C/0.5 h/water quenched. The microstructure was studied using the light microscope Nikon EPIPHOT 300 (LM) and scanning electron microscope JEOL JEM 7600F (SEM). The specimens for microstructural observations were prepared via a standard metallographic process (grinded

Oxidation time [h]	0	0.5	1	2	4
Weight increment [g]	0	0.0074	0.0198	0.0198	0.0267
Estimated oxygen increase [wt%]	0	0.036	0.087	0.102	0.118
Estimated total oxygen content [wt%]	0.31	0.35	0.40	0.41	0.43
Measured oxygen content [wt%]	0.31	0.55	0.55	0.52	0.56

Table 1. The dependence of oxygen content on oxidation time of powder metallurgy processed specimens.

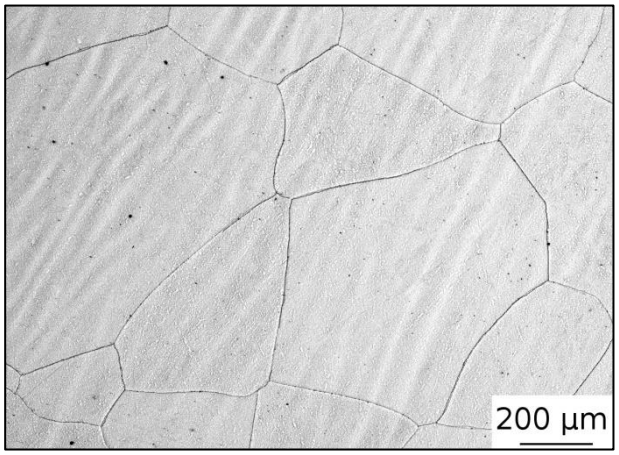

Figure 1. Microstructure of an arc melted alloy with 0.3 wt.% of oxygen after the solution treatment.

up to #4000 with SiC papers and polished with Struers OP-S emulsion with the addition of H_2O_2). 3 ml HF + 8 ml HNO_3 + 100 ml H_2O etchant was used for the etching. Tensile tests have been performed on Instron 1185 machine according to ISO 6892-1:2009 standard. Standard round tensile specimens with a 5 mm diameter gauge and M8 shoulders were used. The oxygen content in final alloys has been determined by Bruker Galileo G8 gas fusion analyser. At least three measurements (specimens of 0.1 g) for each material have been performed. Which gives the final value with a scatter lower than ±0.05 wt% (typically ±0.03 wt%). The declared experimental scatter of the device itself is ±1 % of the measured value. The amount of oxygen added to alloys prepared by powder metallurgy was also determined by the method of weighting. During this, approximately 70 g of titanium powder was weighted, subsequently oxidized and weighted again. This has been carried out by using a weighting machine with an accuracy of 0.0001 g. At least two measurements were repeated two times. The oxygen addition into the alloy was calculated on the basis of those measurements. Basic data are presented in Table 1.

3. Results and Discussion

The microstructures of as-cast and solution treated alloys consist of recrystallized grains of β-Ti (bcc) phase (Figure 1). This microstructure is typical for all arc-melted specimens. No other phases than the β- phase have been observed in the studied specimens. Therefore, it can be assumed that the oxygen has been almost completely dissolved in the matrix as no oxides have been observed. The arc-melted specimens have a quite large grain size after hot forging and the solution treatment. The grain size has been determined to be approximately 500 µm. It can be seen from Figure 2a that the hardness of solution treated arc melted alloy increases significantly with the increasing oxygen content. It can be estimated that the increase in hardness is approximately 160 HV10 per 1 wt% O. The same trend has been observed for both tensile strength and yield strength values where the observed increment corresponds to about 400 MPa per 1 wt% O. However, the influence on Young's modulus was lower (see Figure 2b) with an estimated increase approximately 21 GPa per 1 wt% O. It was also observed that specimens with the highest oxygen content have a ductility close to zero, which could be limiting for many applications and for subsequent technological processing (e.g., cold rolling). In all that cases, the increase can be clearly observed and is supposed to be caused by the interstitial strengthening of the oxygen dissolved in the matrix.

During the specimen preparation via powder metallurgy process, the oxygen addition was performed by different way. The titanium powder oxidation has been used for this purpose. The powder contains a certain amount of oxygen before the oxidation (due to a technological process during powder production). The original oxygen is present in the form of an interstitial solid solution (as in the arc melted specimen). The titanium powder was oxidized at 200 °C on air for 0.5, 1, 2 and 4 hours. The powder was weighted before and after the oxidation. The weight change during the oxidation (70 g of titanium powder was oxidized) shows an increase, which could be ascribed mostly to the oxygen (weight increment in Table 1). Subsequently, the increase of oxygen content in the alloy has been calculated. The measured value of the alloy with an unoxidised powder was then used as the basis for the total estimated oxygen content in the mentioned in Table 1. It can be seen that the measured oxygen content is higher than the content estimated from weighting the powders (and initial content in powders). This may be caused by moisture evaporation that may slightly increase the initial weight (before oxidation). It can be also seen from Table 1 that the real oxygen content is similar for all oxidized specimen regardless of the oxidation period. This could imply that after oxidation of sur-

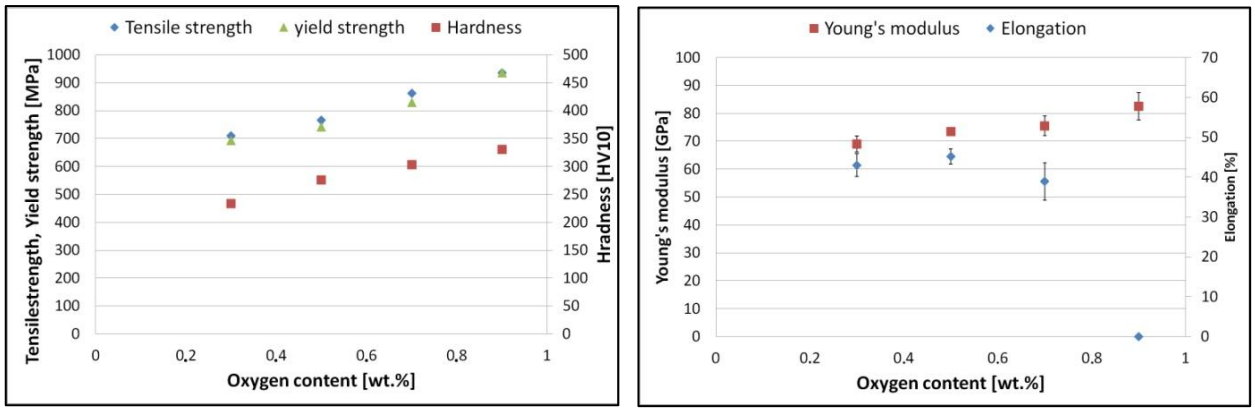

FIGURE 2. (a) Hardness and Tensile strength vs. oxygen content in the arc melted specimen. (b) Young's modulus and elongation values vs. oxygen content in the arc melted specimen.

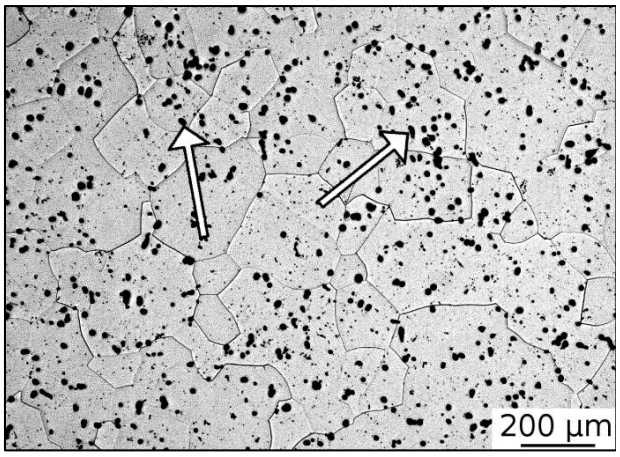

FIGURE 3. Microstructure of powder metallurgy specimen (powder oxidized 200 °C/0.5 h). Titanium oxide particles are marked by arrows.

face powder particles, further oxidation is prevented by those oxide layers as the temperature and time are not sufficient for a significant diffusion of oxygen into the titanium powder.

The typical microstructure of oxidized specimens after solution treatment can be seen in Figure 3. Numerous particles of fine titanium oxides can be seen there (marked by arrows in Figure 3). The composition containing high amount of oxygen and titanium has been determined by EDS (not shown here, however, further characterization (the oxide structure) has not been determined exactly. It can be assumed that most of the added oxygen (added via oxidation) is present in a form of titanium oxide particles. This is caused probably by the fact that the titanium oxides are stable even at the highest temperature used during the experiment (i.e., sintering temperature 1400 °C) and they are not dissolved even after 10 hours of sintering. This could also be derived from the Ti-O binary phase diagram [11]. Only the part of oxygen, which was present in the initial powder (i.e., ~ 0.3 wt%), is supposed to be dissolved in the matrix. The hardness values of solution treated specimens along with tensile strength values can be seen in Figure 3. Those values are plotted as a dependence on the oxidation time. When compared with Table 1, it can be seen that the oxygen content is similar for all oxidized specimens (i.e., ~ 0.55 %) and unoxidised (0 hours) corresponds to initial value of 0.3 %). However, it can be seen that both the tensile strength and hardness values are nearly constant with respect to the experimental scatter. The hardness values of non-oxidized powders well correspond to that of arc melted specimen with the oxygen content of 0.3 %, which is the same as in the initial powder specimens. The tensile strength values of powder metallurgy processed specimens are slightly higher than those of arc melted specimens. This is probably caused by the smaller grain size (150 µm vs. 500 µm) of the arc melted, which may cause the tensile strength according to Hall-Petch equation [7]. It should be pointed out that the increase of oxygen content during the oxidation had no (or very weak) effect on both hardness and tensile (yield) strength values. As mentioned above, the added oxygen is supposed to be almost completely present in the form of titanium oxide particles. On the one hand, the titanium oxide particles mayhave caused the increase of Young's modulus values as can be seen in Figure 4b. It has been reported that the Young's modulus of titanium oxides is higher (~ 250 GPa) than that of beta-titanium alloys [12]. On the other hand, the presence of titanium oxides in the current form (i.e., particle size and particle number) does not significantly deteriorate the plasticity (elongation values) as can be seen from Figure 4b. It can be seen in Figure 3 that the interparticle distance of oxides particles is in order of tens of micrometres. This is quite a big distance (e.g., in comparison with the ~ 10 nm interparticle α-precpitate distance, which caused a significant increase in strength as observed by Coakely et al. [13]), therefore, the strengthening effect of titanium oxide particles in the current work is negligible. This is consistent with the results of Song et al. [14] who studied the strengthening effect

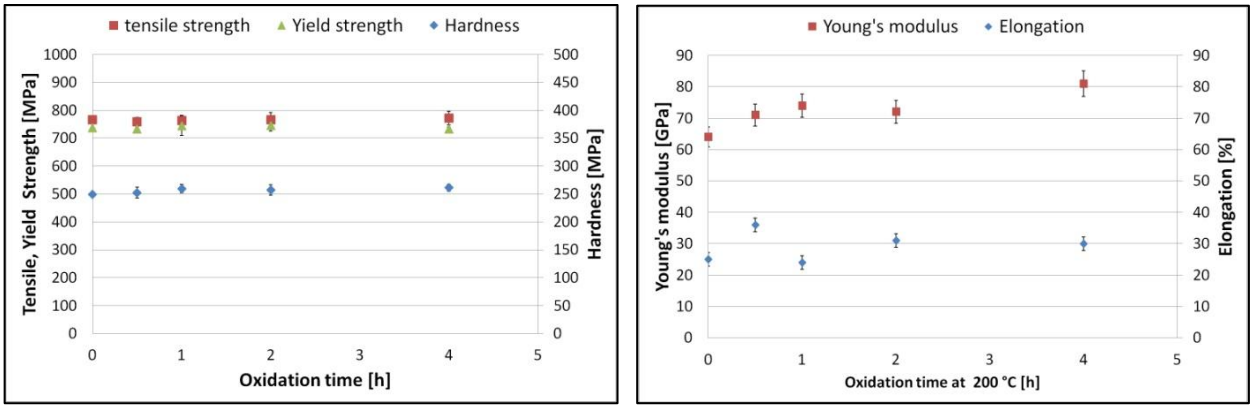

Figure 4. (a) Tensile strength, Yield strength and hardness values vs. oxidation time at 200 °C (powder metallurgy specimens). (b) Young's modulus and elongation values vs. oxidation time at 200 °C (powder metallurgy specimens).

of Y_2O_3 particles (with the comparable interparticle distance as in this paper) on beta-titanium alloys and they found it to be quite small. It can be therefore assumed that the oxygen content has much weaker effect on tensile strength in form of titanium oxide particles than in the form of a solid solution. The ductility values remain sufficiently high (far above 20 %) which is supposed to be enough for most intended applications. Longer oxidation times (or higher oxidation temperatures) could lead to a higher amount of titanium oxides particles, which could generate a more distinct strengthening effect. However, this could have a deteriorate effect on the ductility of the alloy or decrease the fatigue characteristics.

4. Summary

Two ways of oxygen addition has been studied in this work. Accordingly to the way of addition, oxygen was present in form of titanium oxide particles or in a solid solution. It was observed that the oxygen dissolved in the matrix has a strong strengthening effect (~ 400 MPa per wt%), whereas in the form of titanium oxide particles, the strengthening effect is negligible for the currently studied contents and particle size. The tensile strength remains around 750 MPa. However, the elongation values also remains around 30 %. The strengthening effect of oxide particles could be possibly increased with a high amount of fine particles present in the microstructure

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