MICROSTRUCTURE AND MECHANICAL PROPERTIES OF Ti-Nb-Zr-Ta-O BIOMEDICAL ALLOY

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Abstract

Recently developed metastable alloy Ti-35.3Nb-7.3Zr-5.7Ta-0.7O (wt.%) abbreviated TNZTO is unique in its high oxygen content and exhibits promising properties for successful use in biomedicine, namely for total endoprostheses and bone fixation. As-cast material is not fully homogeneous; it shows dendritic structure and high density of micro-sized pores. High O content causes increased strength and, interestingly, good ductility with elongation > 12 %. Tensile tests were performed on the as-cast material and material after high-temperature die forging. As-cast material showed yield stress > 900 MPa, whereas yield stress of die-forged material exceeds 1100 MPa. The microhardness tests were also performed on the as-cast and die-forged conditions. Strength values exceed the most used Ti-6Al-4V alloy and therefore the studied alloy is very perspective for manufacturing load-bearing orthopaedic implants.

Keywords: TNZTO, microstructure, microhardness, tensile properties

1. INTRODUCTION

Titanium alloys were extensively applied in orthopaedics due to their superior mechanical properties, excellent corrosion resistance and favourable biocompatibility for several decades. There are numerous studies reviewing outstanding properties of these materials for medical use [1, 2, 3, 4]. Despite Ti-6Al-4V alloy was developed for the aerospace industry, it is still the workhorse of the orthopaedic implants industry [2]. In spite of generally good properties of these alloys, the principal adverse property is too high elastic modulus (around 115 GPa for both Ti-6Al-4V and Ti-6Al-7Nb) that is much higher than that of cortical bone (10-30 GPa). The load that is normally applied to bone is carried by the stiff implant and the bone tissue atrophies due to lack of functional stimulation. Consequent osteoporosis results in fractures of surrounding bone or loosening the implant. For any of these reasons, the life-time of such orthopaedic implant is limited usually to 15-20 years [5, 6]. The biggest current interest is therefore focused on metastable β-titanium alloys with sufficient strength and decreased elastic modulus.

The Ti-Nb-Ta-Zr alloying system was already mentioned as a highly biocompatible material with favorable mechanical properties. Elastic modulus is as low as 55 GPa. Ti-Nb-Ta-Zr alloy is predetermined for biomedical use also due to low metal release in vitro, which is advantageous especially for long-term implants [7].

On the other hand, the considerable disadvantage of this alloy is its relatively low strength. Despite both Zr and Ta provides some solution strengthening compared to Ti-Nb binary alloys [8, 9], the ultimate tensile strength (UTS) reaches only 550 MPa that is significantly lower than the UTS of Ti-6Al-4V alloy. Increasing the strength is therefore the major issue for using this type of alloy for implants of big joints. In this investigation the strengthening effect of oxygen is investigated.

Increasing stability of β-phase may also lead to an increase in elastic modulus [10]. Increased hardness due to oxygen content changing from 0.3 wt.% to 0.5 wt.% was reported in Ti-Nb-Ta-Zr single crystals [11]. More related to this thesis is study finding that 0.46 wt.% of oxygen content increases the strength of Ti-35Nb-7Zr-5Ta alloy to 1000 MPa for solution treated condition [12].

2. EXPERIMENTAL PROCEDURE

Ti-35.3Nb-5.7Ta-7.3Zr-0.7O (wt.%) alloy was successfully produced on demand by Retech Co., USA by plasma arc melting of elemental materials into form of small compacts followed by so-called sequential pour melting in pure He atmosphere to produce a rod with diameter of 55 mm. Material was investigated in as-cast and as-forged condition. Die-forging was performed in a single step at 1100 °C into a shape of modular orthopaedic implant semi-product with diameter of approx. 31 mm. Microstructure was studied by light microscopy and scanning electron microscopy - Zeiss Auriga Compact with FEG emitter. Samples were ground and polished utilizing 320, 500, 800 and 1200 grit SiC papers. Final polishing for light microscopy was done by diamond pastes 3 µm and 1 µm and OPS. Samples were etched by weak Kroll etchant to reveal microstructural features. Samples for scanning electron microscopy (SEM) were polished using Buehler vibratory polisher in three consequent steps using two alumina solutions (0.2 µm and 0.05 µm alumina) and finally colloidal silica (Allied). Microhardness was measured according to Vickers with load of 500 g using semi-automatic Qness 10A+ hardness tester. Finally, computer controlled Instron 5882 was employed for tensile tests at room temperature with strain rate 10^{-4} s^{-1}.

3. RESULTS AND DISCUSSION

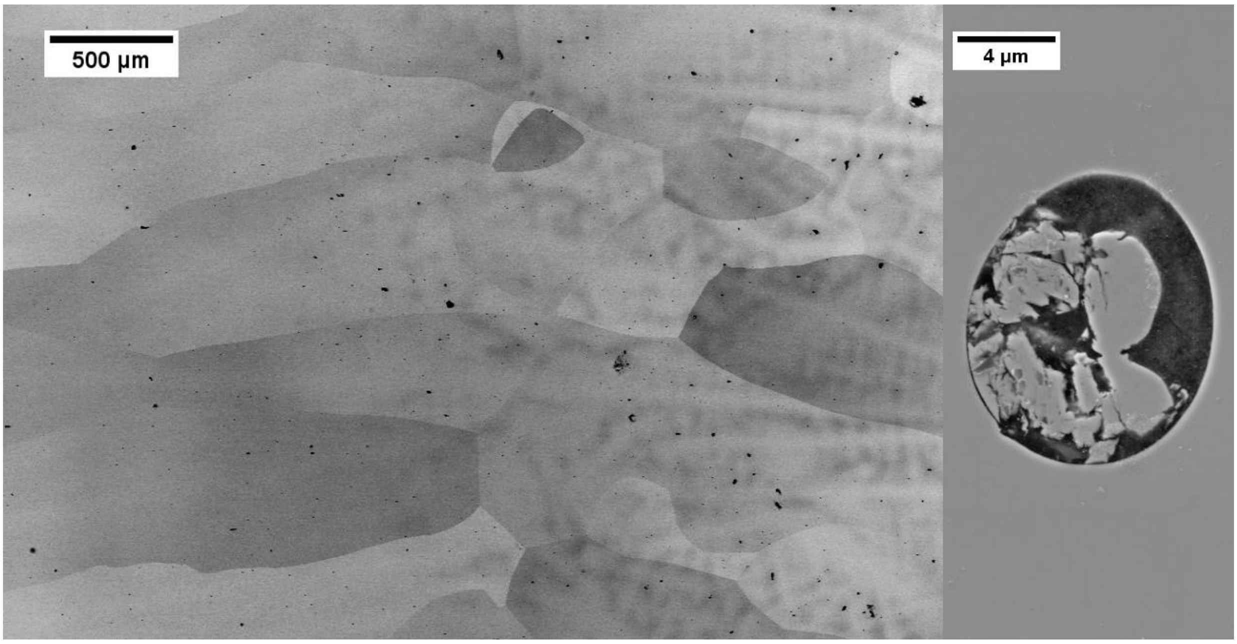
The microstructure of the as-cast sample is shown in **Figure 1a)**. Large elongated grains (up to 2 mm) are visible due to channeling contrast in SEM. Grain elongation is parallel to the radius of cast rod and results from solidification and cooling. Small black spots that can be seen all over the micrograph are pores, which were proven by high magnification SEM observation - **Figure 1b)** and similar porosity was observed in several as-forged samples. Z-contrast in SEM allowed us to observe differences in chemical composition in the sample. It can be seen that in the right part of the image, there are chemical inhomogeneities appearing as blurred lighter dendrites. Point energy dispersive X-ray (EDX) analysis was performed to determine the chemical composition in the dendrites area (light dendrites and darker surrounding) and in the opposite homogeneous area in the left part of the image. The results are shown in **Table 1**.

Table 1 Chemical composition of dark and light regions determined by EDX analysis

wt.%	Ti	Nb	Zr	Ta
light regions	45.8	35.0	8.2	11.0
dark regions	51.3	31.2	10.5	7.0
homogeneous regions	48.3	33.3	9.1	9.4

EDX analysis should be understood only qualitatively as the true alloy composition cannot be quantitatively determined by EDX. Moreover, O content could not be detected. On the other hand, mutual comparison of measurements is appropriate. Light regions (dendrites) are rich in heavy elements Ta, Nb (which could be expected from the lighter shade in Z-contrast) and depleted of comparatively light Ti. Vice-versa, in the darker regions, Ti prevails. Formation of dendrites follows from different melting points of constitutive elements. Melting points of Ta (3020 °C) and Nb (2477 °C) are significantly higher than Ti (1668 °C), even Zr has slightly higher melting point (1855 °C). It is assumed that dendrites form at high cooling rates near the periphery of rod manufactured by sequential pour melting. Right hand side of the **Figure 1a)** indeed heads towards edge of the rod. Similar dendritic structure was observed in [13] at high cooling rates of 10^1-10^3 K / s.

Composition of the homogeneous region - left part of **Figure 1a)** - represents approximately an average of light dendrites and dark surroundings. It follows that the material overall is homogeneous, while fast cooling of the outer part of the rod leads to dendritic solidification.

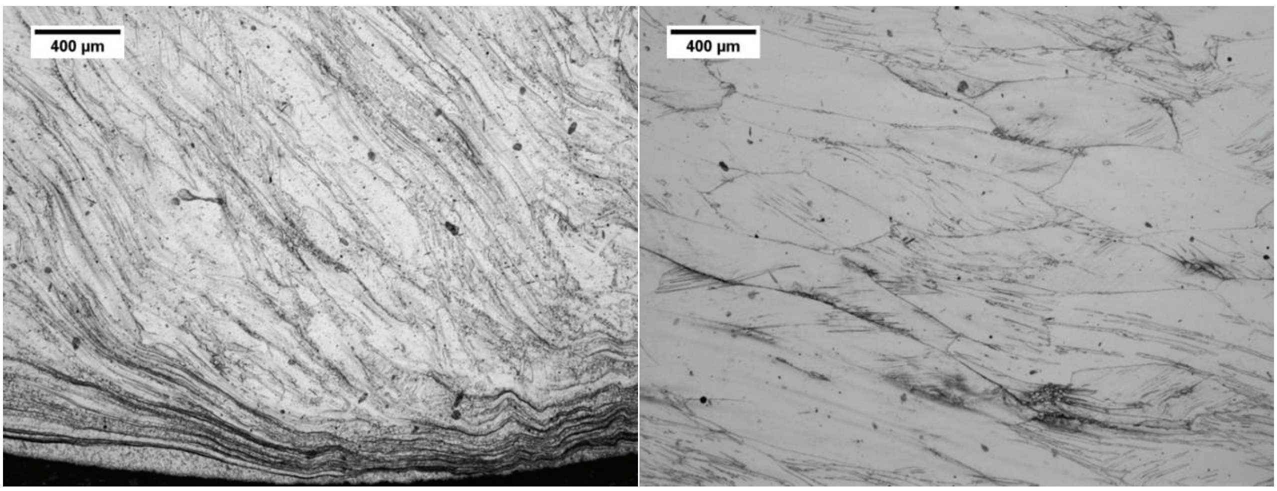


a) b)

Figure 1 Microstructure (EDX analysis) of the as-cast sample: a) overview and b) detail of a pore

Microstructure of the as-forged material was observed by light microscopy. Images from the edge of the forged piece and from the central part are shown in **Figure 2a)** and **b)**, respectively. Edge of the forged piece shows massively deformed microstructure with clearly elongated grains, especially in the vicinity of the surface. Grains in the central part are large and slightly elongated (similar to as-cast condition). Detail observation of **Figure 2b)** reveals apparent twinning in the most of grains (compare to [14]).

Microhardness measurements were performed for the as-cast condition as well as on the as-forged sample. As-cast sample was measured both in the homogeneous and the inhomogeneous region. For the forged piece, both the edge and the central part were measured. Results are shown in **Table 2**. Although there is a difference between grains on the edge and in the centre of the forged piece, it has no effect on the microhardness with respect to experimental uncertainty. Similarly, the as-cast sample exhibits the same microhardness for both the homogeneous and the inhomogeneous region. In contrast, the forged piece has higher microhardness than the as-cast sample, though the difference is small and within statistical error.



a) b)

Figure 2 Microstructure of the forged piece: a) on the edge and b) in the central part

Table 2 Microhardness measurements of the as-cast sample and the forged piece

Sample	as-cast (homogeneous)	as-cast (inhomogeneous)	forged (edge)	forged (central part)
Microhardness (HV 0.5)	326 ± 6	325 ± 7	335 ± 9	336 ± 6

Figure 3 shows the true stress - true strain curves for both the as-cast and as-forged material that were obtained by tensile testing. Forging of the material clearly increases the yield stress as well as the ultimate tensile strength (UTS). Both curves exhibit so-called sharp yield point that is caused by Cottrell atmosphere of interstitial O atoms formed around dislocations [15]. This fact was also reported in Geng et al. [16] for similar alloy. In the as-forged condition, the interaction between interstitial oxygen atoms and higher dislocation density is stronger which leads to more pronounced sharp yield point. The mean values of the yield stress and of the UTS from at least three measured samples per condition are shown in **Table 3**.

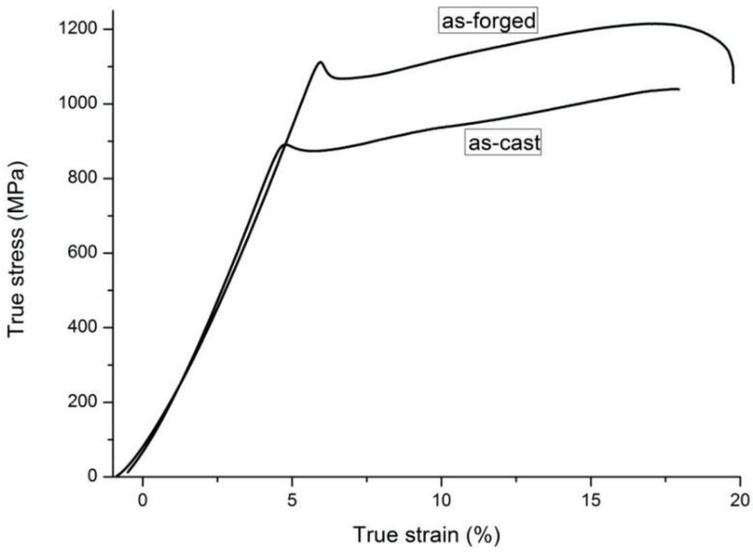


Figure 3 True stress - true strain curves for as-cast and as-forged material

Developed alloy shows yield stress and UTS values exceeding the most commonly used Ti-6Al-4V alloy. Due to decreased elastic modulus, excellent biocompatibility [14, 17], strength and formability the alloy is very perspective for manufacturing load-bearing orthopaedic implants.

Table 3 Values of yield stress and UTS for the as-cast and the as-forged condition

Sample	as-cast	as-forged
Yield stress (MPa)	920 ± 33	1123 ± 19
UTS (MPa)	1041 ± 26	1215 ± 18

4. CONCLUSION

- Biomedical Ti alloy, Ti-35.3Nb-7.3Zr-5.7Ta-0.7O (wt.%) was manufactured by sequential casting and successfully die-forged at 1100 °C.
- As-cast material is not fully homogeneous, it shows dendritic structure, which forms due to high cooling rates, and high density of micro-sized pores.
- Microstructure after forging observed by light microscopy shows partly deformed grains and twinning.
- High oxygen content causes high strength (> 1000 MPa) and good room-temperature ductility with elongation > 12%. Interaction between interstitial oxygen atoms and dislocations results in sharp yield point (especially after hot-forging).
- Strength values surpass the strength of the most used Ti-6Al-4V alloy and the studied alloy is very perspective for manufacturing load-bearing orthopaedic implants.

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