Increasing Strength of Ti-Nb-Zr-Ta Biomedical Alloy via Oxygen Content

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Abstract

Low strength restricts the application of biomedical beta titanium alloys in low-modulus solution treated condition. Commercial Ti-Nb-Zr-Ta biomedical alloy was used for this study. Small additions of iron, silicon and oxygen were used to increase the strength of the alloy. The highest effect was achieved by oxygen content. The strength can be more than doubled after adding 0.7 wt.% of oxygen thanks to interstitial hardening. At the same time, the elastic modulus measured by pulse-echo method is increased from 60 GPa to 80 GPa. The alloys containing 2 wt.% of iron and/or 0.7 wt.% of oxygen show significant work hardening. Scanning electron microscopy was employed for microstructural characterization.

Keywords: titanium alloys, biomedicine, elastic modulus, hardening

1. INTRODUCTION

Titanium alloy are widely used for load-bearing orthopaedic implants thanks to their unique properties. These properties include excellent corrosion resistance, relatively high strength, sufficient biocompatibility and elastic modulus significantly lower than that of steels [1,2]. The most commonly used Ti-6Al-4V alloy was originally developed for aerospace industry and it belongs to alpha + beta alloys [3]. The main disadvantage of this alloy is insufficient biocompatibility both chemically and mechanically. The effect of otherwise toxic vanadium remains unclear and the high elastic modulus of the material causes stress shielding and consequent osteoporosis that results in decreased life-time of orthopaedic implant. On the other hand, too low elastic modulus causes large amounts of shear motion between stem and bone leading to the formation of fibrous tissue and failure [4].

Currently, there is high interest in metastable beta-Ti alloys tailored for biomedical applications. Metastable beta alloys have been developed since 1960s for aerospace industry [5]. Metastable beta-Ti alloys consist of pure beta phase after quenching from temperature above beta transus (typically around 600 - 800 °C). Upon annealing under beta transus temperature, stable alpha phase precipitates. These particles significantly increase elastic modulus and therefore this aged condition should be avoided. Several unstable phases may also be formed in this type of alloys. Omega phase can be formed in solution treated condition right after water quenching or they are formed upon annealing under low temperatures (typically around 300 – 400°C). Omega phase particles also cause an increase of elastic modulus and therefore should also be avoided when low elastic modulus is a concern [6]. Another unstable phase is martensitic alpha” phase. This phase exists in some type of metastable beta alloys that are less stabilized by beta stabilizing elements. Alpha” phase can be formed martensitically upon quenching. However, it might also be formed during deformation – so-called stress induced martensite (SIM). This effect leads to pseudo-elasticity and also shape memory effect [7,8]. Several approaches to design biomedical titanium alloy have been developed. The main findings are that Ti-Nb system avoids formation of omega phase when compared to Ti-Mo system; moreover Nb is regarded as a biocompatible element [9]. Electronic approach based on d-electron bonding describes stability of beta phase close to martensitic transformation and allows designing alloys with extraordinarily low
elastic modulus [10-12]. Achieving sufficient strength in these materials is however problematic. One option is intensive cold-working [13]; the other is utilizing increased oxygen content.

Ti-35Nb-5Ta-7Zr (TNTZ) alloy was used as a benchmark material in this study. The alloy was developed in USA and patented in 1998 [14]. The TNZT alloy contains only biocompatible element in solution treated condition in consists of beta phase only. The elastic modulus can be as low as 55 GPa. The considerable disadvantage is relatively low strength of this alloy that is around 550 MPa. The purpose of this study is to employ small oxygen, iron and silicon additions in order to strengthen the TNTZ alloy.

The effect of oxygen content in TNTZ alloy on phase transformations was studied in [15] and the effect on mechanical properties in [16]. Finally, some studies combined increased oxygen content and cold-working [17,18]. The effect of Fe and Si additions was thoroughly described in our previous work [19].

2. MATERIAL AND EXPERIMENTAL PROCEDURE

Fourteen different alloys were manufactured. A TNZT alloy with chemical composition 51.7Ti-35.3Nb-7.3Zr-5.7Ta (wt.%) or 68.7Ti-24.2Nb-5.1Zr-2.0Ta (at.%) was used as a benchmark. The following scheme describes the 14 tailored alloys utilizing 0 or 2 wt. % Fe, 0-0.25 wt.% Si and 0 or 0.4 or 0.7 wt. % oxygen:

Table 1 The overview of chemical compositions (wt.%) of all prepared alloys. * - alloy could not be successfully forged. ** - this alloy was used for material-demanding in-vivo tests (not presented) and tensile test therefore could not be performed

<table>
<thead>
<tr>
<th>Ti-35Nb-6Ta-7Zr (TNTZ)</th>
<th>TNTZ+2Fe</th>
<th>TNTZ+0.15Si</th>
<th>TNTZ+0.25Si</th>
<th>TNTZ+0.4O</th>
<th>TNTZ+0.25Si+0.4O</th>
<th>TNTZ+0.7O</th>
<th>TNTZ+0.25Si+0.7O</th>
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<tr>
<td>TNTZ+0.15Si</td>
<td>TNTZ+2Fe</td>
<td>TNTZ+0.4O</td>
<td>TNTZ+0.25Si</td>
<td>TNTZ+0.7O*</td>
<td>TNTZ+2Fe+0.4O</td>
<td>TNTZ+0.25Si+0.4O**</td>
<td>TNTZ+2Fe+0.7O*</td>
</tr>
<tr>
<td>TNTZ+0.25Si</td>
<td>TNTZ+2Fe</td>
<td>TNTZ+0.4O</td>
<td>TNTZ+0.25Si</td>
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<td>TNTZ+2Fe+0.7O*</td>
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</table>

All alloys were prepared by arc melting of pure elements under low pressure in clean He atmosphere (350 mbar). Samples were homogenized at 1400 °C for two hours and furnace cooled. Material was then forged using forging hammer into shape of rods with diameter of 14 mm. Material was heated to approximately 1100 °C before forging; however, the forging temperature was not controlled. Samples for SEM observations were carefully polished using SiC abrasive papers. Subsequently, three step procedure using alumina (0.3 μm and 0.05 μm) and colloidal silica on vibratory polisher (Buehler – Vibromet) was employed to obtain as clean surface as possible. Elastic modulus was measured on 3 mm thick samples using pulse-echo method [20]. SEM observations were performed at scanning electron microscope FEI Quanta 200F with FEG cathode at the accelerating voltage of 20 kV. Microhardness was measured using automatic microhardness tester Qness Q10A with Vickers indentor and applied load of 500g. Computer controlled Instron 5882 was employed for the tensile tests utilizing strain rate 10⁻⁴ s⁻¹.

3. RESULTS

Figures 1-4 show the observations of the microstructure of selected alloys after forging. So-called channeling contrast allows observing individual grains. All alloys containing 2% Fe show coarse-grained undeformed microstructure containing pure beta phase disregarding oxygen content. Iron is strong beta-stabilizer; therefore pure beta-phase is retained even in presence of oxygen that is strong alpha stabilizer. Similar appearance was observed for the benchmark TNTZ alloy. On the other hand, the alloys containing oxygen without balancing iron content show microstructure containing either other phases or deformed twinned microstructure. Further experiments are necessary to clarify these microstructural observations.
Elastic modulus of all alloys was measured by pulse-echo method for as-cast material. Results are shown in Fig. 5. Elastic modulus of basic TNTZ alloy is around 65 GPa, which is in accordance with literature [14]. Elastic modulus increased to 80 GPa by either Fe or O content. This is typical value for either stabilized beta phase or beta + alpha” mixture [17]. For combined Fe and O content, the elastic modulus jumps. The origin of this increase is unknown and furthermore this increase is surprisingly removed by small Si addition. It can be concluded that the low beta phase stability of benchmark alloy is broken by Fe or O additions and therefore the increased value of $E = 80$ GPa is observed.

Fig. 6 shows the results of microhardness measurements for as-cast condition. Each elemental addition increases the microhardness of the material and oxygen shows the highest individual effect. Combining additions increase the microhardness when compared to individual effects, but the total effect is lower than the sum of individual effects. Microhardness can be more than doubled by 0.7 wt. % oxygen.
Figure 7 summarizes yield stress and ultimate tensile strength of the investigated alloys determined from tensile test. Each addition significantly increases the strength when compared to benchmark alloy; however, oxygen shows the highest effect. The effect of combined additions is mixed. Iron content, high oxygen content and especially mixed Fe and O additions cause significant work-hardening that can be observed as the difference between yield stress and ultimate tensile strength measured from true-stress - true-strain flow.
curves. 0.7 wt. % of oxygen more than doubles the strength of the alloy. Yield stress of 1000 MPa and ultimate tensile strength of 1200 MPa are superior to the common Ti-6Al-4V alloy.

![Tensile tests - true stress](image)

**Fig. 7 Tensile tests – yield stress and ultimate tensile strength (UTS) evaluated from true-stress – true-strain flow curves**

4. Conclusions

Following conclusions can be drawn from this investigation:

- Benchmark TNTZ alloy and all Fe containing alloys have coarse-grained single phase microstructure.
- Fe, Si and O additions increase elastic modulus due to breaking the low stability of beta phase in the benchmark alloy. The elastic modulus of most alloys is ~80 GPa, but it is significantly increased when Fe and O content is combined.
- Microhardness and strength of TNTZ alloy can be more than doubled when employing 0.7 wt. % oxygen addition.
- Achieved yield stress of 1000 MPa and ultimate tensile strength of 1200 MPa are superior to the common Ti-6Al-4V alloy.

ACKNOWLEDGEMENTS

Financial support by the Czech Science foundation under grant P107/12/1025 and by the Grant agency of the Charles University (project GAUK 158213) is gratefully acknowledged.

LITERATURE


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