THE EFFECT OF CHEMICAL COMPOSITION AND MICROSTRUCTURE ON ELASTIC MODULUS AND HARDNESS OF BIOMEDICAL TITANIUM ALLOYS BASED ON Ti-NB-ZR-TA COMPOSITION WITH SMALL FE AND SI ADDITIONS

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Abstract.
Beta titanium alloys are promising materials for load-bearing orthopaedic implants due to their excellent corrosion resistance and biocompatibility, low elastic modulus and moderate strength. Metastable beta-Ti alloys are hardenable via precipitation of alpha phase; however this has the adverse effect on elastic modulus. Small amounts of Fe (0-2%) and Si (0-1%) were added to Ti-Nb-Zr-Ta biocompatible alloy. SEM observations showed that Si content inhibits the grain growth during beta annealing. Coarse and fine silicide particles were observed using scanning electron microscopy. Fe and Si additions cause an increase in elastic modulus from 65 GPa to 85 GPa, which is still much lower than that of commonly used Ti-6Al-4V alloy. Fe additions and also Si additions cause a significant increase in microhardness. High temperature annealing enhances the positive effect of Si content on microhardness due to higher solubility of Si in beta Ti matrix. Alloy with composition TNTZ+2Fe+0.5Si proves optimal combination of elastic modulus and hardness.

Keywords: titanium alloys, biomedicine, elastic modulus, hardening

1. INTRODUCTION
For several decades, titanium alloys have been the mostly used material for load-bearing orthopedic implants [1]. Unique combination of properties includes extreme corrosion resistance, relatively high strength, sufficient biocompatibility and moderate elastic modulus [2]. Commercially pure titanium is used in some orthopaedic applications. However, limited strength (up to 500 MPa) disallows using commercially pure titanium as a material for orthopaedic endoprostheses, which constitute the majority of the market of metallic implants. The most commonly used is still one of the oldest Ti alloys – Ti-6Al-4V that belongs to alpha + beta alloys. Despite generally good properties of this alloy, there are several limitations. Special concern relates to the presence of vanadium that is considered as toxic element. Similar alpha + beta Ti alloy Ti-6Al-7Nb has been developed to avoid the adverse effect of vanadium [3]. However, another principal adverse property is too high elastic modulus (around 115 GPa for both Ti-6Al-4V and Ti-6Al-7Nb alloys) that is much higher than that of cortical bone (10-30 GPa). Too high elastic modulus 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].

1.1. Metastable beta-Ti alloys
Metastable beta-Ti alloys have been developed since 1960s [5]. The dominant area of application is the aerospace industry. However, in the last two decades, specialized biocompatible alloys have also been developed. 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. Several unstable phases may also be formed in this type of alloys. Omega phase is formed in less stabilized beta alloys upon annealing under low temperatures (typically around 300 – 400°C) and is a precursor of subsequent alpha precipitation. Omega phase particles are very small (~ 10 nm) and causes sharp increase of elastic modulus. Omega phase formation should therefore 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 even 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]. Pseudo-elasticity further decreases the elastic modulus, but its utilization in orthopaedic implants is questionable.

1.2. TNZT alloy

Ti-35Nb-7Zr-5Ta (TNZT) alloy was used as a benchmark material in this study. The alloy was developed in 1990s in USA and patented in 1998 [9]. The TNZT alloy contains only biocompatible element and at room temperature when water quenched from temperature above beta transus it consists of beta phase only. In this condition, the elastic modulus is as low as 55 GPa. The considerable disadvantage is relatively low strength of this alloy that is around 550 MPa, depending on oxygen content [10]. The strength can be significantly improved by omega phase formation and subsequent alpha precipitation. Nevertheless, elastic modulus is increased to above 100 GPa that is similar to common alpha + beta alloys. The purpose of this study is to employ small Fe and Si additions in order to harden TNTZ alloy without excessive increase of elastic modulus.

1.3. Fe and Si additions

Iron is a strong beta stabilizer and even low content causes hardening of alpha alloys via clustering and stabilization of beta phase and in beta alloys via simple solution strengthening [11]. On the other hand, Si has very low solubility in both alpha and beta phase and contributes to hardening via creation of dispersed precipitates Ti$_5$Si$_3$. Moreover, in alloys containing Zr even more stable (Ti,Zr)$_5$Si$_3$ compound is formed [12]. Si content of 0.2-0.4 wt.% is often utilized in high-strength and high-temperature alloys in aerospace industry in order to increase the strength and to suppress excessive creep [13,14]. Combined effect of Fe and Si has been explored by Lee et al. [15]. According to this study, Si content increases the strength up to 2 wt. % and the most pronounced increase is achieved already for 0.5 % content. On the other hand, Si content in excess of 1 wt. % reduces elongation drastically. Fe additions above 2 wt.% increase the strength substantially. As a result, combined alloying by Fe and Si leads to higher strength levels. However, this cited study by Lee et al. [15] considers alpha phase only. Kim et al. [16] studied Ti-(18-28)Nb-(0.5-1.5)Si metastable beta Ti alloys. They reported that Si content up to 1% decreases elastic modulus down to 48 GPa. However, this fact is related to a particular degree of beta stabilization and alpha” phase formation rather than to a special effect of Si.

2. MATERIAL AND EXPERIMENTAL PROCEDURE

Six different alloys were proposed and 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 six tailored alloys utilizing 0-2 wt.% Fe additions and 0-1 wt.% Si additions:

- 1 – TNZT
- 2 – TNZT + 1% Si
- 3 – TNZT + 2% Fe
- 4 – TNZT + 0.5% Si + 1% Fe
- 5 – TNZT + 0.5% Si + 2% Fe
- 6 – TNZT + 1% Si + 1% Fe

All alloys were prepared by arc melting of pure elements under low pressure of clean He atmosphere (350 mbar). Each part of the sample was remelted at least six times by electric arc to ensure the homogeneity. Samples of approximate weight of 200g 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. Finally, samples were sealed into quartz tube and beta solution treated at 1150°C/2h followed by water quenching. Such a high temperature was chosen to ensure full recrystallization that is incomplete after 1000°C/2h [17] and that should be above the solvus of silicide particles as reported by Ankem et al. [12]. Samples for microstructure 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 [18]. Extensive SEM observations were performed at scanning electron microscope FEI Quanta 200F with FEG cathode at the accelerating voltage of 20 kV and EDX analyzer. Microhardness was measured using semi-automatic microhardness tester Leco using Vickers indentor and load of 300g.

3. RESULTS

3.1 SEM observations

![Fig. 1 TNZT alloy](image1)
![Fig. 2 TNZT-1Si](image2)
![Fig. 3 TNZT-2Fe](image3)
![Fig. 4 TNZT-1Fe-0.5Si](image4)
Figures 1-6 show the observations of the microstructure of all prepared alloys. The origin of the contrast is so-called channeling contrast. The microstructure is therefore visible thanks to different orientations of individual grains. Microstructure of alloys without Si content (Figs. 1 and 3) is very coarse with grain sizes > 100 mm. Iron content does not have any observable effect on the grain size. On the other hand, Si serves as grain growth inhibitor. The grain size decreases with increasing Si content (compare Figs. 4 and 5 to Figs. 2 and 6). The mechanism of grain growth suppression is via underpinning of grain boundaries with intermetallic precipitates. Those intermetallic precipitates appear as small black dots in Figs 2, 4, 5 and 6. It is known, that the composition of intermetallic silicides in Ti alloys containing zirconium is (Ti,Zr)₅Si₃ [12].

Fig. 7 TNTZ-2Fe-0.5Si –EDX analysis

<table>
<thead>
<tr>
<th>wt. %</th>
<th>Matrix</th>
<th>1</th>
<th>2</th>
<th>3</th>
<th>4</th>
<th>5</th>
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<tr>
<td>Ti</td>
<td>43.9</td>
<td>61.5</td>
<td>68.5</td>
<td>71.7</td>
<td>24.2</td>
<td>32.5</td>
</tr>
<tr>
<td>Nb</td>
<td>40</td>
<td>24</td>
<td>19.6</td>
<td>16.1</td>
<td>11.8</td>
<td>16.7</td>
</tr>
<tr>
<td>Zr</td>
<td>7.1</td>
<td>7.4</td>
<td>7.5</td>
<td>7.3</td>
<td>45.7</td>
<td>34.9</td>
</tr>
<tr>
<td>Ta</td>
<td>5.5</td>
<td>5.3</td>
<td>2.8</td>
<td>3.5</td>
<td>1.8</td>
<td>3</td>
</tr>
<tr>
<td>Fe</td>
<td>2.5</td>
<td>1.1</td>
<td>4.2</td>
<td>0.9</td>
<td>0.6</td>
<td>1</td>
</tr>
<tr>
<td>Si</td>
<td>1</td>
<td>0.7</td>
<td>0.5</td>
<td>0.6</td>
<td>15.9</td>
<td>12</td>
</tr>
</tbody>
</table>
3.2 EDX measurements

Fig. 7 is a detail backscatter electron image of area close to the surface of the as-forged rod. Surface areas of rods cooled below beta-transus temperature during forging. We can therefore observe two types of particles. First, alpha phase particles that appear as almost black dots and second, silicide particles that appear as darker gray dots in this detail image. 5 particles were chosen for chemical analysis employing EDX. Particles 1 -3 are alpha phase particles, whereas particles 4 and 5 are silicides. Results of measurements by EDX are summarized in Table 1. Alpha phase particles are significantly titanium enriched since all other elements are beta stabilizers that are rejected form the alpha phase. Silicide particles are obviously Si enriched, but also significantly Zr enriched suggesting that Zr is dominant element in these intermetallic particles at the extent of Ti. Note that EDX results cannot be taken quantitatively, but serve only for comparison purposes. Moreover incident area is bigger than some of the particles and herefore presented composition is not solely a composition of the particle.

3.3 Elastic modulus and microhardness

Fig. 8 Elastic modulus measurements

Fig. 9 Microhardness evaluation

Elastic modulus of all alloys was measured by pulse-echo method for as-forged and beta solution treated conditions. Results are shown in Fig. 8. Elastic modulus of basic TNTZ alloy is around 65 GPa, which is in accordance with literature [9]. Elastic modulus increases with increasing Fe and Si content. The highest elastic modulus is observed for TNTZ+2Fe+0.5Si alloy, however, the value of 85 GPa is still significantly lower than that of commonly used Ti-6Al-4V alloy. No systematic difference between as-forged and as-annealed conditions was observed.

Fig. 9 shows the results of microhardness measurements for as-forged condition and for material quenched after 2 hours annealing at 1000°C and 1150°C. The microhardness of basic alloy is comparatively low. Fe and Si additions are capable to more than double the microhardness in beta solution treated condition. Fe additions and Si additions increase microhardness, but Si content above 0.5 wt. % is adverse. The highest microhardness is acheived for TNTZ+2Fe+0.5Si alloy.

Microhardness of alloys without Si content does not depend on the temperature of beta annealing. On the other hand, higher temperature of annealing leads to increased microhardness of alloys with Si content. It is suggested that more Si atoms are dissolved in the matrix causing either solid solution hardening or creating higher density of tiny precipitates upon quenching. Microhardness of Ti alloys with sufficient Si content can therefore be increased by beta solution treatment at high temperature.

4. CONCLUSION

Following conclusions can be drawn from this investigation

- Si content causes creation of intermetallic silicide particles that suppress grain growth
- Silicides paritcles are significantly Zr enriched
Fe and Si additions increase elastic modulus. Maximum achieved elastic modulus was 85 GPa, which is much lower than elastic modulus of common Ti-6Al-4V alloy (115 GPa).

Hardness of TNTZ alloy can be more than doubled when employing small Fe and Si additions.

Alloy with composition TNTZ+2Fe+0.5Si proves optimal combination of elastic modulus and hardness.

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