INVESTIGATION OF MECHANICAL PROPERTIES AND BICOMPATIBILITY IN VITRO OF Ti-NB-TA-ZR ALLOY WITH SMALL Fe AND Si ADDITIONS

Josef STRÁSKÝ, Petr HARCUBA, Michal LANDA, Miloš JANEČEK

a Charles University in Prague, Prague, Czech Republic, EU, josef.strasky@gmail.com
b Academy of Sciences of the Czech Republic, Institute of Thermomechanics, Prague, Czech Republic, EU

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. Six different alloys with Fe and Si additions were prepared by arc melting, hot forging and beta solution treatment. The effect of Fe and Si additions to on microhardness and elastic modulus were studied. Coarse and fine silicide particles were observed using light microscopy. Fe and Si additions cause a significant increase in elastic modulus from 63 GPa to 84 GPa, which is still much lower than that of commonly used Ti-6Al-4V alloy. Fe additions and also Si additions cause an increase in microhardness from 170 to 370 HV0.3. The optimal combination of microhardness and elastic modulus is achieved by utilizing additions of both alloying elements.

Keywords: biocompatible beta-Ti alloy, Fe and Si additions, microhardness, elastic modulus

1. INTRODUCTION

1.1. Titanium in biomedicine
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 orthopaedics 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].

1.2. 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.

1.3. 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.

1.4. 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 Ti₅Si₃. Moreover, in alloys containing Zr even more stable (Ti,Zr)₅Si₃ 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. To our knowledge, no study examining combined effect of Fe and Si additions to biocompatible beta-Ti alloy has been published.

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. Since no alpha phase was observed after forging, the forging temperature did not fall below beta transus temperature. 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 (0.2 μm and 0.05 μm) and colloidal silica on vibratory polisher (Buehler – Vibromet) was employed to obtain as clean surface as possible. For silicides observations, the weak Kroll’s etchant was used: 2 ml of 40% fluoric acid, 4 ml of 65% nitric acid and 50 ml of water, etching for 15 s. Grain structure was observed only using differential interference contrast (Nomarski contrast) after etching in the solution consisting of 2 ml of 40% fluoric acid, 5 ml of 30% hydrogen peroxide and 50 ml of water for 2 mins. Olympus microscope equipped with differential interference contrast – so-called Nomarski contrast was used for all observations. Elastic modulus was measured on 3 mm thick samples using pulse-echo method [18]. Microhardness was measured using semi-automatic Leco M410 A microhardness tester using Vickers indenter and load of 300g.

3. RESULTS

3.1. Light microscopy

![Fig. 1 Optical micrograph of TNZT alloy (benchmark)](image1)

![Fig. 2 TNZT alloy + 1 Si (wt.%), intermetallic particles (silicides) are well visible](image2)
Two types of intermetallic particles are present, big particles preferentially along grain boundaries. Small particles in the grain interiors are visible.

Fig. 1 shows the optical micrograph of TNZT alloy without any additions (benchmark). Despite intensive etching no microstructure is visible. Few dispersed black points are remnants from polishing [17]. Similar figure can be obtained for the alloy with Fe content but without Si. Figs. 2 and 3 show alloys with Si content. Two types of silicide particles are distinguishable. The bigger particles (> 1 µm) are ordered in chains that may correspond to the grain boundaries. Smaller particles are distributed almost homogenously in the areas without bigger particles, possibly in the grain interiors. Fig. 4 shows intermetallic particles in a bigger detail. It is obvious that the area with higher concentration of bigger particles is depleted and no smaller particles are seen.

Fig. 5 uses differential interference contrast (Nomarski contrast) to reveal the microstructure of the TNZT alloy without any additions. Similar microstructure has been observed for the TNZT+2Fe alloy. It contains coarse grains of the size in the range of 50 – 100 µm. Few spots and also thin green lines are believed to be remnants from polishing and etching. Finally, Fig. 6 shows the Nomarski contrast image of material with silicide intermetallic particles. The particles are slightly over-etched for easier identification and their apparent size is bigger than in previous figures. Two types of silicide particles are clearly seen. By careful observation, it might be found that not all bigger particles are distributed along grain boundaries and vice-versa, not each grain boundary contains silicide particles. As a result, we assume that annealing at 1150°C did not attain the solvus temperature of the (Ti,Zr)2Si3 particles. Therefore those particles might have been created during furnace cooling after homogenization annealing (1400°C) or even directly after melting. Partial recrystallization during forging and subsequent annealing led to movement of some grain boundaries which have not been sufficiently pinned by silicides.
3.2. Elastic modulus measurement

![Fig. 5 TNZT alloy - Differential interference contrast (DIC – Nomarski contrast); grain structure and some polishing remnants are visible](image1)

![Fig. 6 TNZT alloy + 1 Fe + 1 Si (wt.%) – two types of silicides particles are well seen](image2)

Fig. 7 shows the result of elastic modulus determination. Basic TNZT alloy has the elastic modulus of 63 GPa, which is approximately 50% of elastic modulus of the most common Ti-6Al-4V alloy. Si and Fe additions increase elastic modulus substantially. However, even the highest attained elastic modulus of 84 GPa for TNZT+1Si+1Fe alloy is significantly lower than that of Ti-6Al-4V alloy (115 GPa).

3.3. Microhardness evaluation

Microhardness was evaluated for two series of samples: the first one - the samples after forging and the second one - the samples after forging and beta solution treatment. Microhardness of basic TNZT alloy is rather low. Both Fe and Si proved to have strong effect on microhardness, especially combined additions of both elements lead to increased material hardness. The highest microhardness was attained for TNZT+0.5Si+2Fe alloy. Comparing the microhardness of as-forged and beta solution treated conditions; we observe systematically higher values in alloys containing Si. This is attributed to the fact that during furnace cooling after homogenization annealing and also during air cooling after forging, the Si content is concentrated in silicide particles of micrometer range. On the other hand, during beta annealing at 1150°C, more Si is dissolved in beta matrix. Si atoms cannot diffuse to remaining bigger silicide particles due to fast...
quenching and possibly form new small particles. Those dispersed particles then contribute to the hardening of the material.

![Graph showing microhardness of alloys](image)

**Fig. 8** Microhardness of all alloys. As-forged condition (forging in beta region) and beta-solution treated condition

4. **CONCLUSIONS**

The following conclusions can be drawn from this investigation:

- Biocompatible metastable beta-Ti alloys Ti-35Nb-7Zr-5Ta-(0-2)Fe-(0-1)Si were developed and successfully manufactured.
- Light microscopy revealed the presence of silicide particles and suggested that their solvus temperature is above 1150°C.
- Elastic modulus of TNZT alloy is 63 GPa. Fe and Si additions increase elastic modulus to 84 GPa that is still significantly lower than the elastic modulus of commonly used Ti-6Al-4V (115 GPa).
- Microhardness of TNZT alloy is more than doubled by small Fe and Si additions.

**ACKNOWLEDGEMENTS**

*Financial support by the Czech Science foundation under grant P107/12/1025 and by the Ministry of Education, Youth and Sports under the project KONTAKT II LH 12217 is gratefully acknowledged.*

**LITERATURE**


[14] CHAUDHURI, K., PEREPEZKO, J.H. Microstructural Study of the Titanium Alloy Ti-15Mo-2.7Nb-3Al-0.2Si (TIMETAL 21S), Metal and Mat Trans, 25, 1994 1109-1117


