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HABILITATION THESIS

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Advanced Titanium Alloys for Medical Applications

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Habilitation Thesis
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Content

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I would like to thank prof. Miloš Janeček for bolstering my scientific career and letting me write on my own several hundreds of pages of manuscripts, chapters, grant applications and grant reports within last ten years. I acknowledge my colleague Petr Harcuba for plenty of experimental work he did and for never-ending fruitful discussions. I acknowledge Jana Šmilauerová and Hanuš Seiner for their kind help with writing this thesis. I would like to thank my hard-working students: Jiří Kozlík, Dalibor Preisler, Anna Veverková and Kristína Bartha who work for their own benefits, but also significantly contributed to this thesis. Above all I would like to express my appreciation to my wife Jitka for a thorough support.

1. Structure of the thesis

This habilitation thesis presents the main achievements of my research at the Department of Physics of Materials during the years 2014 – 2020. My scientific activities focused mainly on the development of titanium-based materials for medical applications. The range of research spans from theoretical considerations and experimental characterization to applied research projects aiming to achieve commercially utilizable materials. I conducted a significant part of this investigation, but a successful research in such a complex topic requires a team consisting of members with different abilities, experiences and interests. Such team at the Department of Physics of Materials made this thesis possible.

The habilitation thesis is a compilation of previously published works. However, the structure of the thesis is affected by the fact that recently I was invited and had the privilege to publish two chapters in the monograph *Titanium in medical and dental applications* published by Woodhead Publishing, Elsevier. Each of these two chapters introduced the topic, reviewed existing literature and presented some of our own experimental results. Based on these two chapters, which are included in this habilitation thesis, the scientific content of the thesis can be divided into two following parts:

1) ***Development of Ti-Nb-Ta-Zr-O biomedical alloys***
2) ***Ultra-fine grained Ti alloys for biomedical use***

How to read this thesis

Chapter 2 ***Introduction*** aims on introducing the reader to the topic of titanium alloys with the focus on medical applications. The text of this chapter is partly based on the introduction to the diploma thesis of my former PhD student Kristina Bartha: *Microstructure and mechanical properties of ultra-fine grained titanium alloys*.

Chapter 3 ***Development of Ti-Nb-Ta-Zr-O biomedical alloys*** first briefly introduces this research topic. More detailed scientific overview is included in the chapter *Biocompatible beta-Ti alloys with enhanced strength due to increased oxygen content* from the monograph *Titanium in medical and dental applications*, which is reprinted in this thesis. The chapter 3 continues with a list of published papers and their annotations. At the end of this chapter, some interesting, yet unpublished, results are presented.

Chapter 4 ***Ultra-fine grained Ti alloys for biomedical use*** has a similar structure to the previous chapter. After a brief overview, the reader is referred to the chapter *Microstructure and lattice defects in ultrafine grained biomedical α+β and metastable β Ti alloys* from the monograph *Titanium in medical and dental applications*, which is attached to this thesis. The description of 7 published papers follows. At the end of this chapter, some unpublished results are presented.

Chapter 5 ***Conclusion and outlook*** summarizes the thesis and describes current activities of myself and my research team in the field of titanium alloys.

2. Introduction

2.1. Titanium and classification of titanium alloys

Titanium was discovered by the English chemist William Gregor in 1791 in the mineral ilmenite ($FeTiO_3$). In 1795 it was named after the Titans due to its resistance to be isolated as a pure metal. Titanium is a transition metal and as a chemical element with the atomic number of 22 it belongs to the Group 4 of the periodic table of elements [Lutjering2007].

Titanium and its alloys are of great interest due to their outstanding properties such as high specific strength and excellent corrosion resistance. Titanium is not a noble metal, but it owes its corrosion resistance to a passivation layer, consisting mainly of TiO_2, which is formed virtually immediately on the exposed surface and is stable at high temperatures and in many chemically aggressive environments [Welsch1993].

Aircraft industry comprises the biggest market for titanium alloys. Other applications include architecture, jewellery, sport goods and, most importantly for this thesis, medicine [Geetha2009].

Under different conditions, titanium can exist in different crystal structures, which are referred to as allotropic modifications. Above so-called β-transus temperature (882°C), the structure of the material is the body-centered cubic (bcc) which is referred to as β phase. Upon cooling, the material transforms to the hexagonal close-packed (hcp) structure referred to as α phase. Nevertheless, the stability ranges of the α and β phases can be affected by additions of alloying elements as schematically shown in Figure 1. The β-transus temperature can be shifted by alloying, and a two phase region α + β is introduced. The β stabilizing elements decrease the β-transus temperature and shift the β-phase field towards lower temperatures. The β stabilizing elements are divided to β-isomorphous and β-eutectoid. Sufficient amount of the β-isomorphous elements can stabilize β phase at room temperature, while the β-eutectoid elements can form a stable intermetallic compound. However, the intermetallic compound usually forms only at elevated temperatures and after a long time and, in many alloys containing β-eutectoid elements, it can be avoided completely [Smilauerova2017].

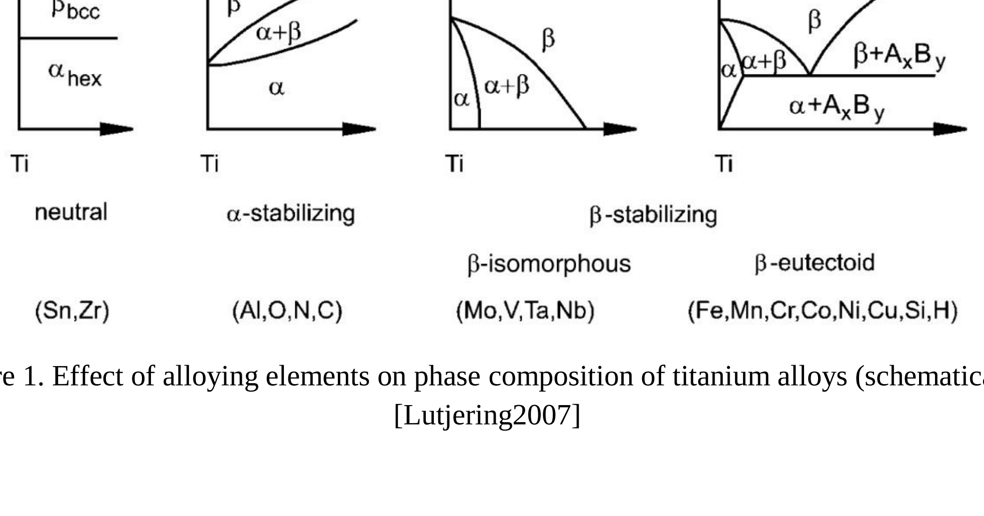

Figure 1. Effect of alloying elements on phase composition of titanium alloys (schematically) [Lutjering2007]

The schematic phase diagram depicted in Figure 2 shows qualitatively the effect of the content of the β-stabilizing elements (horizontal axis) and temperature (vertical axis) on the phase composition. Equilibrium phase diagram is shown by the solid black curves, while the dashed red curve shows a martensite start (M_s) temperature corresponding to the beginning of a β → α" phase transformation. α" is an orthorhombic martensite phase [Davis1979]. The martensite start temperature decreases with increasing content of β-stabilizers.

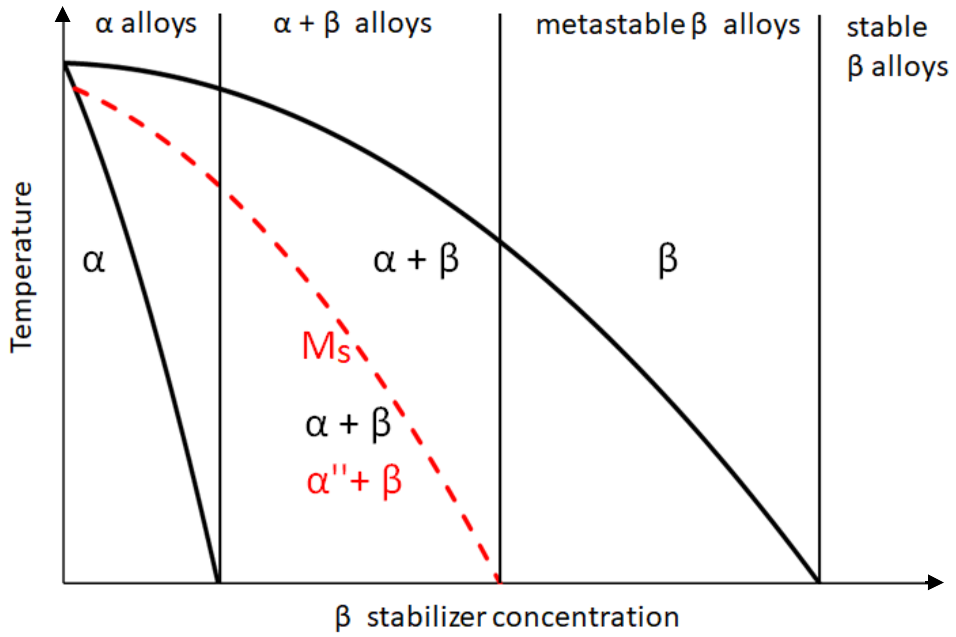

Figure 2. Pseudo-binary β isomorphous phase diagram (schematically)

Based on this phase diagram, titanium alloys are divided into four classes according to their phase composition at room temperature. α phase is the only stable phase at room temperature for pure titanium and α alloys. Increasing content of the β-stabilizing element(s) stabilizes some amount of β phase at room temperature which is characteristic for α + β alloys. When the martensite start temperature is lowered below the room temperature, the formation of α phase and martensitic α" phase can be fully suppressed. Such alloys are called metastable β-Ti alloys and currently represent the most studied group of Ti alloys. Finally, a Ti alloy can be β stabilized to such extent that β phase is thermodynamically stable at ambient temperature, and the alloy is referred to as the stable β-Ti alloy.

2.2. Phase transformations in metastable β-Ti alloys

Apart from above mentioned stable α and β phases, many unstable and metastable phases were found in titanium alloys. Many titanium alloys in commercial practice are intentionally used in a metastable condition (metastable phase composition).

The majority of the results presented in this thesis concerns metastable β-Ti alloys. Metastable β-Ti alloys, by definition, do not contain α, α', or α" phase after quenching from a temperature above the β-transus temperature of the particular alloy (typically around 700 – 800 °C) – this condition is referred to as beta solution treated condition.

After quenching, ω phase can be formed in some metastable β-Ti alloys by a diffusionless displacive transformation (ω athermal phase). ω phase can be also formed via diffusion-assisted process at temperatures 200 – 550 °C depending on the alloy composition (ω isothermal phase). This phase has been thoroughly studied in numerous reports [DeFontaine1971, Devaraj2009]. A comprehensive discussion can be found in the PhD thesis by J. Šmilauerová [Smilauerova2016]. For the purpose of the present thesis, it must be stressed that ω phase causes a significant increase of elastic modulus [Tang2000].

Controlled precipitation of incoherent *α* phase particles in the β matrix is the major strengthening mechanism in metastable β-Ti alloys and has been thoroughly studied by numerous researchers since 1960s. The nucleation of the *α* phase occurs heterogeneously at preferential sites - including grain and subgrain boundaries, dislocations and other types of lattice defects [Makino1996, Ivasishin2005].

In diffusion controlled transformations, such as precipitation of α phase particles in the β matrix, the formation of a new phase is accompanied by a change of composition, which is controlled by diffusion. At high cooling rates, diffusion fails to accomplish required compositional changes and phase transformations are generally suppressed. However, with increasing under-cooling, the driving forces for the transformation increase considerably and the crystal structure may change spontaneously without a change in chemical composition. These transformations are referred to as martensitic. Martensitic transformations involve organized movement (shift) of atoms from their initial positions in the crystal lattice into new positions creating a new crystal structure. The martensitic transformation is athermal, i.e. time-independent at a given temperature. The transformation initiates below M_s (martensite start) temperature, and the material is fully transformed below M_f (martensite finish) temperature [Gottstein2004]. Two main martensite phases occurring in titanium alloys are hexagonal α' phase and orthorhombic α'' (alpha double prime). α'' can be formed martensitically upon quenching in alloys with composition near the borderline between α + β and metastable β-Ti alloys [Kharia2001, Elmay2013]. M_s temperature of the α'' phase formation is schematically shown in Figure 2 by a red dashed line. Martensite can be also formed with the aid of stress which causes organized mutual movement of atomic planes (stress induced martensite - SIM) [Orgeas1998]. α'' martensitic phase might be formed by mechanical loading in some metastable β-Ti alloys [Koul1970], which results in pseudo-elasticity and shape memory effect [Kim2007, Kent2010].

2.3. Strengthening mechanisms in Ti alloys

Plastic deformation in metals is promoted predominantly by dislocation movement. Shear stress necessary for activation of the dislocation slip (Peierls stress τ_p) in a defect-free single-crystal is surprisingly low, and strategies for material strengthening must be employed in order to achieve commercially viable properties.

Deformation strengthening is a basic strengthening mechanism and is utilized in materials prepared by severe plastic deformation (SPD) methods described below. Strength of a polycrystalline material is also increased by grain boundaries. This strengthening effect is related to the mean grain size d via Hall – Petch relationship [Hall1951, Petch1953]:

$$\sigma_y = \sigma_0 + k_y d^{-1/2}, \tag{1}$$

where σ_y is the yield stress of the material, σ_0 represents the friction stress, k_y is a material constant and d is the mean size of grains. Increasing strength via grain refinement is the main motivation for the development and production of so-called ultra-fine grained (UFG) materials [Valiev1993].

In alloys, solute atoms interact with dislocations and increase the stress required for dislocation movement. The absolute increase of the mechanical strength strongly depends on the strength of the obstacle – for instance on the type of solute atom. Moreover, the strengthening effect is significantly enhanced if solute atoms impose large anisotropic distortions.

It must be recalled that β-Ti alloys studied in this thesis have bcc structure and that interstitial strengthening by oxygen is of our primary interest. Oxygen atoms (along with carbon and nitrogen atoms) are interstitial atoms and considered as "heavy" interstitials (contrary to hydrogen or helium atoms). Interstitial oxygen atoms induce anisotropic elastic dipoles with tetragonal symmetry in bcc materials [Savino1981], because an interstitial atom in an octahedral void is closer to the pair of its neighbours and causes a significant asymmetric tetragonal distortion of the lattice. The effect of tetragonal distortions on hardening was described in a seminal paper by Fleischer [Fleisher1962]. The distortion increases the interaction of the interstitial atom with both edge and screw dislocations and promotes strengthening significantly. As a result, strengthening by interstitial atoms is more effective in bcc alloys than, for instance, in face-centered cubic (fcc) materials, where the lattice distortion is more isotropic [Cochardt1955].

Interstitial strengthening by increased oxygen content is used in commercially pure Ti (i.e. in hcp α phase). This type of strengthening is very efficient as recently explained in [Yu2015]. So-called commercially pure titanium (CP Ti) may contain up to 0.4 wt. % of oxygen, which guarantees its strength of 550 MPa. Titanium with higher oxygen content becomes brittle [Welsch1993]. Interstitial hardening by oxygen atoms also affects the strength and the ductility of Ti alloys. In α + β alloys or metastable β-Ti alloys, maximum allowed oxygen content is limited typically to 0.2 wt % [Welsch1993]. Interstitial strengthening by oxygen is also efficient in bcc structure of β alloys as explained above. Moreover, ductility of some β alloys is preserved even for oxygen content exceeding 0.5 wt % [Qazi2004].

In metastable β-Ti alloys used in the commercial practice, the most used strengthening mechanism is the controlled precipitation of homogenously distributed α phase particles [Lutjering2007]. α phase precipitation is usually achieved via elaborated thermal or thermomechanical treatment [Zheng2016]. One of the topics of this thesis is the investigation of the effect of severely deformed microstructure on α phase precipitation.

2.4. *Titanium as an implant material*

Replacement of big joints is considered as a major achievement in orthopaedic surgery in 20^{th} century. One of the most delicate issues in a hip endoprosthesis design is the femoral stem that is crucial for preventing the implant from loosening. Development of orthopaedic implants is a complex and multi-field scientific issue.

Titanium alloys have been extensively applied in the 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 [Long1998, Katti2004, Geetha2009]. Excellent biocompatibility of titanium was proven by many authors both in vitro and in vivo [Rao1997, Okazaki2005, Gepreel2013]. In the last two decades, specialized biocompatible β-Ti alloys were developed. Among commonly used alloying elements, Nb, Ta, Zr and also Mo are regarded as the most biocompatible, whereas V, Cr and Co are considered inappropriate [Steinemann 1998], although Ti-6Al-4V alloy is still used for load-bearing implants [Niinomi2008].

Ti-6Al-4V alloy is a two-phase α + β alloy originally developed for aerospace applications in 1950s and still constitutes the workhorse of titanium industry. The strength of Ti-6Al-4V alloy can exceed 1000 MPa after proper thermomechanical treatment. The elastic modulus of the alloy is around 115 GPa, which is half of the elastic modulus of steels [Welsch1993]. Despite its original application in aerospace industry, Ti-6Al-4V alloy is nowadays used for manufacturing of vast majority of load-bearing body implants such as hip joint implants [Rack2006].

The strength of the implant material is the most important parameter for implant construction. The yield stress above 800 MPa is a typical requirement as this is the low-limit of the strength of Ti-6Al-4V alloy. Common elastic modulus of Ti and Ti alloys is around 100 GPa, which is much higher than the elastic modulus of the cortical bone (10-30 GPa) [Niinomi2012]. This difference in stiffness of the implant and the surrounding bone causes so-called stress shielding effect. The applied load is transmitted through the implant stem, and therefore the surrounding bone is not loaded and becomes atrophied and prone to failure. As a result, a material with a sufficient strength and a reduced elastic modulus is required [Niinomi2008].

Metastable β-Ti alloys have been developed since 1960s [Lutjering2007]. The principal advantages of these alloys is their increased strength. The dominant area of application is the aircraft manufacturing – namely landing gear structures. However, in the last three decades, specialized biocompatible alloys have also been developed [Kaur2019].

2.5. *Ultra-fine grained Ti alloys*

Ultra-fine grained (UFG) materials are defined as polycrystalline materials with grain sizes lower than 1 μm but typically greater than 100 nm. These materials usually have excellent mechanical properties – high strength, hardness and fatigue resistance. A common disadvantage is a reduced ductility of the material [Langdon2013]. The reduction of grain size in polycrystalline materials results in changes in mechanical and physical properties, namely an increase in strength.

UFG bulk materials can be fabricated by severe plastic deformation (SPD) methods, which refer to techniques that introduce intensive plastic deformation to the material by repetitive processing [Valiev2000, Huang2013]. The most used SPD methods are Equal Channel Angular Pressing (ECAP) [Segal1981] and High Pressure Torsion (HPT) [Smirnova1986].

The principle of ECAP is a repetitive pressing of a small rod or billet through a die consisting of two intersecting channels with the same cross-section. The geometry of the die is characterized by two angles: Φ and Ψ shown in Figure 3.

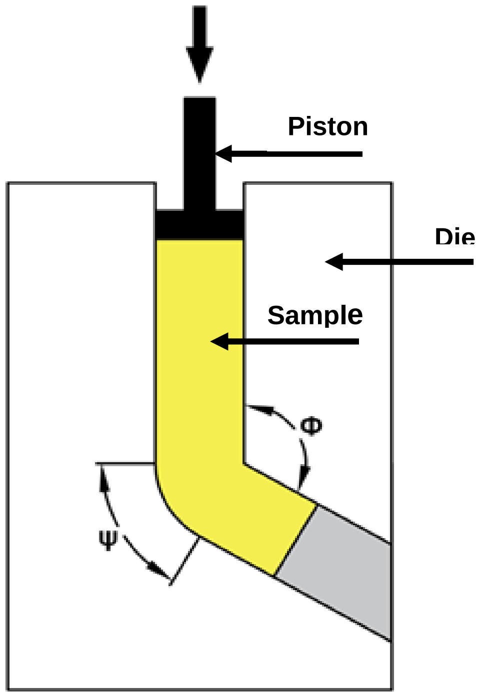

Figure 3. Schematic representation of the ECAP process

A conventional ECAP die has the angle Φ equal to 90°; however, titanium alloys, due to their high strength and limited ductility, can be usually repeatedly successfully processed only using a die with an increased angle Φ (e.g. 120° as shown in Figure 3).

The specimen pressed through the ECAP die is deformed by a simple shear, and the imposed von Mises strain after *N* passes can be expressed [Iwahashi1996]:

$$\varepsilon_{VM} = \frac{N}{\sqrt{3}}\left[2\,\mathrm{cotg}\left(\frac{\phi}{2}+\frac{\psi}{2}\right)+\psi\,\mathrm{cosec}\left(\frac{\phi}{2}+\frac{\psi}{2}\right)\right]. \quad (2)$$

The equivalent von Mises strain calculated from eq. (2) for a die with angles Φ = 120° and ψ = 0° is ε_{VM} = 0.67 for each pass. Pressing temperature is a crucial parameter of the ECAP which influences both the processability and the microstructure of the deformed material.

During high pressure torsion (HPT) a disc-shaped sample is placed between two anvils which compress the sample at high pressure (several GPa). One of the anvils is subsequently rotated and deforms the sample in torsion. The schematic representation of the procedure is shown in Figure 4.

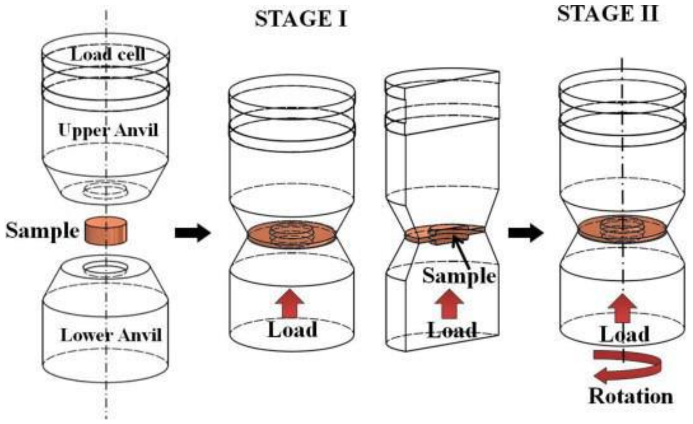

Figure 4. Schematic representation of the HPT process [Song2011]

The total von Mises strain imposed by HPT in the sample can be expressed using a simple torsion model [Valiev1996]:

$$\varepsilon_{VM} = \frac{2\pi N r}{\sqrt{3}h}, \quad (3)$$

where N is the number of rotations, r is the distance from the sample centre and h is the sample thickness. Due to the geometry of the deformation, the imposed strain is not homogeneous and increases from the centre to the edge of the sample. HPT is usually carried out at room temperature and its main advantage is the high degree of imposed deformation. Small size of samples and inhomogeneous deformation which restrict commercial production are the main disadvantages of HPT processing [Zhilyaev2008]. In contrast, ECAP is capable of producing specimens with a reasonable size for various biomedical applications [Valiev2009].

Ultra-fine grained titanium was first prepared by the SPD methods at Ufa State Aviation Technical University (USATU), Ufa, Russia [Popov1997] Ultra-fine grained titanium alloy Ti-6Al-4V was later prepared by ECAP [Semenova2004]. Manufacturing of dental implants benefits from the enhanced strength of UFG titanium [Valiev2009]. Recently, SPD processing has been proposed to fabricate ultra-fine grained metastable β-Ti alloys with high strength, reduced modulus of elasticity and excellent biocompatibility [Xu2009, Zafari2015, Polyakov2019]. It has been shown that severe plastic deformation of these alloys leads to improved strength due to grain refinement and substructure evolution [Valiev2014]. These materials are of significant interest for biomedical use [Xie2013].

3. Development of Ti-Nb-Ta-Zr-O biomedical alloys

This chapter describes our achievements in the field of development and characterization of new biocompatible β-Ti alloys.

Within the last 25 years, the development of biocompatible β-Ti alloys with decreased modulus of elasticity focused mainly on the Ti-Nb-Ta-Zr alloying system due to an excellent biocompatibility of the used alloying elements [Okazaki2005]. The two most investigated alloys are Ti-29Nb-13Ta-4.6Zr [Kuroda1998] (Japan alloy) and Ti-35Nb-7.3Zr-5.7Ta (US alloy). The latter alloy was developed in the 1990s in the USA, patented in 1999 [Ahmed1999] and used as a benchmark material for alloy development described in this thesis. The alloy was designed experimentally by testing many different chemical compositions aiming to achieve the minimum elastic modulus. Ti-35Nb-7Zr-5Ta was the most β-stabilized alloy tested in [Tang2000]. The elastic modulus of this alloy can be as low as 50 GPa, because α, α'' and ω phases are avoided in the β solution treated condition. The main disadvantage of this alloy is its low strength of only 500 MPa that is not sufficient for manufacturing of implants of big joints.

The main objective of our own investigation was to develop strategies for increasing strength of Ti-35Nb-7Zr-6Ta alloy while maintaining low elastic modulus and good biocompatibility. The majority of our research in this field focuses on biocompatible β-Ti alloys with an increased oxygen content. Our findings, along with a comprehensive literature review, are summarized in the chapter in the monograph:

[A0] J. Stráský, M. Janeček, P. Harcuba, D. Preisler, M. Landa, *Chapter 4.2.:* **Biocompatible beta-Ti alloys with enhanced strength due to increased oxygen content**, in *Titanium in Medical and Dental Applications*, Editors: Francis H. Froes, Ma Qian, Woodhead Publishing in Materials, Elsevier 2018

This chapter provides the very first comprehensive review on β-Ti alloys with increased oxygen content. This class of alloys intended for biomedical applications with knowledge-based design is very promising for manufacturing of load-bearing orthopaedic implants. The chapter describes theoretical considerations of interstitial strengthening of bcc materials, which include β-Ti alloys. Moreover, it provides a comprehensive literature review of reports on β-Ti alloys in which the oxygen content was increased (intentionally or unintentionally) and properly measured. The immense effect of interstitial oxygen atoms on the strength enhancement was documented. Our experimental results describing the development of biomedical Ti-Nb-Zr-Ta-O alloys with varied oxygen content are introduced in the text, as well.

I wrote the whole chapter with the help of my student Dalibor Preisler who prepared the overview of the properties of various alloys characterized in available literature. Other co-authors contributed by the experimental characterization.

[A1] I. Kopová, J. Stráský, P. Harcuba, M. Landa, M. Janeček, L. Bačáková: ***Newly developed Ti-Nb-Zr-Ta-Si-Fe biomedical beta titanium alloys with increased strength and enhanced biocompatibility***, Materials Science & Engineering C, Vol. 60, 2016, 230 -238

The paper published already in 2016 represents our first attempt to increase the strength of Ti-35Nb-7Zr-6Ta alloy by utilizing the combined strengthening effect of iron and silicon. Fe causes simple solution strengthening in β-Ti alloys, while Si addition causes precipitation of silicides which may increase the strength via precipitation strengthening. The results show that the strength of the material increased from 500 MPa to 800 MPa. However, the modulus of elasticity increased from 60 GPa to 80 GPa. We ascribe such significant increase of modulus of elasticity to the stabilization of β phase by Fe content.

This contribution resulted from a long-term cooperation between Department of Physics of Materials and the Institute of Physiology, Czech Academy of Sciences. This cooperation initially focused on surface treatment of Ti alloys [Harcuba2012, Stráský2013, Havlíková2014]. Biocompatibility (cell adhesion and toxicity) of the newly developed biomedical Ti-based alloys was assessed at the Institute of Physiology headed by prof. Lucie Bačáková and complemented by the investigation of mechanical properties conducted by our group. The most important original finding is that the addition of other alloying elements does not have any harmful effect on the biomedical response of the alloys, and the biocompatibility of all studied alloys was superior to that of benchmark Ti-6Al-V alloy.

Based on discussions in our team, I designed the new alloys arranged for their manufacturing and managed their experimental characterization. I wrote the introduction to the paper and the part describing the development, microstructure and mechanical properties of the alloys.

[A2] J. Stráský, P. Harcuba, K. Václavová, K. Horváth, M. Landa, O. Srba, M. Janeček: ***Increasing strength of a biomedical Ti-Nb-Ta-Zr alloy by alloying with Fe, Si and O***, Journal of Mechanical Behavior of Biomaterials, Vol. 71, 2017, 329 – 336

This is the key publication in which we describe the strengthening of the Ti-35Nb-7Zr-6Ta titanium alloy by three different mechanisms: substitutional solid solution strengthening by Fe, precipitation hardening by silicide particles and interstitial strengthening by oxygen. It was proven that interstitial strengthening is much more efficient than the other mechanisms, and increased content of oxygen proved to be the most promising for achieving optimal combination of desired mechanical properties. Addition of oxygen, which is obviously a biotolerant element, resulted in doubled strength of the material. At the same time, ductility of the material exceeded 20 %, which is sufficient for practical use. On the other hand, modulus of elasticity increased to 80 GPa due to reasons explained below.

The strategy of designing new alloys was developed by me and my colleague Petr Harcuba. I performed the measurements of mechanical properties, summarized all achieved results, discussed them and wrote the manuscript.

[A3] D. Preisler, J. Stráský, P. Harcuba, F. Warchomicka, M. Janeček, ***Enhancing mechanical properties and microstructure of Ti-Nb-Zr-Ta-O biomedical alloy through hot working***. Acta Physica Polonica A, Vol. 134 (2018)

The newly developed alloy with composition Ti-35Nb-7.3Zr-5.7Ta-0.7O was granted a Czech patent no. 307793 in 2018. The alloy was thoroughly characterized with the focus on its use as a material for manufacturing of load-bearing implants of big joints, namely for the stem of the hip joint endoprosthesis. The paper investigates hot-formability of this alloy. Deformation tests at high temperatures with high strain rates were undertaken to determine parameters of hot-working of the material, which is commonly required for the manufacturing of the implant.

The publication could not be possible without a close cooperation bewteen our team and the team of dr. Fernando Warchomicka, Technical University Graz, Austria. This foreign partner provided us the possibility to use Gleeble machine allowing deformation at high temperatures and at high strain rates, and immediate water quench after the deformation.

[A4] J. Stráský, D. Preisler, K. Bartha, M. Janeček, ***Manufacturing of Biomedical Ti-Based Alloys with High Oxygen Content and Various Amount of Beta-Stabilizing Elements***, Materials Science Forum, Conference proceedings: Thermec 2018, Paris

The above mentioned drawback of oxygen addition is the undesired increase of elastic modulus. We found that elastic modulus can be retained at low level (60 GPa) by decreasing content of the β stabilizing elements. The paper ***Manufacturing of Biomedical Ti-Based Alloys with High Oxygen Content and Various Amount of Beta-Stabilizing Elements*** in the conference proceeding of conference Thermec 2018 represents the first experimental characterization of alloys with reduced content of β stabilizing elements. This paper with limited length shows only initial experimental results. Most achievements remain unpublished and are described below in this thesis.

[A5] D. Preisler, M. Janeček, P. Harcuba, J. Džugan, K. Halmešová, J. Málek, A. Veverková, J. Stráský, ***The Effect of Hot Working on the Mechanical Properties of High Strength Biomedical Ti-Nb-Ta-Zr-O Alloy***, Materials 12 (2019) 4233

Our most recent published contribution in the field of development and characterization of Ti-Nb-Ta-Zr-O based alloys describes the possible thermomechanical treatment of the alloy. Most importantly, this paper includes experimental results from fatigue testing. Fatigue performance is a key property which decides applicability of the developed material and determines the life-time of an implant. Testing of fatigue properties is extremely material demanding and rarely published for newly developed biomedical β-Ti alloys. The publication results from a long-term cooperation between our team and Beznoska Ltd., an important Czech implant manufacturer. Cooperation with industrial partner (currently supported by a project by Ministry of Industry and Trade, Czech Republic) is promising in terms of application and commercialization of achieved results.

My current research in the development of new biocompatible β-Ti alloys with increased oxygen content focuses on the reduction of elastic modulus without sacrificing strength. The majority of this research has not been published yet and therefore is introduced in the rest of this section.

Elastic modulus (E) of different phases in Ti alloy can be ordered as: $E_{\beta} \approx E_{\alpha''} \approx 70$ GPa < $E_{\alpha} \approx 100$ GPa < $E_{\omega} \approx 130$ GPa [Fischer 1970, Niinomi 1998, Tane 2013, Nejezchlebova 2016]. The stability of individual phases is connected to the electron-per-atom ratio (*e/a* ratio) and the elastic modulus decreases with decreasing *e/a* ratio as long as the material retains the pure β phase [Hao 2007]. Therefore, in order to achieve material with a reduced elastic modulus, an alloy should retain the pure β phase, but the stability of this phase must be low: in 'proximity' to β → α" martensitic transformation [Tane 2010].

During elastic deformation, atoms are slightly shifted from their initial positions due to stress, but after relieving the stress, atoms return to their original positions. Elastic deformation in shear is crucial for overall macroscopic Young's modulus of polycrystalline materials. Therefore, in the proximity of the martensitic transformation, which would occur at slightly lower temperature, the atoms can be shifted further away from their initial positions by the shear stress, although they return back after relieving the stress without any change in crystal structure. Such material exhibits lower elastic constants (so-called abnormal softening) due to the 'proximity' to the martensitic transformation, although no martensitic transformation actually occurs [Nakanishi1980].

The effect of 'proximity' of martensitic transformation was studied in different systems such as Ti-Ni [Ren2001] or Co-Ni-Al [Seiner2013]. Abnormal softening of elastic constants was measured in single crystals of biomedical Ti-Nb-Ta-Zr alloy, but it was not ascribed directly to the 'proximity' of martensitic transformation [Tane2010]. Biomedical alloys with the lowest elastic modulus such as Ti-29Nb-13Ta-4.6Zr, Ti-35Nb-7Zr-5Ta or GUM Metal (Ti-35Nb-2Ta-3Zr-0.3O) were developed mostly experimentally and in my opinion these alloys owe their low-modulus property to the 'proximity' of martensitic transformation, although the inventors of these alloys may have not realized this at the time of the alloy development.

In the Ti-35Nb-7Zr-6Ta-0.7O alloy, which we have thoroughly studied, high oxygen content affects the phase stability of the β matrix. Oxygen is an α stabilizing element in terms of increasing the β transus temperature in pure Ti [Waldner1999] and in metastable β-Ti alloys [Qazi2005, Geng2011]. The relationship between oxygen content and β → α" martensitic transformation is less understood. Results from a few experimental studies suggest that in the competition between β and α" phases, interstitial oxygen acts as a β stabilizing element and shifts the martensite start (M_s) temperature of α" formation to lower temperatures [Furuta2007, Tane2016, Abdel-Hady2006, Obbard2011]. Consequently, by adding significant amount of oxygen to a low-modulus β-Ti alloy, the stability of β phase increases, causing an increase of the elastic modulus.

These considerations are depicted in Figure 5 which presents a schematic pseudo-binary phase diagram of Ti-Zr-Nb-Ta-O alloys. The diagram is pseudo-binary in terms that one constituent is not pure Ti (cf. Figure 2), but Ti-7Zr composition. The other constituent is a β-Ti stabilizing element (cf. Figure 2), in this particular case the total Nb + Ta content.

Horizontal axis therefore represents the content of Nb + Ta in wt % (the effect of Ta on phase stability is similar to Nb within the limits used in the studied alloys). This unusual construction allows us to show the position of quaternary Ti-35Nb-7Zr-6Ta alloy in the diagram. Note that blue lines are relevant for the alloys without oxygen.

The effect of oxygen is incorporated into the diagram such that the first constituent in the diagram (along vertical axis on the left hand side) is not Ti-7Zr but Ti-7Zr-0.7O composition, and the diagram is drawn by red lines. It can be observed that oxygen increases the stability of α phase. This diagram allows us to depict the position of Ti-35Nb-7Zr-6Ta-0.7O alloy.

Apart from solid lines representing the equilibrium diagram, the dotted lines represent the start of martensitic transformation β → α" (cf. Figure 2). In the diagram, elastic modulus of Ti-35Nb-7Zr-6Ta and Ti-35Nb-7Zr-6Ta-0.7O is also shown. Low modulus of the former alloy is given by the partial abnormal softening due to the 'proximity' of martensitic transformation. On the other hand, the elastic modulus of Ti-35Nb-7Zr-6Ta-0.7O alloy is much higher, because oxygen is a β stabilizing element with respect to β → α" martensitic transformation (M_s line is shifted to the left).

The key idea is therefore to decrease the total content of β stabilizing elements (Nb and Ta) to restore the low elastic-modulus of the alloy with high oxygen content, which must be kept sufficiently high to retain the high strength. In this respect, Ti-29Nb-7Zr-0.7O alloy was tested, and its elastic modulus of 65 GPa confirms the discussed effects.

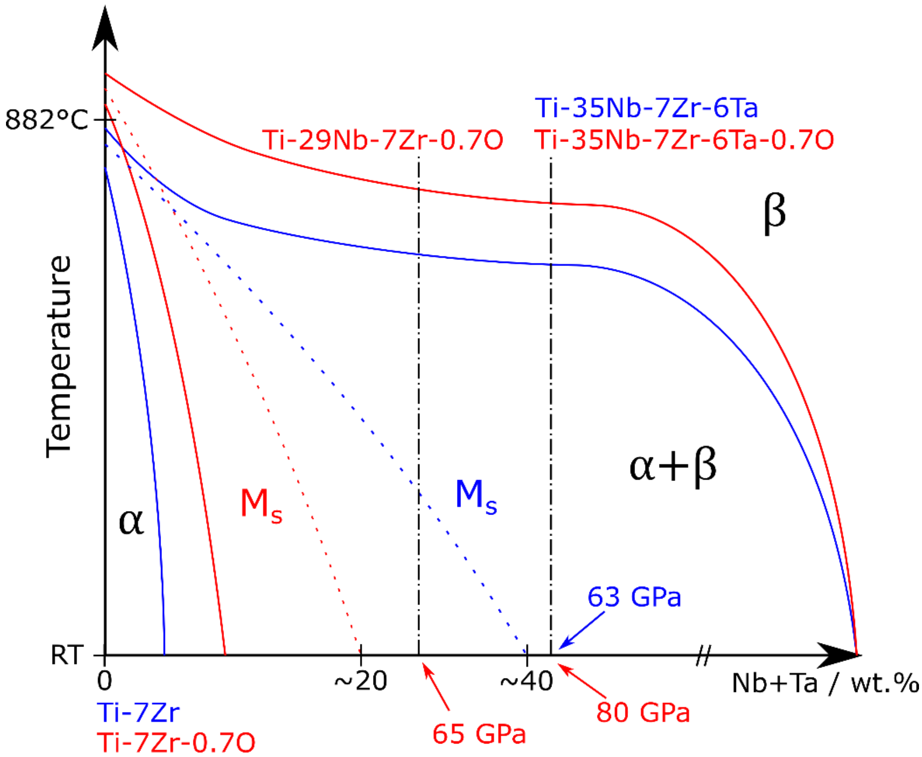

Figure 5. Schematic pseudo-binary phase diagram. Blue lines are drawn for the addition of β-stabilizing Nb/Ta to Ti-7Zr alloy. Red lines correspond to adding of Nb/Ta to Ti-7Zr-0.7O composition.

Recently, we have manufactured and tested several alloys derived from the Ti-35Nb-7Zr-6Ta-0.7O alloy with reduced Nb content (26 – 35 wt % Nb) and reduced Ta content (0 or 6 wt %). Figure 6 shows the elastic moduli of the developed Ti-Nb-(Ta)-Zr-O alloys and clearly demonstrates that the elastic modulus decreases with decreasing Nb content and also when Ta is absent. These alloys were subjected to tensile testing and all of them achieved the high yield strength of at least 800 MPa (Figure 7), which is attributed to the interstitial strengthening by oxygen.

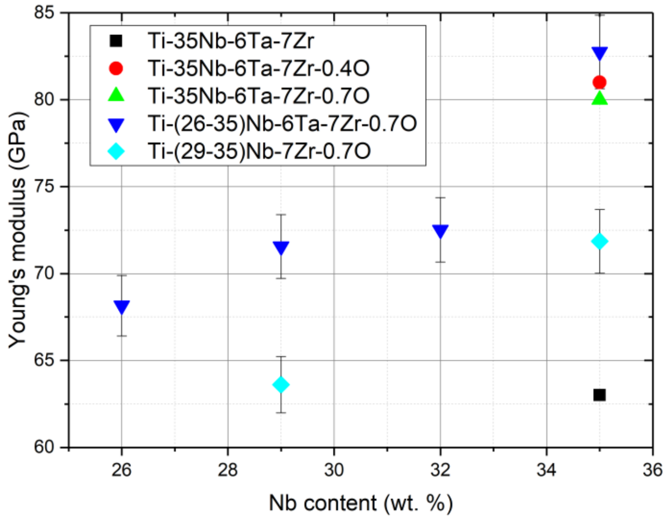

Figure 6. Elastic modulus of Ti-Nb-(Ta)-Zr-O alloys with various content of Nb and Ta

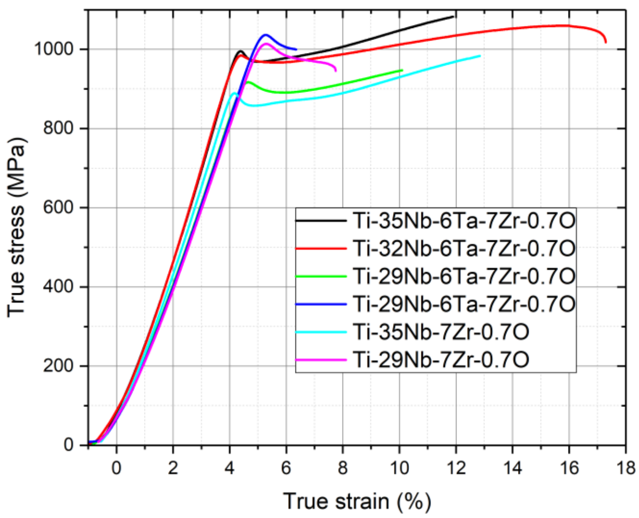

Figure 7. Flow curves for Ti-Nb-(Ta)-Zr-O alloys with various content of Nb and Ta

Simultaneous achievement of low elastic modulus and high strength is very promising in terms of potential application in implant manufacturing. Figure 8 shows a comparison of the newly developed alloys with results from other authors. Our newly developed alloys possess the strength of around 900 MPa and the elastic modulus of around 70 GPa. Such combination of mechanical properties has not been reported, yet.

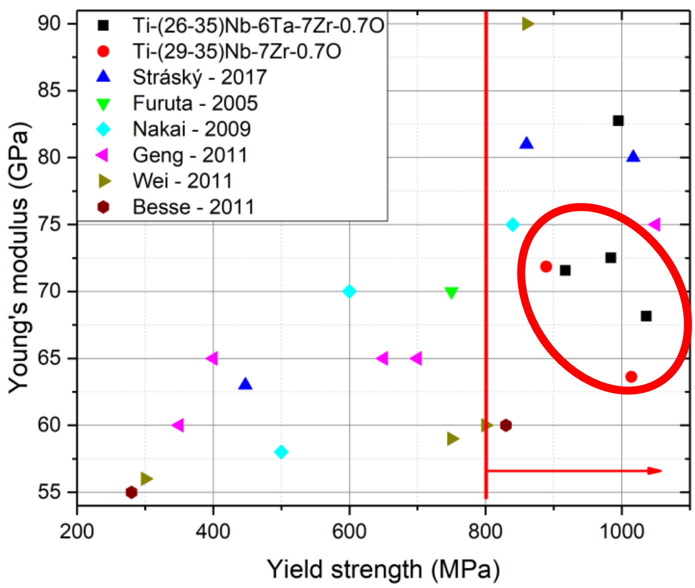

Figure 8. Elastic modulus and yield strength of our Ti-Nb-(Ta)-Zr-O alloys (highlighted by the red circle) in comparison with results of other authors. Materials having the strength above 800 MPa are prospective candidates for load-bearing implants of big joints.

4. Ultra-fine grained Ti alloys for biomedical use

This chapter summarizes our results achieved in the development, manufacturing and characterization of ultra-fine grained (UFG) Ti based materials for biomedical use. Our contribution of this long-term research is mainly in the methodology of experimental characterization.

Ultra-fine grained (UFG) materials contain, by definition, the high amount of grain boundaries. SPD methods for fabrication of UFG materials also typically produce high density of dislocations. Complex characterization of the UFG metallic materials requires utilizing numerous experimental methods such as x-ray diffraction (XRD), scanning electron microscopy (SEM), transmission electron microscopy (TEM) and indirect methods such as electrical resistivity measurement, positron annihilation spectroscopy or microhardness measurement [Čížek2016]. Defect structure significantly affects mechanical properties of materials and is therefore of significant importance.

Our work in investigation of lattice defects and microstructure of UFG titanium alloys is thoroughly reviewed in the chapter:

[B0] J. Stráský, M. Janeček, I. Semenova, J. Čížek, K. Bartha, P. Harcuba, V. Polyakova, S. Gatina, ***Microstructure and lattice defects in ultrafine grained biomedical α+β and metastable β Ti alloys***, in: Titanium in Medical and Dental Applications, ed. F. Froes, M. Qian, pp. 455-475 (2018)

The chapter in the monograph contains a thorough introduction to UFG Ti alloys, methods of their manufacturing and methods of experimental characterization of UFG Ti-based materials. The chapter contains our own experimental data and underlines the importance of employing various complementary experimental techniques. Output of each of the experimental methods must be thoroughly understood in order to get the full picture about microstructure and properties of these novel materials. Superior properties of the UFG materials are based on strengthening via grain refinement and increase of dislocation density.

The chapter was written by me in a cooperation with my former PhD student Kristina Bartha.

[B1] M. Janeček, J. Stráský, J. Čížek, P. Harcuba, K. Václavová, V.V. Polyakova, I.P. Semenova*:* ***Mechanical properties and dislocation structure evolution in Ti6Al7Nb alloy processed by high pressure torsion***, Metallurgical and Materials Transactions, Vol. 45A, 2014, 7 – 15.

As mentioned in the Introduction, the workhorse of Ti industry is Ti-6Al-4V alloy, which is still used for implant manufacturing despite known toxicity of vanadium. Vanadium-free Ti-6Al-7Nb alloy is an α + β alloy for biomedical applications which was developed as a non-toxic alternative to Ti-6Al-4V alloy. Our first study on an UFG biomedical alloy, summarized in the paper, describes the evolution of microstructure and mechanical properties in Ti-6Al-7Nb alloy prepared by high pressure torsion (HPT). The material was studied by microscopic methods, microhardness measurement and an advanced method of positron annihilation spectroscopy, which is able to determine the density of dislocations and also the concentration of vacancies or vacancy clusters. I wrote the majority of the manuscript in cooperation with prof. M. Janeček and I supervised my student K. Bartha (neé Václavová) during preparation of this publication.

The publication is the first outcome of the cooperation between our research group and the research team at the Ufa State Aviation University, Ufa, Russia. This team was formed by one of the leading experts in the field of UFG materials prof. Ruslan Z. Valiev and is headed by prof. Irina P. Semenova. Intensive cooperation is based on the complementarity of the research groups and available equipment. The UFG materials were manufactured by SPD methods in Ufa and thoroughly characterized at the Department of Physics of Materials and at other cooperating institutes in Prague.

[B2] J. Stráský, P. Harcuba, M. Hájek, K. Václavová, P. Zháňal, M. Janeček, V. Polyakova, I. Semenova: ***Microstructure evolution in ultrafine-grained Ti and Ti-6Al-7Nb alloy processed by severe plastic deformation***, NanoSPD6, IOP Conference Series: Materials Science and Engineering, Vol. 63, 2014, pp. UNSP 012072.

The contribution in the conference proceedings from the conference NanoSPD (nanostructured materials prepared by SPD methods) ***Microstructure evolution in ultrafine-grained Ti and Ti-6Al-7Nb alloy processed by severe plastic deformation*** investigates the use of in-situ electrical resistivity measurement to reveal microstructural changes during heating of UFG commercially pure Ti and UFG biomedical Ti-6Al-7Nb alloy. Results from the electrical resistivity measurements were compared to the results from other experimental techniques. The UFG condition is thermodynamically unstable and undergoes processes of recovery and recrystallization at elevated temperatures. Moreover, in the case of Ti-6Al-7Nb alloy, the transition between α and β phases occurs during heating. Enhanced thermal stability of the UFG structure was revealed for the Ti-6Al-7Nb alloy in comparison to commercially pure Ti. Thermal stability at high temperatures discussed in this paper is clearly not important for the use of the material in human body, but it is of significant importance for manufacturing of implants from semi-products which is performed at high temperatures.

[B3] K. Bartha, P. Zháňal, J. Stráský, J. Čížek, M. Dopita, F. Lukáč, P. Harcuba, M. Hájek, V. Polyakova, I. Semenova, M. Janeček: ***Lattice defects in severely deformed biomedical Ti-6Al-7Nb alloy and thermal stability of its ultra-fine grained microstructure,*** Journal of Alloys and Compounds, Vol. 788, 2019, pp. 881-890

This extensive paper underlines the necessity of using several complementary methods for comprehensive microstructural characterization of multi-phase UFG materials. Indirect methods, namely electrical resistivity measurement, x-ray diffraction or positron annihilation spectroscopy are combined with direct observations by scanning electron microscopy. The investigation focused on UFG microstructure and its thermal stability in Ti-6Al-7Nb alloy. The publication completed our investigation of this α + β biomedical Ti alloy. I coordinated the research and wrote the manuscript with significant help of my PhD student K. Bartha.

[B4] K. Václavová, J. Stráský, V. Polyakova, J. Strásk á, J. Nejezchlebová, H. Seiner, I. Semenova, M. Janeček: ***Microhardness and microstructure evolution of ultra-fine grained Ti-15Mo and TIMETAL LCB alloys prepared by high pressure torsion***, Materials Science and Engineering A Vol. 682, 2017, pp. 220-228

Since 2014, our investigation focused on UFG *metastable β-Ti* alloys [Janecek2014]. Two metastable β-Ti alloys were studied. Binary Ti15Mo alloy is intended and currently also certified for biomedical use. Ti-6.8Mo-4.5Fe-1.5Al (TIMETAL LCB) is referred to as low-cost β-Ti alloy (LCB) and is designed for application in aerospace and automotive industry. Both materials were deformed by high pressure torsion (HPT) and thoroughly characterized. The results are summarized in publication ***Microhardness and microstructure evolution of ultra-fine grained Ti-15Mo and TIMETAL LCB alloys prepared by high pressure torsion***. Detailed observations by electron back-scattered diffraction (EBSD) technique proved that the twinning (and multiple twinning – i.e. formation of secondary twins in primary twins) significantly contributes to the grain refinement in these body-centred cubic titanium alloys. This fact was reported for the first time in a β-Ti alloy. The alloys were investigated in the β solution treated condition, which typically exhibits a low strength. Nevertheless, the microhardness of the studied UFG alloys in the β solution treated condition exceeded the microhardness achievable by standard thermomechanical treatment involving precipitation of α phase. It is therefore of significant interest to combine microstructural refinement by SPD methods and subsequent ageing treatment to achieve even higher strength levels.

The manuscript was prepared in a close cooperation between me and my student Kristina Bartha (neé Václavová).

[B5] K. Bartha, A. Veverková, J. Stráský, J. Veselý, P. Minárik C.A. Corrêa, V. Polyakova, I. Semenova, M. Janeček, ***Effect of the severe plastic deformation by ECAP on microstructure and phase transformations in Ti-15Mo alloy***, Materials Today Communications 22 (2020) 100811

The effect of SPD deformation on phase transformations was studied in Ti15Mo alloy prepared by two SPD methods: ECAP and HPT. The article ***Effect of the severe plastic deformation by ECAP on microstructure and phase transformations in Ti-15Mo alloy*** summarizes the characterization of phase transformations in the biomedical Ti15Mo alloy prepared by ECAP in the β solution treated condition, which is a thermodynamically metastable condition. As described in the Introduction, achieving the stable composition requires the precipitation of α phase particles by heterogeneous nucleation and growth. UFG structure significantly affects both the nucleation and growth process.

The publication was prepared by K. Bartha under my supervision. It results from continuing cooperation with the research team in Ufa, Russia.

[B6] K. Bartha, J. Stráský, A. Veverková, P. Barriobero-Vila, F. Lukáč, P. Doležal, P. Sedlák, V. Polyakova, I. Semenova, M. Janeček, ***Effect of the High-Pressure Torsion (HPT) and Subsequent Isothermal Annealing on the Phase Transformation in Biomedical Ti15Mo Alloy***, Metals 9 (2019) 1194

Ti15Mo alloy prepared by high pressure torsion (HPT) contains a high density of dislocations and the grain structure is significantly refined. The nucleation of *α* phase therefore occurs at lower temperatures and results in very fine equiaxed *α* phase precipitates upon isothermal heating due to the dense net of nuclei. Combination of severe deformation, grain refinement and subsequent thermal processing is promising in terms of achieving enhanced mechanical properties of the alloy.

Apart from the isothermal annealing and ex-situ measurements included in the last mentioned publication, the phase transformation in Ti15Mo alloy were studied also in-situ during linear heating by high energy synchrotron x-ray diffraction (HEXRD). These results have not been published yet and therefore are presented here.

Phase transformation in Ti15Mo alloy were studied both in the coarse-grained solution treated condition and the UFG condition prepared by HPT.

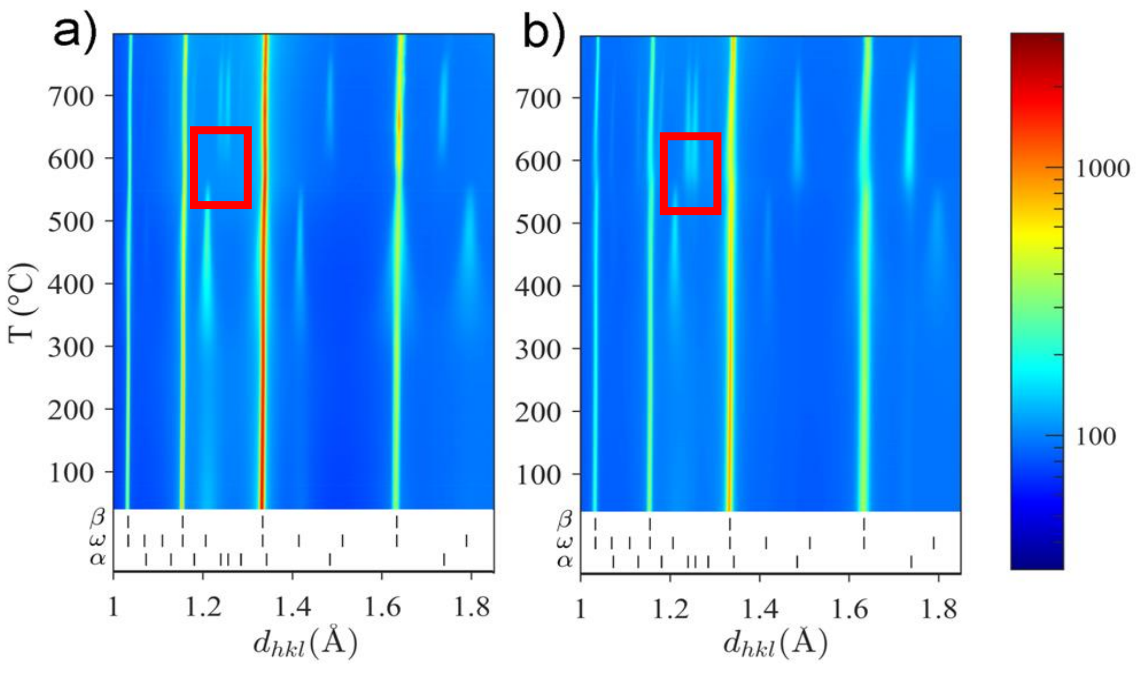

Figure 9 High energy synchrotron x-ray diffraction (HEXRD) of Ti15Mo alloy *in-situ* during linear heating at the rate of 5 °C/min from room temperature to 800 °C.
a) non-deformed material, b) UFG material deformed by HPT. Horizontal axis represents interplane distances d_{hkl}; temperature is shown on the vertical axis and the measured intensity is represented by the colour code.

Figure 9 shows the HEXRD patterns measured *in-situ* during linear heating at the rate of 5 °C/min from room temperature up to 800 °C. The horizontal axis represents the interplane distances d_{hkl}; temperature is shown on the vertical axis and the measured intensity is represented by the colour code. The most intense peaks are those of β phase; however, more interesting peaks are related to ω phase and to α phase. Peaks corresponding to ω phase often coincide with the more intense β phase peaks. A notable exception is the peak at d_{hkl} = 1.2 Å. ω peaks are most intense at 450 °C, while α peaks at 650 °C. Figure 9 a) shows HEXRD patterns for the coarse-grained material, while in Figure 9 b), HEXRD patterns for the UFG material deformed by HPT are presented. Red boxes highlight the biggest difference between the two studied conditions. In the non-deformed material, ω phase dissolves completely at 550 °C and only at a higher temperature, α phase starts to precipitate [Zhanal2018]. On the other hand, in the UFG condition, the severe plastic strain introduced by SPD enhances the α phase precipitation, which occurs at lower temperatures already in the presence of ω particles and the co-existence of all three phases (ω, α and β) was observed.

For a comprehensive description of the effect of microstructure on the α phase precipitation, the reader is referred to the dissertation thesis *Phase transformations in ultra-fine grained titanium alloys* by my former doctoral student Kristina Bartha [Bartha2019].

[B7] R. Z. Valiev, E. A. Prokofiev, N. A. Kazarinov, G. I. Raab, T. B. Minasov, J. Stráský, ***Developing nanostructured Ti alloys for innovative implantable medical devices***, Materials 13 (2020) 967

The last publication included in this habilitation thesis is a review paper by a team of authors headed by prof. Ruslan Z. Valiev. This invited review paper was published in a special issue *Alloys for Biomedical Use* of journal Materials, MDPI. I had the privilege to serve as a guest editor of this issue and used this opportunity to invite prof. Valiev to submit a review paper to this issue. I contributed to this paper by a comprehensive literature review of the UFG β-Ti alloys for biomedical use. The paper discusses not only properties of UFG Ti-based alloys, but also describes specific applications of these materials in practical medical use.

5. Conclusion and outlook

Research and development of titanium alloys still represent a vast scientific field for exploration. This habilitation thesis is devoted to two important scientific areas. The first one – development of biomedical titanium alloys – is of primary interest to the titanium community and I am convinced that our contribution will lead to application of the newly developed alloys in medical practice.

The second part is devoted to ultra-fine grained Ti alloys for biomedical use. UFG materials constitute a very interesting field of materials science as they exhibit superior mechanical properties. Potential application of metallic UFG materials is still in the beginning. Manufactured products suffer from small size and the low efficiency of production. Despite that, first potential biomedical applications of UFG Ti alloys have already emerged.

Apart from continuing research in the areas described in this thesis, my scientific activities in the field of Ti alloys include two other topics.

1. Powder metallurgy (PM) is an emerging processing technology. PM is particularly useful for manufacturing products from Ti alloys, because conventional manufacturing methods (casting, forging and machining) are complicated in Ti alloys due to their affinity to oxygen, high toughness and low thermal conductivity. One of the promising PM methods is so-called Spark Plasma Sintering (SPS) allowing compaction of powder materials at shorter times and lower temperatures than conventional sintering methods. My PhD student Jiří Kozlík demonstrated the feasibility of processing of commercially pure Ti by cryogenic milling followed by compaction by SPS [Kozlik2019, Kozlik2020].

   Currently we focus on manufacturing of bulk material by SPS from Ti alloys – either from a pre-alloyed powder or from elemental powders. We used Ti15Mo alloy powder to show the effect of cryogenic milling and SPS on phase composition and microstructure of the alloy [Veverkova2019] Our recent, yet unpublished, results show that it is possible to manufacture biomedical β-Ti Ti-Nb-Zr-O alloy with homogeneous composition, controlled oxygen content and promising mechanical properties from elemental powders and TiO_2 powder.

   Another important branch of powder metallurgy is the Additive Manufacturing (3D printing), which is believed to be a feasible option for net-shape or near-net-shape production. Apart from interesting technological issues associated with 3D printing, the possibility of additive manufacturing opens a brand new field for alloy development and characterization. Required properties of 3D printed materials will significantly differ from the properties required for 'standard' metallic materials, for instance in terms of high temperature formability. Simultaneously, new issues emerge, such as limited fracture toughness and overall fatigue performance of final products prepared by additive manufacturing. A breakthrough in this field is anticipated – in terms of new technologies, new materials and new applications.

2. The second area of my interest relates to the investigation of plastic deformation mechanisms associated with phase transformations in metastable β-Ti alloys. Although dislocation movement is a major mechanism of plastic deformation in metals, in some advanced metallic materials, other plastic deformation mechanisms such as transformation induced plasticity (TRIP) and twinning induced plasticity (TWIP) operate. Well-known examples include so-called TRIP/TWIP steels. Nevertheless, recently also TRIP/TWIP Ti alloys emerged. It is now qualitatively clear that TRIP and TWIP effects depend on the chemical composition of an alloy – in particular on the degree of its β phase stabilization. However, interrelations between martensitic transformation, twinning in various twinning systems and activity of dislocation slip systems are not fully explored and deserve systematic investigation.

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6. Reprints of included publications

This habilitation thesis includes two authored chapters from book *Titanium in Medical and Dental Applications* published in 2018 and 12 contributions in journals and conference proceedings published in years 2014 – 2020. This section consists of the reprints of the aforementioned publications.

[A0] J. Stráský, M. Janeček, P. Harcuba, D. Preisler, M. Landa, *Chapter 4.2.:* **Biocompatible beta-Ti alloys with enhanced strength due to increased oxygen content**, in *Titanium in Medical and Dental Applications*, Editors: Francis H. Froes, Ma Qian, Woodhead Publishing in Materials, Elsevier 2018

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