Opponent´s Opinion on the Doctoral Dissertation

Author: Dalibor PREISLER

Title: **Beta-Ti alloys for medical applications**

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Ideal biomaterials must include only non-toxic elements with good biocompatibility, but at the same time, they should have suitable mechanical properties and high corrosion resistance. In the case of implants subjected to cyclic loading, such as the hip joint, the tensile strength should be ~1000 MPa and Young's modulus as close to those of natural human bone (20-30 GPa) as possible. However, the elastic modulus of most titanium alloys is much higher (~110 GPa). Consequently, the lack of load-bearing (stress-shielding effect) on the bone adjacent to the implant can lead to bone atrophy and loosening of the implant. Therefore, it is desirable to find a new processing route for Ti alloys with high strength and low Young's modulus, reducing the number of implant failures and revision surgeries. There is no doubt that the topic of the dissertation, which is the development of novel Ti alloys for load-bearing endoprostheses of large joints, is very valuable and up-to-date.

The thesis consists of 124 pages, with 4 figures in the theoretical part and 68 figures in the experimental part. The literature review of the dissertation (12 pages, 128 references) clearly and concisely describes the state of the art of the Ti alloys for medical applications. The aims of the thesis are formulated in six partial points. From 2019 to 2023, the doctoral student co-authored 15 papers related to the topic of the dissertation. Most papers were published in highly respected international journals (Journal of Materials Research and Technology, Journal of Alloys and Compounds, Materials and Design, Materials Science and Engineering A, Materials Letters, Wear, etc.). Dalibor PREISLER is the first author of three papers. Two of them are focused on Ti-Nb-Zr-O-based alloys and one on Nb-Ta-Ti-Zr coatings on Ti substrate.

The microstructure of polymorphous Ti alloys with a β transus in the range from 800 to 1000°C is quite complicated. Besides basic hexagonal α and cubic β structures, there are also other phases present: ω and O′ phases or orthorhombic α" and hexagonal α′ martensite. The martensitic transformation can be not only thermally induced by quenching but also stress-induced. Furthermore, titanium is a very reactive element, so melting, casting and heat treatment of Ti alloys should be carried out in a vacuum or protective atmosphere. For the development of novel biocompatible materials, the author exploited two approaches. A classical route of melting, casting, homogenization, rotary swaging, and recrystallization annealing was used for the preparation of 17 dissimilar Ti alloys. One of these alloys was chosen for a prototype industrial hip implant manufacturing. An alternative high-throughput powder metallurgy method with a field-assisted sintering technique (FAST, also known as spark plasma sintering - SPS) was applied for the preparation of additional 10 alloy compositions.

A variety of methods was used for the characterization of the prepared alloys. Besides custom techniques such as scanning (SEM), transmission (TEM) electron microscopy, energy dispersive spectroscopy (EDS), electron backscattering diffraction (EBSD), or X-ray diffraction (XRD), less common methods of resonant ultrasound spectroscopy (RUS) and scanning acoustic microscopy (SAM) were employed. The content of interstitial elements, especially Oxygen, was measured by inert gas fusion (IGF – also known as carrier gas hot extraction – CGHE). Mechanical properties were monitored by microhardness measurements, tensile testing (also in situ in SEM), compression testing with digital image correlation (DIC), and acoustic emission. The full-scale hip implants were tested in fatigue in a NaCl solution in distilled water kept at 37 °C.

The thesis contains numerous results, presented in three chapters. Chapter 5 describes metastable Ti alloys with lower β phase stability prepared by the classical melting and casting method. The high yield strength was achieved by high oxygen content. The main limiting factor for ductility was found to be the phase composition. If the ω or α″ phase was present in a significant fraction in the material with high O content, it had an embrittling effect. Alloys with β structure only were all sufficiently ductile. Young's modulus was minimized by tailoring the composition to reach the lattice softening due to proximity to martensitic transformation. Avoiding the ω phase formation was the main criterion for the selection of the best alloy. All these findings are beyond the state of the art in the given field. The alloys developed in this thesis have particularly high strength in comparison to most alloys reported in the literature, while some alloys (namely Ti-29Nb-7Zr-0.7O, Ti-26Nb-7Zr-6Ta-0.7O and Ti-35Nb-0.7O) also exhibit low elastic modulus (~65 GPa) and sufficient ductility.

The high-throughput characterization of Ti-Nb-based alloys, presented in Chapter 6, is an original method of testing a high number of different chemical compositions in layered pellet samples prepared by powder metallurgy procedures. The key result is that oxygen and niobium have a very similar contribution to the stabilization of the β phase with respect to the martensitic transformation to α″ phase. Furthermore, the elastic moduli G and E exhibit a systematic dependence on the content of β-stabilizing elements.

The specification of the rules for the design of Ti alloys for implant manufacturing is summarized at the end of Chapter 7. One of the most important findings of the thesis is the nature of the ω phase in O-rich alloys. In water-quenched samples, ω phase should form without any elemental redistribution, which is commonly referred to as athermal ω. The athermal ω has usually only a negligible effect on the mechanical properties of Ti alloys. In contrast, if the Ti alloys contain a higher concentration of oxygen, the presence of higher amounts of athermal ω phase directly results in ductility deterioration.

I have got some comments and questions which could be discussed during the defense of the thesis:

- Page 75, Fig. 46. Zero strain as red and blue color as the maximum is quite uncommon. The reader is confused because usually, it is the opposite.
- Page 80, Figs. 50, 51, 52. What is the reason for the increasing roughness of the surface relief of the samples 0.23O, 0.49O, and 0.85O?
- Page 103, Fig. 71. What are black dots arranged in an arc shape in the bottom right part of the in situ tensile test specimen?

Overall, the results presented in the dissertation prove that the planned research aims were fulfilled. The formal level of the thesis meets high standards, and the English text is written in a very clear and succinct way. Dalibor PREISLER proved the ability to perform numerous well-defined and properly aimed experiments and give a very solid description and interpretation of the observations, which bring new insight to the development of innovative biocompatible Ti alloys. I am confident about the high quality of the work and can recommend the thesis for presentation and defense.

Prague, August 24, 2023