

氏名(本籍地)	Muhammad Farzik Ijaz
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学位論文題目	

**Improvement of superelastic and mechanical properties of biomedical  $\beta$ -Ti alloys through alloying elements adjustment and microstructure control**  
(合金元素調整と微細組織制御による生体用  $\beta$ -Ti 合金の超弾性および機械的特性の改善)

主査	宮崎 修一	工学博士	筑波大学教授
副査	金 熙榮	工学博士	筑波大学教授
副査	古谷野 有	工学博士	筑波大学准教授
副査	鈴木 義和	博士(工学)	筑波大学准教授
副査	御手洗 容子	博士(工学)	物質・材料研究機構グループリーダー

## 論 文 の 要 旨

The present research systematically explored the principal strategies for the enhancement of mechanical biocompatibility of  $\beta$ -Ti alloys. In the area of mechanical biocompatibility the improvement of mechanical and superelastic properties are the key factors to ensure the successful and sustainable performance of indwelling medical devices including cardiovascular implants and artificial bone implants. Consequently, in this thesis special attention has been paid to improve the mechanical and superelastic properties of our newly developed  $\beta$ -Ti alloys through different alloying elements adjustment and subsequent microstructural control so as to meet the high standards required for versatile biomedical applications. The main objective of this thesis is on one hand, to study a novel biocompatible alloying system as a potential substitute of the Ti-Ni alloys used in the biomedical devices such as stents and orthodontic arch wires and on the other hand, to suggest suitable alloying element adjustment for improving the mechanical properties such as reducing the Young's moduli of the conventional  $\beta$ -type Ti-Nb based alloys used for the bone implants. Furthermore, in this study two new different classes of  $\beta$ -Ti alloys have also been rigorously investigated by several thermomechanical methods in order to provide an insightful understanding regarding the optimal microstructural controls required for manipulating the desired mechanical and superelastic properties of  $\beta$ -Ti alloys. Nevertheless, on the basis of current experimental findings, important remedies were also suggested to further improve the superelastic and mechanical properties of conventional  $\beta$ -type Ti alloys. Accordingly, beside detailed introduction chapter this thesis has been further subdivided in two parts:

Part 1 :-( chapters 2 and 3): In the chapter 2 of this thesis, the new alloying element adjustment

such as Sn in the ternary Ti-Nb-Mo alloys has been investigated. Particularly, in this study a new quaternary Ti-Nb-Mo-Sn alloy has been developed in which unique Sn content dependence of the critical stress for inducing martensite is discussed in detail. The stress hysteresis of Ti-Nb-Mo alloys decreased with increasing Sn content due to the suppression of athermal omega phase formation. The addition of Sn was also very effective for increasing superelastic recovery strain. Due to a two-fold role of Sn, i.e. on the martensitic transformation temperature and omega phase, the stress for inducing martensitic transformation decreased with increasing Sn content up to 1at.%, then increased by further addition of Sn which is attributed to the compositional effect of Sn on the martensitic transformation temperature .

In the chapter 3 of this thesis, the research was mainly concentrated to develop a new Ni-free biomedical superelastic alloy with a large recovery strain. Therefore a new class of Ti-Zr base biomedical superelastic alloys was developed. The (Ti-Zr)-Mo-Sn alloys exhibited shape memory effect and superelastic property by adjusting Mo and Sn contents. The (Ti-Zr)-1.5Mo-3Sn alloy revealed the most stable superelasticity among (Ti-Zr)-(1-2)Mo-(2-4)Sn (at.%) alloys. The superelastic recovery strain showed a strong dependence on heat treatment temperature after cold working in the (Ti-Zr)-1.5Mo-3Sn alloy. The superelastic recovery strain increased as the heat treatment temperature increased although the critical stress for slip decreased. The (Ti-Zr)-1.5Mo-3Sn alloy heat treated at 1073 K exhibited excellent superelastic properties with a large recovery strain as large as 7 % which is found to be two times larger than the other conventional  $\beta$ -Ti-based superelastic alloys reported so far. In order to elucidate the correlation between the microstructure on the observed superelastic properties systematic microstructural investigations at different heat treatment temperature have also been carried out. The experimental results concluded that the large recovery strain of 7% for the specimens heat treated at 1073 K for 3.6 ks is due to the strong favorable recrystallization textures  $\{001\}_{\beta} <110>_{\beta}$ , in addition to the large transformation strain.

Part 2:-(chapter 4 and 5): The chapter 4 and 5 of this thesis was focused to discuss the scope and problems of conventional implant alloys in terms of crucial stress shielding effect which is generated due to the large mismatches among the Young's moduli at the human bone/implant interface. Therefore this part of the thesis was to introduce optimum microstructural characteristics required for reducing the Young's modulus of conventional  $\beta$ -type Ti-Nb based alloys. In an attempt to replace traditional ( $\alpha+\beta$ )-type Ti-6Al-4V alloys having much higher Young's modulus value (110 GPa) than that of human bone (10-30 GPa). In this context, part two of this thesis is primarily focused on the development of novel low Young's moduli  $\beta$ -type Ti-Nb based alloys. The experimental results in chapter 4 and 5 demonstrated that the Young's modulus values of Ti-Nb based alloys prepared by arc melting method are highly anisotropic and indicated strong dependence on the microstructures developed during cold rolling and/or following heat treatment. In particular, the attractive combination of attributes like low Young's modulus value and higher ultimate tensile strength, while simultaneously keeping the advantage of fabrication ease makes our newly developed  $\beta$ -type Ti-Nb-based alloy a viable candidate for the future biomedical implant applications.

#### 審 査 の 要 旨

[批評]

本論文は、生体用  $\beta$  チタン合金の超弾性と機械的特性を合金元素調整と微細組織制御により改善することを目的とし、Ti-Nb-Mo 合金、(Ti-Zr)-Mo-Sn 合金およびTi-Nb-Fe-Sn 合金について実験的に研究を行ったものである。まず、Ti-Nb-Mo 合金に Sn を添加することで、Sn にはマルテンサイト変態温度を下げる本来の働きがある上に、オメガ相を抑制することでマルテンサイト変態温度を上げる効果もあることを見出した。これにより、マルテンサイト変態誘起応力と応力ヒステリシスに及ぼす Sn 添加のユニークな効果の原因を解明した。次に、(Ti-Zr)-Mo-Sn 合金について、Mo と Sn の濃度を変えることで超弾性特性の改善を試みた結果、(Ti-Zr)-1.5Mo-3Sn 合金で 7%もの大きな超弾性歪みを実現することに成功した。この値は従来の  $\beta$  チタン合金の 2 倍以上であり、市販されている Ti-Ni 合金の値に匹敵するものである。実用レベルの超弾性特性が  $\beta$  チタン合金で開発されたことになる。また、Ti-Nb-Fe-Sn 合金については、集合組織と合金濃度の調整で、低ヤング率と高強度の特性を実現できることも解明した。開発されたこれらの合金は生体用材料として有用な特性を有し、今後の材料開発の指針についても明らかにしており、価値ある研究であると判断される。よって、著者は学位を受けるのに十分な資格を有すると認められる。

#### 〔最終試験結果〕

平成27年 2月 12日、数理物質科学研究科学位論文審査委員会において審査委員の全員出席のもと、著者に論文について説明を求め、関連事項につき質疑応答を行った。その結果、審査委員全員によって、合格と判定された。

#### 〔結論〕

上記の論文審査ならびに最終試験の結果に基づき、著者は博士(工学)の学位を受けるに十分な資格を有するものと認める。