Design and development of low elastic modulus Ti-Nb-Zr alloys for biomedical applications

A thesis submitted in fulfilment of the requirements for the degree of Doctor of Philosophy

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November 2019
Declaration

I certify that except where due acknowledgement has been made, the work is that of the author alone; the work has not been submitted previously, in whole or in part, to qualify for any other academic award; the content of the thesis is the result of work which has been carried out since the official commencement date of the approved research program; any editorial work, paid or unpaid, carried out by a third party is acknowledged; and, ethics procedures and guidelines have been followed.

I acknowledge the support I have received for my research through the provision of a RMIT research scholarship in support of an Australian Research Council (ARC) discovery grant. I acknowledge the support I have received for my research through the provision of an Australian Government Research Training Program Scholarship.

Afrin Mehjabeen

1st November 2019
Acknowledgements

I would like to express my deepest gratitude and appreciation to my supervisors, friends and family members for their incredible support, sincere guidance and encouragement throughout the tenure of my post graduate research study. I would like to express my special appreciation and thanks to my principal supervisor Professor Ma Qian, who has been a tremendous mentor for me. I would like to thank my associate supervisors, Associate Professor Wei Xu and Dr. Dong Qiu for encouraging my research and providing me excellent research training.

I like to acknowledge the help from University of Science & Technology Beijing (USTB) and Beihang University. I would like to thank the staff in RMIT Microscopy and Microanalysis Facility (RMMF) specially Dr Edwin Mayes, Dr Matthew Field and Mr Peter Rummel for providing me training and support in this research. I would also like to thank all my friends and colleagues specially Dr. Tingting Song, Dr. Na Gui, Dr. Yingying Sun, Dr. Jayyoung Cho, and Xuezhe Zhang.

I would like to thank my family members for their tremendous support throughout this whole journey. I would like to express my deepest gratitude to my husband, Dr. Mohammad Shahriar, my daughter Nayamee Shahriar, and my parents, S.M.G. Amzad Hossain and Anowara Khatoon for their constant support and inspiration.
Abstract

The demand for implants has been increasing globally due to the rising population of the older people (aged ≥80 years), bone diseases, e.g., bone cancers, congenital disabilities, birth defects, revision needs, and accidents. It is essential to select both biologically and mechanically compatible implant materials for such applications. The commonly used implant materials today are austenitic stainless-steel alloys, Co–Cr alloys, Ti, Ta, and their alloys. Recently zirconium (Zr) alloys for biomedical applications are receiving increasing attention due to their two unique properties: 1) the formation of an intrinsic bonelike apatite layer on their surfaces in body environments, and 2) better compatibility with magnetic resonance imaging (MRI) diagnostics due to their intrinsically low magnetic susceptibility, as well as their overall excellent biocompatibility, mechanical properties, and bio-corrosion resistance. In particular, since both of the MRI quality and speed depend on magnetic field strength, there is a compelling drive for the use of high magnetic field strength (>3 Tesla) MRI systems. This requires the availability of implant alloys that can offer much lower susceptibility than the current Ti implant alloys. In that regard, Zr-based alloys offer more promise than Ti-based alloys.

This thesis first presents a comprehensive review of the characteristics of commercially pure (CP) Zr and Zr-based alloys as potential orthopaedic and dental implant materials. These include their 1) phase transformations; 2) unique properties including corrosion resistance, biocompatibility, magnetic susceptibility, shape memory effect, and super-elasticity; 3) mechanical properties; 4) current orthopaedic and dental applications, and; 5) the d-electron theory for Zr alloy design and novel Zr-alloys, and 6) future directions for extending the use of Zr-alloys as orthopaedic and dental implants are discussed. Then following a detailed analysis of the design methods for low elastic modulus Ti alloys, the d-electron theory and
the $e/a$ ratio approach are used together to design nine strong, ductile, and low elastic modulus Ti-Nb-Zr alloys. Among them, five are Zr-based Ti-Nb-Zr alloys, and four are Ti-based Ti-Nb-Zr alloys. To assess Ti-Nb-Zr alloys, it is important to understand the influence of Zr on the $\beta$-phase stability of Ti-Nb-Zr alloys. The concept of the Mo equivalence (Mo-Eq), proposed by Molchanova (Phase Diagrams of Titanium Alloys, 1965), has been commonly used as a general guideline to gauge the stability of a $\beta$-Ti alloy. A critical literature review has shown that all four existing Mo-Eq expressions deviate substantially from experimental observations and the well-established $d$-electron theory in predicting the $\beta$-phase stability of Ti-Nb-Zr alloys. The reasons are that existing Mo-Eq expressions either completely neglect or significantly overestimate the $\beta$-stabilizing effect of Zr. In this thesis, a new Mo-Eq expression, i.e., $(\text{Mo-Eq})_{\text{Ti-Nb-Zr}} = 0.238\text{Nb (wt.\%)} + 0.11\text{Zr (wt.\%)} + 0.97$, has been defined for Ti-Nb-Zr alloys in order to properly address the $\beta$-stabilizing effect of Zr. This new Mo-Eq expression shows good consistency with both experimental observations and the $d$-electron theory in predicting the $\beta$-phase stability of various Ti-Nb-Zr alloys. With necessary modifications, the approach developed is expected to be also applicable to the assessment of the $\beta$-phase stability in other Zr-containing Ti alloys.

Three different methods: tension, compression, and ultrasonic tests, are used to determine the elastic modulus of the five Zr-Ti-Nb alloys (Zr-45Ti-15Nb, Zr-33Ti-15Nb, Zr-28Ti-15Nb, Zr-35Ti-10Nb, and Zr-30Ti-20Nb, in at.%) alloys. The as-cast tensile, compressive and ultrasonic elastic moduli of these alloys range from 58-79GPa, 45-57GPa and 60-95GPa respectively. The two Zr-Ti-Nb alloys (Zr-based Ti-6Nb-53Zr and Ti-18Nb-51Zr) from the literature, which reportedly have the lowest elastic moduli, are prepared and tested for comparison as a point of reference. The dependence of elastic moduli on the test methods, phase constitutes as well as $\overline{B}_0$ and $\overline{M}_d$ and $e/a$ ratio is systematically investigated. The reassessed Mo-Eq. values change linearly with the $e/a$ ratio for the above seven alloys. The
current work also indicates that a small amount of the ω-phase along with β and α"-phases, and the condition of $\frac{e}{a} \approx 4.15$, can lead to low elastic modulus for Zr-Ti-Nb alloys. Therefore, a modified relationship between the phases and the elastic modulus has been suggested, which is: $E_{\omega} \approx 40$ GPa $< E_{\beta} \approx 60-90$ GPa $< E_{\alpha} \approx 100$ GPa $< E_{\omega} \approx 130-220$ GPa.

This study identifies that as-cast Zr-28Ti-15Nb and Zr-33Ti-15Nb alloys can offer low elastic modulus (~60 GPa, tensile and ultrasonic), excellent tensile ductility (~16%), uniform plastic strain (greater than 10%) and sufficiently high tensile yield strength (~650 MPa) for implant applications.

While designing the Zr-Ti-Nb alloys, this thesis author realized that Ti-Nb-Zr alloys could also offer low elastic modulus. As a result, four new Ti-Nb-Zr alloys (Ti-26Zr-10Nb, Ti-25Zr-15Nb, Ti-22Zr-15Nb, and Ti-21Zr-20Nb) are designed by the $d$-electron theory and $\frac{e}{a}$ ratio. The as-cast tensile, compressive and ultrasonic elastic moduli of these alloys are in the range of 58-71GPa, 34-60GPa and 52-83GPa respectively. The effects of alloying elements on microstructures, mechanical properties i.e. tensile strength, yield strength, compressive yield strength, elastic modulus, elastic energy, and microhardness of these newly designed alloys have been investigated. Ti-Nb-Zr alloys also show the linear relationship between Mo-Eq values and $\frac{e}{a}$ ratio. The results also confirm that a small amount of ω-phase is not clearly detrimental in reducing the elastic modulus along with β and α"-phase. Therefore, the results from Ti-Nb-Zr alloys strongly agree with the above proposed relationship sequence between the phases and the elastic modulus for Zr-Ti-Nb alloys.

**Keywords:** Zr-based alloys, Ti-based alloys, bone implant, biomedical applications, Ti-Nb-Zr, Low elastic modulus, $d$-electron theory, Mo-Eq expression, $\frac{e}{a}$ ratio, β-phase, magnetic susceptibility, mechanical properties, tensile test, compressive test, ultrasonic elastic modulus test.
Publications and presentations during candidature

Peer-reviewed Journal Papers


- A. Mehjabeen, S. Liu, M. Qian, D. Qiu, W. Xu, Z. Lu, W. Yuan, Y. Yuan, Y. Sun, M. Brandt, H. P. Tang, Design and development of strong, ductile and low modulus Zr-Ti-Nb alloys for biomedical application. (In preparation)

Conference Presentations

- A. Mehjabeen, M. Qian, W. Xu, D. Qiu, The developments of Zirconium (Zr) and it’s alloys in orthopaedic & dental implants. CAMS-2016, 6-8th December, Swinburne University of Technology, Melbourne, Australia. (Poster)

- A. Mehjabeen, M. Qian, W. Xu, D. Qiu, Zirconium alloys for orthopaedic & dental implants: a review. TMS-2017, 26th February-2nd March, San Diego, California, USA. (Oral presentation)
# Table of contents

Declaration.............................................................................................................................................i

Acknowledgements.................................................................................................................................ii

Abstract.................................................................................................................................................. iii

Table of contents....................................................................................................................................vii

List of Figures ..........................................................................................................................................xi

List of Tables ...........................................................................................................................................xvi

Chapter 1 Introduction ..............................................................................................................................1

1.1. Background ......................................................................................................................................1

1.1 1.2. Aims and objectives ............................................................................................................... 4

1.2 1.3. Structure of the thesis ..............................................................................................................5

Chapter 2 Literature review .....................................................................................................................11

2.1 Introduction .....................................................................................................................................11

2.2 Basic properties of CP Zr and its alloys .........................................................................................13

2.3 Common phases in Zr-alloys and typical alloying elements .............................................................14

2.4 Biocompatibility of Zr and biocompatible alloying elements for Zr ..............................................20

2.4.1 Bioactivity of Zr ..........................................................................................................................23

2.4.2 Corrosion resistance ....................................................................................................................26

2.5 Mechanical properties ......................................................................................................................31

2.5.1 Dense Zr-alloys ..........................................................................................................................31
2.5.2 Porous Zr-alloys .................................................................35
2.5.3 Bulk metallic glasses ..........................................................36
2.6 Magnetic susceptibility ...........................................................36
2.7 Shape memory effect and super-elasticity of Zr-based alloys ........46
2.8 Recent application as biomaterials ..........................................48
2.9 The d-electron theory for Zr-based alloys ................................52
2.10 Future directions for Zr-alloys for implant applications ............58
  2.10.1 Alloy design .................................................................58
  2.10.2 Low magnetic susceptibility ...........................................58
  2.10.3 Low modulus ...............................................................60
  2.10.4 Wear resistance ............................................................60
  2.10.5 Porous Zr-alloys ............................................................60
2.11 Knowledge gaps identified and concluding remarks ..................61

Chapter 3 Alloy design principles and methodology for titanium and zirconium alloys ......83
  3.1 Introduction ........................................................................83
  3.2 Alloy design methods for Titanium and Zirconium alloys ...........84
    3.2.1 The d-electron theory .......................................................84
    3.2.2 The $\epsilon/\alpha$ ratio .......................................................91
    3.2.3 The conventional Mo-Eq approach ..................................94
    3.2.4 The First Principle approach ..........................................98
  3.3 A different design approach proposed for Zr-based and Ti-based Ti-Nb-Zr alloys ....102
Chapter 6 Design and development of low-elastic-modulus as-cast Ti-Nb-Zr alloys for biomedical applications ................................................................. 159

6.1 Introduction .................................................................................................................. 159

6.2. Materials and Methods ............................................................................................... 162

6.2.1. Alloy design ............................................................................................................ 162

6.2.2. Sample fabrication .................................................................................................. 164

6.2.3. Phase and microstructural characterization ............................................................ 166

6.2.4. Mechanical property testing .................................................................................. 166

6.3. Results and Discussion .............................................................................................. 167

6.3.1 Constituent phases and microstructure and of as-cast Ti-Nb-Zr alloys ................. 167

6.3.2. Mechanical properties of as-cast Ti-Nb-Zr alloys .................................................. 171

6.3.3 The dependence of elastic modulus on $\overline{B_o}, \overline{M_d}, \frac{e}{\alpha}$ ratio, and secondary phases .......................................................................................................................... 176

6.4. Conclusions .................................................................................................................. 178

Chapter 7 Summary and future work .................................................................................. 188

7.1 Summary ....................................................................................................................... 188

7.2 Recommendations for future work ............................................................................. 190
List of Figures

Figure 2.1 (a) Binary phase diagram of Zr-O (reproduced with permission from Ref. [25] Copyright (1986), with permission from Springer Nature), and (b) the microstructure of CP Zr (reproduced with permission from Ref.[29] Copyright (1998), Elsevier).

Figure 2.2 Temperature-pressure phase diagram for pure Zr (reproduced with permission from [30] Copyright (1998), Elsevier).

Figure 2.3 (a) Zr-Ti binary phase diagram plotted using Pandat™, superimposed with $T_0$ curves, and (b) Dependence of $T_0$ on biocompatible elements in Zr-X alloys (X = Ti, Fe, Ta, Sn, Mo, and Nb) plotted using Pandat™.

Figure 2.4 (a) Cytotoxicity of pure metals, and (b) Relationship between polarization resistance and biocompatibility of pure metals, Co-Cr alloy and stainless steels (reproduced with permission from Ref.[40] Copyright (1986), Springer Nature).

Figure 2.5 Viabilities of (a) human osteosarcoma cells (HOS) cultured for Zr and Ti for different times (reproduced with permission from Ref. [51] Copyright (1993),The Stomatological Society), and (b) MG 63 osteoblast-like cells cultured in extraction media of CP Zr and Ti and, and Zr–1X alloys for 48, 96 and 168 h (reproduced with permission from Ref.[52] Copyright (2013), Elsevier).

Figure 2.6 Pitting potential of six binary primary Zr-X systems that contain biocompatible elements for Zr vs. alloying content, X (reproduced with permission from Ref.[66] Copyright (2014), Japan Society of Corrosion Engineering).

Figure 2.7 (a) Zr-Nb binary phase diagram plotted using Pandat™, superimposed with the $T_0$ curves, and (b) XRD results of as-cast Zr-Nb alloys (i) Zr, (ii) Zr-3Nb, (iii) Zr-6Nb, (iv) Zr-9Nb, (v) Zr-12Nb, (vi) Zr-16Nb, (vii) Zr-20Nb, and (viii) Zr-24Nb alloys (reproduced with permission from Ref.[82] Copyright (2011), Elsevier).
Figure 2.8 Young’s modulus and micro Vickers hardness of (Ti-Zr)-XNb alloys (reproduced with permission from Ref.[34] Copyright (2015), JIM Material).

Figure 2.9 Magnetic susceptibility spectrum [20].

Figure 2.10 Quantitative relationship between absolute magnetic susceptibility and the artifact volume under both fast spin echo (FSE) and gradient echo (GRE) conditions (reproduced with permission from Ref.[122] Copyright (2013), Elsevier).

Figure 2.11 MRI (3 Tesla) results and 3-D renderings of the Zr, Ag, and Zr–Ag (vol.%) composites swaged at 64% (reproduced with permission from Ref.[90] Copyright (2017), Elsevier).

Figure 2.12 Magnetic susceptibilities of as-cast (a) Zr-Nb alloys (reproduced with permission from Ref.[10] Copyright (2009), JIM Material), and (b) Zr-Mo alloys (reproduced with permission from Ref.[31] Copyright (2010), Elsevier).

Figure 2.13 Magnetic susceptibility of Zr-1X (wt.%) alloys (reproduced with permission from Ref.[52] Copyright (2013), Elsevier).

Figure 2.14 Correlations between magnetic susceptibility, Young’s modulus, valence electron concentration, and phase composition of suction-cast Zr-Ti-Mo-Nb-Sn alloys (reproduced with permission from Ref.[86] Copyright (2015), Elsevier).

Figure 2.15 Mass magnetic susceptibility of cold-rolled Zr–14Nb and Zr as a function of reduction ratio in thickness (reproduced with permission from Ref.[32] Copyright (2013), Elsevier).

Figure 2.16 Tensile stress-strain curves of (a) Ti-50Zr (at.%) at room temperature (reproduced with permission from Ref.[146] Copyright (2011), Elsevier), and (b) (Zr-Ti)–(1.5,2)Mo–(2–4)Sn (at.%) alloys (reproduced with permission from Ref.[33] Copyright (2015), Elsevier).
Figure 2.17 (a) Total hip replacement (THR), (reproduced with permission from Ref.[71] Copyright (2005), Wolters Kluwer Health, Inc), (b) Total knee replacement (TKR), (reproduced with permission from Ref.[147] Copyright (2005), Springer Nature), (c) Z-Systems Z-Look3 Evo implant, [152] (d) Bredent whiteSKY implant, [152] and (e) Oral Iceberg CeraRoot implant (CeraRoot 21 design) [152].

Figure 2.18 A scanning electron micrograph of the cross-section of the oxinium™ femoral component (a), and a typical cathodoluminescence overall intensity (at 500 nm) profile (b). The oxygen profile detected on oxinium™, according to glow discharge optical emission spectroscopy, is also plotted (gray-dottedline) for a qualitative comparison (reproduced with permission from Ref.[154] Copyright (2014), Elsevier).

Figure 2.19 $\overline{B_o} - \overline{M_d}$ diagram for Ti and its alloys (reproduced with permission from Ref. [171] Copyright (2006), Elsevier).

Figure 2.20 $\overline{B_o} - \overline{M_d}$ diagram constructed for (a) binary Zr-X alloys (reproduced with permission from Ref.[172] Copyright (2006), Atomic Energy Society of Japan), and (b) Zr and its alloys from the literature data to show the $\alpha$-zone,[52, 82, 84, 85] $\beta$-zone [7, 82, 83, 85, 86, 91] and ($\alpha+$-$\beta$)-zone [82, 85, 86, 91].

Figure 3.1 (a) bond order, $Bo$ and (b) $d$-orbital energy level, $Md$ [8].

Figure 3.2 $\overline{B_o} - \overline{M_d}$ diagram [11].

Figure 3.3 $\overline{B_o} - \overline{M_d}$ diagram constructed for (a) binary Ti-X alloys, (b) binary Zr-X alloys [13].

Figure 3.4 Relationship between corrosion rate and $\overline{B_o}$ for (a) bcc and (b) hcp Ti-M binary alloys in 10% $H_2SO_4$ at 343K [8].

Figure 3.5 The elastic modulus vs. electron to atom ratio [22].

Figure 3.6 Expected phases in Ti alloys after water quenching with respect to $e/\alpha$ (Adapted and redrawn from Ref.[23]).
Figure 3.7 The changes of elastic moduli with the alloying element for bcc (a) Ti-X (X= W, Mo, Ta, Nb, V) and (b) Zr-X binary alloys (X=Nb and Mo). [36].

Figure 3.8 The elastic modulus of β bcc Ti–25(at.%)Nb–xZr system as a function of Zr content [38].

Figure 3.9 $\overline{B_o} - \overline{M_d}$ diagram with newly designed alloys.

Figure 4.1 Dependence of the quantity of $\Delta = 10 - \psi \times \text{Nb (wt.%) on Zr content in Ti-Nb-Zr alloys.}$

Figure 4.2 XRD results of (a) two Zr-based Ti-Nb-Zr alloys and (b) four Ti-based Ti-Nb-Zr alloys. and optical micrographs of (c) Water-quenched Ti-15Nb-40Zr (at.%), nearly single β. (d) Water-quenched Ti-10Nb-26Zr (at.%), noticeable $\alpha''$-martensite.

Figure 4.3 Ti-Nb-Zr alloys in the $\overline{B_o} - \overline{M_d}$ map [13-16].

Figure 5.1 Recently developed ternary Ti-Nb-Zr System and their elastic Modulus (where ST: Solution treated, HT: Heat treated and CR: Cold rolled) [10-18]. Unspecified compositions are given in at.%.

Figure 5.2 $\overline{B_o} - \overline{M_d}$ diagram for Ti-Nb-Zr alloys adapted from literature [21-29].

Figure 5.3 $\overline{B_o} - \overline{M_d} - e/a$ diagram for the five new designed Zr-Ti-Nb alloys.

Figure 5.4 (a) XRD patterns of the new designed as-cast Zr-Ti-Nb alloys and two as-cast Zr-based alloys (Ti-18Nb-51Zr and Ti-6Nb-53Zr) from the literature, (b) Zr-Ti phase diagram obtained using Pandat™ CompuTherm database.

Figure 5.5 Correlation between the Mo-Eq. and $ea$ ratio for the seven alloys studied.

Figure 5.6 Optical micrographs of each as-cast Zr-Ti-Nb alloy.

Figure 5.7 Engineering and true stress - strain curves of as-cast Zr-Ti-Nb alloys: a) tensile test, and b) compression test.

Figure 5.8 Compressive, tensile and ultrasonic elastic moduli of Zr-Ti-Nb alloys.
Figure 5.9 Relationship between $e/\alpha$ ratio and elastic modulus [40], with superimposed experimental data from this study.

Figure 6.1 $\overline{B}_o - \overline{M}_d - e/\alpha$ diagram for the four new designed Ti-Nb-Zr alloys.

Figure 6.2 XRD patterns of as-cast Ti-Nb-Zr alloys.

Figure 6.3 Optical micrographs of as-cast Ti-Nb-Zr alloys: (a) and (a') Ti-26Zr-10Nb, (b) Ti-25Zr-15Nb, (c) Ti-22Zr-15Nb, and (d) Ti-21Zr-20Nb.

Figure 6.4 Correlation between the Mo-Eq. values and $e/\alpha$ ratio for these four alloys.

Figure 6.5 Engineering and true stress-strain curves of as-cast Ti-Nb-Zr alloys by (a) tensile test, and (b) compressive test.

Figure 6.6 Compressive, tensile and ultrasonic elastic modulus of as-cast Ti-Nb-Zr alloys.

Figure 6.7 Schematic relationship between $e/\alpha$ ratio and elastic modulus, with superimposed experimental data from this study [48].

Figure 7.1 Schematic diagram of future work
List of Tables

Table 1.1 Australian joint replacement records in 2018 [1].
Table 2.1 Basic properties of CP Zr (R60702) and CP Ti Grade-1 [10, 11, 13, 14].
Table 2.2 Chemical compositions of industrial and nuclear grades of Zr-alloys [11, 12].
Table 2.3 Tensile properties of industrial and nuclear grades of Zr-alloys [11, 23].
Table 2.4 Solubility limits of O, N, H, and C in α-Zr and β-Zr [25-28].
Table 2.5 Electrochemical parameters of CP Zr, Zr-1X (X = Ti, Nb, Mo, Cu, Au, Pd, Ag, Ru, Hf, and Bi), CP Ti, Ti-6Al-4V, 316L stainless steel and Co-29Cr-8Mo [52, 67].
Table 2.6 Electrochemical parameters obtained from potentiodynamic polarization curves.
Table 2.7 Mechanical properties of recently developed Zr-based alloys by compressive test, tensile test, bending test, and nanoindentation test.
Table 2.8 Conditions for MRI magnetic compatibility for MRI applications [20].
Table 2.9 Magnetic Susceptibility of different metals.
Table 2.10 Magnetic susceptibility of as-cast Zr–Ta alloys [136].
Table 2.11 Zr-based alloys and their α” martensite phase.
Table 2.12 List of $\overline{B}_{o}$ and $\overline{M}_{d}$ values for different alloying elements M in hcp Zr and bcc Zr [172].
Table 3.1 List of $\overline{B}_{o}$ and $\overline{M}_{d}$ values for different alloying elements X in hcp Ti and Zr and bcc Ti and Zr [11, 13].
Table 3.2 Mo-Eq coefficients of alloying elements proposed by Bania [27], Zhou [28], Mo [29], and Wang [30].
Table 3.3 Calculated and experimental equilibrium lattice constants $a$ and $c$ and elastic constants of hcp Ti and Zr.
Table 3.4 New alloy composition and their $\overline{B}_{o}$, $\overline{M}_{d}$, and $e/a$ ratio.
Table 4.1 Metastable β-region for Ti-Nb-Zr alloy systems and their Mo-Eq [9, 11].

Table 4.2 Newly designed metastable Ti-Nb-Zr alloys and corresponding Mo-Eq values.

Table 5.1 Newly designed alloy compositions and their $\overline{B_o}$, $\overline{M_d}$, and $e/\alpha$ values.

Table 5.2 Mechanical properties of Zr-Ti-Nb alloys.

Table 6.1 Newly designed alloy compositions and their $\overline{B_o}$, $\overline{M_d}$, $e/\alpha$, and Mo-Eq values.

Table 6.2 Comparison of mechanical properties of Ti-Nb-Zr alloys with those of Ti-6Al-4V ELI (mill annealed) [10, 66].
Chapter 1 Introduction

1.1. Background

According to the annual report of Australian orthopaedic association (AOA), in the year 2018, joint replacements procedures have increased from the previous year as shown in Table 1.1 [1]. This happens because of the increased number of the aging population (aged ≥80 years), bone disease, including bone cancer and congenital disabilities, birth defects, accidents and revision needs. Aging population suffers from various types of age-related degenerative bone problems [2], and sometimes, a person requires extensive rehabilitation due to accidents [2]. The joint replacement surgery can be beneficial for the older people (80% of those in the 80-89 age group and 60% of the ≥90 age group) to survive at another least five years [3]. After ten years of the surgery, over 40% of the 80-89 age group and almost 15% of the ≥90 age group are still alive [3]. As a result, the selection of metallic implant is crucial when used for a prolonged period. After healing, sometimes a revision surgery is required to remove the metal implant. To avoid revision surgery, biodegradable metals, which can dissolve in the body environment, can be used for certain types of the implants but not for the majority [4]. Therefore, it is essential to select implant materials that are both biologically and mechanically compatible but non-biodegradable for biomedical applications.
Table 1.1 Australian joint replacement records in 2018 [1].

<table>
<thead>
<tr>
<th>Total hip, knee and shoulder replacement procedure in 2018: 122,281 procedure</th>
</tr>
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<tbody>
<tr>
<td><strong>Hip</strong></td>
</tr>
<tr>
<td>49,764 replacement procedure</td>
</tr>
<tr>
<td>Procedure increased by 1.7%</td>
</tr>
<tr>
<td>Revision surgery decreased to 8.4%</td>
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</table>

An orthopaedic implant requires some essential properties such as 1) proper osseointegration; 2) excellent biocompatibility, i.e., non-toxicity and not causing any adverse reactions in the human body [5], 3) comparable mechanical properties, and 4) low magnetic susceptibility. Currently, the representative non-biodegradable metallic implant materials used today are austenitic stainless-steel alloys, Co–Cr alloys, Ti, Ta, and their alloys. Among them, Co–Cr alloys are the best wear-resistant implant alloy. However, Smith Nephew’s oxinium (oxidized Zr-2.5Nb (wt. %)) has found good applications in knee and hip replacement procedures [6, 7] due to its excellent wear resistance over traditional Co–Cr alloys [8]. Austenitic stainless steels show maximum ductility compared with other representative alloys. However, the adverse effect of metal ions, such as Ni, Co, and Cr released from stainless steels and Co–Cr alloys to human body restricts the more widespread use of these alloys as implant materials [9]. Moreover, the elastic moduli of stainless steel (190-210GPa) [5] and Co-Cr alloys (210-253GPa) [5] are about 5-7 times that of healthy human cortical bones (13-35 GPa) [10, 11], which can cause the “stress shielding” effect. The “stress shielding” effect can be defined as insufficient load transfer from artificial implants to adjacent remodelling bone [12], which may result in bone resorption and potential loosening of the prosthetic device. Although Ta exhibits better biocompatibility than other metals [13], due to its high density (16.4 g cm$^{-3}$),
Ta is more suitable in highly porous forms for low strength implant applications. Commercially pure (CP) Ti and Ti-alloys exhibit excellent properties [14]. However, they risk getting partially magnetized in the intense magnetic field of MRI (magnetic resonance imaging) machine due to their relatively high magnetic susceptibility [15, 16]. This can cause heat generation in the implants [17], dislocation of implants [18], and low-quality images or artifacts in the images [15]. All these risks could be minimized by using a material with much lower magnetic susceptibility [16]. Since MRI is becoming an essential diagnostic tool, alloys with low magnetic susceptibility are receiving increasing attention for orthopaedic and dental implant applications.

As one of the most common Al- and V-free Ti-based alloy systems, Ti-Nb-Zr, has been widely investigated [19-22] due to the excellent biocompatibility of each element involved. This system offers several attractive characteristics. For example, the binary Ti-Nb alloys exhibit the lowest elastic modulus compared with other binary Ti alloys [23, 24]. Zr exhibits low magnetic susceptibility, and can act as a β-stabilizing element in β-Ti-Nb alloys in both the solution-treated and aged conditions [25]. As a result, researchers have developed different compositions of Ti-Nb-Zr alloys [19-22]. However, the potential of this alloy system as implant material has not been fully explored yet.

A substantial amount of research has been carried out on Ti-based Ti-Nb-Zr alloys [19-22], whereas only three studies focused on the Zr-based Ti-Nb-Zr alloy system [26-28]. Recent studies have shown that Zr-based alloys are very promising as implants for high-intensity MRI diagnosis [29, 30]. In that regard, Zr-based Ti-Nb-Zr alloys have the potential to offer a good combination of low elastic modulus, low magnetic susceptibility, and suitable mechanical properties. It would be more attractive if these properties could be achieved in the as-cast state.
The emphasis on the as-cast condition is significant as powder bed fusion metal additive manufacturing (PBF-MAM) has become the popular choice of manufacturing custom-made implants as a layer-melting and layer-solidification process. The as-printed part can approximately be considered as an as-cast part, although the cyclic heating effect from subsequent layers can significantly change the microstructure. It would be ideal to use the additively manufactured implants in the as-printed state without resort to subsequent heat treatment or thermomechanical processing (impractical for intricate implants) to alter the mechanical properties including elastic modulus. However, this has not been investigated in detail.

Finally, it is useful to note that both medium entropy alloys (MEAs) and high entropy alloys (HEAs) that contain Ti, Nb and Zr as principal constituent elements are receiving good attention as novel implant alloys [31-34]. They are complementary to the conventional Ti-Nb-Zr alloys and could further stimulate development of this alloy system in the future.

1.1 1.2. Aims and objectives

The main aims and objectives of this study are to design low elastic modulus Ti-Nb-Zr alloys with sufficient tensile and compressive mechanical properties in the as-cast condition and potentially low magnetic susceptibility. This study also focuses on the design approach and factors (i.e., design approach, secondary phases, elastic modulus measurement method) affecting the elastic modulus of both Ti-based Ti-Nb-Zr alloys and Zr-based Zr-Ti-Nb alloys in the as-cast state. Specific objectives of this study are given as follows:

- To assess and study the current implant alloy design methods and identify, improve or develop an approach for the design of both Ti-based and Zr-based Ti-Nb-Zr alloys with low elastic modulus as a start point.
To identify the factors that affect the elastic modulus and how these factors are controlled to reduce the elastic modulus in the as-cast state for both Ti-based and Zr-based Ti-Nb-Zr alloys.

To understand the influence of Zr on the β-stability of the Ti-Nb-Zr alloy system.

To design low elastic modulus Zr-based and Ti-based Ti-Nb-Zr alloys and assess their mechanical properties in detail.

1.2 1.3. Structure of the thesis

This thesis is composed of seven chapters, and they are introduced as follows:

Chapter 1 Introduction, which concisely describes the background and objectives of this thesis.

Chapter 2 Literature review, which delivers a comprehensive literature review of Zr alloys for orthopaedic and dental applications. It also provides relevant basic metallurgy, biocompatibility, mechanical properties, super-elasticity and shape memory effect and magnetic susceptibility of Zr-alloys. In addition, this chapter discusses the recent application of Zr alloys as an implant material and the use of the d-electron theory for the design of Zr-based alloys. Finally, this chapter identifies the research gaps and future directions for the Zr-based alloys for orthopaedic and dental application.

Chapter 3 Alloy design principles and methodology for titanium and zirconium alloys, which describes the design method (i.e., the d-electron theory, $e/A$ ratio, Mo-Eq approach, first principle studies) used in the literature for developing new implant alloys. On this basis, this chapter identifies the design approach (the combination of the d-electron theory, $e/A$ ratio, and Mo-Eq approach) used in this study to develop low elastic modulus Ti-based Ti-Nb-Zr alloys and Zr-based Ti-Nb-Zr alloys.
Chapter 4 The beta-phase stability in Ti-Nb-Zr alloys for alloy design and microstructural prediction, which discusses the existing Mo-Eq expressions and their deficiency in defining the β-phase stability for Ti-alloys. This chapter considers the β-stabilizing effect of Zr and re-define the β-phase stability of Ti-Nb-Zr alloys by proposing a new Mo-Eq expression. A set of experimental results and data available from literature are used to validate this newly proposed Mo-Eq equation. Finally, this chapter shows that the new Mo-Eq expression proposed is consistent with the d-electron theory.

Chapter 5 Strong, ductile (tensile) and low-elastic-modulus as-cast Zr-Ti-Nb alloys for biomedical applications, which studies the design and development of strong, ductile and low elastic modulus Zr-based Ti-Nb-Zr alloys for biomedical application. This chapter also critically analyses the available literature data on low elastic modulus Ti-Nb-Zr alloys and compares them with the experimental results of this study. The dependence of elastic modulus on the electronic parameters, i.e., $\frac{\overline{B}_0}{M_d}$, $e/\alpha$ ratio, and secondary phases is further discussed in this chapter.

Chapter 6 Design and development of low-elastic-modulus as-cast Ti-Nb-Zr alloys for biomedical applications, which analyses the low elastic modulus Ti-based Ti-Nb-Zr alloys for biomedical application. The mechanical properties of these newly developed Ti-Nb-Zr alloys are discussed. The factors affecting the elastic modulus are also broadly discussed. This chapter is an indirect outcome of this approach developed in this thesis.

Chapter 7 Summary and future work, which summarizes the significant findings of the entire thesis and recommends a range of future research activities.

References


Chapter 2 Literature review

2.1 Introduction

A large number of populations in the world suffer from various types of bone issues including age related degenerative bone problems [1]. In addition, accidents can lead a person to extensive rehabilitation [1]. For example, in 2018, primary total knee and hip replacements in Australia alone have increased by 1.2% and 1.7% respectively from the previous year [2]. In the rehabilitation process, the use of metallic implants for a prolonged period of time can be a significant concern, because a revision surgery is necessary to remove the supporting metal implant after healing. Biodegradable implants, which can dissolve in the body environment, are a novel solution to avoid revision surgery for certain types of implants but not for the majority [3]. Therefore, it remains essential to consider both biologically and mechanically compatible but non-biodegradable metallic materials for orthopaedic and dental implant applications.

Austenitic stainless-steel alloys, Co-Cr alloys, Ti, Ta and their alloys are representative metallic implant materials developed to date. Among them, Co-Cr alloys possess the best wear resistance, while austenitic stainless steels exhibit the maximum ductility. However, metal ions, such as Ni, Co, and Cr released from stainless steels and Co-Cr alloys entail adverse effect [4]. Ta is the most biocompatible metal [5] but its exceptional density (16.4 g cm$^{-3}$) dictates that it is better used in highly porous forms for applications that require relatively low strengths. As a result, CP Ti and Ti-alloys have essentially become the metal of choice for implant applications due to their excellent biocompatibility, bio-corrosion resistance, low density (4.5 g cm$^{-3}$) and extensive mechanical properties [6].

*This work has been published in *Advanced Engineering Materials*. Mehjabeen, Afrin, Tingting Song, Wei Xu, Hui Ping Tang, and Ma Qian. "Zirconium Alloys for Orthopaedic and Dental Applications." *Advanced Engineering Materials* 20.9 (2018)
Zr is conventionally alloyed to biocompatible β-Ti-alloys for improved mechanical properties [7]. However, recently Zr-alloys have received increasing attention as alternative implant materials due to two unique properties: (i) the formation of an intrinsic bone-like apatite layer on their surfaces in body environments, confirmed by in vivo studies [7-9] and (ii) their intrinsically low magnetic susceptibility versus all implant metals including Ti [10], which offers better MRI compatibility.

Briefly, Zr was discovered by Martin Heinrich Klaproth in 1789 while analysing the precious stone jargon [11]. Later in 1824 Berzelius [11] managed to isolate impure Zr. However, it was not until 1947 that ductile Zr sponge was produced through the Kroll process, which has since remained [11]. Zr offers a low thermal neutron capture cross section, which is about 30 times lower than that of Ti and has therefore enabled its wide application in nuclear power plants for a much better thermal reactor neutron efficiency [11, 12]. In addition, Zr exhibits superior corrosion resistance in nitric acid environments to Ti, making it preferable for related applications [11].

Zr and Ti possess the same outer shell valence electron structure. Their oxides, e.g., TiO$_2$ and ZrO$_2$, are both bio-inert and exhibit similar thermodynamical and biological characteristics [7]. Table 2.1 lists the basic properties of CP Zr and CP Ti at similar oxygen content (Grade-1) [10, 11, 13, 14]. In general, Zr has lower hardness and Young’s modulus than Ti but superior corrosion resistance [15]. The magnetic susceptibility (\(\chi\)) of an implant material is critical for MRI diagnosis through which in vivo images of the human body with or without implants can be taken without making any incision. Most current MRI scanners operate at a field strength of 1.5 Tesla, although 3-Tesla MRI systems are already clinically available (improvements in magnet design and shielding are still needed [16]). Since both the image quality and imaging speed depend on the magnetic field strength, there is a constant drive for
even much higher field strength whole-body scanners (7-11 Tesla) from the industry [16]. However, such high Tesla MRI can lead to heat generation in the implants,[17] dislocation of implants,[18] and low quality images [19] if the magnetic susceptibility of the implant material is not sufficiently low, such as Ti and 316L stainless steel implants ($\chi = 151 \times 10^{-6}$ cm$^3$mol$^{-1}$ for Ti [14] and $\chi = 3520-6700 \times 10^{-6}$ cm$^3$mol$^{-1}$ for 316L [20]). The magnetic susceptibility of CP Zr is about half of that of CP Ti and one thirtieth to one sixtieth of that of stainless steel [20]. In addition, alloying with selected biocompatible elements can further reduce the magnetic susceptibility of the resultant Zr-alloys to meet the MRI magnetic compatibility of the second kind (see Section 5, Table 2.8). This makes Zr-based alloys particularly attractive as an emerging group of implant materials for high Tesla MRI diagnoses [21].

This chapter reviews recent development in Zr-based alloys and their application as biomaterials. This includes the physical and chemical properties of CP Zr, and the phase transformations, microstructures, mechanical properties, biocompatibility, magnetic susceptibility and super-elasticity of CP Zr and its alloys. In addition, the advantage of using the $d$-electron theory in the design of new Zr-based alloys is discussed. Future directions are suggested together with a discussion of challenges.

### 2.2 Basic properties of CP Zr and its alloys

There are two types of grade for Zr-based alloys, industrial grades and nuclear grades (Table 2.2) [11, 12]. For industrial grades, R60702 is unalloyed or CP Zr and the rest are alloyed with Nb and Sn. Both grades are differentiated by their Hf content, where industrial grades can contain up to 4.5 wt.% Hf, while Hf is limited to 0.01 wt.% for nuclear grades as Hf increases the thermal neutron cross section of Zr-alloys, which is undesired for maintaining a high thermal reactor neutron efficiency [11]. Similar to CP Ti that limits the content of
Fe,[22] the specification for CP Zr limits Fe together with Cr. Table 2.3 lists the tensile properties of both grades of Zr [11, 23]. The tensile strength of CP Zr ranges from 380 to 785 MPa, yield strength from 200 to 660 MPa and tensile elongation from 14% to 17%, sufficient for most bone implant applications [11, 23].

Fig. 2.1a shows the Zr-O binary phase diagram. Zr can form a dense and continuous surface oxide layer by reaction with O. In the initial stage of reaction (260-400 °C), the oxide layer is black but turns ash grey as temperatures increases [11]. Then the adhesion at the metal-oxide interface will become weak [11]. The introduction of a high amount of oxygen (≥ 8 at.%) increases solid-solution strengthening but can result in the formation of large pores and cracks [24].

As a transition metal, Zr has an incomplete shell in its electronic structure (4d^25s^2), which permits it to form solid solutions with other elements and also makes it paramagnetic. Similar to Ti, Zr can dissolve interstitial elements (O, N, C, and H) over a wide range of temperature up to a substantial level. Table 2.4 summarizes the solubility data extracted from binary phase diagrams of Zr-O, Zr-N, Zr-H and Zr-C [25-28].

### 2.3 Common phases in Zr-alloys and typical alloying elements

Zr undergoes a similar allotropic transformation as Ti [6] and exhibits a hexagonal close-packed (hcp) crystal structure (α-phase) up to 862°C (Fig. 2.1a) [25]. The body-centered cubic (bcc) structure of Zr (β-phase) is stable from 862°C to melting point (~1860°C). At room temperature, the lattice parameters of Zr are \( a = 0.3233 \) nm and \( c = 0.5149 \) nm [11]. Fig. 2.1b displays an optical micrograph of annealed CP Zr, which contains equiaxed grains and the mean diameter of grain is about 25 µm [29].
### Table 2.1 Basic properties of CP Zr (R60702) and CP Ti Grade-1 [10, 11, 13, 14].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Oxygen Content (wt.%)</th>
<th>Atomic Number</th>
<th>Atomic Weight</th>
<th>Valence Electron</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
<th>Density (g/cm³)</th>
<th>Tensile Strength (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Elongation at Break (%)</th>
<th>Young’s Modulus (GPa)</th>
<th>Shear Modulus (GPa)</th>
<th>Magnetic Susceptibility $10^6$(cm³/g⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CP Zr</td>
<td>≤ 0.16</td>
<td>40</td>
<td>91.224</td>
<td>4</td>
<td>1852</td>
<td>4377</td>
<td>6.7</td>
<td>440</td>
<td>240</td>
<td>18</td>
<td>88</td>
<td>35.3</td>
<td>1.3</td>
</tr>
<tr>
<td>CP Ti Grade 1</td>
<td>≤ 0.18</td>
<td>22</td>
<td>47.867</td>
<td>4</td>
<td>1668</td>
<td>3287</td>
<td>4.51</td>
<td>240</td>
<td>170</td>
<td>24</td>
<td>102.7</td>
<td>44</td>
<td>3.2</td>
</tr>
</tbody>
</table>
Table 2.2 Chemical compositions of industrial and nuclear grades of Zr-alloys [11, 12].

<table>
<thead>
<tr>
<th>Element</th>
<th>Industrial grades (wt.%)</th>
<th>Nuclear grades (wt.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>CP Zr (R60702)</td>
<td>Zr-Sn (R60704)</td>
</tr>
<tr>
<td>Zr + Hf, min</td>
<td>99.2</td>
<td>97.5</td>
</tr>
<tr>
<td>Hf, max</td>
<td>4.5</td>
<td>4.5</td>
</tr>
<tr>
<td>Fe + Cr</td>
<td>0.2, max</td>
<td>0.2-0.4</td>
</tr>
<tr>
<td>Sn</td>
<td>1.0-2.0</td>
<td></td>
</tr>
<tr>
<td>H, max</td>
<td>0.005</td>
<td>0.005</td>
</tr>
<tr>
<td>N, max</td>
<td>0.025</td>
<td>0.025</td>
</tr>
<tr>
<td>C, max</td>
<td>0.05</td>
<td>0.05</td>
</tr>
<tr>
<td>Nb</td>
<td>2-3</td>
<td></td>
</tr>
<tr>
<td>O, max</td>
<td>0.16</td>
<td>0.18</td>
</tr>
</tbody>
</table>

Table 2.3 Tensile properties of industrial and nuclear grades of Zr-alloys [11, 23].

<table>
<thead>
<tr>
<th>Tensile properties</th>
<th>CP Zr (R60702)</th>
<th>Zr-Sn (R60704)</th>
<th>Zr-Nb (R60705)</th>
<th>Zircaloy-2 (R60802); annealed at 20°C</th>
<th>Zircaloy-4 (R60804); annealed at 20°C</th>
<th>Zr-Nb (R60901)</th>
</tr>
</thead>
<tbody>
<tr>
<td>UTS, min (MPa)</td>
<td>379</td>
<td>413</td>
<td>552</td>
<td>785</td>
<td>785</td>
<td>450</td>
</tr>
<tr>
<td>Yield Strength, min (MPa)</td>
<td>207</td>
<td>241</td>
<td>379</td>
<td>600</td>
<td>600</td>
<td>310</td>
</tr>
<tr>
<td>Elongation, min (%)</td>
<td>16</td>
<td>14</td>
<td>16</td>
<td>17</td>
<td>17</td>
<td>15</td>
</tr>
</tbody>
</table>
Figure 2.1 (a) Binary phase diagram of Zr-O (reproduced with permission from Ref. [25] Copyright (1986), with permission from Springer Nature), and (b) the microstructure of CP Zr (reproduced with permission from Ref.[29] Copyright (1998), Elsevier).
Table 2.4 Solubility limits of O, N, H, and C in α-Zr and β-Zr [25-28].

<table>
<thead>
<tr>
<th>Element</th>
<th>Solubility in α-Zr (at.%)</th>
<th>Solubility in α-Zr from 550°C to 800°C (at.%)</th>
<th>Solubility in β-Zr (at.%)</th>
<th>Solubility in β-Zr from 1000°C to 1300°C (at.%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>35 at 2065°C</td>
<td>28.5</td>
<td>10.5 at 1970°C</td>
<td>2-6</td>
</tr>
<tr>
<td>N</td>
<td>24.7 at 1988°C</td>
<td>20.9-22.2</td>
<td>5 at 1883°C</td>
<td>0.65-1.6</td>
</tr>
<tr>
<td>H</td>
<td>5.93 at 550°C</td>
<td>-</td>
<td>37.5 at 550°C</td>
<td>-</td>
</tr>
<tr>
<td>C</td>
<td>Around 1 at 886°C</td>
<td>-</td>
<td>Around 0.5</td>
<td>1855°C</td>
</tr>
</tbody>
</table>

High pressure can change the phase stability of Zr over a wide range of temperature as shown in Fig. 2.2. High pressure (4.5-16.5 GPa, 1 GPa = 9870 standard atmospheres) can change bcc β-Zr into amorphous Zr [30] (Section 4.3 for Zr-based amorphous alloys). The application of high pressure (4.5-18GPa) decreases the ω-phase formation temperature (700-500°C).

Apart from pressure, alloying elements can play a significant role in determining the phase composition and stability in Zr-alloys. Similarly, they can be classified into α-stabilizers, β-stabilizers and neutral. α-stabilizers (e.g., Al, Sn and O) increases the allotropic transformation temperature (ATT) while β-stabilizers (e.g., Nb, Ta, Mo, Fe, and Ti) decreases [11]. Neutral elements (Si and Hf) have no strong effect. By adding both α- and β-stabilizers to Zr, the resultant Zr-alloys can have the co-existence of α and β. Consequently, Zr-alloys can be classified as α-, (α+β) - and β-Zr-alloys. β-phase exhibits lower Young’s modulus than α-phase because its bcc structure contains a lower number density of atoms [6]. This property is useful for developing low modulus Zr-alloys for implant applications.
The β-phase in Zr-alloys can transform into ω (hexagonal but not close packed), α' (hcp), α″ (orthorhombic) by cold rolling, annealing, solution treatment, quenching or ageing [10, 31-34]. The ω-phase increases Young’s modulus but favours low magnetic susceptibility [11]. Martensitic α″-phase can exhibit lower Young’s modulus than martensitic α'-phase for Ti-based alloys [35, 36]. In addition, α″-phase is essential for realizing the shape memory effect [37, 38]. Finally, massive transformation (α_m) may also occur in Zr-alloys when cooled from the β-phase region at sufficiently high cooling rates but slower than that for α' transformation.

**Figure 2.2** Temperature-pressure phase diagram for pure Zr (reproduced with permission from [30] Copyright (1998), Elsevier).
The temperature $T_o$ (at which two phases have the same Gibbs free energy but are in unstable equilibrium) can provide an indication for the $\alpha_m$ or $\alpha'$ start temperature. In addition, a detailed assessment of the dependence of $T_o$ on each alloying element can inform alloy design for controlled transformations. The predicted $T_o$ curves for bcc $\rightarrow$ hcp and Liquid $\rightarrow$ bcc in Zr-Ti-alloys using Pandat$^\text{TM}$ CompuTherm database are superimposed on the phase diagram of Zr-Ti (Fig. 2.3a). The $T_o$ for bcc $\rightarrow$ hcp changes with changing Zr or Ti content, namely, Ti is not neutral for Zr and nor Zr is neutral for Ti. Fig. 2.3b summarises the $T_o$ values for Zr-X ($X = \text{Ti, Fe, Ta, Sn, Mo, Nb}$) calculated using the Pandat$^\text{TM}$ CompuTherm database. The following observations are most notable: (i) $T_o$ decreases with increasing content of Fe, Mo, Ta, or Nb; (ii) there exists a minimum point (30 wt.% of Ti) for the influence of the Ti content on $T_o$; and (iii) there exists a maximum point for the influence of Sn content on $T_o$. The influence of Ti and Sn on $T_o$ changes in opposite directions and has the potential to cancel each other out. These observations are informative for design of Zr-alloys as will be shown later.

2.4 Biocompatibility of Zr and biocompatible alloying elements for Zr

The biocompatibility of a material depends on two factors,[39] i.e., the response of human body and its degradation in human body. There has been a renewed interest in determining the biocompatibility of a pure metal. Fig. 2.4a shows the relationship between coefficient of fibroblastic outgrowth in embryo heart muscle and relative growth rate of L929 cells (fibroblastic cells of mouse),[40] while Fig. 2.4b exhibits the relationship between polarization resistance and biocompatibility of surgical implant materials [40]. The data presented in Fig. 2.4a and 4b leads to slightly different conclusions for some elements but Zr is highly biocompatible by either criterion, along with Ti and Ta.
Figure 2.3 (a) Zr-Ti binary phase diagram plotted using Pandat™, superimposed with $T_0$ curves, and (b) Dependence of $T_0$ on biocompatible elements in Zr-X alloys ($X = Ti, Fe, Ta, Sn, Mo, and Nb$) plotted using Pandat™.
Figure 2.4 (a) Cytotoxicity of pure metals, and (b) Relationship between polarization resistance and biocompatibility of pure metals, Co-Cr alloy and stainless steels (reproduced with permission from Ref.[40] Copyright (1986), Springer Nature).
Li et al. [41] investigated the cytotoxicity of Ti, Ta, Nb, Zr, Sn, Mo, and Si in both bulk and powder forms. Owing to their large curvatures and therefore increased activity, metal powder particles can show more cytotoxicity than their bulk forms [42]. In particular, Zr, Ta and Sn were the only three metals that showed good biocompatibility in both powder and bulk forms. Conversely, both Ti and Nb exhibited slight cytotoxicity in powder form, although biocompatible in bulk form. Mo and Si displayed significant cytotoxicity in powder form but slight cytotoxicity in bulk form. Clarifying the biocompatibility of a metal in its powder form is important because the surface of a metal implant, whether it is manufactured additively or subtractively, is often made rough or porous or micro-surface-patterned in order to enhance cell responses [13, 42]. These surface features have curvatures similar to those of metal powders. In this regard, both Zr and Ta are more biocompatible than Ti. Sn does not offer the same level of strength as Ti, Zr and Ta. Therefore, it is mainly used as an alloying element. Apart from Sn, other biocompatible alloying elements for Zr may include Ti, B, Mg, Si, P, Ca, Sr, Nb, Mo, Pd, In, Sn, Ta, Pt, and Au, depending on concentration, while those that should be excluded may include Be, Al, V, Cr, Mn, Fe, Co, Ni, Cu, Zn, and Ag [36].

2.4.1 Bioactivity of Zr

Bioactivity refers to the ability to produce a bone-like apatite layer on its surface in the body environment [43, 44] or in a simulated body fluid (SBF) [45, 46]. This bone-like apatite layer is critical for adhesion of the implant to the bone [47] and subsequent new bone growth on the implant surface in the initial stage of implantation. Uchida et al. [48] studied NaOH-treated Zr samples in a SBF, and found that, the surface oxide layer reacted with the NaOH solution, accompanied by the formation of a Na-free zirconia hydrogel (Zr-OH) surface layer. This hydrogel led to nucleation of the bone-like apatite. On a different note, Zr-OH has been used as a material for concentrating human enteric viruses [49].
ZrO\textsubscript{2} exhibits similar bioactivity to that of TiO\textsubscript{2} and Ta\textsubscript{2}O\textsubscript{5} [50]. Annealing of nanostructured ZrO\textsubscript{2} and TiO\textsubscript{2} showed no change in their bioactivity; however, annealing enhanced the bioactivity of nanostructured Ta\textsubscript{2}O\textsubscript{5}. Nb\textsubscript{2}O\textsubscript{3} was not bioactive either before or after annealing because of its low propensity to form Nb-OH. Another comparative in vitro study shown in Fig. 2.5a further indicates the similarity in biocompatibility between Zr and Ti [51].

Zhou et al. [52] assessed the viability of osteoblast-like cells (MG 63) after culturing in extraction media of CP Zr and Zr-based binary alloys (Zr–1X) for 48 h, 96 h and 168 h. Cell culture medium (MEM) was used as a negative control which was considered biocompatible. If the elemental metal exhibits similar or higher cell viability than that of the control group, then it could be considered biocompatible. As shown in Fig. 2.5b, no significant difference was found in cell viabilities between Zr and Ti. In particular, all Zr-1X alloys exhibited a high level of cell viability which is over 87% or no adverse effect on osteoblast-like cells (MG 63). Other Zr-based binary alloys including Zr-Nb [53] and oxidized Zr-Sn [54] and porous Zr-Ti-Nb alloys [55] all exhibited excellent biocompatibility.

Hemocompatibility refers to the compatibility to blood and is another critically important requirement for implant materials. The hemocompatibility of three Zr-X alloys, Zr-10Nb, Zr-2.5Nb and Zr-12Ta, in human blood have been assessed and found acceptable,[56] which confirms the compatibility of Zr-alloys. Zr-coated Ti alloy implants resulted in enhanced cell responses in the early stages due to improved wettability [57, 58]. In addition, Zr-coating improves wear résistance [58].
Figure 2.5 Viabilities of (a) human osteosarcoma cells (HOS) cultured for Zr and Ti for different times (reproduced with permission from Ref. [51] Copyright (1993), The Stomatological Society), and (b) MG 63 osteoblast-like cells cultured in extraction media of CP Zr and Ti and, and Zr–1X alloys for 48, 96 and 168 h (reproduced with permission from Ref.[52] Copyright (2013), Elsevier).
Grain size affects cell responses to Zr-alloys. Ultrafine-grained Zr samples can exhibit both excellent mechanical properties and good in vitro biocompatibility [59]. For example, by tailoring the grain size of Zircaloy-2 (Zr-(1.3–1.6%) Sn-(0.07–0.20%) Fe-(005–0.16%) Cr-(0.03–0.08%) Ni-0.006%N), it is possible to achieve both good mechanical properties and improved protein absorption [60]. Protein absorption is essential for cell adhesion and cell proliferation, because the implant material has its first contact with the proteins available in the human body fluid, followed by subsequent cell adhesion through these proteins.

Bacterial adhesion depends on the specific resistivity of an implant material [61]. An orthopaedic implant can fail just because of bacterial adhesion to its surface [62]. Hence information about bacterial adhesion to an implant material is important for determining antibacterial treatment regimens and the expected comfort level of patients. During adhesion, a bacterium either donates or accepts electrons from the implant material. Those which donate electrons to the implant material will be attached strongly compared with those which accept electrons from the implant material. A study of bacterial adhesion to CP Ti and Zr oxides revealed that Zr oxide is more resistant to bacterial adhesion than CP Ti or TiO₂ [63, 64] due to its electric conductivity [65].

2.4.2 Corrosion resistance

Corrosion of implant materials can reduce their expected life or lead to a revision surgery. In addition, the released metallic ions, if excessive, can be problematic. Tsutsumi [66] assessed in detail the corrosion behaviour of Zr and its binary alloys. Pitting was observed during the potentiodynamic anodic polarization measurement of CP Zr in Hanks’ solution. However, the pitting potential of Zr is much higher than that of 316L stainless steel and can be increased substantially through alloying with other elements. Fig. 2.6 shows that an addition of more than 10 at.% of Ti, Nb or Ta resulted in higher pitting potential than that of CP Zr. On the
contrary, Zr-Pd and Zr-Au alloys showed lower pitting potential values than that of CP Zr at low concentrations (≤ 5 at.%). In brief, the three favourable alloying elements for Zr are Ti, Nb, and Ta for enhanced resistance to pitting in physiological environments [66].

![Graphs showing pitting potential vs concentration for various Zr-X systems](image)

**Figure 2.6** Pitting potential of six binary primary Zr-X systems that contain biocompatible elements for Zr vs. alloying content, X (reproduced with permission from Ref.[66] Copyright (2014), Japan Society of Corrosion Engineering).
The corrosion behaviour of CP Zr and Zr-1X alloys (wt.%) (X = Ti, Nb, Mo, Cu, Au, Pd, Ag, Ru, Hf, and Bi) has been studied [56]. Table 2.5 summarizes the electrochemical parameters of Zr-1X (X = Ti, Nb, Mo, Cu, Au, Pd, Ag, Ru, Hf, and Bi) alloys [52, 67]. The open circuit potential (OCP) values of Zr-1X alloys (X = Ti, Nb, Mo, Au, Pd, Ru, Hf and Bi) were found to be higher than that of CP Zr as shown in Table 2.5. This means that the spontaneous passive film produced by these alloying elements were thermodynamically stable. For this reason, these alloys had a lower corroding tendency than CP Zr. On the other hand, Zr-1Cu and Zr-1Ag showed lower OCP values than CP Zr. It should be noted that Zr-1X (X = Ti, Nb, Cu, Au, Pd, Ag, Ru, Hf, and Bi) alloys showed lower OCP values than those of CP Ti, 316L and Co-Cr-Mo. Their corrosion current density, $i_{corr}$, was lower than that of CP Zr, which confirms that alloying can improve the corrosion resistance of Zr.

The corrosion resistance of ternary Zr-based alloys has been studied recently. The open circuit potential and polarization resistance of Zr-1.5Nb-1X (X = Ti, Mo, Ta, W)(at.%) were found to be both higher than the respective values of Grade 2 CP Ti [68]. Among these ternary alloys, Zr-1.5Nb-1Ta showed the highest open circuit potential and polarization resistance. In addition, Zr-40Ti-6Ag showed increased pitting corrosion resistance compared with binary Zr-40Ti because of the formation of a thick, dense and stable passive film [69].

Invented by Smith & Nephew (a medical device supplier), oxinium refers to oxidized Zr, which has been used as replacement joints [70, 71]. The success of oxinium has attracted much attention to investigate the corrosion resistance of oxidized Zr-based alloys. Table 2.6 summarizes the work on the corrosion resistance of oxidized Zr-based alloys [54, 72, 73]. The $i_{corr}$ values of these oxidized alloys are significantly lower than without oxidation, i.e., oxidized Zr-alloys possess excellent corrosion resistance.
Table 2.5 Electrochemical parameters of CP Zr, Zr-1X (X = Ti, Nb, Mo, Cu, Au, Pd, Ag, Ru, Hf, and Bi), CP Ti, Ti-6Al-4V, 316L stainless steel and Co-29Cr-8Mo [52, 67].

<table>
<thead>
<tr>
<th>Alloy composition, Wt. %</th>
<th>Pure Zr</th>
<th>Zr–1Ti</th>
<th>Zr–1Nb</th>
<th>Zr–1Mo</th>
<th>Zr–1Cu</th>
<th>Zr–1Au</th>
<th>Zr–1Pd</th>
<th>Zr–1Ag</th>
<th>Zr–1Ru</th>
<th>Zr–1Hf</th>
<th>Zr–1Bi</th>
<th>Pure Ti</th>
<th>Ti–6Al–4V</th>
<th>316 L SS</th>
<th>Co–Cr–Mo</th>
</tr>
</thead>
<tbody>
<tr>
<td>Corrosion potential, E_{corr}(V)</td>
<td>-0.450 (0.017)</td>
<td>-0.452 (0.002)</td>
<td>-0.466 (0.009)</td>
<td>-0.341 (0.021)</td>
<td>-0.457 (0.029)</td>
<td>-0.408 (0.054)</td>
<td>-0.389 (0.014)</td>
<td>-0.452 (0.041)</td>
<td>-0.428 (0.024)</td>
<td>-0.463 (0.019)</td>
<td>-0.435 (0.039)</td>
<td>-0.381 (0.021)</td>
<td>-0.393 (0.043)</td>
<td>-0.303 (0.017)</td>
<td>-0.377 (0.821)</td>
</tr>
<tr>
<td>Corrosion current density, I_{corr}(10^{-7} A cm^{-2})</td>
<td>1.963 (0.931)</td>
<td>0.961 (0.675)</td>
<td>1.189 (0.608)</td>
<td>1.406 (0.690)</td>
<td>1.363 (0.184)</td>
<td>1.868 (0.464)</td>
<td>1.388 (0.766)</td>
<td>1.451 (0.174)</td>
<td>1.343 (0.089)</td>
<td>1.847 (0.169)</td>
<td>1.413 (0.507)</td>
<td>0.751 (0.196)</td>
<td>0.895 (0.230)</td>
<td>3.095 (0.687)</td>
<td>0.495</td>
</tr>
<tr>
<td>Open circuit potential, OCP (V)</td>
<td>-0.447</td>
<td>-0.429</td>
<td>-0.446</td>
<td>-0.343</td>
<td>-0.451</td>
<td>-0.394</td>
<td>-0.402</td>
<td>-0.449</td>
<td>-0.427</td>
<td>-0.384</td>
<td>-0.44</td>
<td>-0.336</td>
<td>-0.358</td>
<td>-0.21</td>
<td>-0.34</td>
</tr>
<tr>
<td>Electrolyte</td>
<td>Alloy composition, (at. %)</td>
<td>Corrosion potentials, $E_{\text{corr}}$(V)</td>
<td>Corrosion current density, $i_{\text{corr}}$(μA/cm$^2$)</td>
<td>Reference</td>
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<tr>
<td>Artificial saliva</td>
<td>Untreated Zr-2.3Sn</td>
<td>$-0.552\pm0.067$</td>
<td>$0.0564\pm0.0151$</td>
<td>[54]</td>
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<tr>
<td></td>
<td>Oxidized Zr-2.3Sn</td>
<td>$-0.296\pm0.114$</td>
<td>$0.00315\pm0.00029$</td>
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<tr>
<td>Artificial saliva containing 0.1 M H$_2$O$_2$</td>
<td>Untreated Zr-2.3Sn</td>
<td>$-0.483\pm0.045$</td>
<td>$0.188\pm0.0527$</td>
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<tr>
<td></td>
<td>Oxidized Zr-2.3Sn</td>
<td>$-0.140\pm0.015$</td>
<td>$0.0121\pm0.0029$</td>
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<tr>
<td>Acidified Ringer’s solution(pH = 3)</td>
<td>Untreated Zr-7.8Ti-0.3Nb-0.3Mo</td>
<td>$-0.256 (0.017)$</td>
<td>$14.5 (0.7)$</td>
<td>[73]</td>
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<tr>
<td></td>
<td>Oxidized Zr-7.8Ti-0.3Nb-0.3Mo</td>
<td>$-0.172 (0.016)$</td>
<td>$2.4 (0.2)$</td>
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<tr>
<td></td>
<td>Untreated Zr-37.3Ti-0.3Nb-0.55Mo</td>
<td>$-0.291 (0.017)$</td>
<td>$5.3 (0.4)$</td>
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<tr>
<td></td>
<td>Oxidized Zr-37.3Ti-0.3Nb-0.55Mo</td>
<td>$-0.354 (0.019)$</td>
<td>$0.9 (0.2)$</td>
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<tr>
<td></td>
<td>Untreated Zr-60-0.3Nb-0.3Mo</td>
<td>$-0.325 (0.019)$</td>
<td>$1.4 (0.2)$</td>
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<tr>
<td></td>
<td>Oxidized Zr-60-0.3Nb-0.3Mo</td>
<td>$-0.376 (0.021)$</td>
<td>$0.4 (0.1)$</td>
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<tr>
<td>0.1% NaF containing acidified artificial saliva</td>
<td>Untreated Zr-32.2Ti</td>
<td>$-1.11 \pm 0.03$</td>
<td>$38 \pm 0.7$</td>
<td>[72]</td>
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<tr>
<td>(pH = 4)</td>
<td>Oxidized Zr-32.2Ti</td>
<td>$0.04 \pm 0.05$</td>
<td>$0.25 \pm 0.08$</td>
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<td></td>
<td>Untreated Zr-56Ti</td>
<td>$-0.63 \pm 0.06$</td>
<td>$2.6 \pm 0.6$</td>
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<td></td>
<td>Oxidized Zr-56Ti</td>
<td>$-0.05 \pm 0.04$</td>
<td>$0.25 \pm 0.04$</td>
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<tr>
<td>Artificial saliva (pH = 6.8)</td>
<td>Untreated Zr-20Nb</td>
<td>$-0.46935$</td>
<td>$0.91046$</td>
<td>[74]</td>
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<td></td>
<td>Oxidized Zr-20Nb</td>
<td>$-0.29472$</td>
<td>$5.5361$</td>
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<tr>
<td></td>
<td>Untreated Zr-20Nb-3Ti</td>
<td>$-0.45992$</td>
<td>$1.7757$</td>
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<tr>
<td></td>
<td>Oxidized Zr-20Nb-3Ti</td>
<td>$-0.35319$</td>
<td>$0.054929$</td>
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</table>
2.5 Mechanical properties

2.5.1 Dense Zr-alloys

The mechanical properties play a critical role in materials selection for implant application. The Young’s modulus of cortical bone ranges from 6 to 26.6 GPa [75, 76]. If an implant exhibits higher Young’s modulus, then most of the loads will be carried out by implant rather than the bone. This will cause resorption in bone tissue, known as stress shielding [77]. Consequently, the implant material may loosen from the bone or the bone may re-fracture. The lack of sufficient strength can result in implant fracture [78, 79]. In particular, when the bone-implant interface begins to fail, the development of a soft fibrous tissue at the interface can make more relative movements between the implant and bone under loading. These movements can entail unbearable pain for the patient leading to a revision surgery. Similarly, fatigue induced fracture can cause implant loosening, stress shielding, and ultimate implant failure [80]. For Ti-based alloys, the ratio of fatigue strength to tensile strength is between 0.5-0.65 [22]. It is expected that Zr-based alloy may show similar ratios. Table 2.7 summarises the mechanical properties of recently developed Zr-based alloys for biomedical applications [7, 52, 81-92].

Binary Zr-Nb alloys showed different mechanical responses, depending on their Nb content because of change in phase constituent. The tensile strength and elongation of Zr-(3-6)Nb alloys, which contain α-phase, first increased and then decreased with increasing Nb content [82]. Fig. 2.7a shows the Zr-Nb phase diagram, which suggests that the amount of β-phase in Zr-Nb alloys increases with increasing Nb content [82]. Fig. 2.7b shows the phases detected in as-cast Zr-(9-16)Nb (wt.%) by XRD. The strong peak intensity from the ω-phase in Zr-9Nb alloy resulted in higher hardness. The decrease in intensity of the ω-phase with increasing Nb content led to a decrease in tensile elongation, hardness and strength [82].
However, there is a slight increase in strength and hardness when the Nb content is more than 20%. XRD detected no ω-phase at 20%Nb content. Hsu et al. [93] pointed out that as-cast Zr-alloys can have different structures and mechanical properties compared with heat-treated conditions. Data on fatigue properties is still very limited.

Much attention has been paid to the equi-atomic Zr-50Ti (at.%) binary alloy recently [34, 94] because of the complete mutual solubility of Zr and Ti in either the β-phase or α-phase regions as shown in Fig. 2.3a [95]. Literature suggests that Zr-50Ti (at.%) can exhibit hardness that is 2-3 times higher than that of CP Ti and CP Zr due to the large lattice misfit between Ti and Zr [95]. In addition, a variety of high Zr-containing (> 15 at.%) Ti-based alloys have recently been developed for biomedical application [96-99]. Theoretical studies [100] indicated that Zr can help to reduce Young’s modulus and increase strength. For example, Zr-based Ti-60Zr (at.%) alloy exhibited the lowest Young’s modulus in the Ti-Zr binary alloys [101].

Hisata et al. [34] investigated the microstructure of (Zr-Ti)-(0-8)Nb (at.%). The phase changes with increasing Nb content as follows: α′ → α″ + α′ + β → β + α″ → β. The Young’s modulus of the as-quenched alloy samples changes according to their phase constituents as shown in Fig. 2.8. After cold rolling, stress-induced martensitic transformations (β → α and/or β → α″) were observed, which led to lower Young’s modulus. For example, cold-rolled (Zr-Ti)-6Nb, which contained α'-phase as its main phase, exhibited the lowest Young’s modulus (59.5GPa).
Figure 2.7 (a) Zr-Nb binary phase diagram plotted using Pandat™, superimposed with the T₀ curves, and (b) XRD results of as-cast Zr-Nb alloys (i) Zr, (ii) Zr-3Nb, (iii) Zr-6Nb, (iv) Zr-9Nb, (v) Zr-12Nb, (vi) Zr-16Nb, (vii) Zr-20Nb, and (viii) Zr-24Nb alloys (reproduced with permission from Ref.[82] Copyright (2011), Elsevier).
Table 2.7 Mechanical properties of recently developed Zr-based alloys by compressive test, tensile test, bending test, and nanoindentation test.

<table>
<thead>
<tr>
<th>Test method</th>
<th>Alloy Composition</th>
<th>Condition</th>
<th>Strength (MPa)</th>
<th>Yield Strength (MPa)</th>
<th>Young’s modulus (GPa)</th>
<th>Hardness</th>
<th>Elongation, (%)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compressive test</td>
<td>Zr-8.8Si-(0-0.9)Nb</td>
<td>As-cast</td>
<td>1169 - 1257</td>
<td>790 - 953</td>
<td>25.08–29.63 GPa</td>
<td></td>
<td></td>
<td>[81]</td>
</tr>
<tr>
<td></td>
<td>Zr-4Cu-(0-0.9)Nb</td>
<td>As-cast</td>
<td>1542-1485</td>
<td>1200-1363</td>
<td>33.075-34.13</td>
<td></td>
<td></td>
<td>[84]</td>
</tr>
<tr>
<td></td>
<td>Zr-20Nb-(0-15)Ti</td>
<td>As-cast</td>
<td>1100 -</td>
<td>473 -508</td>
<td>24.89 -24.91</td>
<td></td>
<td></td>
<td>[83]</td>
</tr>
<tr>
<td></td>
<td>Zr-5Al-(10-15)Fe-10Nb</td>
<td>As-cast</td>
<td>1300-1260</td>
<td>1040-1140</td>
<td>50-58</td>
<td></td>
<td></td>
<td>[89]</td>
</tr>
<tr>
<td>Tensile test</td>
<td>Zr-(3-24)Nb</td>
<td>As-cast</td>
<td>786-663</td>
<td>604-649</td>
<td>84.8-72.12</td>
<td>266-231</td>
<td>6.5-17.9</td>
<td>[82]</td>
</tr>
<tr>
<td></td>
<td>Zr-1X(X=Ti, Nb, Mo, Cu, Au, Pd and Ag)</td>
<td>Annealed</td>
<td>564-591</td>
<td>456-452</td>
<td>259-258</td>
<td>24-22</td>
<td></td>
<td>[52]</td>
</tr>
<tr>
<td></td>
<td>Zr-41Ti-5Al-4V</td>
<td>ST-35%CR</td>
<td>680-1185</td>
<td>850-1000</td>
<td>70-45</td>
<td>17.3-9</td>
<td></td>
<td>[87]</td>
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<tr>
<td></td>
<td>Zr-(16-64)Ag</td>
<td>Swaged at 96%</td>
<td>686-395</td>
<td>574-368</td>
<td>78-56</td>
<td>3.4-1.5</td>
<td></td>
<td>[90]</td>
</tr>
<tr>
<td>Bending test</td>
<td>Zr-(10-40)Ti</td>
<td>As-cast</td>
<td>1726-1433</td>
<td>69-78</td>
<td>291-278</td>
<td></td>
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<td>[85]</td>
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<tr>
<td></td>
<td>Zr-(1-10)Mo</td>
<td>Hot rolled, Solution treated and quenched</td>
<td>1781-1307</td>
<td>422-323</td>
<td>98.8-73.2</td>
<td></td>
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<td>[91]</td>
</tr>
<tr>
<td>Nanoindentation test</td>
<td>[(Mo,Sn)-(Zr,Ti)14]Nb_x (x=1, 3)</td>
<td>As-cast</td>
<td>61-98</td>
<td>231-268</td>
<td></td>
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<td>[86]</td>
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<tr>
<td></td>
<td>Zr-1X(X=Ti, Nb, Mo, Cu, Au, Pd and Ag)</td>
<td>Annealed</td>
<td>102-109</td>
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<td></td>
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<td>[52]</td>
</tr>
<tr>
<td>Dynamic mechanical analyser / Microindentation</td>
<td>Ti-18Nb-51Zr</td>
<td>Annealed at 1000°C, 2 h</td>
<td>62.5/59.7</td>
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<td>[92]</td>
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<tr>
<td></td>
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<td>Water quenched at 1000°C, 2 h</td>
<td>73.5/63.2</td>
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<td>Water quenched at 680°C, 10 min</td>
<td>68/61</td>
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<td>Multi stage treatment</td>
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Figure 2.8 Young’s modulus and micro Vickers hardness of (Ti-Zr)-XNb alloys (reproduced with permission from Ref.[34] Copyright (2015),JIM Material).

2.5.2 Porous Zr-alloys

Porosity beyond a critical level can play an important role in reducing Young’s modulus because the amount of material that supports same cross-sectional area will become much less. As a result, when stress is increased, deformation becomes larger and Young’s modulus becomes smaller. Besides, interconnected open pores can facilitate bone tissues ingrowth to permit stress transfer between bone and implants in a smoother style [102, 103]. Maya et al. [55] investigated Zr-Nb-Ti porous alloys for biomedical application with an average pore size of 260 µm. The Young’s modulus and compressive plateau stress of these alloys vary in the ranges of 0.3-1.4GPa and 11-32MPa, respectively, depending on porosity as well as the Nb content. There are a variety of techniques that can be used to fabricate porous Zr (see Section 9.2).
2.5.3 Bulk metallic glasses

Zr-based bulk metallic glasses (BMG) have also attracted attention for biomedical applications due to their high compression strength (~2GPa), corrosion and wear resistance, low elastic modulus (50–100 GPa) and excellent formability in the supercooled liquid region [104-109]. Since many BMGs contain Ni, which is carcinogenic to human body,[110] Ni-free Zr-based BMGs have been developed including Zr-5Nb-22.5Cu-5Pd-7.5Al,[111] Zr-5Nb-20Cu-5Fe-10Al,[112] and (Zr$_{0.62}$Cu$_{0.23}$Fe$_{0.05}$Al$_{0.10}$)$_{100-x}$Ag$_x$ ($x = 0, 1, 3, 5, 7$) [113]. However, their potential needs to be further assessed due to the lack of sufficient tensile ductility [114].

2.6 Magnetic susceptibility

Magnetic susceptibility measures a material’s propensity to respond to an applied magnetic field. This property was not considered until the MRI technique was invented. MRI is a commonly used diagnostic tool in orthopaedics and surgery. It can get cross-sectional perspectives of the human body without invasive X-ray irradiation [115]. However, MRI diagnostics are hindered when metals such as stainless steel and Co-Cr alloys are implanted in the body because metallic implants get magnetized in the intense magnetic field of the MRI systems. As pointed out earlier, this can result in heat generation in the implants,[17] dislocation of implants [18] and artifacts in the image [116, 117].

The magnetization of a material can be expressed as $M = M_o + \chi H$, where $M_o$ is defined as natural magnetization, which can be found in some materials even without an applied magnetic field, $\chi$ is magnetic susceptibility and $H$ is applied magnetic field. The selection of a material for use in, or near, an MRI system depends on $\chi$ and $M_o$. Theoretically if $M_o$ is not precisely zero but relatively close to zero, then the material can exhibit magnetic field compatibility. Table 2.8 provides reasonable guidance for selecting suitable implant materials [20]. Here $\chi_{water}$ is taken as $-9.05 \times 10^{-6}$, which is close to the susceptibility of human tissues.
Table 2.8 Conditions for MRI magnetic compatibility for MRI applications [20].

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Property</th>
<th>Examples</th>
<th>Comments</th>
</tr>
</thead>
<tbody>
<tr>
<td>$M_0 \neq 0$ and/or $</td>
<td>\chi</td>
<td>&gt; 10^{-2}$</td>
<td>MRI magnetic incompatibility</td>
</tr>
<tr>
<td>$10^{-5} &lt;</td>
<td>\chi - \chi_{\text{water}}</td>
<td>&lt; 10^{-2}$</td>
<td>MRI magnetic compatibility of the first kind</td>
</tr>
<tr>
<td>$</td>
<td>\chi - \chi_{\text{water}}</td>
<td>&lt; 10^{-5}$</td>
<td>MRI magnetic compatibility of the second kind</td>
</tr>
</tbody>
</table>

Fig. 2.9 shows the magnetic susceptibility spectrum for a variety of materials including Zr and soft tissue [20]. The top diagram displayed the full range of magnetic susceptibility by using logarithmic scale, while the bottom diagram contained information about materials which had $|\chi| < 20$ ppm by using linear scale (ppm by weight, mg/kg).

The magnetic susceptibility of most human tissues varies in the range of -7 to -11 ppm [20]. Although implant materials that fall into the category of MRI magnetic compatibility of the first kind (Table 2.8) do not experience any forces or torques, they can produce significant artifacts. Artifacts can change the image of organs near implant without providing the exact diagnosis [118-120]. This happens because of the difference in magnetic susceptibility between the metals and living cells [121].
Imai et al. [122] studied the effect of magnetic susceptibility on artifacts in MRI. They investigated ten metals (316L, Co-29Cr-6Mo, Nb, Ti, Zr, Mo, Al, Sn, Cu and Ag) by using 1.5 Tesla and 3.0 Tesla MR scanners under both fast spin echo (FSE) and gradient echo (GRE) conditions and the results are shown in Fig. 2.10 [122]. They confirmed that the artifacts in MRI increased with increasing magnetic susceptibility [122].

![Magnetic susceptibility spectrum](image)

**Figure 2.9** Magnetic susceptibility spectrum [20].

The correspondence between magnetic susceptibility and volume of artifacts for Zr–Ag composites with different swaged ratios have been investigated [90]. The magnetic susceptibility of these swaged alloys decreases with increasing volume fraction of Ag. Fig. 2.11 shows the reversed configuration of the MRI (3 Tesla) artifacts for Zr and Ag. The size of artifacts decreases with the increasing volume fraction of Ag or with decreasing magnetic susceptibility. This case study shows the significant influence of magnetic susceptibility on
MRI artifacts. The use of a higher field strength MRI scanner can augment the artifacts, making the diagnosis much more challenging.

**Figure 2.10** Quantitative relationship between absolute magnetic susceptibility and the artifact volume under both fast spin echo (FSE) and gradient echo (GRE) conditions (reproduced with permission from Ref. [122] Copyright (2013), Elsevier).

**Figure 2.11** MRI (3 Tesla) results and 3-D renderings of the Zr, Ag, and Zr–Ag (vol.%) composites swaged at 64% (reproduced with permission from Ref. [90] Copyright (2017), Elsevier).

Table 2.9 provides the information of magnetic susceptibility of different metals [10, 14, 123-128]. The magnetic susceptibility of Zr is low \(1.3 \times 10^{-6} \text{cm}^3 \text{g}^{-1}\) [10, 14]) compared to other
conventional implant materials. Heyse et al. [129] analysed the MRI (1.5 Tesla) results of the implant-bone interface after total knee arthroplasty (TKA). Out of the 55 patients who experienced MRI after TKA, 27 patients had oxinium femoral implants and the rest 28 patients had conventional Co-Cr-Mo alloy femoral implants. Excellent visibility and reliability were obtained in Zr-based TKA than in Co-Cr-Mo one. Raphael et al. [130] did similar tests and observed 14 patients who had Zr knee prostheses and seven patients who had conventional Co-Cr knee prostheses. Similarly, Zr prostheses had greater reliability, inter-observer agreement, and less variability than Co-Cr knee prostheses. For this reason, Zr-based alloys such as Zr-Nb,[10, 82] Zr-Mo [31] and Zr-Cu [131] have been investigated.

Collings [132] suggested that magnetic susceptibility of an alloy (χ) relies on the constituent phases and the respective volume fractions and can be assessed as [132]

\[ \chi = V_{\alpha'} \cdot \chi_{\alpha'} + V_{\beta} \cdot \chi_{\beta} + V_{\omega} \cdot \chi_{\omega} \]  

(2.1)

where \( V_{\alpha'} \), \( V_{\beta} \), and \( V_{\omega} \) are volume fractions of the \( \alpha' \), \( \beta \) and \( \omega \) phases, respectively, and \( \chi_{\alpha'} \), \( \chi_{\beta} \), and \( \chi_{\omega} \) are the magnetic susceptibility of each corresponding phase.

Fig. 2.12a [10] shows the dependence of magnetic susceptibility on Nb content for Zr-Nb binary alloys. Two minimum points were observed, one at 3% Nb and the other at 20% Nb. This was due to the phase constituents of binary Zr-Nb alloys. The magnetic susceptibility values (χ) of the \( \alpha' \), \( \beta \), and \( \omega \) phases in Zr-based alloys follow the sequence of \( \chi_{\omega} < \chi_{\alpha'} < \chi_{\beta} \) [10].

Similar observations were made with binary Zr-Mo alloys,[31] as shown in Fig. 2.12b. A minimum magnetic susceptibility value was observed at 3 wt.% Mo. However, it levelled off from about 10 wt.% Mo. The magnetic susceptibility of Mo is lower than that of Zr but still the magnetic susceptibility increases with increasing Mo from 3% to 10% because of change in phase constituent. This shows the importance of controlling the phase constituent in a Zr-
based alloy, rather than the intrinsic magnetic susceptibility of each alloying element. Encouragingly, the magnetic susceptibility of large Zr-1Mo alloy ingots after HIP processing [133] is almost the same as that of small ingots [31]. This suggests that thick-section ingots can be made having low magnetic susceptibility [133]. Furthermore, cold swaging can be applied to Zr-1Mo alloy to achieve a combination of good mechanical properties and low magnetic susceptibility [134].

**Table 2.9 Magnetic Susceptibility of different metals.**

<table>
<thead>
<tr>
<th>Metal</th>
<th>Magnetic susceptibility $\times 10^{-6}$ (cm$^3$ g$^{-1}$)</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>3.2</td>
<td>[14]</td>
</tr>
<tr>
<td>Nb</td>
<td>2.24</td>
<td>[123, 124]</td>
</tr>
<tr>
<td>Zr</td>
<td>1.3</td>
<td>[10, 14]</td>
</tr>
<tr>
<td>Ta</td>
<td>0.85</td>
<td>[123, 125]</td>
</tr>
<tr>
<td>Mo</td>
<td>0.94</td>
<td>[123, 124]</td>
</tr>
<tr>
<td>Sn</td>
<td>-0.32</td>
<td>[126]</td>
</tr>
<tr>
<td>Si</td>
<td>-0.11</td>
<td>[126]</td>
</tr>
<tr>
<td>Ru</td>
<td>0.43</td>
<td>[127]</td>
</tr>
<tr>
<td>Au</td>
<td>-0.28</td>
<td>[126]</td>
</tr>
<tr>
<td>Cu</td>
<td>-0.09</td>
<td>[126]</td>
</tr>
<tr>
<td>Pd</td>
<td>5.23</td>
<td>[125]</td>
</tr>
<tr>
<td>Ag</td>
<td>-0.18</td>
<td>[126]</td>
</tr>
<tr>
<td>Hf</td>
<td>0.42</td>
<td>[128]</td>
</tr>
<tr>
<td>Bi</td>
<td>-1.34</td>
<td>[126]</td>
</tr>
</tbody>
</table>
Figure 2.12 Magnetic susceptibilities of as-cast (a) Zr-Nb alloys (reproduced with permission from Ref.[10] Copyright (2009), JIM Material), and (b) Zr-Mo alloys (reproduced with permission from Ref.[31] Copyright (2010), Elsevier).

Zhou et al. [52] investigated the magnetic susceptibility of Zr-1X alloys where X = Ti, Nb, Mo, Cu, Au, Pd, Ag, Ru, Hf and Bi. As shown in Fig. 2.13, except Zr-1Ag, all other binary alloys exhibited lower magnetic susceptibility than did CP Zr and Zr-1Cu, Zr-1Pt and Zr-1Ru.
exhibited similar low magnetic susceptibility. In fact, the magnetic susceptibility of Cu is close to that of human tissue and Cu possesses the lowest magnetic susceptibility by Table 2.9, but unfortunately Cu is not biocompatible for implant application [135].

![Figure 2.13 Magnetic susceptibility of Zr-1X (wt.%) alloys (reproduced with permission from Ref.[52] Copyright (2013), Elsevier).](image)

Until 2014 all the investigations conducted on magnetic susceptibility of Zr-based alloys dealt with only binary Zr-alloys. More recently, Pang et al. [86] designed a number of multicomponent Zr-based alloys (see Fig. 2.14) based on a cluster-plus-atom-glue model and investigated their mechanical properties and magnetic susceptibility. Among them, Zr-6.25Nb-3.13Mo-3.13Sn (No. 5) and Zr-6.25Nb-6.25Ti-3.13Mo-3.13Sn (No. 6) exhibited both low magnetic susceptibility values ($2.12 \times 10^{-6}$ and $2.13 \times 10^{-6}$ cm$^3$ g$^{-1}$ respectively) and low Young’s modulus values (77GPa and 79GPa respectively). They both fall in the metastable β-region (Fig. 2.14).
Tsuno et al. [136] investigated the magnetic susceptibility of as-cast Zr-Ta binary alloys. As shown in Table 2.10, there is a sudden decline in magnetic susceptibility in Group B, which contained ω-phase. This is similar to previous studies [10, 31]. In other words, in order to achieve low magnetic susceptibility, the presence of ω-phase is important. The ω-phase can be classified as isothermal ω, athermal ω and strain-induced ω-phases based on the formation process [22, 137]. The isothermal ω-phase in Ti alloys can form during heat treatment over the range of 100–500 °C as a very fine distribution of ellipsoidal or cuboidal particles [138-140].
Table 2.10 Magnetic susceptibility of as-cast Zr–Ta alloys [136].

<table>
<thead>
<tr>
<th>Alloy (wt.%)</th>
<th>Group-A</th>
<th>Group-B</th>
<th>Group-C</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Zr-10Ta</td>
<td>Zr-13Ta</td>
<td>Zr-15Ta</td>
</tr>
<tr>
<td>Magnetic susceptibility $\times 10^{-6}\text{(cm}^3\text{g}^{-1})$</td>
<td>1.4</td>
<td>1.05</td>
<td>1.02</td>
</tr>
<tr>
<td></td>
<td>Zr-18Ta</td>
<td>Zr-20Ta</td>
<td>Zr-25Ta</td>
</tr>
<tr>
<td></td>
<td>1.07</td>
<td>0.94</td>
<td>1.06</td>
</tr>
</tbody>
</table>
The athermal ω-phase can form martensitically by quenching from the β-phase field to room temperature [10, 21]. However, the athermal ω-phase can also form during isothermal ageing heat treatment. The strain-induced ω-phase is observed during plastic deformation as plate like precipitates [141-143]. More detailed information about the formation of ω-phase in Zr-based alloys and its effect on magnetic susceptibility can be found in Refs.[10, 31, 32].

Fig. 2.15 shows an example, where the magnetic susceptibility of cold-rolled Zr-14Nb decreased with increasing reduction ratio. This can be explained by the formation of the ω-phase after cold rolling at reduction ratio of 5% [32]. Similarly heat treatment of Zr-16Nb alloys assisted in the formation of the ω-phase which decreased the magnetic susceptibility. Suyalatu et al. [31] reported that Zr-3Mo, containing α and β phases, possessed higher magnetic susceptibility than Zr-3Mo containing ω-phase by aging at 700°C.

2.7 Shape memory effect and super-elasticity of Zr-based alloys

Ni-free shape memory alloys (SMAs) are more attractive than Nitinol, which contains approximately equal atomic percentages of Ti and Ni and has been widely used in implant fabrication [144]. Ni can lead to cytotoxicity [110, 145]. Literature suggests that αʺ-martensite transformation provides promising shape memory effect and super-elasticity [37, 38]. αʺ-martensite transformation can occur in Zr-based alloys as shown in Table 2.11 [33, 34]. This means that these Zr-based alloys have the potential to show the shape memory effect.
Figure 2.15 Mass magnetic susceptibility of cold-rolled Zr–14Nb and Zr as a function of reduction ratio in thickness (reproduced with permission from Ref.[32] Copyright (2013), Elsevier).

Table 2.11 Zr-based alloys and their $\alpha''$ martensite phase.

<table>
<thead>
<tr>
<th>Alloy (at.%)</th>
<th>Phases</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-48Ti-4Nb[34]</td>
<td>$\alpha''$, $\alpha'$, $\beta$</td>
</tr>
<tr>
<td>Zr-47Ti-6Nb[34]</td>
<td>$\beta$, $\alpha''$</td>
</tr>
<tr>
<td>Zr-48Ti-1Mo-3Sn [33]</td>
<td>$\alpha''$</td>
</tr>
<tr>
<td>Zr-48.5Ti-1Mo-2Sn [33]</td>
<td>$\alpha''$</td>
</tr>
</tbody>
</table>

Li et al. [146] reported the shape memory effect of the Ti-50Zr (at.%) binary alloy whose tensile stress-strain curve is shown in Fig. 2.16a. At high temperature, this alloy can experience a reversible martensitic transformation between hcp $\alpha'$-martensite and $\beta$-(parent) phase, which results in a maximum shape memory strain of 1.4% and good plasticity. The
shape memory strain of Zr-Ti based alloys can be improved by alloying and applying proper thermo-mechanical treatments.

Recently Ijaz et al. [33] investigated the shape memory behaviour of (Zr-Ti)-(1-2)Mo-(2-4)Sn (at.%). The results shown in Fig. 2.16b indicate that (Zr-Ti)-1.5Mo-2Sn (at.%) possessed shape memory effect while (Zr-Ti)-1.5Mo-3Sn and (Ti-Zr)-2Mo-2Sn (at.%) exhibited super-elasticity. The authors suggested that (Zr-Ti)–1.5Mo–3Sn can exhibit excellent superelastic properties with recovery strain up to 7% at 1073K. This happens because of their strong \{001\}_\beta <110>\beta recrystallization texture. The shape memory behaviour of Zr-based alloys is expected to receive increasing attention in future due to their Ni-free nature.

2.8 Recent application as biomaterials

An oxidized Zr-based alloy (Zr-2.5Nb, wt.%), known as oxinium, has been used in total knee replacement (TKR) and total hip replacement (THR) procedures for more than a decade. This implant material was developed in 1997 by Smith & Nephew for TKR, which was first used for THR in 2002 [11] as shown in Fig. 2.17a[71] and b [147]. It was claimed that the life of an oxinium implant was about 20-25 years, [71, 148] about 10 years longer than that of Co-Cr alloys and polyethylene implants.
Figure 2.16 Tensile stress-strain curves of (a) Ti-50Zr (at.%.) at room temperature (reproduced with permission from Ref.[146] Copyright (2011), Elsevier) and (b) (Zr-Ti)–(1.5,2)Mo–(2–4)Sn (at.%) alloys (reproduced with permission from Ref.[33] Copyright (2015), Elsevier).
The development of oxinium was inspired by the property of zirconia (ZrO$_2$, density: 5.68 g/cm$^3$; melting point: 2715°C; hardness: 12 GPa [149]), which has a tooth-like colour, suitable mechanical properties, and excellent biocompatibility [150]. In addition, it is inert in body fluids with negligible ion release compared with other metallic implants [151]. Besides, fine zirconium particles released from the implant surface have less inflammatory response and bone resorption than Ti particles, which suggests superior biocompatibility. As a result, a variety of commercially available zirconia-based dental implant systems have been developed, including the Sigma implant, the Z-systems, the ReImplant system, the White Sky system, the Goei system, the Konus system, CeraRoot system and the Ziterion system [151]. Fig. 2.17c, d and e show a few such examples.
Inspired by the attractive properties of ZrO$_2$, Smith & Nephew introduced a thick layer of Zr oxide (4-6 μm) on Zr-2.5Nb(wt.%) alloy (i.e. R60901, see Table 2.2) implants by heat treatment at 773K in air [153]. Fig. 2.18 shows the microstructure of the resultant cross...
section and the typical Cathodoluminescence (CL) intensity profile of the oxinium femoral component [154]. The Cathodoluminescence intensity is raised by the presence of the O content and vice versa [155, 156]. This ZrO₂ layer offers high hardens and therefore excellent wear resistance and high hardness compared to Co-Cr alloys and Ti-alloys. In addition, it generates a relatively high compressive stress, which contributes to the adherence to the base material [157]. As a result, oxidized Zr femoral heads have proved to be more wear resistant than Co-Cr heads in vitro [70]. In a rabbit tibia model, oxidized Zr-alloys exhibited bone responses similar to, or better than, that Co-Cr alloys [9].

Aside from this oxinium, other Zr-based alloys, which are patented for biomedical application but not yet in clinical application, include Zr-(18.46-18.79)Nb-(0.47-1.1)Si (wt.%)[158] Zr-(19.5-20.5)Nb-(0.1-1.5)Ti (wt.%)[159] Zr-(16-50)Ta (wt.%)[160] and Ti-(10-20)Nb-(1-50)Zr (wt.%) [161]. In addition, there are Zr-based BMGs, which are patented for biomedical application such as Zr₅₀₋ₓ Al₁₀ Cu₄₀ Reₓ (at.%) (RE = Y or La or Ce or Nd, Sm, Gd or Dy or Ho or Er, Tm or Lu; x is 0 < x ≤10)[162] (60-70)Zr-25Ti-2.5Nb-7.5Al-15Fe-15Cu-10Ag-10Pd,[163] Zr₄₈ Cu₄₅₋ₓ Alₓ Agₙ, (1 < x <10),[164] (Zrₓ Tiₙ)₁₋ₓ (Beₓ Cₓ₁₋ₓ)ₓ (X = Y/Co/ Fe/ Cr/ Mo/ Mg/ Al/ Hf/ Ta/ Nb/ V; c = 25 at.% ; z = 20-25 at.% ; a: b = 1.16),[165] [(Zrₓ Cu₁₀₀₋ₓ)ₐ(Eₓ G₁₀₀₋ₓ)₁₀₀₋ₓ]₁₀₀₋ₓZᵧ, (70≤a≤90, x≥50, y>0, and 0≤b≤6) [166].

2.9 The d-electron theory for Zr-based alloys

In order to overcome the time-consuming trial-and-error alloy design methods, Morinaga et al. [167] developed a theoretical method for alloy design known as the ‘d-electron theory’, based on the DV-Xα molecular orbital calculations of electronic structures. The approach was first used to predict the phase stability and elastic modulus of Ti-alloys through two parameters Bₒ and Mₓ ,[168] where Bₒ is the bond order which displays the covalent bond strength between Ti and other alloying element M, and Mₓ is the d-orbital energy level which
correlates electronegativity and the metallic radius of the elements. Each alloying element has a specific set of $B_o$ and $M_d$ values, and the compositional average of the $B_o$ and $M_d$ values can be obtained by using the following formula [169]

$$
\overline{B_o} = \sum X_i(B_o)_i 
$$

$$
\overline{M_d} = \sum X_i(M_d)_i
$$

where $X_i$ is the atomic fraction of a given element. A $\overline{B_o}$-$\overline{M_d}$ diagram can then be constructed by taking the compositional average of the $B_o$ and $M_d$ values of each element in the alloy.

Existing alloys are used to determine the phase boundary of the $\overline{B_o}$-$\overline{M_d}$ diagram. In the diagram constructed for Ti-alloys (Fig. 2.19), there are three regions, i.e., $\alpha$, $\beta$ and $\alpha+\beta$, where the $\beta$-phase field is clearly isolated from the $\beta+\omega$-phase. The $\beta/\beta+ \omega$-phase region is in the neighbourhood of the twin or slip boundary. The $\alpha$-phase coincides with the $\beta$-and/or $\omega$-phase at room temperature (RT) below the boundary of $M_s = RT$ ($M_s$: martensitic transformation start temperature). Below the boundary of $M_f = RT$ ($M_f$: martensitic transformation finish temperature), the martensite phase can usually be found in the alloy at RT. $\beta$-phase is metastable around the $\alpha+\beta/\beta$ boundary and can transform into omega phase ($\omega$) and martensitic phase ($\alpha'$, $\alpha''$) by water quenching [170].
**Figure 2.18** A scanning electron micrograph of the cross-section of the oxinium™ femoral component (a), and a typical cathodoluminescence overall intensity (at 500 nm) profile (b).

The oxygen profile detected on oxinium™, according to glow discharge optical emission spectroscopy, is also plotted (gray-dotted line) for a qualitative comparison (reproduced with permission from Ref.[154] Copyright (2014), Elsevier).
The $d$-electron theory has proved to be effective in the design of new Ti implant alloys. However, until now no report has been found on using the $d$-electron theory to design Zr-based implant alloys. Table 2.12 lists the $B_o$ and $M_d$ values for different alloying elements in Zr [172].

A $\overline{B}_o - \overline{M}_d$ diagram has been plotted for Zr-X binary system, [172] as shown in Fig. 2.20a, to understand the alloying effect of each element. The $\beta$-stabilizing isomorphous elements and
the eutectoid elements are directed towards the leftward direction while the neutral element, Hf, is directed towards the upward and rightward direction.

The data available from literature on Zr-based alloys have been used to develop an informative \( \overline{B}_o - \overline{M}_d \) diagram (Fig. 2.20b) using the \( B_o \) and \( M_d \) values listed in Table 2.12. Similarly, Fig. 2.20b shows that there exist three regions for Zr-based alloys (\( \alpha \), \( \beta \), and \( \alpha+\beta \)) and the stability of the \( \beta \)-phase depends on the amount of the \( \beta \)-stabilizing elements. The \( \beta \)-type alloys are usually deformed by either the slip or twinning mechanism based on the phase stability of these alloys [168, 173]. The twinning mechanism will change to the slip mechanism when the stability of the \( \beta \)-phase increases [171]. This is because both martensitic and athermal \( \omega \)-phase transformations are significantly restrained with increasing \( \beta \)-stabilizing elements [173]. In this diagram, single \( \beta \)-phase and single \( \alpha \)-phase are clearly separated from the (\( \alpha+\beta \))-phase region. However, slip and twin boundaries need to be identified with the assistance of experimental data. In that regard, detailed experimental research needs to be carried out to establish the relationship between phase stability and deformation behaviour for Zr-based alloys. As the first \( \overline{B}_o - \overline{M}_d \) diagram for Zr-alloys, Fig. 2.20b can be used to assist in the design of low modulus Zr-based alloys in the future.
Figure 2.20 A $B_o-M_d$ diagram constructed for (a) binary Zr-X alloys (reproduced with permission from Ref. [172] Copyright (2006), Atomic Energy Society of Japan), and (b) Zr and its alloys from the literature data to show the $\alpha$-zone, [52, 82, 84, 85] $\beta$-zone [7, 82, 83, 85, 86, 91] and ($\alpha+\beta$)-zone [82, 85, 86, 91].
2.10 Future directions for Zr-alloys for implant applications

2.10.1 Alloy design

The alloy design approaches developed for Ti-alloys can be used for the design of Zr-based alloys for implant application. For instance, the $d$-electron theory is well established today for Ti-based alloys. However, no use of this theory has been reported as yet for design of Zr-based alloys. This is expected to change soon. The use of Zircobase, a thermodynamic database [174] for Zr-alloys, coupled with Thermo-Calc software can predict thermodynamic and metallurgical properties of Zr-based alloys (e.g., formation enthalpies, phase transformation temperatures, solubility limits, and chemical compositions of second phase precipitates). It can be a useful thermodynamic tool in the design of Zr-based alloys. In addition, since additive manufacturing (AM) has become an increasingly important manufacture method for orthopaedic implants, it is necessary for any new Zr alloy design to also take into account the influence of the AM process on the selection of alloying elements and evolution of microstructures.

2.10.2 Low magnetic susceptibility

MRI, a non-invasive diagnostic tool, provides precise images with excellent contrast details of soft tissue and anatomic structures. This diagnostic technique is continually growing by offering much improved resolutions (initially from ~4 mm to below 0.5 mm today) to enable the study of more body parts, including the ability to take images of the structural properties and/or functions of brain at the cellular scale or even at the cortical columns level [175]. These improvements depend largely on the use of intense magnetic fields [175]. However, metal implants can get magnetized in an intense MRI magnetic field, which can produce low quality images leading to wrong diagnostics. In this regard, Zr-alloys with low magnetic susceptibility (of the second kind in Table 2.8) are essential for such biomedical applications.
As pointed out earlier, in order to achieve low magnetic susceptibility, the presence of \( \omega \)-phase is necessary, although it leads to increased modulus. Research should focus on the development of new Zr-based alloys with sufficiently low magnetic susceptibility while the increased modulus could be addressed separately, e.g., through AM of strong Zr-alloy lattices [176].

**Table 2.12** List of \( B_o \) and \( M_d \) values for different alloying elements M in hcp Zr and bcc Zr [172].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Bond order, ( B_o )</th>
<th>Bond order, ( B_o )</th>
<th>d orbital energy level, ( M_d ) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>hcp Zr</td>
<td>bcc Zr</td>
<td></td>
</tr>
<tr>
<td>3d</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti</td>
<td>3.48</td>
<td>4.01</td>
<td>2.50</td>
</tr>
<tr>
<td>V</td>
<td>3.51</td>
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<td>Other</td>
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</tr>
</tbody>
</table>
2.10.3 Low modulus

The $\overline{B}_o-M_d$ diagram has worked efficiently for design of low modulus Ti-based alloys. It is expected that the $\overline{B}_o-M_d$ diagram constructed for Zr-alloys as shown in Fig. 2.20b will work similarly satisfactorily as well for the design of low modulus Zr-based alloys subject to necessary improvements. In order to improve this $\overline{B}_o-M_d$ diagram, more Zr-based alloys should be investigated for identification of the metastable β-region, $M_s = RT$ line and $M_f = RT$ line. Besides, it is necessary to develop an empirical Molybdenum Equivalent (Mo-Eq) parameter for Zr-based alloys in order to easily gauge the β-phase stability in Zr-based alloys.

2.10.4 Wear resistance

Wear resistance is another critical property for many implant applications. Wear debris can create severe inflammatory response in a biological environment, which can lead to bone failure [78, 177]. Also, accelerated wear can take place under excessive loading [178]. For example, the consequence of accumulated wear of artificial hip implants after 10–15 years of implantation often lead to revision surgery [179]. However, the oxidized Zr-based alloys, oxinium, can achieve outstanding wear resistance, similar to that of ceramic surfaces due to their oxide layer. For instance, oxinium exhibited 4900 times less volumetric wear and 640 times less deep scratches than traditional Co-Cr alloys in laboratory wear testing [180]. In fact, owing to the poor wear resistance of Ti-alloys compared to Co-Cr alloys,[181] it is essential to modify their surfaces for many implant applications. In this regard, oxidized Zr-based alloys offer an ideal solution for implant applications.

2.10.5 Porous Zr-alloys

Porous Ti-alloys [182, 183] including Ti lattices [184-186] have already found wide application as bone implants. In general, porous structures can eliminate the bone-implant
stiffness mismatch and also enhance bone-implant fixation due to bone ingrowth into the pores [13]. In addition, they can offer an effective pathway to insert and deliver antibiotic (through porous structures) to control infections [187]. Up till now, porous Zr-alloys have not received much attention because of the limited overall applications of Zr-alloys as implant materials. As a group of emerging implant alloys, porous Zr-alloys are expected to find significant applications in the future, similar to porous Ti implants. In principle, the methods used to produce porous biomedical Ti-alloys are all applicable to Zr-alloys, including sintering, templating, solidification-based foaming processes, additive manufacturing, dealloying and the integration of them. In particular, dealloying can be used to produce pore size ranging from about 10 nm to a few hundred micrometres [188] in various product forms such as ribbon, rod and strip [189]. In contrast, AM offers unlimited freedom in porous structures but the minimum pore size is limited to ~250 µm.

2.11 Knowledge gaps identified and concluding remarks

This chapter has reviewed the major characteristics of CP Zr and Zr-alloys as implant materials in the context of both the current 1.5 Tesla MRI and future high field strength (> 3 Tesla) MRI diagnostics. These include the phase transformations in Zr and its alloys, their biocompatibility in both bulk and powder forms, effect of alloying elements, microstructures and mechanical properties, magnetic susceptibility, shape memory effect, super-elasticity, and current applications as implant alloys. The importance of the $d$-electron theory for design of new Zr-based implant alloys is highlighted through a newly constructed $\overline{B_o-M_d}$ diagram using the data from literature. Future research directions are suggested from an alloy performance perspective. This chapter also identifies the research gaps of this study and they are as follows:
• Less effort has been put on the development of Zr-based biomedical alloys whereas Zr-based alloys can be potential implant material because of their good biocompatibility, excellent mechanical properties along with low magnetic susceptibilities.

• There is a lack of understanding on how various factors affect the elastic modulus of alloys. This indicates the necessity of studying the effect of various factors on elastic modulus of alloys and to develop a method based on the understanding to design alloys with low elastic modulus.

• The conventional Mo-Eq expression quantifies the β-stabilizing effect of all the β-stabilizing elements excluding Zr. However, Zr is not a neutral element and it acts as a β-stabilizing element with the presence of other β-stabilizing element (i.e. Nb, Mo, Ta) in Ti-based alloys. The β-stabilizing effect of Zr on other Ti-based alloys needs to be investigated.

Based on the developments to date, it can be concluded that Zr-alloys offer unique opportunities for researchers to develop a novel class of orthopaedic implant alloys that can meet all major desired requirements, including biocompatibility, strength, ductility, modulus, wear resistance, and magnetic susceptibility for high field strength MRI diagnostics. This is due to the unique attributes of Zr, such as: (i) Zr is biocompatible in both bulk and powder forms (Ti exhibits slight cytotoxicity in powder form); (ii) its oxidized surface (zirconia) is more resistant to bacterial adhesion than titania as an intrinsic bone-like apatite layer forms on its surface in body environments; (iii) its magnetic susceptibility is about half of that of CP Ti and one thirtieth to one sixtieth of that of stainless steel, which can be further lowered by appropriate alloying; and (iv) its oxidized surface exhibits 4900 times less volumetric wear and 640 times less deep scratches than the current most wear resistant Co-Cr implant alloys.

Along with the drive for use of high magnetic field strength MRI systems and inspired by the
demonstrated MRI advantages of Zr-alloys over other metallic implants, we forecast that the
next decade will witness significant developments in Zr-based alloys for implant
applications with the assistance of both the d-electron theory and the Zircobase
thermodynamic database.

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Chapter 3 Alloy design principles and methodology for titanium and zirconium alloys

3.1 Introduction

The replacement of and repair to injured bones with artificial implant materials have now become a commonly used procedure to provide relief in pain and disability. Moreover, the aging population has increased the demand for implant materials. Implant failures are seldom triggered by structural material failures, such as metal implant fatigue fracture or fast destruction of a polyethylene cup [1]. Rather, one of the most probable causes of implant failures is the aseptic loosening of the implant [1]. This pathogenesis of the aseptic loosening can be caused by mechanical [2], biological [2], and magnetic factors. Mechanical variables include comparative micromotion between the implant and the host bone, stress shielding effect and wear-induced material loss from the different implant components [1]. Biological variables include biocompatibility, particle wear reaction or resistance to corrosion [1]. Magnetic factor includes the highly desired low magnetic susceptibility, without which an implant material can get magnetized to the immense magnetic field of MRI (Magnetic Resonance Imaging) machine [3, 4]. To avoid such undesirable events, it is desirable to develop implant alloys with excellent biocompatibility, low elastic modulus and low magnetic susceptibility.

Ti and its alloys always have proved to be important biomaterials due to their excellent biocompatibility, good corrosion resistance, and good mechanical properties. To avoid the stress shielding effect, the idea of using metastable β-Ti alloys has attracted tremendous attention to researchers. A wide variety of Ti-based alloys have been developed as biomaterials over the last few decades [5]. Many were developed based the on trial and error method, which is time-consuming and not cost-effective. Moreover, in order to focus on low
elastic modulus, sometimes the importance of the low magnetic susceptibility is overlooked. Thus, a more comprehensive theoretical approach is needed to develop implant alloys.

In this chapter, different types of theoretical alloy design criteria (d-electron theory, $e/\alpha$ ratio, Mo-Eq approach, and first principle study) are broadly discussed. An improved approach for the design of Ti-Nb-Zr alloys, is discussed by combining the d-electron theory and the $e/\alpha$ ratio and considering other phase stability parameters.

3.2 Alloy design methods for Titanium and Zirconium alloys

3.2.1 The d-electron theory

Ti-based alloys have long received special attention towards bio-implant applications because of their super-elasticity, shape memory effect, low elastic modulus, bio-corrosion resistance, and their excellent biocompatibility. Extensive investigations have been carried out to develop β-type Ti alloys with low elastic modulus. The development of new alloys by using the trial-and-error method was popular until Morinaga et al. [6] developed the d-electron theory, which was based on DV-Xα molecular orbital calculations of electronic structures. This theory describes the potential relationship between phase stability and elastic properties of Ti alloys through two electronic properties, bond order, $B_o$, and d orbital energy level, $M_d$ [7] as shown in Fig. 3.1[8]. From Fig. 3.1, $B_o$ can be defined as overlapping of the electron clouds between the alloying element (M) and mother metal (X), which is a measure of the covalent bond strength between alloying elements. A high $B_o$ value indicates the stronger chemical bond between the alloying element and the mother metal [8].
Figure 3.1 (a) bond order, $B_o$ and (b) $d$-orbital energy level, $M_d$ [8].

In an M-X molecule, both the bonding level at low energy state and the antibonding level at high energy state are developed by the combination of the $d$-orbitals of isolated M and X atoms. If an M atom possess higher $d$ level than that of the X atom, the electrons transfer from M to X to release the energy. Thus, M and X atoms exhibit the positive and negative effective charges, respectively. This suggests that the order of charge transfer depends on the energy level of the atoms and it is linked to electronegativity [9]. An element with higher electronegativity should have lower $M_d$ value. The $M_d$ value also correlates with the atomic radius. The atomic radius of an element corresponds to the average radius of the $d$-orbital of that element. As a result, with a larger atomic radius, the average distance between $d$-electrons and the nucleus increases, which weakens the Coulomb force operating between them. Thus, an alloy with a high $M_d$ value should have a high atomic radius [8]. Table 3.1 represents the $B_o$ and $M_d$ values for different alloying elements X in hcp Ti, Zr and bcc Ti, Zr. By taking these $B_o$ and $M_d$, the compositional average of $B_o$ and $M_d$ values can be calculated using the following formula [10]

$$
\overline{B_o} = \sum X_i(B_o)_i
$$

(3.1)

$$
\overline{M_d} = \sum X_i(M_d)_i
$$

(3.2)
where, \( X_i \), \( (B_o)_i \), and \( (M_d)_i \) are the atomic fractions, bond order and \( d \)-orbital energy level of that given element, respectively. A \( B_o - M_d \) diagram can then be constructed by taking the compositional average of the \( B_o \) and \( M_d \) values of each element in the titanium alloy. Abdel et al. [11] reported that elastic modulus would decrease along the \( \beta/\beta+\omega \) phase boundary with increasing \( B_o \) and \( M_d \) values, as shown in Fig. 3.2.

To understand the alloying effect of each element, a \( B_o - M_d \) diagram is constructed in Fig. 3.3 for Ti-X and Zr-X binary systems. Fig. 3.3 clearly shows that the \( \beta \)-stabilizing isomorphous elements (i.e., Nb, Ta) and the eutectoid elements are directed towards upward and leftward, respectively. The alloying vectors of Si and Al are directed to downward with

**Figure 3.2** \( B_o - M_d \) diagram [11].

---

**Table 3.2**

<table>
<thead>
<tr>
<th>Element Composition</th>
<th>Bond Order ( B_o ) Range</th>
<th>Orbital Energy Level ( M_d ) Range</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-7.5Mo</td>
<td>2.86 - 2.90</td>
<td>2.45 - 2.50</td>
</tr>
<tr>
<td>Ti-14Mo</td>
<td>2.88 - 2.92</td>
<td>2.47 - 2.52</td>
</tr>
<tr>
<td>Ti-15Mo</td>
<td>2.90 - 2.94</td>
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</tr>
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<td>2.47 - 2.52</td>
</tr>
<tr>
<td>Ti-27.5Nb</td>
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<td>2.47 - 2.52</td>
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<td>2.47 - 2.52</td>
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<td>2.88 - 2.92</td>
<td>2.47 - 2.52</td>
</tr>
<tr>
<td>Ti-80Ta</td>
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<td>2.47 - 2.52</td>
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</table>
increasing composition of Si and Al, which indicates that Si and Al are $\alpha$-stabilizing elements. On the other hand, neutral elements (i.e., Zr, Hf) are heading towards an upward and rightward direction, which is completely different from the other elements. Fig. 3.3 suggests that the same alloying element, X, shows a similar stability effect on both Ti and Zr.

The $d$-electron theory can also help to develop corrosion-resistant Ti alloys. Morishita et al. [12] found that $\overline{B}_o$ could be used as an essential parameter to predict corrosion resistance. To understand the relationship between the electronic parameters and corrosion resistance, sets of polarization curves were plotted at 343K in both 10 wt. % H$_2$SO$_4$ and 10 wt.% HCl solutions with a variety of binary Ti-M alloys (M 5 Al, V, Cr, Fe, Co, Ni, Zr, Nb, Mo, Hf, and Ta) [12]. From the polarization curve, it is confirmed that Ti alloys with higher $\overline{B}_o$ values exhibit lower critical anodic current density, which results in higher corrosion resistance even in a 10 wt. % H$_2$SO$_4$ solution at 343K, as shown in Fig. 3.4 [8]. A similar observation was also found in a 10 wt.% HCl solution at 343K [12]. Thus, the $d$-electron theory can help to predict the corrosion resistance of Ti alloys in the acid environments.
Table 3.1 List of $B_o$ and $M_d$ values for different alloying elements X in hcp Ti and Zr and bcc Ti and Zr [11, 13].

<table>
<thead>
<tr>
<th>Elements</th>
<th>Ti</th>
<th>Zr</th>
<th>Hcp Zr</th>
<th>Bcc Zr</th>
<th>d orbital energy level, $M_d$ (eV)</th>
</tr>
</thead>
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<td>Bond order, $B_o$</td>
<td>d orbital energy level, $M_d$ (eV)</td>
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<td></td>
<td>hcp Ti</td>
<td>bcc Ti</td>
<td></td>
<td>Hcp Zr</td>
<td>Bcc Zr</td>
</tr>
<tr>
<td>3d</td>
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<td></td>
<td></td>
<td></td>
<td></td>
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</tr>
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</table>
Figure 3.3 A $\overline{B_o-M_d}$ diagram constructed for (a) binary Ti-X alloys, (b) binary Zr-X alloys [13].
Figure 3.4 Relationship between corrosion rate and $\overline{B_0}$ for (a) bcc and (b) hcp Ti-M binary alloys in 10% H$_2$SO$_4$ at 343K [8].
You et al. [14] proposed a new parameter, interatomic bonding force, by combining Coulomb’s law and the $d$-electron theory, which can be estimated by

$$\text{Bonding force} \propto \frac{Z_{\text{eff}} \cdot B_o}{M_d^2}$$

(3.3)

Where $\overline{Z_{\text{eff}}}$, $\overline{B_o}$, and $\overline{M_d}$ are the compositional average values of $Z_{\text{eff}}$, $B_o$ and $M_d$ in a Ti alloy, respectively. $Z_{\text{eff}}$ is the effective nuclei charges felt by each valence electron which can be calculated by the following equation:

$$Z_{\text{eff}} = Z - s$$

(3.4)

where $Z$ is the atomic number and $s$ is the Slater shielding constant [15]. It is expected that if an alloy has lower bonding force, it will have low elastic modulus.

Until now several promising Ti-based alloys have been developed for the biomedical application using the $d$-electron theory. For example, the alloy Ti-13\%V-3\%Cr-2\%Nb-(2-3)\%Al [16] designed using the $\overline{B_o}$-$\overline{M_d}$ diagram, has higher tensile strength and fracture toughness than the commercial alloy, Ti-15\%V-3\%Cr-3\%Sn-3\%Al (Ti-15-3-3-3). Niinomi [17] has developed a new $\beta$-type Ti-alloy Ti-29Nb-13Ta-4.6Zr (wt.%), which has very low elastic modulus (50 GPa). Saito et al. [18] have invented the gum metals (Ti-12Ta-9Nb-3V-6Zr-1.5O and Ti-23Nb-0.7Ta-2Zr-1.2O(at.%)), which sit near the bioimplant alloy Ti-29Nb-13Ta-4.6Zr (wt.%) ($\overline{B_o}$ and $\overline{M_d}$ value of 2.87 and 2.45 respectively) on the $\overline{B_o}$-$\overline{M_d}$ diagram. These gum metals show superelasticity and ultra-low elastic modulus with their other super properties when they are 90\% cold rolled.

### 3.2.2 The $e/\alpha$ ratio

Apart from the parameters of $B_o$, $M_d$ and the bonding force, another critical parameter to consider in alloy design is the electron to atom ratio ($e/\alpha$ ratio) [11]. Literature suggests that
\( e/\alpha \) can affect the elastic modulus. You et al. [19] reported that an \( e/\alpha \) range from 4.06-4.17 is required to obtain low elastic modulus for the Ti-Nb-Zr alloy system. However, Ozan et al. [20] contradicted this and suggested a range between 4.18 and 4.25. On the other hand, Hou et al. [21] reported that non-linear elastic behaviour of the alloy is not dependent on \( e/\alpha \) ratio. Taking these results together suggests that there are other factors that affect the elastic modulus. Fig. 3.5 [22] explains the schematic relationship between the elastic modulus and \( e/\alpha \) ratio for most of the Ti-TM (TM: \( d \)-electron rich transition metal element) binary alloys. 

\( \beta \)-phase becomes unstable with decreasing solute concentration at low \( e/\alpha \). The formation of \( \alpha \) and \( \alpha' \) martensite raises the elastic modulus. On the other hand, \( \beta \)-phase is stabilized at high \( e/\alpha \), and the elastic modulus increases with the increasing solute content. The observed peak in the middle could be attributed to the formation of the metastable \( \omega \) phase. The lowest elastic modulus of the \( \beta \) phase can only be obtained (the dotted line in Fig. 3.5) when proper alloying element can suppress the \( \omega \)-phase.
Laheurte et al. [23] addressed the expected water quenched microstructure with respect to $e/\alpha$ ratio for Ti alloys. Fig. 3.6 (adapted and redrawn from Ref.[23]) clearly shows that the $\beta$-phase becomes more stable with increasing value of $e/\alpha$ ratio. When $e/\alpha$ value is 4.2, the $\beta$ phase becomes sufficiently stable for Ti alloys.

**Figure 3.5** The elastic modulus vs. electron to atom ratio [22].
3.2.3 The conventional Mo-Eq approach

β-titanium (β-Ti) alloys are one of the most promising metallic biomaterials for orthopaedic applications. Ti alloys that contain sufficient β-stabilizing element(s) to enable the β-phase to be retained in a metastable condition by water quenching are known as β-Ti alloys [24]. To understand the stability of β-Ti alloy, Mo Equivalent (Mo-Eq) can be used as a general guideline. Molybdenum is well known as a β-stabilizing element in titanium alloys. The critical minimum molybdenum content required to retain 100% β in Ti-Mo binary alloys on water quenching is at 10% for small samples. By arbitrarily using this critical minimum molybdenum content as a point of reference, Mo Equivalent (Mo-Eq) was defined to gauge the β-phase stability on water quenching.

E. K. Molchanova proposed the concept of the Mo Equivalence (Mo-Eq) in "Phase Diagrams of Titanium Alloys" (Figure 193 and Figure 194, p. 158) [25], which was translated from "Atlas Diagramm Sostoyaniya Titanovykh Splavov" (Israel Program for Scientific Translations, Jerusalem, 1965). Boyer et al. [26] proposed the Mo equivalence equation for

![Graph showing expected phases in Ti alloys after water quenching with respect to \( \epsilon/a \) (Adapted and redrawn from Ref.[23]).]
Ti alloys in the well-known *Materials Properties Handbook: Titanium Alloys* (1994) using the data shown in Figure 193 of Ref. [25] in the following form:

\[
(Mo\text{-Eq})^{\text{Molchanova}} = 1.0(\%\text{Mo}) + 0.2(\%\text{Ta}) + 0.28(\%\text{Nb}) + 0.4(\%\text{W}) + 0.67(\%\text{V}) + \\
1.25(\%\text{Cr}) + 1.25(\%\text{Ni}) + 1.7(\%\text{Mn}) + 1.7(\%\text{Co}) + 2.5(\%\text{Fe})
\]  

(3.5)

Bania [27] then expressed the Mo-Eq concept in the form of Eq. (2). In this equation, the prefix coefficient of each β-stabilizer is defined by the ratio of the β_c value of Mo (i.e., 10 wt.%) to that of respective β-stabilizer. Al is also added to this equation to show its α-stabilizing effect.

\[
(Mo\text{-Eq})^{\text{Bania}} = 1.0(\%\text{Mo}) + 0.67(\%\text{V}) + 0.44(\%\text{W}) + 0.28(\%\text{Nb}) + 0.22(\%\text{Ta}) + \\
2.9(\%\text{Fe}) + 1.6(\%\text{Cr}) + 0.77(\%\text{Cu}) + 1.11(\%\text{Ni}) + 1.43(\%\text{Co}) + 1.54(\%\text{Mn}) - 1.0(\%\text{Al})
\]  

(3.6)

Eq. (2) overrides the original Eq. (1) as a commonly used expression to estimate the Mo-Eq of a Ti alloy. Apart from Eq. (2), three other expressions for Mo-Eq have also been proposed [28-30], namely

\[
(Mo\text{-Eq})^{\text{Zhou}} = 1.0(\%\text{Mo}) + 0.74(\%\text{V}) + 0.5(\%\text{W}) + 0.39(\%\text{Nb}) + 0.28(\%\text{Ta}) + 2.2(\%\text{Fe}) + \\
1.69(\%\text{Cr}) + 0.85(\%\text{Cu}) + 1.22(\%\text{Ni}) + 1.57(\%\text{Co}) + 1.69(\%\text{Mn})
\]  

(3.7)

\[
(Mo\text{-Eq})^{\text{Mo}} = 1.0(\%\text{Mo}) + 0.73(\%\text{V}) + 0.5(\%\text{W}) + 0.31(\%\text{Nb}) + 0.24(\%\text{Ta}) + 2(\%\text{Fe}) + \\
1.69(\%\text{Cr}) + 1.29(\%\text{Ni}) + 1.16(\%\text{Co}) + 1.69(\%\text{Mn})
\]  

(3.8)

and

\[
(Mo\text{-Eq})^{\text{Wang}} = 1.0(\%\text{Mo}) + 1.25(\%\text{V}) + 0.59(\%\text{W}) + 0.28(\%\text{Nb}) + 0.22(\%\text{Ta}) + \\
1.93(\%\text{Fe}) + 1.84(\%\text{Cr}) + 1.5(\%\text{Cu}) + 2.46(\%\text{Ni}) + 2.67(\%\text{Co}) + 2.26(\%\text{Mn}) + 3.01(\%\text{Si}) + \\
0.3(\%\text{Sn}) + 0.47(\%\text{Zr}) - 1.47(\%\text{Al})
\]  

(3.9)
Equations (3.5) to (3.8) are based on experimental data while Eq. (3.9) is derived from phase diagrams. Table 3.2 summarises the (Mo-Eq) coefficient of each element and the $\beta_c$ value defined by Molchanova [17], Bania [27], Zhou [28], and Mo [29] and the (Mo-Eq) coefficient of each element and the slope of the $[\beta/(\alpha + \beta)]$ phase boundary from the phase diagrams of various binary Ti-X alloys used by Wang et al. [30] to determine the corresponding Mo-Eq coefficients. Equations (3.5) to (3.8) are substantially similar to each other, which all treated Zr as a neutral element and therefore excluded it. However, Zr was included in Eq. (3.9) as a $\beta$-stabilizer with a significant coefficient of 0.47. Such a large discrepancy resulted from the use of a different theoretical approach to obtaining the coefficient of Mo-Eq [30]. Wang et al. [30] has suggested that the slope of the $[\beta/(\alpha + \beta)]$ phase-boundary line, from pure Ti to some particular point, such as the monotectoid, eutectoid, peritectoid or congruent point on a Ti-X binary phase diagram, can be used as an indicator of the $\beta$-stabilizing capability of solute X. After normalizing this $[\beta/(\alpha + \beta)]$ slope in this Ti-X binary system by that from the Ti-Mo system, Wang et al. [30] developed a different measure of $\beta$-phase stability as shown in Table 3.2. On the other hand, Equations (3.5) to (3.8) are similar. The differences are variations in the relative importance of the $\beta$-stabilizing effect of each element including that for the reference element Mo, where the $\beta_c$ value for Ti-Mo binary alloys suggested by Zhou [28] and Mo [29] is 11 wt.% compared to 10 wt.% proposed by Bania [27]. The key question about these four different Mo-Eq equations is thus the role of Zr.
Table 3.2 Mo-Eq coefficients of alloying elements proposed by Bania [27], Zhou [28], Mo [29], and Wang [30].

<table>
<thead>
<tr>
<th>Alloying element</th>
<th>(Mo-Eq) coefficient</th>
<th>( \beta_c ) (wt.%)</th>
<th>Slope of ([\beta / (\alpha + \beta)]) line, (K/wt. %)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo</td>
<td>1</td>
<td>1.0</td>
<td>1.0</td>
</tr>
<tr>
<td>V</td>
<td>0.67</td>
<td>0.67</td>
<td>0.74</td>
</tr>
<tr>
<td>W</td>
<td>0.4</td>
<td>0.44</td>
<td>0.5</td>
</tr>
<tr>
<td>Nb</td>
<td>0.28</td>
<td>0.28</td>
<td>0.39</td>
</tr>
<tr>
<td>Ta</td>
<td>0.2</td>
<td>0.22</td>
<td>0.28</td>
</tr>
<tr>
<td>Fe</td>
<td>2.5</td>
<td>2.9</td>
<td>2.2</td>
</tr>
<tr>
<td>Cr</td>
<td>1.25</td>
<td>1.6</td>
<td>1.69</td>
</tr>
<tr>
<td>Cu</td>
<td>-</td>
<td>0.77</td>
<td>0.85</td>
</tr>
<tr>
<td>Ni</td>
<td>1.25</td>
<td>1.11</td>
<td>1.22</td>
</tr>
<tr>
<td>Co</td>
<td>1.7</td>
<td>1.43</td>
<td>1.57</td>
</tr>
<tr>
<td>Mn</td>
<td>1.7</td>
<td>1.54</td>
<td>1.69</td>
</tr>
<tr>
<td>Si</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>Sn</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Zr</td>
<td>-</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>Al</td>
<td>-</td>
<td>-1.0</td>
<td>-1.0</td>
</tr>
</tbody>
</table>

\( \beta_c \) values in bold indicate a slope of \([\beta / (\alpha + \beta)]\) not available in the literature (N/A).
Up till now, the β-stabilizing effect of Zr in Ti alloys remains to be an open question. Several controversies can be identified from the literature where the predicted Mo-Eq values contrasted with the water-quenched microstructures. In Chapter 4 of this Thesis, an equation has been developed to quantify the β-stabilizing effect of Zr in Ti alloys based on the literature data and some experimental results.

3.2.4 The First Principle approach

The elastic modulus of Ti alloys depends on their phase stability [31]. Pure Ti contains the hexagonal-close-packed (hcp) phase at ambient temperature and pressure, which is known as α-phase. This α-phase changes to non-equilibrium phases (hcp α’, orthorhombic α”, and ω) with the addition of the transition metal (TM) alloying elements such as V, Nb, and Mo. With a high TM concentration, the non-equilibrium phases transform into body-centered-cubic, β-phase, and the elastic modulus decreases [32]. However, in the single β-phase area, higher TM concentration may result in hardening, which is contradictory to the previous statement. To achieve the low elastic modulus, a proper alloy design method should be identified, and an understanding of the relationship among alloying elements, phase stability, and elastic modulus is essential. Recently, the theoretical design approach, i.e., computational material design based on first principles quantum mechanical methods, has been considered as a lucrative tool to design elastic properties of materials [33, 34]. Although most of the investigations on biocompatible Ti alloys are experimental, very few first principles approach of them have been reported.

First principle studies have been conducted on different Ti-based alloy systems for example Ti-X (X = V, Cr, Mn, Fe, Zr, Nb, Mo, W, Ta, or Sn) [32, 35-38], Ti-Nb-Zr [32, 38], Ti-Nb-Zr-Sn [32], Ti-Mo-Nb [39], Ti-Mo-Zr [39], Ti-Mo-Nb-Zr [39] on Ti-Nb-Zr-Sn [39] alloys. All these alloys can be a potential candidate material for low elastic modulus biomedical
applications if the compositions of these alloys are carefully designed. However, the conventional correlation between the $e/a$ ratio and both elastic modulus and phase stabilities is not applicable to Ti-Sn binary alloys [39].

Song et al. [35] conducted first-principles calculation on β-type bio Ti alloys and reported that Nb, Mo, Zr, and Ta were suitable alloying elements for β-type titanium alloys, which can help to increase strength and decrease elastic modulus. Recently the directional elastic moduli for binary Ti–Nb and Ti–Mo alloys were predicted by first-principle calculations which were quite close to the experimental results [40]. Ikehata et al. [36] calculated the elastic constants of pure Ti and Zr and Ti$_{(1-x)}$X$_{x}$ (X=V, Nb, Ta, Mo, and W) and Zr$_{(1-x)}$X$_{x}$ (X=Nb and Mo) binary alloys where $x = 0.0, 0.25, 0.5, 0.75,$ and $1.0$ and compared them with each other. Both the calculated and experimental elastic constants ($C_{11}, C_{12}, C_{13}, C_{33},$ and $C_{44}$) of pure Ti are higher than pure Zr, as shown in Table 3.3. On the other hand, both the Ti-X or Zr-X alloys exhibit lower elastic modulus when $x = 0.25$ (Fig. 3.7). It is also suggested that $C_{11}−C_{12}$ depends on valence electron number per atom or $e/a$ ratio, and when $e/a$ ratio is around 4.20-4.24, the value of $C_{11}−C_{12}$ becomes nearly zero. $C_{11}−C_{12}$ also exhibits the stability of the β-phase in these alloys. As a result, it is suggested that the $e/a$ ratio should be around 4.20-4.24 to achieve the low elastic modulus in the Ti or Zr binary alloys having β-phase. Although the compositional variation in these binary alloys was significant, not all possible structural configurations were included in this study.
Table 3.3 Calculated and experimental equilibrium lattice constants $a$ and $c$ and elastic constants of hcp Ti and Zr.

<table>
<thead>
<tr>
<th></th>
<th>$a$ (Å)</th>
<th>$c$ (Å)</th>
<th>$C_{11}$ (GPa)</th>
<th>$C_{12}$ (GPa)</th>
<th>$C_{13}$ (GPa)</th>
<th>$C_{33}$ (GPa)</th>
<th>$C_{44}$ (GPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti</td>
<td>Calculated [36]</td>
<td>2.946</td>
<td>4.666</td>
<td>171.6</td>
<td>86.6</td>
<td>72.6</td>
<td>190.6</td>
</tr>
<tr>
<td></td>
<td>Expt.[41]</td>
<td>2.951</td>
<td>4.684</td>
<td>162.4</td>
<td>92.0</td>
<td>69.0</td>
<td>180.7</td>
</tr>
<tr>
<td>Zr</td>
<td>Calculated [36]</td>
<td>3.232</td>
<td>5.182</td>
<td>139.4</td>
<td>71.3</td>
<td>66.3</td>
<td>162.7</td>
</tr>
<tr>
<td></td>
<td>Expt.[41]</td>
<td>3.231</td>
<td>5.148</td>
<td>143.4</td>
<td>65.3</td>
<td>65.3</td>
<td>164.8</td>
</tr>
</tbody>
</table>

*measured at room temperature

Figure 3.7 The changes of elastic moduli with the alloying element for bcc (a) Ti-$X$ ($X= W, Mo, Ta, Nb, V$) and (b) Zr-$X$ binary alloys ($X=$Nb and Mo). [36].
Sun et al. [37] investigated the elastic properties of β, α” and ω phases in Ti–25 at.% Nb with first principles studies and found that the phase stability follows the order of α” > ω > β from the aspects of energetic and electronic structures. Although the bulk moduli of β, α”, and ω phases are close, the shear and elastic moduli of β, α” and ω phases are very different. The shear and elastic moduli follow the order of ω > α” > β in the Ti–25 at. % Nb alloy.

To understand the effect of Zr in the Ti–25(at.%)Nb system on the elastic modulus, ternary Ti–25Nb–xZr with x varying from 6.25, 12.5, 18.75 to 25 at.% and with maximum possible structural configurations are studied using first-principles studies [38]. Fig.3.8 [38] showed that the $e/\alpha$ ratio did not change with increasing Zr content, but density does. It has been suggested that higher $\overline{B_0}$ values should give rise to low elastic modulus among the least stable β-Ti alloys [42].

![Graph showing Young's modulus of bcc Ti–25(at.%)Nb–xZr system as a function of Zr content](image)

**Figure 3.8** The elastic modulus of β bcc Ti–25(at.%)Nb–xZr system as a function of Zr content [38].
3.3 A different design approach proposed for Zr-based and Ti-based Ti-Nb-Zr alloys

In general, the mechanical properties of Ti-based alloys depend on their phase stability and microstructure. The addition of an alloying element can change both features. As a β stabilizing element, Nb, has attracted much attention to be added to many β Ti-based alloys and near β Ti-based alloys. Zr is another important alloying element in Ti-based alloys. Zr acts as a β stabilizing element in β Ti alloys in both the solution treated and aged conditions [43]. Zr is well known as a neutral element for a long period. Hady at al. [43] reported a stronger average chemical bond between atoms in the β phase of the Ti-Nb-Zr ternary system than in binary Ti-Nb and Ti-Zr systems. He also reported that Zr suppresses ω phase formation. For instance, in the Ti-23Nb (at.%) alloy system, the ω phase disappeared with an addition of only 6 at.% Zr [43]. Moreover, when the Zr content is more than 30 at.%, ω phase never came back in the alloys [43]. Recently Zr-based alloys are attracting more attention for biomedical application because of their lower magnetic susceptibility than that of Ti [3].

In this study, new sets of Ti-Nb-Zr alloys have been designed and developed based on the $d$-electron theory and the $e/\alpha$ ratio to achieve low elastic modulus with potentially low magnetic susceptibility, as shown in Table 3.4. The rationales for the design of these compositions are summarised below:

- All the alloying elements (Ti, Nb and Zr) are biocompatible.
- The binary Ti-Nb alloys exhibit the lowest elastic modulus compared with other binary Ti-alloys [44, 45] and Zr acts as a β-stabilizer in Ti-Nb alloys [43]. Hence, Zr can work with Nb to further lower the elastic modulus.
- The elastic modulus of commercially pure (CP) Zr is ~20% lower than that of CP Ti (88 [46] vs. 105 GPa ) while having similar biocompatibility [47]. This 20% lower
elastic modulus of the matrix metal can be an important advantage for the design of low elastic modulus and biocompatible $\beta$-Zr-Ti-Nb alloys in the as-cast condition.

- Both Nb and Zr exhibit low magnetic susceptibility compared to Ti. Hence, Zr-Ti-Nb alloy compositions are developed to achieve low magnetic susceptibility.

- It is well established that $\omega$-phase is responsible for high elastic modulus and when Zr content is more than 30 at.% , then the $\omega$-phase disappears. Hence to avoid $\omega$-phase formation Zr-Ti-Nb alloy compositions are developed.

- Along the metastable $\beta$-phase boundary of the $\overline{B}_o - \overline{M}_d$ diagram if an alloy has high $\overline{B}_o$ and $\overline{M}_d$ values, then the alloy should possess low elastic modulus.

- From Fig. 3.5, an alloy should have lowest elastic modulus, when the $e/\alpha$ value is 4.1-4.25 and the $\omega$-phase is suppressed.

- High $\overline{B}_o$ value is required for good corrosion resistance. Hence alloys with high $\overline{B}_o$ value are developed to achieve good corrosion resistance.

- The ductility of Zr-Ti-Nb or Ti-Zr-Nb system is insensitive to oxygen (O) and can achieve more than 10% tensile ductility with 0.4-0.6 wt.%O [48]

- The powder bed fusion metal additive manufacturing (PBF-MAM) has become famous for custom-made implants as a layer-melting and layer-solidification process. The as-printed part can approximately be considered as an as-solidified or as-cast part. As a result, the emphasis is given on the as-cast condition.

Here the Ti-Nb-Zr alloy system can be divided into two categories - Ti-based Ti-Nb-Zr (Ti-Nb-Zr) alloys and Zr-based Ti-Nb-Zr (Zr-Ti-Nb) alloys. As Zr exhibits lower magnetic susceptibility compared to Ti, more emphasis is given on the Zr-based alloys. The design is based on the $\overline{B}_o - \overline{M}_d$ diagram but with $e/\alpha$ lines added to the diagram for the Ti-Nb-Zr system, as shown in Fig.3.9 [11]. As a result, the $e/\alpha$ values of different potential Ti-Nb-Zr
alloys can be easily determined by using the $e/\alpha$ lines in the $\overline{B}_o - \overline{M}_d$ diagram. For the Ti-Nb-Zr system, the $e/\alpha$ ratio depends on the Nb content. On this basis, the newly developed Mo-Eq. parameter that incorporates the latent influence of Zr on the $\beta$-phase stability in Ti-Nb-Zr alloys will be used together to finalise the design or understand the resultant phase stability or microstructure.

\textbf{Table 3.4} New alloy composition and their $\overline{B}_o$, $\overline{M}_d$, and $e/\alpha$ ratio.

<table>
<thead>
<tr>
<th></th>
<th>Alloy composition (at%)</th>
<th>Alloy composition (wt%)</th>
<th>Bond order, $\overline{B}_o$</th>
<th>d-orbital energy level, $\overline{M}_d$, eV</th>
<th>$e/\alpha$ ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Ti-40Zr-15Nb</td>
<td>Ti-50.7Zr-19.3Nb</td>
<td>2.95</td>
<td>2.64</td>
<td>4.15</td>
</tr>
<tr>
<td>2</td>
<td>Ti-52Zr-15Nb</td>
<td>Ti-61.4Zr-18Nb</td>
<td>2.99</td>
<td>2.70</td>
<td>4.15</td>
</tr>
<tr>
<td>3</td>
<td>Ti-57Zr-15Nb</td>
<td>Ti-65.4Zr-17.6Nb</td>
<td>3.00</td>
<td>2.72</td>
<td>4.15</td>
</tr>
<tr>
<td>4</td>
<td>Ti-55Zr-10Nb</td>
<td>Ti-65.8Zr-12.2Nb</td>
<td>2.98</td>
<td>2.71</td>
<td>4.1</td>
</tr>
<tr>
<td>5</td>
<td>Ti-50Zr-20Nb</td>
<td>Ti-58Zr-23.6Nb</td>
<td>2.99</td>
<td>2.69</td>
<td>4.2</td>
</tr>
<tr>
<td>6</td>
<td>Ti-26Zr-10Nb</td>
<td>Ti-37Zr-15Nb</td>
<td>2.90</td>
<td>2.57</td>
<td>4.1</td>
</tr>
<tr>
<td>7</td>
<td>Ti-25Zr-15Nb</td>
<td>Ti-34.8Zr-21.3Nb</td>
<td>2.91</td>
<td>2.57</td>
<td>4.15</td>
</tr>
<tr>
<td>8</td>
<td>Ti-22Zr-15Nb</td>
<td>Ti-31.3Zr-22Nb</td>
<td>2.90</td>
<td>2.55</td>
<td>4.15</td>
</tr>
<tr>
<td>9</td>
<td>Ti-21Zr-20Nb</td>
<td>Ti-29Zr-28Nb</td>
<td>2.91</td>
<td>2.54</td>
<td>4.2</td>
</tr>
</tbody>
</table>
3.4 Summary

In this chapter, all the design approaches used in the literature for the design of Ti-based implant material are broadly discussed. Nine Ti-Nb-Zr alloy compositions have been developed using the $d$-electron theory and the $e/a$ ratio. Among them, four are Ti-based Ti-Nb-Zr (Ti-Nb-Zr) alloys, and five are Zr-based Ti-Nb-Zr (Zr-Ti-Nb) alloys. However, detailed experimental assessments should be carried out to evaluate each designed composition. To evaluate the significance of the design approach used in this thesis, the
elastic modulus of these newly designed alloys should be measured. Factors that affect elastic modulus should be widely investigated to achieve a new pathway to design low modulus Ti-Nb-Zr and Zr-Ti-Nb alloys. This forms the basis for the rest of this thesis project.

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Chapter 4 The beta-phase stability in Ti-Nb-Zr alloys for alloy design and microstructural prediction

4.1 Introduction

β-titanium (β-Ti) alloys that are free of vanadium (V), nickel (Ni) and aluminium (Al) are one of the most promising groups of metallic biomaterials for orthopaedic applications. By definition, β-Ti alloys refer to those which contain sufficient β-stabilizing element(s) to enable the β-phase to be retained in a metastable condition by water quenching [1]. They are generally divided into metastable (age hardenable) and stable β-Ti alloys (not age-hardenable) [2]. The critical minimum amount of β-stabilizers needed to retain 100% β-phase on water quenching is technically denoted as $\beta_c$, while the minimum content of β-stabilizers needed to form stable β-Ti alloys is referred to as $\beta_s$. Metastable β-Ti alloys are those that fall in between $\beta_c$ and $\beta_s$, within which α can precipitate upon ageing. As the values of $\beta_c$ and $\beta_s$ depend on alloy chemistry, a parameter known as Mo Equivalent (Mo-Eq) has been defined and commonly used as a general guideline to assess the β-phase stability of a Ti alloy for both alloy design and processing [3-5]. It is therefore an important design parameter for Ti alloys. This paper first examines all existing Mo-Eq expressions and then focuses on the development of a new Mo-Eq equation proposed specifically for the Ti-Nb-Zr system. This is followed by a detailed experimental assessment and comparison with Morinaga’s $d$-electron theory for alloy design.

*This work has been published in JOM.

4.2 Existing Mo-Eq expressions and their deficiencies

The concept of the Mo Equivalence (Mo-Eq) was proposed by E. K. Molchanova in "Phase Diagrams of Titanium Alloys" (Figure 193 and Figure 194, p. 158) [3], which was a translation from “Atlas Diagramm Sostoyaniya Titanovykh Splavov” (Israel Program for Scientific Translations, Jerusalem, 1965). Boyer et al. [4] presented the data shown in Figure 193 of Ref. [3] as the Mo equivalence of a titanium alloy in the well-known Materials properties handbook: titanium alloys (1994), (p. 10) in the following form:

\[(\text{Mo-Eq})_{\text{Molchanova}[3]} = 1.0(\%\text{Mo}) + 0.2(\%\text{Ta}) + 0.28(\%\text{Nb}) + 0.4(\%\text{W}) + 0.67(\%\text{V}) + 1.25(\%\text{Cr}) + 1.25(\%\text{Ni}) + 1.7(\%\text{Mn}) + 1.7(\%\text{Co}) + 2.5(\%\text{Fe})\] (4.1)

Bania [5] then further discussed the Mo-Eq concept and expressed it in the form of Eq. (4.2) in which the prefix coefficient of each β-stabilizer represents the ratio of the β_c value of Mo (i.e. 10 wt.%) to that of respective β-stabilizer. As an α-stabilizer, Al is also included to show its opposing effect when it is present in a β-Ti alloy.

\[(\text{Mo-Eq})_{\text{Bania}[5]} = 1.0(\%\text{Mo}) + 0.67(\%\text{V}) + 0.44(\%\text{W}) + 0.28(\%\text{Nb}) + 0.22(\%\text{Ta}) + 2.9(\%\text{Fe}) + 1.6(\%\text{Cr}) + 0.77(\%\text{Cu}) + 1.11(\%\text{Ni}) + 1.43(\%\text{Co}) + 1.54(\%\text{Mn}) - 1.0(\%\text{Al})\] (4.2)

Eq.(4.2) overrides the original Eq. (4.1) as a commonly used expression to estimate the Mo-Eq of a Ti alloy. Apart from Eq. (4.2), three other expressions for Mo-Eq have also been proposed [6-8], namely

\[(\text{Mo-Eq})_{\text{Zhou}[6]} = 1.0(\%\text{Mo}) + 0.74(\%\text{V}) + 0.5(\%\text{W}) + 0.39(\%\text{Nb}) + 0.28(\%\text{Ta}) + 2.2(\%\text{Fe}) + 1.69(\%\text{Cr}) + 0.85(\%\text{Cu}) + 1.22(\%\text{Ni}) + 1.57(\%\text{Co}) + 1.69(\%\text{Mn})\] (4.3)
(Mo-Eq)_{Mo}^{[7]} = 1.0(\%Mo) + 0.73(\%V) + 0.5(\%W) + 0.31(\%Nb) + 0.24(\%Ta) + 2(\%Fe) + 1.69(\%Cr) + 1.29(\%Ni) + 1.16(\%Co) + 1.69(\%Mn) \quad (4.4) \\

and

(Mo-Eq)_{Wang}^{[8]} = 1.0(\%Mo) + 1.25(\%V) + 0.59(\%W) + 0.28(\%Nb) + 0.22(\%Ta) + 1.93(\%Fe) + 1.84(\%Cr) + 1.5(\%Cu) + 2.46(\%Ni) + 2.67(\%Co) + 2.26(\%Mn) + 3.01(\%Si) + 0.3(\%Sn) + 0.47(\%Zr) - 1.47(\%Al) \quad (4.5) \\

eqs. (4.2-4.4) are similar and they were all formulated on the basis of experimental data, where Zr was treated as a neutral element and therefore excluded. It should be pointed out that no information was given about the sample size used in the water quenching experiments, which affects the resultant microstructure. However, Eq. (4.3) considered that the $\beta_c$ value of Mo should be 11 (rather than 10), which was also mentioned in Ref. [3]. The slight difference between Eqs. (4.2), (4.3) and (4.4) resulted from experimental and analytical errors. In contrast, Eq. (4.5) combines both experimental and phase diagram data. For example, the coefficients for Nb and Ta were taken from Eq. (4.2), while the coefficient for Zr was derived from the Ti-Zr phase diagram [8]. As a result, Zr was treated as a $\beta$-stabilizer that is more potent than Nb (0.28) and Ta (0.22) but no experimental support was given. Limited evidence suggests [9, 10] that the $\beta$-stabilizing effect of Zr depends on the quantity of other $\beta$-stabilizers present in the alloy.

Table 4.1 summarises nine different Ti-Nb-Zr alloys reported in the literature with identified phase constituents in the water-quenched state [9, 11]. They provide an experimental basis for a detailed assessment of Eqs. (4.2-4.5). As can be seen from Table 4.1, despite the high Mo-Eq values predicted by Eq. (4.5), e.g., 24.12 for Ti-12Nb-30Zr (at.%), $\alpha''$-martensite still forms on water quenching. In other words, Eq. (4.5) significantly overestimates the $\beta$-stabilizing effect of the alloying elements in these alloys. With regards to Eq. (4.2), it
substantially underestimates the overall β-stabilizing effect of the alloying elements in Ti-Nb-Zr alloys. For example, Eq. (4.2) predicts Mo-Eq values of 3.64 and 5.43 for Ti-10Nb-45Zr (at.%) and Ti-14Nb-30Zr (at.%), respectively, which are much lower than 10. However, the β-phase was fully retained in both alloys upon water quenching. Eq. (4.4) and Eq. (4.2) offer similar predictions. Eq. (4.3) shows a serious underestimation of the β-stabilizing effect too. For instance, the Mo-Eq of Ti-14Nb-30Zr (at.%) is predicted to be 7.57 but full β phase is retained. So is the case for Ti-10Nb-45Zr (at.%), where Mo-Eq = 5.07 but full β phase is retained. On the other hand, Eq. (4.3) overestimates the β-stabilizing effect in Ti-20.9Nb-9Zr (at.%) (clear formation of α’ although Mo-Eq = 12.36). In summary, none of the existing Mo-Eq equations offers predictions that are consistent with experimental observations for Ti-Nb-Zr alloys. In addition, when all these predictions based on Eqs. (4.2-4.5) are compared with the d-electron theory diagram, there is substantial inconsistency as well.
Table 4.1 Metastable β-region for Ti-Nb-Zr alloy systems and their Mo-Eq [9, 11].

<table>
<thead>
<tr>
<th>Alloy compositions at.%</th>
<th>Alloy compositions wt.%</th>
<th>Phases (water quenched)</th>
<th>Mo-Eq values by existing expressions (wt.%)</th>
<th>New Mo-Eq by Eq. (4.77)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-12Nb-30Zr</td>
<td>Ti-16.82Nb-41.29Zr</td>
<td>α″,β</td>
<td>4.71, 6.56, 5.21, 24.12</td>
<td>9.5</td>
</tr>
<tr>
<td>Ti-14Nb-30Zr</td>
<td>Ti-19.4Nb-40.7Zr</td>
<td>β</td>
<td>5.430, 7.57, 6.01, 24.56</td>
<td>10.1</td>
</tr>
<tr>
<td>Ti-8Nb-46Zr</td>
<td>Ti-10.4Nb-58.8Zr</td>
<td>α″,β</td>
<td>2.91, 4.06, 3.22, 30.55</td>
<td>9.9</td>
</tr>
<tr>
<td>Ti-10Nb-45Zr</td>
<td>Ti-13Nb-57.1Zr</td>
<td>β</td>
<td>3.64, 5.07, 4.03, 30.48</td>
<td>10.1</td>
</tr>
<tr>
<td>Ti-20.2Nb-12Zr</td>
<td>Ti-30.18Nb-17.6Zr</td>
<td>β</td>
<td>8.45, 11.77, 9.36, 16.72</td>
<td>10.1</td>
</tr>
<tr>
<td>Ti-22Nb-4Zr</td>
<td>Ti-34.4Nb-6.13Zr</td>
<td>β</td>
<td>9.63, 13.42, 10.66, 12.51</td>
<td>9.8</td>
</tr>
<tr>
<td>Ti-22Nb-6Zr</td>
<td>Ti-33.9Nb-9.1Zr</td>
<td>β</td>
<td>9.49, 13.22, 10.51, 13.77</td>
<td>10</td>
</tr>
<tr>
<td>Ti-22Nb-8Zr</td>
<td>Ti-33.4Nb-11.92Zr</td>
<td>β</td>
<td>9.35, 13.03, 10.35, 14.95</td>
<td>10.2</td>
</tr>
</tbody>
</table>
4.3 New Mo-Eq expression for Ti-Nb-Zr alloys

We first determine the Mo-Eq coefficient of Nb. Three different values were used previously in Eqs. (4.2-4.5), namely, 0.28%, 0.31% and 0.39%. Recent experimental work has defined that the $\beta_c$ value for Ti-Nb binary alloys is 42 wt.% [12]. Consequently, the Mo-Eq coefficient of Nb can be defined as

$$\psi = (10/42) = 0.238$$

We then need to consider the $\beta$-stabilizing effect of Zr properly. As can be seen from Table 4.1, a small increase (e.g., 1-3 at.%) in the content of Zr or Nb+Zr can change the phase constituents from $\alpha'' + \beta$ to single $\beta$ under water quenching conditions. For instance, a single $\beta$-phase was retained in the Ti-22Nb-4Zr (at.%) alloy but not in the Ti-22Nb-2Zr (at.%) alloy. Similarly, a single $\beta$-phase was retained in the Ti-14Nb-30Zr (at.%) alloy but not in the Ti-12Nb-30Zr (at.%) alloy. Considering that Nb and Zr are generally weak $\beta$-stabilizers, it can be assumed that the Mo-Eq values of the Ti-Nb-Zr alloys listed in Table 4.1 are all in the vicinity of the critical value, i.e., 10 wt.%. Consequently, the $\beta$-stabilizing effect of Zr in these Ti-Nb-Zr alloys can be estimated by the quantity, $\Delta = 10 - \psi \times \text{Nb (wt.%)}$. Fig. 4.1 shows the dependence of the quantity, $\Delta = 10 - \psi \times \text{Nb (wt.%)}$, on the Zr content for all the Ti-Nb-Zr alloys listed in Table 4.1. The resultant significant linear relationship identifies the contribution of Zr in stabilizing the $\beta$ phase in Ti-Nb-Zr alloys considered in Table 4.1. Accordingly, a new Mo-Eq for Ti-Nb-Zr alloys can be defined from Fig. 4.1 as

$$(\text{Mo-Eq})_{\text{Ti-Nb-Zr}} = 0.238 \text{Nb (wt.%)} + 0.11 \text{Zr (wt.%)} + 0.97$$

Eq. (4.7) was applied to all the Ti-Nb-Zr alloys listed in Table 4.1. Good consistency was observed with experimental observations, where when the new Mo-Eq parameter is close to or above 10, the alloy contains $\beta$-phase as primary phase (along with some other secondary
phases) after water quenching, while when it is clearly below 10, there martensite is the dominant phase.

![Graph](image)

**Figure 4.1** Dependence of the quantity of $\Delta = 10 - \psi \times \text{Nb (wt.%) on Zr content in Ti-Nb-Zr alloys.}

### 4.4 Applying the new Mo-Eq to the design of Ti-Nb-Zr alloys and validation

Table 4.2 summarises the Mo-Eq values predicted by Eqs. (4.2-4.5) and (4.7) for six newly designed Ti-Nb-Zr alloys in this study (the first six alloys in Table 4.2) and those available in the literature. Ingot samples of these alloys were made by arc-melting of a mixture of pure metals (purity > 99.9 wt.%) in a Ti-gettered high-purity argon atmosphere. The ingots were re-melted four times to ensure chemical homogeneity. Then the melted alloys were cast into a copper mould with a cylindrical cavity of 10 mm in diameter and 60 mm in depth. The as-cast samples with a diameter of 10 mm and thickness of 2 mm were homogenized at 1000°C.
for 4 h and then solution-treated at 900°C for 0.5 h, followed by water quenching. Samples were ground with SiC grinding papers of up to 4000 grit for microstructural characterization. Final polish was performed with a mixture of colloidal silica and H₂O₂. The samples were subsequently cleaned in an ultrasonic bath using ethanol and etched with Kroll’s reagent. Phase identification was conducted using a Bruker D8 Advance X-ray diffractometer (XRD) with a Cu Kα radiation source at room temperature, and the resultant XRD data was analysed by Material Analysis Using Diffraction (MAUD) software.

Fig. 4.2 shows the XRD data of six water-quenched Ti-Nb-Zr alloys and optical micrographs of two of them. Ti-10Nb-26Zr (at.%) was predicted to have martensite due to its low Mo-Eq (8.6, Table 4.2) while the rest should essentially be single β-phase in the water-quenched state. Both the XRD data and microstructural observations have confirmed these predictions, where the β-phase is predominant in each of the other five alloys (e.g., Fig. 4.2c) plus a small amount of secondary phases (α”, ω) while Ti-10Nb-26Zr (at.%) contains significant α”-martensite (Fig. 4.2d). The newly defined Mo-Eq expression by Eq. (4.7) is in good agreement with the experimental observations of each alloy.

With regard to the alloys from the literature (Table 4.2), they were all reported to be nearly single β-phase alloys (i.e., may contain a small amount of α” and/or ω) [13-15]. By the definition of the Mo-Eq, their Mo-Eq values should be equal to or above 10 wt.%. As can be seen from Table 4.2, the new Mo-Eq (Eq. (4.7)) shows excellent consistency with experimental observations too.
Table 4.2 Newly designed metastable Ti-Nb-Zr alloys and corresponding Mo-Eq values.

<table>
<thead>
<tr>
<th>References</th>
<th>Alloy compositions</th>
<th>Mo-Eq values by different expressions</th>
<th>Phase constitution</th>
<th>Microstructural feature</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>Eq.(4.2)</td>
<td>Eq.(4.3)</td>
<td>Eq.(4.4)</td>
</tr>
<tr>
<td>Zr-based alloys [This study]</td>
<td>Ti-15Nb-40Zr</td>
<td>Ti-19.3Nb-50.7Zr</td>
<td>5.44</td>
<td>7.53</td>
</tr>
<tr>
<td></td>
<td>Ti-10Nb-55Zr</td>
<td>Ti-12.2Nb-65.8Zr</td>
<td>3.42</td>
<td>4.76</td>
</tr>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-based alloys [This study]</td>
<td>Ti-10Nb-26Zr</td>
<td>Ti-15Nb-37Zr</td>
<td>4.2</td>
<td>5.85</td>
</tr>
<tr>
<td></td>
<td>Ti-15Nb-25Zr</td>
<td>Ti-21.3Nb-34.8Zr</td>
<td>5.96</td>
<td>8.31</td>
</tr>
<tr>
<td></td>
<td>Ti-15Nb-22Zr</td>
<td>Ti-22Nb-31.3Zr</td>
<td>6.16</td>
<td>8.58</td>
</tr>
<tr>
<td></td>
<td>Ti-20Nb-21Zr</td>
<td>Ti-28Nb-29Zr</td>
<td>7.84</td>
<td>10.92</td>
</tr>
<tr>
<td></td>
<td>Ti-22Nb-24Zr</td>
<td>Ti-30Nb-32Zr</td>
<td>8.4</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Ti-20.7Nb-26.7Zr</td>
<td>Ti-28Nb-35.4Zr</td>
<td>7.84</td>
<td>10.92</td>
</tr>
<tr>
<td></td>
<td>Ti-18.6Nb-31.1Zr</td>
<td>Ti-24.8Nb-40.7Zr</td>
<td>6.94</td>
<td>9.67</td>
</tr>
<tr>
<td>[14]</td>
<td>Ti-20Nb-12Zr</td>
<td>Ti-29.9Nb-17.6Zr</td>
<td>8.4</td>
<td>11.7</td>
</tr>
<tr>
<td></td>
<td>Ti-17Nb-21Zr</td>
<td>Ti-24.4Nb-29.6Zr</td>
<td>6.72</td>
<td>9.36</td>
</tr>
<tr>
<td></td>
<td>Ti-11Nb-38Zr</td>
<td>Ti-14.7Nb-50Zr</td>
<td>4.2</td>
<td>5.85</td>
</tr>
<tr>
<td></td>
<td>Ti-6Nb-53Zr</td>
<td>Ti-7.6Nb-65.7Zr</td>
<td>2.24</td>
<td>3.12</td>
</tr>
</tbody>
</table>

119
(a) 

Intensity (a.u.)

2θ (degrees)

Ti-10Nb-55Zr (at.%)

Ti-15Nb-40Zr (at.%)

(b) 

Intensity (a.u.)

2θ (degrees)

Ti-20Nb-21Zr (at.%)

Ti-15Nb-22Zr (at.%)

Ti-15Nb-25Zr (at.%)

Ti-10Nb-26Zr (at.%)

120
Figure 4.2 XRD results of (a) two Zr-based Ti-Nb-Zr alloys and (b) four Ti-based Ti-Nb-Zr alloys and optical micrographs of (c) Water-quenched Ti-15Nb-40Zr (at.%), nearly single β. (d) Water-quenched Ti-10Nb-26Zr (at.%), noticeable α″-martensite.

4.5 The newly proposed Mo-Eq and the d-electron theory

The d-electron theory describes the potential relationship between phase stability and elastic properties of Ti alloys through two electronic properties, bond order, $B_o$, and d-orbital energy level, $M_d$ [12, 16]. It was developed by Morinaga [16] on the basis of the DV-Xα molecular orbital calculations of electronic structures. The theory has become an essential fundamental tool for the design of β-Ti alloys [1, 12]. In this approach, $B_o$ denotes the covalent bond strength between Ti and a specific alloying element and $M_d$ correlates the electronegativity and metallic radius of that element. $B_o$ and $M_d$ values for all the alloying elements of Ti can be found in the Ref. [16]. Using these $B_o$ and $M_d$ values, compositional average of $B_o$ and $M_d$ can be calculated based on alloy composition through the following equations [16].

\[
\overline{B_o} = \sum X_i(B_o)_i \tag{4.8}
\]

\[
\overline{M_d} = \sum X_i(M_d)_i \tag{4.9}
\]
where, $X_i$, $(B_o)_i$ and $(M_d)_i$ are the atomic fraction, bond order and $d$-orbital energy level of that given element respectively. Then a $B_o - M_d$ diagram can be plotted by taking $B_o$ and $M_d$ values of different Ti alloy. Several sets of Ti alloys is used to define the three regions, $\alpha$, $\alpha + \beta$, $\beta$ of this $B_o - M_d$ diagram. Along the $(\alpha + \beta)/\beta$ boundary in the $B_o - M_d$ diagram the $\beta$-phase is considered metastable.

Fig. 4.3 shows the $B_o - M_d$ diagram plotted for this study on the basis of Ref. [12, 14]. A triangle is drawn by connecting the $B_o$ and $M_d$ values for pure Ti, Nb and Zr, which define the regime of Ti-Nb-Zr alloys, similar to ternary phase diagrams. Each side of this triangle indicates the compositional average values of $B_o$ and $M_d$ of Ti-Nb, Ti-Zr and Zr-Nb binary alloys. The dotted line in blue represents the boundary of critical compositions for metastable $\beta$ alloys according to the inventor of the $d$-electron theory [12]. This boundary may shift upwards or downwards depending on exact alloying compositions. In the Ti-Nb-Zr system, adding Zr was found to shift this boundary downwards [14], as shown by the dashed line in black in Fig. 4.3. The Mo-Eq values predicted by Eq. (4.7) are superimposed onto Fig. 4.3, which indicates that the newly developed Mo-Eq expression is also in good agreement with the metastable $\beta$ line in $d$-electron theory proposed by You and Song et al. [14] in predicting the $\beta$-phase stability. This is a good coincidence because the same conclusion has been arrived by using completely different methods. For example, Ti-Nb-Zr alloys having Mo-Eq values higher than 10 wt.% are situated above the dashed line in black and vice versa. The new Mo-Eq is thus consistent with the $d$-electron theory for Ti-Nb-Zr alloys, which was not the case for all other four Mo-Eq expressions.
Figure 4.3 Ti-Nb-Zr alloys in the $\bar{B}_o - \bar{M}_d$ map [13-16].
4.6 Summary

A new Mo-Eq expression has been formulated for the Ti-Nb-Zr system, i.e., $(\text{Mo-Eq})_{\text{Ti-Nb-Zr}} = 0.238\text{Nb (wt.%)} + 0.11\text{Zr (wt.%)} + 0.97$, which shows good consistency with experimental observations as well as literature data. In addition, it is highly consistent with the well-established $d$-electron theory in predicting the $\beta$-phase stability of various Ti-Nb-Zr alloys. In contrast, none of the existing four Mo-Eq expressions is consistent the $d$-electron theory, as well as experimental observations. However, caution should be exercised when the alloy composition goes significantly beyond the bounds of the chemistries discussed in this study. It is proposed that the approach developed in this work can also be applied to the assessment of the $\beta$-phase stability in other Zr-containing Ti alloys.

References


Chapter 5 Strong, ductile and low-elastic-modulus as-cast Zr-Ti-Nb alloys for biomedical applications

5.1 Introduction

The development of orthopaedic biomaterials continues to draw significant attention due to the increasing demand for bone replacements and repairs [1]. Such implant materials need to be both biologically and mechanically compatible [2]. Biocompatibility can be measured by considering the genotoxic (DNA damaging), cytotoxic (cell destruction/killing), carcinogenic (cancer causing), mutagenic (mutation causing), allergenic (allergic response), and neurological effects of a material in human body [3]. At the same time, mechanical compatibility requires match of a range of important properties including elastic modulus, strengths and ductility under tension and compression, response to loading and unloading, fracture toughness, fatigue strength, Poisson's ratio etc. It is thus tremendously challenging to be both biologically and mechanically compatible. Consequently, new alloy designs for biomedical applications have been focused on elastic modulus (E) match, which can otherwise lead to most of the load being carried by the implant material and therefore resorption in bone tissue [4]. The elastic modulus of healthy human cortical bones fall in the range of 13-35 GPa [5, 6]. Ti-6Al-4V has been the most widely implant alloy in recent years. Although it offers much lower elastic modulus (110 GPa) than 316L stainless steel (190-210GPa) and Co-Cr alloys (210-253GPa), its elastic modulus is still about 3-8 times that of healthy cortical bones. 3D-printed Ti-6Al-4V lattice implants can readily overcome this mismatch [7]. However, it has been found that mismatches with other mechanical properties will occur with those of the cortical bones including strengths and ductility [7].
β-Ti alloys can offer lower elastic modulus (60-80 GPa) \(^8, \, 9\) than \((α + β)\)-Ti-6Al-4V. As such, much effort has been made to develop biomedical β-Ti alloys. In that context, one of the most studied biomedical β-Ti alloy systems is that of the Ti-Nb-Zr system \([10-18]\). There are unique reasons. One is that binary Ti-Nb alloys exhibit the lowest elastic modulus compared with other binary Ti alloys \([19, \, 20]\). The other is that Zr can act as an effective β-stabilizer in Ti-Nb alloys \([21]\), rather than a neutral element in other Ti alloys. Therefore, it can work with Nb to further lower the elastic modulus. Fig. 5.1 summarizes the recently assessed Ti-Nb-Zr alloys and their elastic moduli, including both Ti-based (by weight percent) Ti-Nb-Zr or Ti-Nb-Zr and Zr-based Ti-Nb-Zr or Zr-Ti-Nb alloys. The elastic moduli achieved by compression tests are much lower compared with those obtained by tensile testing or ultrasonic testing. Moreover, low elastic modulus can also be achieved after post processing from the as-cast state. Only three alloys, Ti-6Nb-53Zr (at.% \([11]\) and Ti-11Nb-38Zr (at.% \([11]\), and Ti-18Nb-51Zr (at.% \([22]\), all of which are Zr-based by weight percent, have reportedly achieved elastic modulus lower than 60 GPa in the as-cast state. This is not surprising because Zr-based Ti-Nb-Zr alloys are generally expected to offer lower elastic modulus than Ti-based Ti-Nb-Zr alloys in the as-cast state. This is because the elastic modulus of commercially pure (CP) Zr is ~20% lower than that of CP Ti \((88 \, [23] \text{ vs. } 105 \, \text{GPa})\) while having similar biocompatibility \([24]\). This 20% lower elastic modulus of the matrix metal can be an important advantage for the design of low elastic modulus and biocompatible β-Zr-Ti-Nb alloys in the as-cast condition. The emphasis on the as-cast condition is important as the as-cast condition can approximately be regarded as a as printed condition.
Figure 5.1 Recently developed ternary Ti-Nb-Zr System and their elastic Modulus (where ST: Solution treated, HT: Heat treated and CR: Cold rolled) [10-18]. Unspecified compositions are given in at.%.

Another emerging important requirement is that due to the ever-increasing demands for better and faster diagnostics of implants in patients, magnetic resonance imaging (MRI) requires the use of high magnetic intensity (5-7 Tesla) systems for faster and high-resolution imaging. MRI has become an essential diagnostic tool in modern orthopaedics and surgery. As a result, Ti-based alloys risk being partially magnetised by such future high-intensity MRI systems. The consequences are heat generation in the implants [25], dislocation of implants [26] and artifacts in the image [27, 28]. Artifacts can change the image of organs near the implant leading to incorrect diagnosis [29-31], due to the difference in magnetic susceptibility [32]. Fortunately, Zr possesses much lower magnetic susceptibility than Ti [33]. At the same time,
Zr is strong, ductile and corrosion-resistant, which can easily meet the requirements for strength and ductility for orthopaedic applications [34]. Hence, Zr alloys provide an important potential solution for future high-intensity MRI diagnostics, in addition to the good biocompatibility and low elastic modulus discussed above. An additional consideration of choosing the Zr-Ti-Nb or Ti-Zr-Nb system is that their ductility is insensitive to oxygen (O) and can attain tensile ductility of more than 10% even containing 0.4-0.6 wt.%O [35].

As shown in Fig. 5.1, only two existing Zr-Ti-Nb alloys showed low tensile elastic modulus in the as-cast condition. Hence, more experimental research is needed in the design of Zr-based alloys in order to explore their potential as low elastic modulus implant alloys in the as-cast condition. In this study, five Zr-Ti-Nb alloys are designed based on the $d$-electron theory and the $e/\alpha$ ratio approach for low elastic modulus and high mechanical strength. The elastic moduli of these alloys were measured using three different methods, i.e., tension, compression and ultrasonic vibration. The phase constituents, microstructure and resulting mechanical properties of the designed alloys were investigated. For comparison, two low elastic modulus Zr-based Zr-Ti-Nb alloys (Zr-31Ti-18Nb or Ti-18Nb-51Zr, 59.7 GPa, and Zr-41Ti-6Nb or Ti-6Nb-53Zr, 48 GPa) from the literature were investigated as well [11, 15].

5.2 Design of low-elastic-modulus Zr-based alloys by using a $\overline{B_o}\cdot\overline{M_d} = e/\alpha$ diagram

The $d$-electron theory developed by Morinaga et al [36] based on DV-Xα molecular orbital calculations of the electronic structures for a potential alloy allows for prediction of the plausible relationship between the phase stability and elastic properties of the alloy. In practice, the theory is implemented by plotting two electronic property parameters of existing alloys of the same group, $\overline{B_o}$ (compositional average of bond order) vs. $\overline{M_d}$ (compositional average of the $d$ orbital energy level) [37], known as the $\overline{B_o} - \overline{M_d}$ map. Then, the map can be used to link to the experimentally determined elastic modulus
or other mechanical properties of each existing alloy to establish a predictive trend. For an alloy, the formula for calculating the compositional average values of $B_o$ and $M_d$ are given below [38]

$$\overline{B}_o = \sum X_i (B_o)_i \quad (5.1)$$

$$\overline{M}_d = \sum X_i (M_d)_i \quad (5.2)$$

where, $X_i$, $(B_o)_i$ and $(M_d)_i$ are the atomic fraction, bond order and $d$-orbital energy level of the given element $i$, respectively. For Ti alloys, $B_o$ reflects the covalent bond strength between Ti and introduced alloying elements. The value of $M_d$ is related to both the electronegativity (higher electronegativity elements have lower $d$ orbital energy levels) and the atomic radius of each element (a larger atomic radius has the larger average radius of the $d$ orbital, which corresponds to a higher $d$ orbital energy level) [39].

Fig. 5.2 replots a basic $\overline{B}_o - \overline{M}_d$ diagram for Ti-Nb-Zr alloys from literature [21-29] but is superimposed with a Zr-Nb-Ti triangle, which includes all the Ti-Nb-Zr alloys shown in Fig. 5.1. By referring to the elastic modulus values of these alloys in Fig. 5.1, this diagram reveals that their elastic modulus first decreases along the $\beta/\beta+\omega$ phase boundary with increasing both $\overline{B}_o$ and $\overline{M}_d$, and then the decreasing trend goes well beyond the $\beta/\beta+\omega$ phase boundary into the Zr-based Ti-Nb-Zr region in the triangle. On the other hand, at least for binary Ti alloys, the lowest elastic modulus tends to correspond to a specific range of the electron/atom ($e/\alpha$) ratio if the $\omega$-phase is suppressed [40]. On this basis, using the phase boundaries defined in Fig. 5.2 for Ti-Nb-Zr alloys as a starting point, we introduced the $e/\alpha$ boundaries from 4.1 to 4.3 in the form of four equal zones as shown in Fig. 5.3. In addition to assisting in defining elastic modulus, these $e/\alpha$ lines can further assist in predicting the formation of $\alpha$, $\beta$, $\alpha'$, and $\omega$ (the formation of $\alpha''$ can be inferred from other information). For example, for binary Ti-M (M = $\beta$ stabiliser) alloys, at the $e/\alpha$ range of $4.04 < e/\alpha < 4.1$, $\alpha'$ tends to form
while $\alpha''$ tends to form in the range of $4.1 < \frac{e}{a} < 4.15$ and reaches its maximum stability at $\frac{e}{a} = \sim 4.15$ [40, 41]. The formation of the $\omega$ phase occurs over a broad range but reaches its maximum stability over the $\frac{e}{a}$ range of $4.13 < \frac{e}{a} < 4.15$ [40, 41], beyond which the formation of the $\omega$ phase will be progressively suppressed towards increasing stabilisation of the $\beta$ phase [41].

The two low-elastic-modulus Zr-based Ti-6Nb-53Zr and Ti-18Nb-51Zr alloys from Fig. 5.1 are superimposed on Fig. 5.3 to further inform our alloy design. The superimposed data suggest a potential region for the design of low-elastic-modulus Zr-Ti-Nb alloys. Based on the above theoretical analyses, five new alloys are finally designed, which are designated as Alloys 1-5 in Fig. 5.3, defined by $\overline{B_o}$, $\overline{M_d}$, and $\frac{e}{a}$. Table 5.1 lists these five designed alloys (Alloys 1-5) plus those two (Alloys 6 and 7) from the literature and their $\overline{B_o}$, $\overline{M_d}$, and $\frac{e}{a}$ values, liquidus and solidus temperatures, and $T_0$ values.
Figure 5.2 $B_0 - \bar{M}_d$ diagram for Ti-Nb-Zr alloys adapted from literature [21-29].
Figure 5.3 $B_o - M_d - e/a$ diagram for the five new designed Zr-Ti-Nb alloys.
Table 5.1 Newly designed alloy compositions and their $\overline{B_o}, \overline{M_d}$ and $e/\alpha$ values.

<table>
<thead>
<tr>
<th>Alloy Composition (at.%)</th>
<th>Alloy Composition (wt.%)</th>
<th>Composition by detailed EDS analysis (at.%)</th>
<th>$\overline{M_d}$ (eV)</th>
<th>$\overline{B_o}$</th>
<th>$e/\alpha$</th>
<th>$T_0^*$ (°C)</th>
<th>Liquidus $T_L^*$ (°C)</th>
<th>Solidus $T_S^*$ (°C)</th>
<th>Mo-Eq. values</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Zr-45Ti-15Nb</td>
<td>Zr-30Ti-19.3Nb</td>
<td>38.35 ± 0.4 Zr 46.85 ± 0.3 Ti 14.85 ± 0.2 Nb</td>
<td>2.64</td>
<td>2.95</td>
<td>4.15</td>
<td>193</td>
<td>1653</td>
<td>1622</td>
<td>11.14</td>
</tr>
<tr>
<td>2. Zr-33Ti-15Nb</td>
<td>Zr-20.6Ti-18Nb</td>
<td>50.3 ± 0.1 Zr 34.75 ± 0.1 Ti 14.85 ± 0.1 Nb</td>
<td>2.7</td>
<td>2.99</td>
<td>4.15</td>
<td>190</td>
<td>1675</td>
<td>1647</td>
<td>12.0</td>
</tr>
<tr>
<td>3. Zr-28Ti-15Nb</td>
<td>Zr-17Ti-17.6Nb</td>
<td>55.55 ± 0.3 Zr 29.55 ± 0.1 Ti 14.9 ± 0.2 Nb</td>
<td>2.72</td>
<td>3.01</td>
<td>4.15</td>
<td>201</td>
<td>1690</td>
<td>1662</td>
<td>12.35</td>
</tr>
<tr>
<td>4. Zr-35Ti-10Nb</td>
<td>Zr-22Ti-12.2Nb</td>
<td>53.7 ± 0.1 Zr 36.25 ± 0.1 Ti 10.05 ± 0.2 Nb</td>
<td>2.71</td>
<td>2.98</td>
<td>4.1</td>
<td>326</td>
<td>1652</td>
<td>1628</td>
<td>11.11</td>
</tr>
<tr>
<td>5. Zr-30Ti-20Nb</td>
<td>Zr-18.4Ti-23.6Nb</td>
<td>48.85 ± 0.2 Zr 31.6 ± 0.2 Ti 19.55 ± 0.1 Nb</td>
<td>2.69</td>
<td>3.00</td>
<td>4.2</td>
<td>53</td>
<td>1703</td>
<td>1668</td>
<td>12.97</td>
</tr>
<tr>
<td>6. Zr-41Ti-6Nb</td>
<td>Zr-26.7Ti-7.6Nb</td>
<td></td>
<td>2.70</td>
<td>2.97</td>
<td>4.06</td>
<td></td>
<td></td>
<td></td>
<td>10</td>
</tr>
<tr>
<td>7. Zr-31Ti-18Nb</td>
<td>Zr-19Ti-21.4Nb</td>
<td></td>
<td>2.69</td>
<td>2.99</td>
<td>4.18</td>
<td></td>
<td></td>
<td></td>
<td>12.62</td>
</tr>
</tbody>
</table>

*Calculated using Pandat™ CompuTherm database
5.3 Materials and Methods

5.3.1 Sample fabrication

Sample ingots of each new alloy in Table 5.1 were synthesized by arc-melting of a mixture of pure metals (purity > 99.9 wt.%) in a Ti-gettered high-purity argon atmosphere. Each ingot was re-melted four times to ensure chemical homogeneity. The melt was finally drop-cast into a cylindrical copper mould with dimensions of \( \Phi 10 \text{ mm} \times 60 \text{ mm} \) to produce test samples for characterisation of mechanical properties and ultrasonic elastic modulus. The oxygen content was estimated to be about 0.1-0.15 wt.%.

5.3.2 Phase and microstructural characterization

Disc samples with a diameter of 10 mm and a thickness of 3 mm were ground with SiC abrasive papers of up to 4000 grit and then polished using a mixture of colloidal silica and \( \text{H}_2\text{O}_2 \) for microstructural characterization. All as-polished samples were cleaned in an ultrasonic bath using ethanol. Kroll solution was used to etch the samples for microstructural characterization.

Phase identification was conducted using a Bruker D8 Advance X-ray diffractometer (XRD) with a Cu K\( \alpha \) radiation source at room temperature and the data was analysed using the MAUD software. The microstructure of each alloy was analysed by an optical microscope (Leica- DM2500) equipped with a Leica DFC310 FX camera and a FEI NanoSEM scanning electron microscope (SEM) equipped with an Oxford Instruments X-MaxN 20 energy dispersive X-ray spectroscopy (EDS) detector. According to the EDS spatial resolution calculated using the equation given in the literature [35], the radius of volume detected by EDS for Nb is \(~0.83 \ \mu \text{m} \) at 25 kV (\( k\alpha = 16.581 \text{ kV} \) for Nb) and that for Zr is \(~1.19 \ \mu \text{m} \) at 25 kV (\( k\alpha = \text{kV} \) for Nb). For Ti, this resolution radius at 25 kV reaches 2.99 \( \mu \text{m} \). Therefore,
although it is EDS analysis, it is essentially small bulk-volume analysis. On the other hand, after solution treatment, each alloy is homogeneous. Hence, it is justified to do this small bulk-volume compositional analysis by EDS at multiple areas. In this study, at least three regions with an area of 2.2 mm$^2$ (each region) were analysed for each alloy.

5.3.3 Mechanical property testing

Dog-bone-shaped tensile samples with a gauge length of 20 mm, a width of 5 mm and an approximate thickness of 1.3 mm were prepared via electric discharging machining. Tensile tests were carried out on a CMT4105 universal electronic tensile testing machine with a strain rate of $1 \times 10^{-3}$ s$^{-1}$. A strain gauge was used to measure the strain and the strain was evaluated at low stress. This measurement was repeated several times for validity check. Tensile strength, yield strength, elastic modulus, elastic energy, toughness and strain-to-fracture of each Zr-Ti-Nb alloy were measured from stress strain curves. Compression tests of samples (Φ2mm × 4mm) were conducted on a CMT4305 machine at a strain rate of $2 \times 10^{-4}$ s$^{-1}$. The compressive elastic modulus and strength were measured from compressive stress strain curves. The strength was determined by taking the average of two samples for each alloy.

The elastic modulus (E) of each Zr-Ti-Nb alloy was further determined by ultrasonic modulus measurements (Model RAM-5000, RITEC, USA) from cylindrical samples of Φ10mm × 10mm. The elastic modulus can be calculated using Eq. (5.3):

$$E = \frac{\rho V_s^2 (3V_L^2 - 4V_s^2)}{V_L^2 - V_s^2}$$ (5.3)

where $\rho$ is the density of the material which has been obtained by the Archimedes method, and $V_L$ and $V_s$ are the ultrasonic longitudinal and shear wave velocities, respectively. They can be determined from Eq. (5.4):
\[ V = \frac{2t}{t} \]  

where \( t \) is the time interval between the contiguous peaks of an ultrasonic longitudinal or shear wave and \( l \) is the length of the sample.

5.4 Results and discussion

5.4.1 Constituent phases and microstructures of as-cast Zr-Ti-Nb alloys

Detailed EDS compositional analyses of the designed Zr-Ti-Nb alloys are listed in Table 5.1, which are consistent with the nominal composition of each alloy. Fig. 5.4a shows the XRD patterns obtained from the as-cast seven Zr-Ti-Nb alloys in Table 5.1. To help understand the constituent phases detected, Fig. 5.4b displays the Zr-Ti phase diagram plotted using the Pandat\textsuperscript{TM} CompuTherm database. \( \beta \)-Zr phase was found to be prevalent in each alloy. This is consistent with the expectations based on the molybdenum-equivalence (Mo-Eq.) listed in Table 5.1 (>10 for each alloy) and the fast cooling rate used to fabricate these alloys.

The \( 2\Theta \) for the \( \beta \)-Zr phase shifts towards higher values with increasing Ti content and decreasing Nb content. At the given Nb content of 15 at.\%, the \( 2\Theta \) for \( \beta \)-Zr similarly moves towards higher values with increasing Ti content. In addition, XRD detected the presence of both \( \omega \) and \( \alpha'' \) phases in three of the new designed alloys and the presence of the \( \alpha'' \)-phase in the Zr-45Ti-15Nb alloy, while only Zr-30Ti-20Nb was free of both \( \omega \) and \( \alpha'' \) phases. Zr-31Ti-18Nb and Zr-30Ti-20Nb were able to retain the single \( \beta \)-Zr phase state due to their high Nb content (18-20 at.\%) or higher Mo-Eq. values (Table 5.1). The \( \alpha' \)-phase was detected only in the Zr-41Ti-6Nb alloy due to its lower Nb content (< 10at. \%) and the copper mould casting process. The formation of these different second phases is in line with the predictions based on the \( e/a \) value discussed earlier. For example, Zr-41Ti-6Nb has an \( e/a \) ratio of 4.06 (Table 5.1), which is clearly below 4.10. Therefore, only \( \alpha' \) is expected to form on fast cooling,
which was confirmed by XRD (Fig. 5.4a). Another example is that Zr-30Ti-20Nb has the highest $\varepsilon/\alpha$ ratio (4.20, Table 5.1) of the seven alloys investigated and its $\varepsilon/\alpha$ ratio is at about the minimum value for the disappearance of $\omega$ towards forming an essentially single $\beta$ phase. Indeed, XRD detected no presence of $\omega$ and $\alpha''$ in this alloy. Split peaks from $\beta$-phase were found at several alloys suggesting the existence of $\beta$-phases with different compositions, which can be attributed to local micro-segregation. These microstructural features are expected to result in different elastic moduli and tensile and compressive strengths and ductility.
Figure 5.4 (a) XRD patterns of the new designed as-cast Zr-Ti-Nb alloys and two as-cast Zr-based alloys (Ti-18Nb-51Zr and Ti-6Nb-53Zr) from the literature, (b) Zr-Ti phase diagram obtained using Pandat™ CompuTherm database.

It should be noted that Zr is normally treated as a neutral element in Ti and vice versa. However, the presence of Nb can convert Zr into an effective β-stabilizer in Ti, which has recently been assessed in detail [21, 42]. The same is expected for Ti in Zr. Hence, the phases detected by XRD in Fig. 5.4a include the influence of Zr as a β-stabilizer of Ti. The calculated Mo-Eq. values for each alloy based on Ref. [42] are listed in Table 5.1, which are equal to or greater than 10 wt.% Hence, β-phase is retained as the predominant phase in each alloy during copper mould casting (Fig. 5.4a).
In the above analyses, both the $e/\alpha$ ratio and the Mo-Eq. have been used to discuss the stability of the $\beta$-phase. Fig. 5.5 shows the correlation between the Mo-Eq. and $e/\alpha$ ratio for the seven alloys studied. An approximate linear trend existed between them. Since an increased Mo-Eq. implies increased $\beta$-phase stability, together they provide a more informative prediction of the $\beta$-phase stability in these alloys.

![Graph showing correlation between Mo-Eq. and $e/\alpha$ ratio](image)

**Figure 5.5** Correlation between the Mo-Eq. and $e/\alpha$ ratio for the seven alloys studied.

Fig. 5.6 shows the representative optical microstructure of each alloy. The prior $\beta$ grain boundaries are unclear in Zr-30Ti-20Nb and Zr-45Ti-15Nb, which both showed fine equiaxed dendrites (Fig. 5.6a and b). In contrast, the prior $\beta$ grain boundaries are distinct in both Zr-33Ti-15Nb and Zr-28Ti-15Nb (Fig. 5.6c and d). The two low Nb-containing alloys of
Zr-41Ti-6Nb and Zr-35Ti-10Nb displayed clear columnar grains Fig. 5.6e and f), which can be attributed to the low growth restriction effect of Nb because of the low Nb content. In addition, Zr-41Ti-6Nb showed α′-martensite inside the columnar β-grains due to its lowest Mo-Eq. value (Table 5.1). The Zr-31Ti-18Nb (Ti-18Nb-51Zr) alloy exhibited a mixed structure of elongated and equiaxed grains (Fig. 5.6g). No martensite plates or needles were observed due to its high Mo-Eq. value (12.62 wt.%), consistent with the XRD results (Fig. 5.4a).

In summary, the phase constituents in each as-solidified Zr-Ti-Nb alloy can be reasonably understood based on the $e/a$ ratio and Mo-Eq. of each alloy, where these two parameters exhibited an approximate linear relationship. The optical microstructure showed significant variations. Limited information is available in the literature about the solidification of Zr-based alloys.
(a) Zr-30Ti-20Nb  
(b) Zr-45Ti-15Nb  
(c) Zr-28Ti-15Nb  
(d) Zr-33Ti-15Nb  
(e) Zr-35Ti-10Nb  
(f) Zr-41Ti-6Nb (Zr-based Ti-6Nb-53Zr)
(g) Zr-31Ti-18Nb (Zr-based Ti-18Nb-51Zr)

**Figure 5.6** Optical micrographs of each as-cast Zr-Ti-Nb alloy.

### 5.4.2 Elastic modulus, strength and ductility of as-cast Zr-Ti-Nb alloys

The elastic modulus is an important property in the selection of an implant material. It is largely determined by the bonding force between principal constituent atoms and can be affected by alloying additions, heat treatment and plastic deformation [43, 44]. In this study, the elastic modulus of each alloy is measured by three different methods, i.e., ultrasonic testing, tensile testing, and compression testing. The ultrasonic testing procedure has been detailed under Section 5.3.3 while the elastic modulus values under tension and compression were obtained from the tensile and compressive stress-strain curves. Fig. 5.7 (a, b) shows representative tensile and compressive stress-strain curves, while the elastic modulus values obtained by all three different methods are summarised in Fig. 5.8. Table 5.2 lists the basic tensile and compressive property values.

The elastic modulus under compression is known to be always much lower than that obtained from either ultrasonic testing or tensile testing. The same observations were made with the Zr-Ti-Nb alloys in this study. Therefore, the discussion below will focus on the ultrasonic elastic modulus and tensile elastic modulus.
Zr-28Ti-15Nb and Zr-33Ti-15Nb exhibited the lowest ultrasonic elastic modulus. In addition, their tensile elastic modulus was measured to be ~60 GPa, consistent with the ultrasonically measured. It is ~30% lower than the elastic modulus of CP Zr. It should be stressed that this low elastic modulus (~60 GPa, both ultrasonic and tensile) is achieved in the as-cast state.

Zr-45Ti-15Nb showed marginally higher elastic modulus than Zr-28Ti-15Nb and Zr-33Ti-15Nb but the absolute elastic modulus value remains low (~65 GPa, ultrasonic). In contrast, the low-elastic-modulus Zr-41Ti-6Nb and Zr-31Ti-18Nb alloys reported in the literature [11, 15, 22] both exhibited much higher elastic modulus in the as-cast state (Fig. 5.8). In fact, to the authors’ knowledge, almost all the low-elastic-modulus titanium alloys reported in the literature refer to severely deformed conditions, rather than the as-cast state. The low elastic modulus of the as-cast Zr-28Ti-15Nb and Zr-33Ti-15Nb alloys implies that both alloys can be made into intricate implants by metal casting or PBF-MAM without resort to subsequent heat treatment or plastic deformation to reduce elastic modulus. This can be a significant advantage in the manufacture of custom-made low-elastic-modulus implants. On the other hand, in the as-cast state, both alloys showed excellent tensile ductility (~16%) with the uniform plastic strain of greater than 10% and sufficiently high tensile yield strength (~650 MPa). Together with the intrinsically low magnetic susceptibility of Zr, they have the potential to be used as desired implant alloys.

Zr-45Ti-15Nb and Zr-35Ti-10Nb both showed higher elastic modulus (~70 GPa) by ultrasonic and tensile testing measurements but they can still be regarded as low elastic modulus alloys. Zr-30Ti-20Nb exhibited the highest elastic modulus by both ultrasonic testing (94 GPa) and tensile testing (~80 GPa). It had the highest Mo-Eq. value due to its high Nb content. The alloy from the literature, Zr-31Ti-18Nb, which contained the second highest level of Nb, was also fully β-phase by XRD. Similarly, it displayed the highest elastic
modulus by ultrasonic testing (94 GPa). The two alloys of Zr-30Ti-20Nb and Zr-31Ti-18Nb are similar in both composition and as-cast microstructure and both exhibited high elastic modulus by ultrasonic testing. The effect of the second phase on elastic modulus will be discussed separately in Section 5.4.3.

Table 5.2 Mechanical properties of Zr-Ti-Nb alloys.

<table>
<thead>
<tr>
<th>Alloy composition (at.%)</th>
<th>Yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Elongation (%)</th>
<th>Elastic admissible strain (%)</th>
<th>Elastic energy (MJ/m³)</th>
<th>Compressive strength (MPa)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Zr-45Ti-15Nb</td>
<td>680</td>
<td>690</td>
<td>18.5</td>
<td>0.97</td>
<td>3.31</td>
<td>986±29.1</td>
</tr>
<tr>
<td>Zr-33Ti-15Nb</td>
<td>650</td>
<td>658</td>
<td>15.6</td>
<td>1.11</td>
<td>3.6</td>
<td>777.41±40.3</td>
</tr>
<tr>
<td>Zr-28Ti-15Nb</td>
<td>655</td>
<td>662</td>
<td>17.2</td>
<td>1.00</td>
<td>3.29</td>
<td>935±7.3</td>
</tr>
<tr>
<td>Zr-35Ti-10Nb</td>
<td>720</td>
<td>740</td>
<td>12.9</td>
<td>1.13</td>
<td>4.08</td>
<td>548.4±86.3</td>
</tr>
<tr>
<td>Zr-30Ti-20Nb</td>
<td>778</td>
<td>778</td>
<td>15.8</td>
<td>0.99</td>
<td>3.86</td>
<td>852.7±37.8</td>
</tr>
</tbody>
</table>
(a)
Figure 5.7 Engineering and true stress - strain curves of as-cast Zr-Ti-Nb alloys: a) tensile test, and b) compression test.
In biomedical applications, a preferred implant material is expected to show high tensile yield strength and low elastic modulus. The elastic admissible strain is defined as the ratio of yield strength to elastic modulus, which is an important selection parameter for implant materials. The elastic admissible strain values of these Zr-Ti-Nb alloys range from 0.97% to 1.13% (Table 5.2), which are clearly higher than those of commercially available Ti-based alloys (0.47%-0.99%) [14].

Elastic energy plays an important role in understanding the mechanical behaviour of hard tissue replacements, which usually work in the elastic deformation mode. During the deformation, the external force stores their work in the solid as elastic energy ($\delta_e$), which can be expressed as:

$$\delta_e = \frac{\sigma_y^2}{2E}$$

Figure 5.8 Compressive, tensile and ultrasonic elastic moduli of Zr-Ti-Nb alloys.
where $\sigma_y$ is yield strength and $E$ is elastic modulus. High elastic energy implant materials are always preferred. The elastic energy of the Zr-Ti-Nb alloys is calculated to be in the range of 3.29 to 4.08 MJ/m$^3$ (Table 5.2), which is clearly higher than that of the medical grade extra low interstitial (ELI) Ti-6Al-4V (~3.28 MJ/m$^3$) [45].

The compression stress-strain curves of the Zr-Ti-Nb alloys are shown in Fig. 5.7b. Their compressive yield strength ranges from 550 MPa to 985 MPa compared to less than 210 MPa for cortical bones [7]. Hence, they are sufficient as cortical bone replacements including in various porous or lattice forms for a close match in terms of both strengths and elastic modulus.

5.4.3 The dependence of elastic modulus on \( \bar{B}_o - \bar{M}_d \), \( e/\alpha \) ratio and secondary phases

According to the discussion in Section 5.2, alloys with higher values of \( \bar{B}_o \) and \( \bar{M}_d \) along the metastable $\beta$-phase boundary and an $e/\alpha$ ratio from 4.1 to 4.25 have the high potential to achieve low elastic modulus. Fig. 5.9 reproduces the expected schematic relationship between the $e/\alpha$ ratio and elastic modulus together with the influence of secondary phases established primarily for Ti alloys [40]. In general, if the alloy has an $e/\alpha$ ratio of 4.15, the presence of both $\omega$ and $\alpha''$ in the $\beta$-matrix is expected to lead to the highest elastic modulus. In contrast, if the formation of the $\omega$-phase is suppressed at $e/\alpha$= 4.15 or close to 4.15, then the elastic modulus is expected to follow the dashed line in Fig. 5.9, i.e., the lowest values. Alternatively, the formation of the $\alpha''$-martensite in the $\beta$-matrix at $e/\alpha$ ratio = 4.1 could also lead to low elastic modulus, so could a single $\beta$-phase matrix with $e/\alpha = 4.2 - 4.25$ by Fig. 5.9.

The results from this study suggest that the as-cast Zr-Ti-Nb alloys with an $e/\alpha$ ratio of 4.15 can exhibit low elastic modulus when measured by all three methods (tensile, compression
and ultrasonic). Following the empirical rule of $\varepsilon/\alpha = 4.15$, Zr-45Ti-15Nb, Zr-33Ti-15Nb and Zr-28Ti-15Nb alloys should offer the lowest elastic modulus. This agrees well with the experimental data in Fig. 5.8. Based on the $B_o$ and $M_d$ values, the elastic modulus of both Zr-33Ti-15Nb and Zr-28Ti-15Nb should be lower than that of Zr-45Ti-15Nb as high values of $B_o$ and $M_d$ are expected to lead to low elastic modulus. Again, the experimental results supported these two cases (Fig. 5.8). Hence, the combination of high values of $B_o$ and $M_d$ in conjunction with $\varepsilon/\alpha = 4.15$ has proved to be effective in the design of low-elastic-modulus Zr-Ti-Nb alloys in the as-cast state.

![Graph](image)

**Figure 5.9** Relationship between $\varepsilon/\alpha$ ratio and elastic modulus [40], with superimposed experimental data from this study.

It has been suggested that the elastic modulus (E) of different phases in Ti alloys follows the sequence of $E_\beta \approx E_{\alpha''} \approx 60\text{-}90$ GPa $< E_{\alpha} \approx 100$ GPa $< E_\omega \approx 130\text{-}220$ GPa [5, 46]. On this basis, Tane et al. [47] further suggested that Ti alloys that can retain all the $\beta$-phase at room temperature but have low $\beta$-phase stability, i.e., having a high tendency to the $\beta \rightarrow \alpha''$
transformation, can offer the lowest elastic modulus. Zhou et al. [48] suggested that both $\alpha'$ + $\alpha''$ and $\alpha'' + \beta$ phases can offer a good combination of high tensile strength and low elastic modulus. However, this suggestion remains controversial. Matsumoto [49] and Hao et al. [50] pointed out that the relationship regarding the elastic modulus of metastable $\beta$, $\alpha'$ and $\alpha''$ is not straightforward, whereas Hisata et al. [19] showed that the elastic modulus of these metastable phases should follow the sequence of $\alpha'' < \beta < \alpha'$. Indeed, low elastic modulus was achieved with 100% $\alpha''$-martensite with no retained metastable $\beta$-phase by some researchers [51, 52]. In this study, the two low-elastic-modulus alloys Zr-28Ti-15Nb and Zr-33Ti-15Nb both contained $\omega$-phase and $\alpha''$-martensite. The same occurred to the Zr-35Ti-10Nb alloy, which showed the presence of both $\omega$-phase and $\alpha''$-martensite by XRD. However, all these three alloys exhibited low elastic modulus by both ultrasonic testing and tensile testing (~60 GPa, Fig. 5.8). Considering that $\beta$-phase is still the major phase in these three alloys, according to the experimental results shown in Fig. 5.8, it can be inferred that the elastic modulus of the $\alpha''$-martensite should be smaller than 40 GPa. On the other hand, the presence of the $\omega$-phase is known to increase elastic modulus. Hence, if the $\omega$-phase can be completely suppressed in the above three alloys, their elastic modulus could become even lower. In any case, having the single $\beta$-phase at room temperature gave rise to high elastic modulus. For instance, both Zr-30Ti-20Nb and Zr-31Ti-18Nb displayed high elastic modulus (~90 GPa, ultrasonic).

The experimental elastic modulus values have been superimposed onto Fig. 5.8. Based on the above analyses, we suggest the following slightly modified sequence for the elastic modulus of different phases: $E_{\omega''} < 40$ GPa $< E_{\beta} \approx 60-90$ GPa $< E_{\alpha} \approx 100$ GPa $< E_{\omega} \approx 130-220$ GPa. As a result, $E_{\beta + \alpha'' + \omega}$ can still be easily smaller than $E_{\beta}$ because the contribution from the $\omega$ phase can be assumed to be small in most cases due to its small volume fraction. The experimental
data in Fig. 5.8 supports the concept that the minimum elastic modulus corresponds to $\frac{e}{a} = 4.15$.

### 5.5 Conclusions

In order to develop low elastic modulus Zr alloys in the as-cast state, a new set of Zr-based Ti-Nb-Zr alloys were designed using the $d$-electron theory together with the $\frac{e}{a}$ ratio criterion and evaluated experimentally. In addition, the effects of the alloying elements on the microstructure and mechanical properties of these alloys were investigated. The major findings of this study are summarised as follows:

- Five new low elastic modulus Zr-Ti-Nb alloys (Zr-45Ti-15Nb, Zr-33Ti-15Nb, Zr-28Ti-15Nb, Zr-35Ti-10Nb, and Zr-30Ti-20Nb) were designed and assessed. The elastic modulus of these alloys in the as-cast state ranges from 58-79GPa (tensile), 45-57GPa (compressive) and 60-95GPa (ultrasonic). Of them, Zr-33Ti-15Nb and Zr-28Ti-15Nb alloys showed the lowest elastic modulus (~60 GPa, tensile and ultrasonic) in the as-cast state but they both contained a small amount of the $\omega$-phase.

- A modified relationship between each constituent phase and its elastic modulus has been proposed, which is given by $E_{\alpha''} < 40$ GPa $< E_{\beta} \approx 60-90$ GPa $< E_{\alpha} \approx 100$ GPa $< E_{\omega} \approx 130-220$ GPa. Having the single $\beta$-phase at room temperature gave rise to higher elastic modulus than also having the presence of $\alpha''$ and a small amount of $\omega$ for the seven alloys studied.

- A linear relationship was found to exist between the Mo-Eq. and the $\frac{e}{a}$ ratio for the seven Zr-Ti-Nb alloys investigated. Together they provide a more informative tool for assessing the stability of the $\beta$-phase in the Zr-Ti-Nb alloys studied.

- Both Zr-28Ti-15Nb and Zr-33Ti-15Nb alloys in the as-cast state offer low elastic modulus (~60 GPa, tensile and ultrasonic), excellent tensile ductility (~16%), uniform
plastic strain (greater than 10%) and sufficiently high tensile yield strength (~650 MPa). In addition, Zr offers low magnetic susceptibility. Compared with Ti-6Al-4V, they further offer much higher elastic admission strain and elastic energy.

- The combination of the \(d\)-electron theory with the \(e^2/\alpha\) ratio can be a critical design tool for the development of low elastic modulus and strong and ductile Zr-Ti-Nb alloys in the as-cast condition. This tool can be further improved by incorporating the predicted phase constituents in the designed alloy.

References


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Chapter 6 Design and development of low-elastic-modulus as-cast Ti-Nb-Zr alloys for biomedical applications

6.1 Introduction

The recent increase of bone replacements and repairs results in increased demand for the development of orthopaedic biomaterials, which has attracted much attention [5]. However, these biomaterials should be biologically and mechanically compatible with human bones [36]. An implant material can be considered as biologically compatible when it is free from genotoxic (DNA damaging), cytotoxic (cell destruction/ killing), carcinogenic (cancer-causing), mutagenic (mutation causing), allergenic (allergic response), and neurological effects in the human body [37]. On the other hand, when the mechanical properties of an implant material match with those of human bone, then it can be considered as a mechanically compatible implant material. The mechanical properties (elastic modulus, tensile strength, fracture toughness and fatigue strength) play a critical role in materials selection for implant application.

The most commonly used orthopaedic biomaterials are conventional (α + β) titanium (Ti) alloys (such as Ti-6Al-4V alloy), Co-Cr alloys or stainless steels. Ti alloys are preferable in the biomedical field due to their unique combination of mechanical properties, superior biocompatibility and excellent corrosion resistance. Currently, Ti alloys (mostly Ti-6Al-4V) are used to manufacture approximately 70–80% of total hip replacement implants; for example, acetabular cups and femoral stems [38]. However, the potential adverse effect [39] of vanadium (V) and neurological side effects [40] and genotoxic effects [41] of aluminium (Al) have been a strong driving force for the development of implant alloys with no toxic element. Another primary concern is the “stress shielding” effect [12]. Long-term clinical
investigations have indicated that insufficient load transfer from artificial implants to adjacent remodelling bone might result in bone resorption and potential loosening of the prosthetic device. This effect is caused by the mismatch of elastic modulus between the implant material and the bone [12]. Although Ti-6Al-4V offers much lower elastic modulus (110 GPa) [10] compared with 316L stainless steel (190-210GPa) [5] and Co-Cr alloys (210-253GPa) [5], its elastic modulus is still about 3-8 times higher than that of healthy cortical bones (13-35 GPa) [10, 11].

The superior cold-forming ability of β-Ti alloys (e.g. Ti–15Mo–5Zr–3Al) over (α + β)-Ti alloys (e.g. Ti–6Al–4V) [42] decreases the manufacturing cost, which is an advantage for commercial products [36]. Moreover, metastable β-Ti alloys (β-matrix along with α, α’, ω, and α”) exhibit lower elastic moduli than that of other Ti-alloys [43, 44] due to the lower lattice atomic density and weaker bonds in the body-centred cubic (BCC) crystal structure of the β-phase versus the α-phase [45]. One of the most common β-Ti alloy systems is Ti-Nb-Zr. It has been reported that the binary Ti-Nb alloys contain lower elastic modulus than that of other binary Ti alloys [23, 24]. Zr is a unique alloying element for Ti-Nb alloys. It can act as a β-stabilizing element in Ti-Nb based alloys [25] although Zr is commonly known as a neutral element. However, the β stabilizing effect of Zr in Ti-based alloys is not straightforward [25]. As a result, the Ti-Nb-Zr system has been widely investigated, and researchers have developed many Ti-Nb-Zr alloys with different combinations of Nb and Zr [17-20]. However, an ideal alloy composition from this system is still elusive.

The approach used for the design of low elastic modulus implant Ti alloys is crucial. In the course of designing low modulus Zr-based Ti-Nb-Zr alloys (Chapter 5), we realized that Ti-based Ti-Nb-Zr alloys could also have the potential to offer low elastic modulus with good tensile mechanical strength and high tensile ductility in the as-cast condition, without
subsequent heat treatment or thermo-mechanical processing. In addition to elastic modulus and mechanical strength, the tensile ductility is also important in that human cortical bone shows tensile ductility up to 4% [46]. It is clear that 3D printing will become a predominant fabrication method for custom-made implants. However, 3D-printed dense Ti-6Al-4V implants by selective laser melting (SLM) cannot always ensure more than 4% of tensile ductility in the as-built state due to the formation of the $\alpha'$-martensite. On the other hand, 3D-printed Ti-6Al-4V lattice implants, which are more commonly used as implants, offer much lower tensile ductility than 4% or even no tensile ductility [46]. The current hypothesis behind this mechanical deficiency is that human cortical bones mainly experience compressive loading in normal daily life. This is a potential risk for the widespread applications of SLM-fabricated Ti-6Al-4V lattice implants because compressive loading can lead to large local tensile strain. Currently, the minimum tensile ductility required for dense mill-annealed Ti-6Al-4V is 10%, which is clearly insufficient when the alloy is printed into an implant by SLM. Considering that powder bed fusion metal 3D printing is an additive layer melting and solidification process, similar to layer casting, we propose that any potential titanium implant alloy designed for 3D printing should offer the minimum tensile ductility of 10% in the as-cast condition. As-cast Ti-6Al-4V does not meet this requirement [47] and therefore leaves a potential risk in tensile ductility after 3D printing by SLM.

In this study, four different Ti-based Ti-Nb-Zr alloys are designed based on the combined use of the $d$-electron theory [48] and the $\frac{\mu}{\alpha}$ ratio [49]. Their molybdenum-equivalence (Mo-Eq.) values (Mo-Eq.) values are assessed as well. The elastic modulus of each alloy is measured in three different methods (i. e tensile, compression and ultrasonic vibration). The phase composition, microstructure and other mechanical properties of these alloys are also investigated. The purpose is to design and develop a simple and suitable ternary Ti-Nb-Zr alloy that can offer low elastic modulus, excellent ductility and enough strength in the as-cast
condition for fabrication by metal additive manufacturing or 3D printing. To the authors’ knowledge, few such as-cast biocompatible titanium alloy exists at present.

6.2. Materials and Methods

6.2.1. Alloy design

Previously, the development of new alloys was time-consuming and expensive, as the trial-and-error method was used to design new alloys. Since Morinaga et al. [50] developed the d-electron theory, the new alloy development has become more realistic. The d-electron theory was developed based on DV-Xα molecular orbital calculations of the electronic structures of an alloy which describes the dependence of elastic properties of alloys on the phase stability of those alloys. This theory can be explained through two electronic parameters bond order, $B_o$ and d-orbital energy level, $M_d$ [51]. $B_o$ can be defined by the covalent bond strength between Ti and other alloying elements, and $M_d$ can correlate the electronegativity and metallic radius of the elements. The compositional average of these $B_o$ and $M_d$ values can be obtained by

$$\bar{B}_o = \sum X_i (B_o)_i$$

$$\bar{M}_d = \sum X_i (M_d)_i$$

where, $X_i$, $(B_o)_i$, and $(M_d)_i$ are the atomic fractions, bond order and d-orbital energy level of the given element $i$, respectively. By considering the compositional average of the $B_o$ and $M_d$ values of each alloying element in the titanium alloy, a $\bar{B}_o$-$\bar{M}_d$ diagram has been reconstructed, as shown in Fig. 6.1.

According to Abdel et al. [52], alloys with low elastic modulus can be found along the $\beta/\beta+\omega$ phase boundary with increasing $\bar{B}_o$ and $\bar{M}_d$ values, in the $\bar{B}_o$-$\bar{M}_d$ diagram. Another important criterion for alloy design is electron to atom ration ($E/A$) ratio. Yang et al. [53] reported that
Ti-based binary alloys with $e/\alpha$ ratio between 4.1 to 4.25 could have the lowest elastic modulus if the $\omega$-phase is suppressed. On this basis, the $e/\alpha$ boundaries from 4.1 to 4.3 in the form of four equal zones were introduced in the $\overline{B_o-M_d}$ diagram for Ti-Nb-Zr alloy system as shown in Fig. 6.1. Any alloy hosting on the $e/\alpha = 4.1$ line in the $\overline{B_o-M_d}$ diagram, indicates that $e/\alpha$ ratio of that alloy is 4.1. Thus, $e/\alpha$ values of different Ti-Nb-Zr alloys can be easily determined from this modified $\overline{B_o-M_d}$ diagram. In addition, these $e/\alpha$ lines can further assist to predict the formation of $\alpha$, $\beta$, $\alpha'$, and $\omega$-phase. For instance, in binary Ti-M (M = $\beta$ stabiliser) alloys, $\alpha'$ forms at of $4.04 < e/\alpha < 4.1$. On the other hand, $\alpha''$ forms at $4.1 < e/\alpha < 4.15$ and maximum stability occurs at $e/\alpha = \sim 4.15$ [49, 54]. The $\omega$ phase formation attains maximum stability at $4.13 < e/\alpha < 4.15$ [49, 54], beyond which the $\omega$ phase formation will be suppressed in order to increase the stabilisation of the $\beta$ phase [54]. In this study, four new Ti-based Ti-Nb-Zr alloys were developed based on $\overline{B_o-M_d}$ diagram and $e/\alpha$ ratio as shown in Fig. 6.1. The $\overline{B_o}$, $\overline{M_d}$, and $e/\alpha$ ratio values of these four newly developed alloys are listed in Table 6.1.
Figure 6.1 $\overline{B}_o - \overline{M}_d - e/\alpha$ diagram for the four new designed Ti-Nb-Zr alloys.

6.2.2. Sample fabrication

Alloy ingots were melted by arc-melting of a mixture of pure metals (purity > 99.9 wt.%) in a Ti-gettered high-purity argon atmosphere. The chemical homogeneity was confirmed by remelting the alloy ingots at least four times. The melted alloys were then drop-cast into copper moulds with the dimensions of $\Phi 10\text{mm} \times 60\text{mm}$ and samples were produced to test the mechanical properties and ultrasonic elastic modulus. The nominal compositions of these alloys are given in Table 6.1. The oxygen content was about 0.1-0.15 wt.%.
Table 6.1 Newly designed alloy compositions and their $\overline{B_o}$, $M_d$, $e/\alpha$ and Mo-Eq values.

<table>
<thead>
<tr>
<th>Alloy Composition (at. %)</th>
<th>Alloy Composition (wt.%)</th>
<th>Elements (at.%: normalized)</th>
<th>$d$-orbital energy level, $\overline{M_d}$ (eV)</th>
<th>Bond Order, $\overline{B_o}$</th>
<th>$e/\alpha$ Ratio</th>
<th>Mo-Eq [55]</th>
</tr>
</thead>
<tbody>
<tr>
<td>1. Ti-26Zr-10Nb</td>
<td>Ti-37Zr-15Nb</td>
<td>Zr 25.15 ± 0.05, Ti 65.35 ± 0.15, Nb 9.5 ± 0.1</td>
<td>2.57</td>
<td>2.90</td>
<td>4.1</td>
<td>8.61</td>
</tr>
<tr>
<td>2. Ti-25Zr-15Nb</td>
<td>Ti-34.8Zr-21.3Nb</td>
<td>Zr 23.8 ± 0.1, Ti 61.55 ± 0.05, Nb 14.65 ± 0.05</td>
<td>2.57</td>
<td>2.91</td>
<td>4.15</td>
<td>9.87</td>
</tr>
<tr>
<td>3. Ti-22Zr-15Nb</td>
<td>Ti-31.3Zr-22Nb</td>
<td>Zr 21.25 ± 0.05, Ti 64 ± 0.1, Nb 14.85 ± 0.05</td>
<td>2.55</td>
<td>2.90</td>
<td>4.15</td>
<td>9.65</td>
</tr>
<tr>
<td>4. Ti-21Zr-20Nb</td>
<td>Ti-29Zr-28Nb</td>
<td>Zr 20.05 ± 0.05, Ti 60.3 ± 0.1, Nb 19.65 ± 0.15</td>
<td>2.54</td>
<td>2.91</td>
<td>4.2</td>
<td>10.82</td>
</tr>
</tbody>
</table>
6.2.3. Phase and microstructural characterization

For microstructural characterization, the disc samples (3mm thick and 10mm in diameter) were ground with SiC grinding papers (of up to 4000 grit) and then polished with a mixture of colloidal silica and H$_2$O$_2$. Later, the samples were cleaned with ethanol in an ultrasonic bath. Kroll solution was used to etch the samples to characterize the microstructure of the samples.

Phases were identified using a Bruker D8 Advance X-ray diffractometer (XRD) with a Cu Kα radiation source at room temperature, and the results were analysed through MAUD software. FEI Nova Nano SEM scanning electron microscope (SEM) equipped with an Oxford Instruments X-Max 20 energy dispersive X-ray spectroscopy (EDS) detector was used to examine the composition of the samples. An optical microscope (Leica- DM2500) with Leica DFC310 FX camera was used to analyse the microstructures and to take the images of Ti-Nb-Zr alloys.

6.2.4. Mechanical property testing

The electric discharging machine was used to prepare the dog bone-shaped tensile samples with a gauge length of 20 mm, a width of 5 mm and an approximate thickness of 1.3 mm. CMT4105 universal electronic tensile testing machine was used to conduct the tensile test with a strain rate of $1 \times 10^{-3}$ s$^{-1}$. Tensile strength, yield strength, elastic modulus, elastic energy, toughness and strain-to-fracture of Ti-Nb-Zr alloys were obtained from the stress-strain curve from the tensile test. Compression tests of the samples (Φ2mm × 4mm) were carried out in a CMT4305 machine at a strain rate of $2 \times 10^{-4}$ s$^{-1}$. The compressive yield strength was measured by taking the averages of two samples for each alloy.
The ultrasonic elastic modulus measurement (Model RAM-5000, RITEC, USA) was also used to measure the elastic modulus of these Ti-Nb-Zr alloys (Φ10mm × 10mm). The following equation can be used to calculate the elastic modulus of these alloys:

\[
E = \frac{\rho V_s^2 (3V_L^2 - 4V_s^2)}{V_L^2 - V_s^2}
\]  

(6.3)

where \(\rho\) indicates the density of the material which can be calculated using Archimedes principle. \(V_L\) and \(V_s\) are the ultrasonic longitudinal and shear wave velocities, respectively, and they can be calculated by the following equation:

\[
V = \frac{2d}{t}
\]  

(6.4)

where \(t\) is the time lag between the contiguous peaks of ultrasonic longitudinal or shear wave, and \(d\) is the length of the sample.

Microhardness measurements were conducted using microhardness tester (Future-Tech Corp. FV-700) by taking the averages of five measurements for each alloy.

6.3. Results and Discussion

6.3.1 Constituent phases and microstructure and of as-cast Ti-Nb-Zr alloys

Detailed EDS compositional analyses of the four Ti-Nb-Zr alloys are summarised in Table 6.1. The results consistently confirm the nominal composition of each Ti-Nb-Zr alloy prepared. Fig. 6.2 shows the XRD patterns for the four as-cast Ti-based Ti-Nb-Zr alloys. A predominant presence of the \(\beta\)-phase is observed in Ti-25Zr-15Nb, Ti-22Zr-15Nb and Ti-21Zr-20Nb, while the \(\alpha''\)-martensite phase is prevalent in Ti-26Zr-10Nb. The formation of this predominant \(\alpha''\)-martensite phase is due to the small amount of the \(\beta\)-stabilizer Nb added to the alloy. For binary Ti-Nb alloys, which differs from ternary Ti-Nb-Zr alloys, the minimum Nb content to achieve single \(\beta\)-phase is 27at.% [52]. Zr can act as a \(\beta\)-stabilizer in
Ti-Nb alloys [25, 55] and the Mo-Eq. expression for Ti-Nb-Zr alloys has been established as follows:

$$(\text{Mo-Eq})_{\text{Ti-Nb-Zr}} = 0.238\text{Nb (wt.\%)} + 0.11\text{Zr (wt.\%)} + 0.97$$ \hspace{1cm} (6.5)

Based on Eq. (6.5), when the Nb content is 10 at.\% (13.2 wt.\%), the minimum Zr content required to achieve predominant $\beta$-phase is 41 at.\% (53.3 wt.\%) [55]. The Mo-Eq. values for each alloy were calculated using Eq. (6.5) [55] and listed in Table 6.1. Apart from Ti-26Zr-10Nb, the Mo-Eq. values for all other three alloys were close to 10 wt.\%. Hence, after copper mould casting, $\beta$-phase was detected as the predominant phase by XRD, along with some martensite in some alloys (Fig. 6.2), while due to the low Mo-Eq. value (8.61 wt.\%), significant $\alpha''$ formed in Ti-26Zr-10Nb. Another observation from the XRD patterns is that the $\omega$-phase is present in all the four Ti-Nb-Zr alloys investigated. The results suggest that Ti-Nb-Zr alloys in the composition ranges listed in Table 6.1 are prone to the formation of the $\omega$-phase.
Fig. 6.2 XRD patterns of as-cast Ti-Nb-Zr alloys.

Fig. 6.3 shows the representative optical microstructures of these four alloys in the as-cast condition. A dendritic structure was observed in each alloy. A closer inspection of the microstructure of Ti-26Zr-10Nb (Fig. 6.2 (a')) confirmed the XRD results that it contains significant \(\alpha''\)-martensitic phase.
Figure 6.3 Optical micrographs of as-cast Ti-Nb-Zr alloys: (a) and (a’) Ti-26Zr-10Nb, (b) Ti-25Zr-15Nb, (c) Ti-22Zr-15Nb, and (d) Ti-21Zr-20Nb.
In the above analyses, both the $e/\alpha$ ratio and the Mo-Eq. have been used to discuss the stability of the $\beta$-phase. Fig. 6.4 shows an approximate linear trend between the Mo-Eq. values and the $e/\alpha$ ratio for these four alloys. Since an increased Mo-Eq. value or $e/\alpha$ ratio implies increased $\beta$-phase stability, together, they can be a useful tool to better predict the $\beta$-phase stability in these alloys.

![Graph showing correlation between Mo-Eq. values and $e/\alpha$ ratio for four alloys.](image)

**Figure 6.4** Correlation between the Mo-Eq. values and $e/\alpha$ ratio for these four alloys.

### 6.3.2. Mechanical properties of as-cast Ti-Nb-Zr alloys

The Vickers hardness of each alloy is listed in Table 6.2. Ti-25Zr-15Nb exhibited the highest hardness (280.6 ± 11.5) while Ti-26Zr-10Nb registered the lowest hardness (185 ± 7). Lee et al. [30] studied as-cast binary Ti-Nb alloys in the composition range of 5-35 wt.%Nb and concluded that the microhardness of each phase follows the sequence of $\omega > \alpha' > \alpha'' > \beta > \alpha$, where the microhardness of the $\alpha$-phase was measured from commercially pure Ti. However, Ho et al. [56] reported that the $\alpha''$-martensite phase offers the lowest hardness among the $\alpha'$-phase, $\beta$-phase and $\alpha''$-phase. The results of this study agree with Ho et al. [27], the Ti-26Zr-10Nb alloy with $\alpha''$-phase being the predominant phase exhibited the lowest hardness value. The $\alpha''$-phase may be regarded as an intermediate phase between $\alpha'$ and $\beta$ [57,
The strain required in the phase transition from the β-phase to the twinned α″-phase is small compared to the strain involved in producing the dislocated α′-phase [56]. This could be a reason for the lower hardness value of the α″-phase compared with the α′-phase, in addition to the effect of the crystal structure and composition (α′ and α″ typically have different solute contents). Another possibility is that suggested by Hisata et al. [59], who proposed that the difference in the hardness values of two Ti-Zr based alloys with Nb additions, containing similar phases (α′-phase), could be caused by the relaxation of lattice strain due to the introduction of Nb.

Fig. 6.5(a) shows the representative tensile stress-strain curves for the four Ti-Nb-Zr alloys. The tensile properties are summarised in Table 6.2. As can be seen, Ti-26Zr-10Nb exhibits double yielding, which supports the observation that this alloy contains orthorhombic α″-phase as the main phase [60]. The XRD results of this alloy have confirmed that the α″-phase is the main phase before loading. Therefore, it was not transformed from the β-phase after loading. The alloy also shows the lowest elastic modulus. However, its tensile strength and yield strength values are low compared with other three Ti-Nb-Zr alloys. Each as-cast Ti-Nb-Zr alloy showed excellent tensile ductility (17% to 31%), which is important for processing. In general, as-cast Ti-alloys often exhibit much lower tensile ductility. It is recognised that alloys with good castability are in general printable by additive manufacturing. In that regard, it is expected that all these alloys can be processed by metal additive manufacturing [61]. The yield strength and tensile strength of these newly designed alloys are lower than those of ELI Ti-6Al-4V and Ti-(15.5-16.5)Nb-(9-10)Hf (wt.%, aged) (Tiadyne 1610) [65]. However, one of the low elastic modulus TNTZ β-Ti alloys, Ti–35.3Nb–5.1Ta–7.1Zr [10], exhibits yield strength and tensile strength values similar to the experimental results of this study. However, they are still much higher than those of human cortical bones.
Figure 6.5 Engineering and true stress-strain curves of as-cast Ti-Nb-Zr alloys by (a) tensile test, and (b) compressive test.

In biomedical applications, an implant material should exhibit a combination of high tensile strength, good ductility and a low elastic modulus. The elastic admissible strain can be defined as the ratio of strength to elastic modulus, which has a significant influence on the selection of implant material. A high elastic admissible strain is preferred. In this study, the elastic admissible strains for all the four alloys range from 0.6% to 1.1%, which are better than recent implant material for example Ti-6Al-4V (0.8%) [62], stainless steel (0.17%) [63], and Co-Cr alloys (0.21-0.31%) [63].
Elastic strain energy (\(\delta_e\)) plays an important role in understanding the mechanical behaviour of hard tissue replacement (HTR) material. Usually, the HTR material works in the elastic deformation mode. During deformation, the external force stores their work in the solid as elastic strain energy, which releases on unloading or when the applied force decreases [35]. \(\delta_e\) can be calculated as follows:

\[
\delta_e = \frac{1}{2} \varepsilon_e \sigma_y = \frac{\sigma_y^2}{2E}
\]  

(6.6)

Where \(\delta_e\) is the elastic energy, \(\varepsilon_e\) is the elastic strain, \(\sigma_y\) is the yield strength, and \(E\) is elastic modulus [64]. Using Eq. (6.6), the elastic strain energy values of Ti-Nb-Zr alloys were calculated and listed in Table 6.2. They range from 0.6 to 3.6 MJ/m\(^3\), which are close to the elastic energy of Ti-6Al-4V (~ 3.28 MJ/m\(^3\)) [64]. However, elastic energy values of other bio Ti-alloys range from 1–5 MJ/m\(^3\) [64, 65].

The compressive stress-strain curves obtained for the four alloys are presented in Fig. 6.5 (b). Except the Ti-26Zr-10Nb alloy, the other three alloys all experienced the highest load that the compression testing machine can apply but still, there was no sign of fracture. Ozan et al. [62] reported similar observations with different \(\beta\)-phased Ti-Nb-Zr alloys. In contrast, the Ti-26Zr-10Nb alloy, which exhibited the lowest hardness, broke after reaching 38% strain with an ultimate compressive strength of 1918.8 MPa.

The compressive yield strength values of these Ti-Nb-Zr alloys ranged from 388.4 ± 2 MPa to 1103.14 ± 45MPa (Table 6.2), compared with ~210 MPa (maximum) for human cortical bones [46].
Table 6.2 Comparison of mechanical properties of Ti-Nb-Zr alloys with those of Ti-6Al-4V ELI (mill annealed) [10, 66].

<table>
<thead>
<tr>
<th>Alloy composition (at. %)</th>
<th>Tensile yield strength (MPa)</th>
<th>Tensile strength (MPa)</th>
<th>Tensile ductility (%)</th>
<th>Tensile elastic admissible Strain (%)</th>
<th>Tensile elastic Energy (MJ/m³)</th>
<th>Compressive strength (MPa)</th>
<th>Hardness (HV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ti-26Zr-10Nb</td>
<td>205</td>
<td>595</td>
<td>31</td>
<td>0.6</td>
<td>0.615</td>
<td>388</td>
<td>185</td>
</tr>
<tr>
<td>Ti-25Zr-15Nb</td>
<td>650</td>
<td>670</td>
<td>18</td>
<td>1.1</td>
<td>3.575</td>
<td>1103</td>
<td>281</td>
</tr>
<tr>
<td>Ti-22Zr-15Nb</td>
<td>550</td>
<td>610</td>
<td>17</td>
<td>1</td>
<td>2.75</td>
<td>1189</td>
<td>262</td>
</tr>
<tr>
<td>Ti-21Zr-20Nb</td>
<td>612</td>
<td>620</td>
<td>20</td>
<td>1</td>
<td>3.06</td>
<td>1035</td>
<td>193</td>
</tr>
<tr>
<td>Ti-6Al–4V ELI (mill annealed) [65]</td>
<td>875</td>
<td>965</td>
<td>10-15</td>
<td>0.80</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti-(15.5-16.5)Nb-(9-10)Hf (wt.%, aged) [65]</td>
<td>736</td>
<td>851</td>
<td>10</td>
<td>0.91</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ti–35.3Nb–5.1Ta–7.1Zr (annealed) [10]</td>
<td>547</td>
<td>597</td>
<td>19</td>
<td>0.99</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
6.3.3 The dependence of elastic modulus on $B_o$, $M_d$, $e/a$ ratio, and secondary phases

Elastic modulus is an essential parameter in the selection of implant material and can be determined by the bonding force among atoms. This bonding force is closely related to the crystal structure and the distances among atoms. However, alloying element, heat treatment, and plastic deformation can affect this bonding force [67, 68] which results in the changes in elastic modulus. Fig. 6.6 shows the elastic modulus values of the four Ti-Nb-Zr. Generally, ultrasonic elastic modulus values are higher than the tensile elastic modulus, while tensile elastic modulus values are higher than compressive elastic modulus values. The results from this study follow a similar trend, excluding Ti-26Zr-10Nb. According to the $d$-electron theory and the $e/a$ ratio, the alloys that have high values of $B_o$ and $M_d$, the $e/a$ ratio in the range from 4.1 to 4.25, should exhibit low elastic modulus. Fig. 6.7 shows the schematic relationship between the $e/a$ ratio, elastic modulus, and secondary phases [49]. The experimental results of this study were superimposed on Fig. 6.7. In general, an alloy with $e/a$ ratio of 4.15, is expected to exhibit the highest elastic modulus due to the formation of the $\omega$-phase in the $\beta$-matrix. However, if the $\omega$-phase can be suppressed at the $e/a= 4.15$, then the elastic modulus is expected to follow the dashed line in Fig. 6.7. Alternatively, an $\alpha''$-martensite matrix with an $e/a$ ratio of 4.1 and a $\beta$-phase matrix with an $e/a$ ratio in the range of 4.2 - 4.25 could also exhibit low elastic modulus by Fig. 6.7. The research data of this study did not follow the trend shown in Ref. [40]. However, it showed that the minimum elastic modulus occurred near $e/a =4.15$, which was suggested by the Ref [40].

In this study, the alloys with an $e/a$ ratio of 4.15, exhibited higher elastic modulus than the alloys having an $e/a$ ratio of 4.1 or 4.2 for all three elastic modulus measurement methods. These high elastic moduli could be attributed to the $\omega$-phase present in the $\beta$-matrix of these
alloys. The alloy with an $\frac{e}{a}$ ratio of 4.1 (Ti-26Zr-10Nb) exhibited the lowest elastic modulus by tensile, compressive and ultrasonic testing due to the predominant $\alpha''$-phase in the alloy.

Figure 6.6 Compressive, tensile and ultrasonic elastic modulus of as-cast Ti-Nb-Zr alloys.

The elastic modulus (E) of different phases for titanium alloys can be arranged as $E_\beta \approx E_{\alpha''} \approx 60-90$ GPa $< E_\alpha \approx 100$ GPa $< E_{\omega} \approx 130-220$ GPa [10, 69]. Tane at al. [70] suggested that titanium alloys, which can retain the $\beta$-phase but with low $\beta$-phase stability (i.e., high tendency to the $\beta \rightarrow \alpha''$ martensitic transformation), can have the lowest elastic modulus. Zhou et al. [71] suggested that both $\alpha' + \alpha''$ and $\alpha'' + \beta$ phases could exhibit high tensile strength and low elastic modulus. Few studies [72, 73] showed that low elastic modulus could be achieved at 100% $\alpha''$-martensite. However, Matsumoto [74] and Hao et al. [75] reported that the elastic modulus of metastable $\beta$, $\alpha'$ and $\alpha''$ might not follow a fixed trend or sequence. In contrast, Hisata et al. [59] showed that the elastic modulus of these metastable phases followed the sequence of $\alpha'' < \beta < \alpha'$. 

177
It is well documented that the presence of the $\omega$-phase results in high elastic modulus. However, Kondo et al. [29] showed that the alloy that has the lowest elastic modulus value contained a small amount of the $\omega$-phase in the $\beta$-phase matrix. In this study, the lowest elastic modulus alloy (Ti-26Zr-10Nb) contained a small amount of the $\omega$-phase, which is similar to the results obtained in Chapter 5. This means that a small amount of $\omega$-phase is not necessarily harmful to the effort of reducing the elastic modulus. From the above observations, this chapter supports the sequence proposed in Chapter 5 for the elastic modulus of different phases in Ti alloys, i.e., $E_{\alpha'} < 40 \text{ GPa} < E_\beta \approx 60-90 \text{ GPa} < E_\alpha \approx 100 \text{ GPa} < E_\omega \approx 130-220 \text{ GPa}$.

6.4. Conclusions

In order to develop low elastic modulus and high strength bio-materials, four Ti-based Ti-Nb-Zr alloys were designed using the $d$-electron theory and the $e/\alpha$ ratio criterion and experimentally evaluated. The effects of the alloying elements on the microstructure and
mechanical properties of these alloys were investigated. The major results are summarised as follows:

- Four new Ti-Nb-Zr alloys (Ti-26Zr-10Nb, Ti-25Zr-15Nb, Ti-22Zr-15Nb, and Ti-21Zr-20Nb) were designed and assessed in the as-cast condition. The as-cast tensile, compressive and ultrasonic elastic moduli of these alloys are in the ranges of 58-71GPa, 34-60GPa and 52-83GPa respectively, which are lower than those of other as-cast Ti-Nb-Zr alloys reported in the literature.

- It is confirmed that a small amount of ω-phase is not harmful in reducing elastic modulus along with β and α″-phase for the Ti-Nb-Zr alloys.

- This study supports the sequence proposed in Chapter 5 for the elastic modulus of different phases in Ti alloys, i.e., $E_{\alpha″} < 40 \text{ GPa} < E_\beta \approx 60-90 \text{ GPa} < E_\alpha \approx 100 \text{ GPa} < E_\omega \approx 130-220 \text{ GPa}$. The presence of a small amount of ω-phase was not found to be harmful in terms of decreasing the elastic modulus.

- A linear relationship between Mo-Eq. and $\varepsilon/\alpha$ ratio was observed for the four Ti-Nb-Zr alloys studied.

- The four new Ti-Nb-Zr alloys (Ti-26Zr-10Nb, Ti-25Zr-15Nb, Ti-22Zr-15Nb, and Ti-21Zr-20Nb) showed excellent tensile ductility and enough strengths for implant applications in the as-cast condition. This suggests that these alloys can be used to make intricate implant shapes by casting or 3D printing processes without the need for subsequent heat treatment or thermo-mechanical processing.

**References**


[53] R. Yang, S. Li, Y. Hao, Development and application of low-modulus biomedical titanium alloy Ti2448, INTECH Open Access Publisher2011.


Chapter 7 Summary and future work

7.1 Summary

The research presented in this thesis investigates five Zr-based and four Ti-based Ti-Nb-Zr alloys that are designed to achieve low elastic modulus for biomedical application. An informative literature review, presented in Chapter 2, discusses the current status of Zr-based alloys for biomedical application. This review identifies the research gaps and accordingly, the research questions and objectives of this project, which are presented in Chapter 1. The recent design approaches (i.e. $d$-electron theory, $e/a$ ratio, Mo-Eq approach, first principle studies) for low elastic modulus implant alloy are discussed in Chapter 3. On this basis, Chapter 3 also identifies the design approach used in this study. Chapter 4 addresses the β-stabilizing effect of Zr in Ti-Nb alloys and develops a new Mo-Eq expression for the Ti-Nb-Zr alloy system, which is validated by experimental results. Chapter 5 focuses on the design and development of strong, ductile and low elastic modulus Zr-based Ti-Nb-Zr alloys for biomedical application. Chapter 6 is similar to Chapter 5 but centred on the design and development of low elastic modulus Ti-based Ti-Nb-Zr alloys for biomedical application. The factors affecting the elastic modulus of both Zr-based and Ti-based Ti-Nb-Zr are broadly discussed in these two chapters.

The key findings of this project are summarised as follows:

- To understand the effect of Zr on β-phase stability of Ti-Nb binary alloys, a modified Mo-Eq expression has been formulated for the Ti-Nb-Zr system, i.e., 
  $$(\text{Mo-Eq})_{\text{Ti-Nb-Zr}} = 0.238\text{Nb(wt.\%)} + 0.11\text{Zr (wt.\%)} + 0.97.$$  
  This expression shows good consistency with experimental observations, literature data, and the well-established $d$-electron theory in predicting the β-phase stability of different Ti-Nb-Zr alloys. It provides a
simple but effective tool for assessing the stability of the β-phase in Ti-Nb-Zr based alloys.

- Five new low elastic modulus Zr-Ti-Nb alloys (Zr-45Ti-15Nb, Zr-33Ti-15Nb, Zr-28Ti-15Nb, Zr-35Ti-10Nb, and Zr-30Ti-20Nb) have been designed and evaluated. The elastic modulus of these alloys in the as-cast state falls in the range of 58-79 GPa (tensile), 45-57 GPa (compressive) and 60-95 GPa (ultrasonic). Of them, Zr-33Ti-15Nb and Zr-28Ti-15Nb alloys exhibit low elastic modulus (~60 GPa, by both tensile and ultrasonic testing) compared with other three alloys in the as-cast state. It is useful to note that both alloys contained a small amount of the ω-phase.

- Four new Ti-based Ti-Nb-Zr alloys (Ti-26Zr-10Nb, Ti-25Zr-15Nb, Ti-22Zr-15Nb, and Ti-21Zr-20Nb) have been designed and evaluated using the d-electron theory and the $e/a$ ratio parameter. The as-cast tensile, compressive and ultrasonic elastic moduli of these alloys (ranging from 58-71 GPa, 34-60 GPa and 52-83 GPa respectively) are lower than those of the as-cast Ti-Nb-Zr alloys reported in the literature. Among them, the as-cast Ti-26Zr-10Nb alloy, which contains a small amount of ω-phase, exhibited the lowest elastic modulus.

- A modified relationship between each constituent phase and its elastic modulus was suggested to be $E_{α''} < 40$ GPa $< E_β \approx 60-90$ GPa $< E_α \approx 100$ GPa $< E_ω \approx 130-220$ GPa. The stable single β-phase at room temperature resulted in higher elastic modulus than metastable β-phase containing α'' and a small amount of ω for both the Ti-based and Zr-based Ti-Nb-Zr alloys.

- A linear relationship exists between the Mo-Eq. value and the $e/a$ ratio for both the Zr-based and Ti-based Ti-Nb-Zr alloys. The combination of the Mo-Eq. and the
$e/a$ ratio can be used as an informative tool for evaluating the stability of the $\beta$-phase in the Ti-Nb-Zr alloy system.

- Both Zr-28Ti-15Nb and Zr-33Ti-15Nb alloys in the as-cast condition delivered low elastic modulus (~60 GPa, tensile and ultrasonic), outstanding tensile ductility (~16%), uniform plastic strain (higher than 10%) and adequately high tensile yield strength (~650 MPa), in addition to the intrinsically low magnetic susceptibility of Zr. They further offer much greater elastic admission strain and elastic energy compared with Ti-6Al-4V. Hence, they can be considered as attractive candidate implant materials by casting or 3D printing without subsequent heat treatment or severe deformation.

- The $d$-electron theory and the $e/a$ ratio together offer a critical design tool for developing low elastic modulus, strong and ductile Zr-Ti-Nb and Ti-Nb-Zr alloys in the as-cast condition.

### 7.2 Recommendations for future work

Further studies are needed to address some unresolved issues for the design of both Zr-Ti-Nb and Ti-Nb-Zr based implants and explained in a schematic diagram in Fig. 7.1. These include:

- The approach developed in this thesis, to estimate the influence of Zr on the $\beta$-phase stability of Ti-Nb alloys, can also be applied to the assessment of the $\beta$-phase stability of other Zr-containing Ti alloys. Besides, it is necessary to develop an empirical Molybdenum Equivalent (Mo-Eq) parameter for Zr-based alloys in order to quickly assess the $\beta$-phase stability of Zr-based alloys.
The alloy design methods developed for Ti-alloys can apply to the design of Zr-based alloys for the implant application. Zircobase, a thermodynamic database for Zr-alloys, coupled with Thermo-Calc software, can be a useful thermodynamic tool for the design of Zr-based alloys, in conjunction with the d-electron theory. It is anticipated that more Zr-based implant alloys will be developed in the near future. Furthermore, since additive manufacturing (AM) has become an increasingly important manufacturing method for orthopedic implants, the influence of the AM process on the selection of alloying elements and the evolution of microstructures should also be considered in any new Zr alloy design.

MRI, a non-invasive diagnostic tool, is continuously growing by providing much-enhanced resolutions (originally from ~4 mm to below 0.5 mm today) to allow more body components to be studied. Recent MRI machines can take pictures of the structural characteristics and/or functions of the brain at the cellular or even at the cortical column stage. These improvements mainly depend on the use of intense magnetic fields. However, in an intense MRI magnetic field, metal implants can be magnetized, which can generate pictures of low quality, leading to an incorrect diagnosis. For such biomedical applications, Zr-alloys with low magnetic susceptibility may offer improved imaging quality. In order to attain low magnetic susceptibility, research should also concentrate on developing new low elastic modulus Zr-based alloys with sufficiently low magnetic susceptibility, which could be a challenging task.
• Develop new Mo-Eq equations for other Zr-based alloy system.
• Improve the $\overline{B_o} - M_d$ diagram for Zr-based alloys proposed in this study.
• Focus on the Zr-based alloys with low magnetic susceptibility.
• Consider alloy design from a metal 3D printing perspective.

Figure 7.1 Schematic diagram of future work

- The $\overline{B_o} - M_d$ diagram has proved to be very effective for the design of low elastic modulus Ti-based alloys. The preliminary $\overline{B_o} - M_d$ diagram constructed in this thesis for Zr-alloys has the potential to become similarly effective for the design of low elastic modulus Zr-based alloys subject to necessary continuous improvements. To improve this $\overline{B_o} - M_d$ diagram and make it more informative, more experimental Zr-based alloys should be assessed in order to identify the metastable $\beta$-region, $M_s =$ room temperature (RT) line and $M_f = RT$ line.

- Wear resistance is another essential property for biomedical application. In a biological environment, wear debris can generate serious inflammatory response that can result in bone failure. Excessive loading may also result in accelerated wear. For instance, the consequence of accumulated wear of artificial hip implants after 10–15 years of implantation is often a costly and painful revision surgery. However, the oxidized Zr-2.5Nb (wt.%) alloys, oxinium, exhibits 4900 times less volumetric wear...
and 640 times fewer deep scratches than traditional Co-Cr alloys in laboratory wear testing [1]. In fact, it is essential to modify the surfaces for many implant materials due to their poor wear resistance. In this regard, oxidized Zr-based alloys can be an ideal solution for biomedical applications.

- Porous Ti-alloys, including Ti lattices, have been widely used as bone implants. Porous structures can generally eliminate bone-implant stiffness mismatch and improve bone-implant fixation due to bone ingrowth into the pores. In addition, they can provide an efficient route for inserting and delivering antibiotics (through porous structures) to combat infections. Due to the limited applications of Zr-alloys as an implant material, porous Zr-alloys have not earned much attention so far. In the future, porous Zr-alloys are anticipated to discover critical applications, comparable to porous Ti implants. All the techniques used to create porous biomedical Ti-alloys are relevant to Zr-alloys, including procedures of sintering, tempering, solidification-based foaming, additive manufacturing, dealloying and the integration of them.

**Reference**