

## PREFACE

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Biomedical implants are devices or tissues engineered to be placed inside or on the surface of the human body for the purpose of replacing, supporting, or enhancing the function of a biological structure. These implants can range from joint replacements and dental implants to more complex devices like cardiac pacemakers and cochlear implants. Designed from materials such as metals, ceramics, polymers, or composites, biomedical implants are tailored to interact safely with the human body, promoting healing or restoring function. However, metallic materials are preferred over ceramics and polymers for biomedical implants due to their superior mechanical strength, durability, and resistance to fatigue, which are essential for long-term stability in load-bearing applications like orthopedic and dental implants. The major metallic materials used in present for biomedical implants are 316L stainless steel (SS 316L), cobalt chromium (Co-Cr) alloys, titanium and its alloys (cpTi and Ti-6Al-4V). These materials are widely employed due to their favorable mechanical properties, corrosion resistance, and biocompatibility. Unfortunately, the long-term application presents a challenge due to the fact that these alloys give out toxic ions release of Cr, Ni, Al, and V. Moreover, pure Ti offers excellent biocompatibility and corrosion resistance. However, its lower wear resistance and moderate strength are unfavorable for load-bearing implant applications. Titanium alloys are categorized into three major types:  $\alpha$ -type,  $\beta$ -type, and  $\alpha+\beta$ -type. Pure titanium has a hexagonal close-packed (HCP) crystal structure ( $\alpha$  phase) at room temperature. When heated to a specific temperature, titanium undergoes a phase transformation from the HCP  $\alpha$  phase to the body-centered cubic (BCC)  $\beta$  phase. The minimum temperature at which this transformation occurs is known as the  $\beta$ -transus temperature. For pure titanium, the  $\alpha$  to  $\beta$  phase transformation happens at 882 °C. However, this transformation temperature can be influenced by

alloying elements. Elements like aluminium (Al), boron (B), carbon (C), oxygen (O), and nitrogen (N) raise the transus temperature, stabilizing the  $\alpha$  phase. These elements are referred to as  $\alpha$  stabilizers, and alloys that contain them are known as  $\alpha$ -type titanium alloys. Conversely, elements such as copper (Cu), chromium (Cr), niobium (Nb), tantalum (Ta), iron (Fe), vanadium (V), nickel (Ni), molybdenum (Mo), tungsten (W), and cobalt (Co) lower the transformation temperature, stabilizing the  $\beta$  phase. These are called  $\beta$  stabilizers, and alloys that contain them are known as  $\beta$ -type titanium alloys. Additionally, elements like zirconium (Zr) and tin (Sn) do not significantly affect the transformation temperature and are considered neutral stabilizers. Alloys containing both  $\alpha$  and  $\beta$  phases are classified as  $\alpha+\beta$  type titanium alloys. Furthermore, depending on the alloying elements, their composition, and specific properties, titanium alloys can be grouped into binary, ternary, or high-entropy Ti alloys. In binary category, two types of Ti alloys; Ti-xNb and Ti-xZr alloys, where  $x = 5, 10, 15, 20,$  and  $25$  wt.%. In ternary category, Ti-10Zr-xNb ( $x = 5, 10, 15,$  and  $20$  wt.%) alloys were developed. Moreover, two high entropy Ti alloys with specific combinations of elements as  $\text{TiNb}_{1.5}\text{Mo}_{1.1}\text{Zr}_{1.15}\text{Cu}_{0.25}$  and  $\text{TiNbZr}_{0.8}\text{Mo}_{0.92}\text{Sn}_{0.28}$  was developed with the same techniques. These binary, ternary, and high entropy alloys were comprehensively examined for microstructure, phase composition, density, hardness, elastic modulus, electrochemical corrosion, tribological, and tribocorrosion behaviour to check their suitability for biomedical implants. All the studies carried out are arranged into seven chapters inclusive of conclusions. Summarized view of each chapter is given below:

**Chapter 1:** This chapter comprises the introduction of biomedical implants and its classifications with specific highlights on load-bearing implants such as orthopedic and dental implants. It includes the physiological conditions and required desirable features for an implant biomaterial. In addition, it also discusses the economic perspective,

international standards, and advisories for these implants in a global market.

**Chapter 2:** This chapter deals with the literature review carried out for the present study. It includes brief history of biomaterials, metallic implants, advantages and disadvantages of metallic implants over ceramic and polymeric implants, the crystal structure of titanium, the effect of alloying different elements on the behaviour of titanium alloy are reviewed in this chapter. Furthermore, the detailed literature survey of the mechanical behaviour, corrosion, and wear behaviour, cytocompatibility, and antibacterial study of recently developed titanium alloys are discussed. Additionally, the chapter discusses the limitations of existing implant materials and highlights advancements in titanium alloys for load-bearing applications. At the end, it summarizes the research gaps and motivations for the current study, outlining the defined objectives.

**Chapter 3:** This chapter gives the brief of materials and methodology used for the completion of this work. It includes the detailed procedure of alloys preparation through powder metallurgy processing route along with the detailed characterizations and experiments carried out, including phase composition, microstructural analysis, physical, mechanical, tribological, electrochemical corrosion, and tribocorrosion behaviour to investigate their suitability for biomedical implant applications.

**Chapter 4:** This chapter presents the results from the phase analysis of both the milled powder and sintered alloys, as well as the microstructural examination of the sintered alloys. It includes phase formation in different Ti alloys along with microstructural characterization after sintering. The chapter also covers detailed analysis on the density, microhardness, and elastic modulus of the alloys.

**Chapter 5:** This chapter discuss the electrochemical corrosion and tribological behaviour of the alloys in detail. It includes the open circuit potential, electrochemical

impedance spectroscopy, potentiodynamic polarization, friction, and wear behaviour of the developed alloys. Furthermore, the alloys surfaces after corrosion and wear were analysed through electron microscopy and elemental mapping to ascertain the mechanism of wear and corrosion.

**Chapter 6:** This chapter deals with the study of synergistic action of wear and corrosion primarily called as tribo-corrosion. It includes the analysis of corrosion, wear, and synergistic effect to the materials degradation in simulated body fluids. It includes the study of OCP and potentiodynamic tribocorrosion behaviour under reciprocating motion and constant normal load.

**Chapter 7:** This chapter presents the key conclusions drawn from the tests conducted on the alloys in this study. The results highlighted here indicate that the newly developed alloys are well-suited to fulfil their intended purpose, which is to replicate the natural load-bearing function of bones and hard tissues in the human body. Additionally, the potential directions for future research related to this study are discussed in this chapter.

## ABSTRACT

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This research explores the design, synthesis, and comprehensive evaluation of titanium-based binary alloys (Ti-xNb, Ti-xZr), ternary alloys (Ti-10Zr-xNb), and high entropy alloys (TiNb<sub>1.5</sub>Mo<sub>0.1</sub>Zr<sub>1.15</sub>Cu<sub>0.25</sub> and TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub>) for biomedical implant applications, employing powder metallurgy techniques involving high-energy ball milling followed by sintering. X-ray diffraction and microstructural analyses confirmed the formation of stable  $\alpha+\beta$  dual-phase structures in Ti-Nb and Ti-Zr-Nb alloys, with increased  $\beta$ -phase stabilization with higher Nb content, while Ti-Zr alloys retained a primarily  $\alpha$ -phase structure. The TiNb<sub>1.5</sub>Mo<sub>0.1</sub>Zr<sub>1.15</sub>Cu<sub>0.25</sub> HEA exhibited a multiphase microstructure comprising BCC1, orthorhombic, and tetragonal phases, while TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub> showed BCC1, BCC2, and orthorhombic phases, with all alloys displaying uniform elemental distribution. Mechanical testing revealed significantly enhanced hardness in binary and ternary alloys, with Ti-10Zr exhibiting the highest hardness (~539 HV), followed by Ti-10Nb (~403 HV) and Ti-10Zr-15Nb (~380 HV). Both HEAs demonstrated high hardness (~470–481 HV) due to solid solution and multiphase strengthening. The elastic modulus was notably reduced in alloys containing Nb, Zr, and Sn, falling between 30–70 GPa, closely approximating human cortical bone and thereby reducing the risk of stress shielding. Electrochemical corrosion tests conducted in simulated body fluid (SBF) revealed that Ti-20Zr, Ti-10Zr-5Nb, and TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub> exhibited superior passive behavior. Ti-20Zr showed the lowest corrosion rate (0.00129 mm/year), followed by Ti-15Zr (0.00146 mm/year). In the Ti-Nb series, Ti-5Nb had the lowest corrosion rate (0.0075 mm/year), which increased with Nb content. Similarly, in the Ti-10Zr-xNb series, Ti-10Zr-5Nb showed the least corrosion (0.207 mm/year). Among HEAs, TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub> had a lower corrosion current density (2.71  $\mu\text{A}/\text{cm}^2$ ) than TiNb<sub>1.5</sub>Mo<sub>0.1</sub>Zr<sub>1.15</sub>Cu<sub>0.25</sub> (5.28  $\mu\text{A}/\text{cm}^2$ ).

Tribocorrosion analysis revealed distinct performance trends across alloy systems. Among binary alloys, Ti-10Nb and Ti-15Zr demonstrated the lowest wear volumes under potentiostatic conditions (0.0526 mm<sup>3</sup> and 0.0080 mm<sup>3</sup>, respectively) due to stable Nb- and Zr-rich passive films. In the Ti-10Zr-xNb ternary series, Ti-10Zr-15Nb showed optimal resistance with wear volumes of 0.193 mm<sup>3</sup> (OCP) and 0.088 mm<sup>3</sup> (PDP). The high entropy alloy TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub> outperformed its Cu-containing counterpart, with lower wear volumes (0.0142 mm<sup>3</sup> vs. 0.0109 mm<sup>3</sup> at PDP), attributed to improved passivation and reduced electrochemical degradation.

Overall, alloys such as Ti-10Nb, Ti-15Zr, Ti-10Zr-15Nb, and especially TiNbZr<sub>0.8</sub>Mo<sub>0.92</sub>Sn<sub>0.28</sub> emerged as promising candidates for biomedical implants due to their optimized combination of mechanical strength, low elastic modulus, excellent corrosion resistance, and superior tribocorrosion behavior. These materials offer a compelling alternative to conventional implant alloys such as commercially pure titanium and Ti-6Al-4V.