

Bio-tribocorrosion behavior of low-cost titanium alloys in simulated body fluids

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Declaration

I, Nicola Ruvimbo Rundora, hereby declare that this master's dissertation is my own original work. The dissertation is submitted for the award of Master of Science in Metallurgical Engineering in the School of Chemical and Metallurgical Engineering, University of the Witwatersrand, Johannesburg, South Africa. This work has not been submitted for any other degree in any other University.

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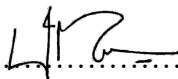
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Abstract

Titanium and its alloys are considered the gold-standard material in the manufacturing of biomedical implants. This is due to their superior mechanical properties and resistance to corrosion in comparison to the other biomaterials on the market. Titanium and its alloys are however very expensive in comparison and their application and accessibility is thus limited. Issues of toxicity as in the case of the commercial alloy (Ti-6Al-4V) have also been reported. One approach to combat these issues has been the development of new low-cost and less expensive $\alpha+\beta$ type titanium alloys through the modification of the commercial alloy composition. These efforts led to the development of the following alloys: Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe. To determine whether these alloys can be utilised for the manufacturing of biomedical implants, they have to undergo a series of screening tests. Some of those tests include wear, corrosion, and tribocorrosion tests. This is the basis of this study. Dry sliding ball-on-disk wear tests were conducted on these alloys. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe had superior wear resistance to Ti-3Fe, the alloy where the full substitution of V with Fe was employed. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe alloys wear resistance was closely comparable to that of the commercial alloy, Ti-6Al-4V. The corrosion behavior of the experimental alloys was investigated in 0.9 wt.% NaCl solution, Hanks Balanced Salt Solution, prediabetic Hanks Balanced Salt Solution, and diabetic Hanks Balanced Salt Solution. It was important to study the behavior of these alloys in a simulated diabetic environment because of the increase in the number of people living with diabetes and their increased risk of developing different bone and joint disorders. The corrosion behavior of Ti-3Fe was superior to that of the commercial alloy and the other experimental alloys in 0.9 wt.% NaCl solution and Hanks Balanced Salt Solution. In the prediabetic and diabetic Hanks Balanced Salt Solution, the experimental alloys resistance to corrosion was comparable to that of the commercial alloy with Ti-4.5Al-1V-3Fe having the best resistance to corrosion in the prediabetic solution and Ti-6Al-1V-3Fe having the best resistance to corrosion in the diabetic solution. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe showed tribocorrosion resistance that was comparable to the commercial alloy in both the normal HBSS and diabetic HBSS under both open circuit potential and potentiostatic conditions. These alloys showed better tribocorrosion behavior in the normal HBSS under potentiostatic conditions compared to Ti-3Fe and the commercial alloy. In the diabetic HBSS under potentiostatic conditions, Ti-4.5Al-1V-3Fe had the best resistance to tribocorrosion. The

glucose addition had a slightly negative effect on the tribocorrosion behavior as the wear rates and total worn volume values in such solutions were slightly higher than in the normal solutions. Ultimately, under corrosion and tribocorrosion testing conditions, the partial substitution of V with Fe as beta stabilisers in low-cost titanium alloy designs offered superior properties over the total replacement of V with Fe.

Dedication

Dedicated to my unwavering pillars of support and inspiration, my parents, whose boundless encouragement, and love have been the driving force behind my pursuit of knowledge.

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Contributions from this study

Journal Articles

- N. R. Rundora, J. W. Van der Merwe, D. E. P. Klenam, and M. O. Bodunrin, “Enhanced corrosion performance of low-cost titanium alloys in a simulated diabetic environment,” *Mater. Corros.*, no. May, pp. 1–13, 2023, doi: 10.1002/maco.202313927.
- N.R. Rundora, D.E.P. Klenam, S. Polat, N.M. Mathabathe, J. van der Merwe, M.O. Bodunrin, “Dry sliding wear behavior of experimental low-cost titanium alloys.” Submitted to *Tribology Transactions*. Status: Under Review
- N.R. Rundora, M.O. Bodunrin, Tribocorrosion behavior of low-cost experimental titanium alloys in simulated body fluids. To be submitted to the journal of *Mechanical Behavior of Biomedical Materials*.

Oral and poster presentations given, and awards stemming from this MSc work are detailed in Appendix D: Awards, presentations, and publications.

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Chapter 1: Introduction

This chapter introduces the whole dissertation by providing a brief background and problem statement, the justification of the research, the research questions, and objectives, and it provides the dissertation structure.

1.1. Background and Problem Statement

Owing to the expanding geriatric population, an increase in the number of diseases such as cardiovascular diseases and common joint disorders like osteoarthritis and osteoporosis, the demand for implantable medical devices that will support or replace the damaged body organs is rapidly increasing (Chew, Zein and Ahmad, 2012). Since the advent of the biomedical implants in 1895 (Hermawan, Ramdan and Djuansjah, 2011), different materials have been tried and tested for the making of biomedical implants. The most popular among these materials are ceramics, polymers, and metals. Metals are currently at the forefront in the making of biomedical implants because of their durability, high strength and toughness (Pandey *et al.*, 2020; Anene *et al.*, 2021). Biocompatibility is essentially a measure of a biomaterial's ability to carry out its desired purpose in the human body without causing an adverse reaction (Kaur and Singh, 2019). This, together with excellent mechanical properties are the main determinants in biomaterial's selection.

A group of Co-based alloys, namely the CoCrMo alloy has been used in the biomedical industry particularly in the making of hip replacement implants because of their good resistance to corrosion and wear and good fatigue strength (Kaur and Singh, 2019). However, their toxicity, high cost and high Young's modulus has significantly limited their use in the biomedical industry (Pandey *et al.*, 2020; Bahl *et al.*, 2021). A popular stainless-steel grade, 316L stainless steel is commonly used in the making of bioimplants and is set apart from the CoCrMo alloy because it is inexpensive. Thus, it is accessible to patients, and it has an acceptable biocompatibility. However, its major disadvantages are a high elastic modulus, high density, and low corrosion resistance. This has created some concern on its use in the industry (Pandey *et al.*, 2020; Bahl *et al.*, 2021). Since the 1950's, titanium and its alloys have gained popularity in a vast number of industries due to their low density (4.54 g/cm³), high strength and toughness, and excellent resistance to corrosion (Soundararajan *et al.*, 2018). The alloys are grouped into α -type, near α , ($\alpha+\beta$), metastable β and

stable β type alloys (Geetha *et al.*, 2009). Owing to their good biocompatibility and excellent corrosion resistance, the commercially pure α -Ti and ($\alpha+\beta$) Ti-6Al-4V extra low interstitial (ELI) alloys were the first titanium alloys used in the biomedical industry (Kolli and Devaraj, 2018). Titanium and its alloys are currently considered gold-standard materials in the biomedical implant industry due to their high strength-to-weight ratio, good mechanical properties, excellent biocompatibility and resistance to corrosion (Ahmed *et al.*, 2014; Anene *et al.*, 2021).

Human bones are known to provide internal support as well as protection of the vital organs and are thus required to be stiff enough to avoid bending whilst being flexible enough for energy absorption (Kaur and Singh, 2019). The two major classifications of human bones are the cortical bone which possesses a high strength and stiffness and the highly porous cancellous bone which possess a smaller Young's modulus and ultimate compressive strength (Kaur and Singh, 2019; Anene *et al.*, 2021). The implant applications of Ti and its alloys are mostly structural as in the case of hip and knee implants, thus they interact with the bones (Anene *et al.*, 2021). Therefore, to avoid a mechanical mismatch between the bone and bioimplant, the biomaterial is required to possess mechanical properties similar to that of the human bone. The elastic modulus must be very similar to that of the human bone which is known to range between 4 and 30 GPa for cortical bone and between 0.2 and 2 GPa for cancellous bone (Kaur and Singh, 2019). Like many other metallic bioimplant material, the elastic modulus of the common biomedical grade titanium alloys, especially Ti-6Al-4V, is far greater than that of the human bone, thus posing a problem to the use of these alloys in the making of bioimplants (Kolli and Devaraj, 2018). In addition to this, the risk of toxicity of the commercial ($\alpha+\beta$) Ti-6Al-4V alloy results from the release of aluminium and vanadium ions. This results in adverse reactions in the body as well as diseases like Alzheimer's disease (Kolli and Devaraj, 2018).

The drive to prevent or reduce exposure to toxicity has resulted in the modification of Ti-6Al-4V alloy compositions (Kaur and Singh, 2019). These modifications led to the development of ($\alpha+\beta$) Ti alloys without vanadium. Examples include Ti-6Al-7Nb and Ti-5Al-2.5Fe alloys (Kolli and Devaraj, 2018). However, due to the inferior wear resistance and elastic modulus mismatch between the ($\alpha+\beta$) Ti alloys and cortical bone, metastable β Ti alloys were developed (Kolli and Devaraj, 2018; Soundararajan *et al.*, 2018). These alloys have improved resistance to corrosion, biocompatibility, and are non-toxic due to the absence of toxic elements. Their alloying elements

increase the strength of the alloys and makes the elastic modulus comparable to that of human bone (Kaur and Singh, 2019).

Despite the advantages of the β Ti alloys, they have only found use in a limited number of applications due to their high cost that is firstly associated with the extraction of titanium (Froes *et al.*, 2004; Wang *et al.*, 2012), and secondly, many of the alloying elements used in the making of these alloys are expensive refractory elements (Kolli and Devaraj, 2018). Some of these alloys are the Ti-29Nb-13Ta, Ti-29Nb-13Ta-4.6Zr, Ti-13Nb-13Zr, Ti-13Nb-5Ta-7Zr, and Ti-4.5Sn-6Zr-11.5Mo alloy containing Ta, Nb, Zr, and Mo (Kolli and Devaraj, 2018). The focus is therefore on the development of low-cost non-toxic ($\alpha+\beta$) type titanium alloys which are mainly modified versions of the common ($\alpha+\beta$) Ti-6Al-4V alloy. Some of these ($\alpha+\beta$) alloys include the Ti-10Fe-0.35O-0.01N alloy developed by Fujii *et al.* (2002) and Ti-3.5Al-1Fe and Ti-5.5Al-1Fe alloys developed by Fujii and Takahashi (2002) as a possible substitute for the most widely used Ti-3Al-2.5V and Ti-6Al-4V alloys respectively.

The main concern with the afore-mentioned alloys is the risk of developing brittle intermetallic phases such as FeTi phase. Bodunrin *et al.* (2018) developed a group of low cost ($\alpha+\beta$) Ti alloys, namely Ti-6Al-1V-3Fe, Ti-4.5Al-1V-3Fe. They found that the partial substitution of the isomorphous beta stabilising elements with the less expensive eutectoid beta stabilizing elements, inhibited the formation of the brittle intermetallic phases while improving mechanical properties as well as improving the alloys resistance to corrosion when compared with the commercially available Ti-6Al-4V alloy (Bodunrin *et al.*, 2018; Bodunrin *et al.*, 2020). This research aims to perform further investigation on these alloys for their potential use in the biomedical industry.

Depending on the function, implants may experience corrosion alone as indicated in jaw, cranial and chin implants or a combination of corrosion and wear as reported in dental, knee, and hip implants (Carquigny, Takadoun and Ivanescu, 2019). The human body is a highly intricate environment as it contains various complex ions and biomolecules. These molecules ultimately influence the corrosion and tribocorrosion resistance of the implants. Investigations on the effect of albumin, a common protein found in the human body, on the corrosion and tribocorrosion performance of metallic biomaterials have been conducted (Carquigny, Takadoun and Ivanescu, 2019). Some researchers found that the presence of albumin had a negative effect on the corrosion resistance of CP-Ti as well as some Ti alloys such as Ti-6Al-4V, Ti-6Al-7Nb, Ti-13Nb-13Zr and

Ti-10Zr-10Nb-5Ta (Williams *et al.*, 1988; Cheng and Roscoe, 2005; Takadoun *et al.*, 2012; Carquigny *et al.*, 2019). Because proteins are known to be easily adsorbed onto solid surfaces, Cheng and Roscoe. (2005) concluded that the detrimental influence of proteins on the corrosion resistance of the biomaterials could be because of the chelation effects of the proteins which accelerate the dissolution of the metals.

In contrast, some researchers found the proteins to have a positive effect on the corrosion resistance of some titanium alloys (Khan, Williams and Williams, 1999a; Carquigny, Takadoun and Ivanescu, 2019). Khan *et al.* (1999b) found that the addition of protein enhanced the corrosion and tribocorrosion resistance of Ti-6Al-4V alloy because the biological molecules provided lubrication during wear. This is consistent with the studies performed by Carquigny *et al.* (2019). Conversely, Takadoun *et al.* (2012) found that the proteins did not provide any lubrication during the tribocorrosion of CP-Ti, Ti-6Al-4V and Ti-10Zr-10Nb-5Ta alloys. Due to these contradictions, further studies on the mechanism of enhancement or inhibition of corrosion and tribocorrosion of implants in physiological fluids containing albumin is required.

In similar terms, the amount of glucose in human fluid is used to rank diabetic patients. It is projected that the total number of people living with diabetes will rise from 537 million in 2021 to 643 million by 2030 and 783 million by 2045 (International Diabetes Federation, 2021). The majority of which are living in low-and-middle income countries which includes South Africa (International Diabetes Federation, 2021). Diabetic people are more at risk of developing various bone and joint disorders such as osteoporosis and osteoarthritis. These issues are already found in the older population due to ageing, however, these effects are enhanced by their susceptibility to developing diabetes as it is well known that diabetes is commonly diagnosed in older adults (International Diabetes Federation, 2021). It is therefore crucial to understand the effects of glucose on corrosion and tribocorrosion of biomaterials as these materials are commonly subjected to diabetic body environments.

The purpose of this research work was to therefore investigate the corrosion and the bio-tribocorrosion performance of the low-cost experimental ($\alpha+\beta$) titanium alloys and to discover the effect of different glucose concentrations on the surface properties of the alloys. The Ti-6Al-4V alloy was used as a reference alloy since it is the most studied and most utilized titanium alloy.

1.2. Justification of Research

The field of biomaterials is growing at quite a rapid rate. A very prominent scientist in the field of biomaterials, Professor Buddy Ratner, found the field to be characterised by multidisciplinary (Ratner *et al.*, 2004). He specifically stated that: “The field of biomaterials started with physicians, then embraced engineers, and was energised and legitimised by the molecular biology revolution” (Ratner, 2019). This coming together of experts from different fields is a good indication of how the biomaterials field is growing. By 2023, the compound annual growth rate (CAGR) of the bioimplant market is projected to rise to 8.6% (Sumayli, 2021). This growth is of course attributed to a vast number of factors that are discussed in the subsequent paragraphs.

Over the past few decades, the rise in the use of machines that are self-operated, the increase in the number of people in sports, defence activities, amplified use of motorcycles and bicycles and rising traffic which increases the number of road accidents, has led to the increasing demand for bio implants which will aid in quick recovery and subsequent early resumption of routine activities. According to the World Health Organization (WHO), approximately 1.3 million people lose their lives each year as a result of road traffic crashes (World Health Organization, 2018). In addition to this, approximately 20 to 50 million more people suffer injuries which are non-fatal. These injuries are mainly related to bone fractures which ultimately lead to the need for biomedical implants. Because of the considerable economic loss associated with biomedical implant surgeries, it is important to utilise low-cost affordable alloys that have good mechanical properties and are biocompatible to avoid the high costs and physical pain associated with revision surgeries (Bhat, Liss and Beredjiklian, 2018).

Another major contribution to the growing biomaterial field is the pace of population ageing. The aging population is growing at a much faster rate than in the past. Globally, it is projected that people aged 60 years and older will double from 1 billion in 2020 to 2.1 billion by 2050 (World Health Organization, 2023). This is a major factor as older people experience problems like hearing loss, cataracts, and refractive errors, back and neck pain, osteoarthritis, and chronic obstructive pulmonary disease (Beard *et al.*, 2016). Osteoarthritis is a joint disease which in most cases will result in joint replacement surgeries. Old people are also prone to frequent injuries which may cause bone fractures as they are quite fragile (Beard *et al.*, 2016). A common disease that does not only affect old people is known as diabetes. This disease is known to affect both young and old

people. Diabetes results in a vast number of complications in the human body, some of which result in the need for bioimplant surgery such as joint diseases like arthritis. Because of these factors, it is imperative to develop inexpensive titanium alloys and low-density stainless-steel alloys (Komane *et al.*, 2023) that are highly biocompatible to ensure that the implants last a lifetime in the human body or at least get replaced after 30 years or more.

1.3. Research Questions

- i) What is the effect of alloy compositions on the corrosion, wear and tribocorrosion of the low-cost Ti-Al-V-Fe and Ti-Fe alloys?
- ii) What is the effect of different glucose concentrations on the corrosion and tribocorrosion of the low-cost Ti-Al-V-Fe and Ti-Fe alloys?
- iii) What are the mechanisms influencing the corrosion, wear and tribocorrosion behavior of Ti-Al-V-Fe and Ti-Fe alloys?

1.4. Research Hypothesis

It is envisaged that the low-cost experimental Ti-Al-V-Fe alloys possess comparable corrosion resistance and tribocorrosion resistance to that of commercial Ti-6Al-4V alloys when exposed to different simulated body fluids.

1.5. Aim and Objectives

The aim of this project was to investigate how the simulated physiological environment including the common biomolecule, glucose, can influence the corrosion and tribocorrosion behaviour of low-cost Ti-Al-V-Fe alloys.

This was achieved through the following objectives:

- i) Assessing the wear behavior of the low-cost Ti-Al-V-Fe alloys and the dominant mechanisms in comparison with Ti-6Al-4V alloy.

- ii) Assessing the influence of composition on the corrosion and tribocorrosion behavior of low-cost Ti-Al-V-Fe alloys in simulated body fluid with and without glucose addition.
- iii) Establishing the mechanisms influencing the corrosion and tribocorrosion performance of Ti-Al-V-Fe alloys in simulated body fluids with and without glucose addition.

1.6. Structure of the Dissertation

- Chapter 2: *Literature review*. This chapter presents an overview of biomedical implants and the various biomaterials on the market today. Detailed classification and insight into the various biomaterials are given. The advantages and disadvantages of the various biomaterials are given in this chapter. A comprehensive overview of the metallurgy of titanium and its alloys is presented. A review of the corrosion, wear, and tribocorrosion of the titanium biomaterials is detailed in this chapter.
- Chapter 3: *Experimental Procedure*. This chapter presents the detailed materials used in this study. The testing methodologies and the characterisation techniques are given in this chapter.
- Chapter 4: *Dry sliding wear tests: Dry sliding wear behavior of experimental low-cost titanium alloys (Paper 2)*. This chapter provides insights into the wear behavior of the experimental alloys in comparison to the commercial Ti-6Al-4V alloy. The influence of the alloy composition on the wear behavior is discussed in this chapter. This chapter is linked to objective 1.
- Chapter 5: *Corrosion tests: Enhanced corrosion performance of low-cost titanium alloys in a simulated diabetic environment (Paper 1)*. This chapter gives insight into the corrosion resistance of the experimental alloys in comparison to that of the commercial Ti-6Al-4V alloy. The assessment of the suitability of these alloys for bioimplant use in relation their corrosion behavior is given. The influence of composition on the corrosion behavior as well as the mechanisms influencing the corrosion resistance and behavior of these alloys, which is linked to objective 2 and 3 is given in this chapter. The influence of the different

concentrations of glucose on the corrosion behavior of the titanium alloys is also presented in this chapter.

- Chapter 6: *Tribocorrosion tests: Tribocorrosion behavior of low-cost experimental titanium alloys in simulated body fluids (Paper 3)*. In this chapter, the tribocorrosion behavior of the experimental alloys in comparison to the commercial alloys is discussed. The influence of the different alloy compositions on the tribocorrosion resistance of the alloys is assessed. The various wear mechanisms driving the tribocorrosion of the titanium alloys are identified and discussed in this chapter. The effects of the different testing conditions (OCP and Potentiostatic) on the tribocorrosion behavior of the alloys are discussed in this chapter. This chapter is linked to objectives 1,2 and 3.
- Chapter 7: *Conclusions and Recommendations*. This chapter presents the overall conclusions of the research as well as the recommendations for future works.

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Chapter 2: Literature Review

This chapter gives an overview of the various biomedical implants and the current status of biomaterials. It also presents a general overview of titanium alloys; their metallurgy, corrosion, wear, and tribocorrosion properties. The research gap is also established in this chapter.

2.1 Biomedical Implants

2.1.1 Background of biomedical implants

A biomedical implant is a medical device which is manufactured to replace a missing biological structure, support a damaged biological structure, or enhance an existing biological structure (Ibrahim *et al.*, 2017; Li *et al.*, 2021). Biomedical implants are used in almost every organ of the human body. Ideally, they should have biomechanical properties comparable to those of autogenous tissues without any adverse effects. Human beings unfortunately fall subject to a vast number of issues and problems which ultimately lead to the need for bio-implants. Human beings suffering from acute heart diseases require bioimplants to survive (Manivasagam *et al.*, 2010). Others suffering from degenerative joint issues such as arthritis and osteoporosis also need implants. Arthritis is known as one of the major illnesses that is generally faced by the aged population (Pandey *et al.*, 2020). They also face several other ailments because of their bodies having performed their expected tasks for long years thus becoming worn out. However, arthritis does not affect the old alone, some young people also find themselves having to deal with the immobility and unbearable joint pain that arises from arthritis. Apart from the aged population as well as diseased people, young, healthy, and dynamic people such as sportspersons often require bioimplants due to bone fractures and excessive strain caused by over or incorrect exercise. Road traffic and other accidents are another reason for the need of biomedical implants (Pandey *et al.*, 2020). This goes to show that biomedical implants are a great necessity amongst the human population.

The issues mentioned above affect various areas and parts of the human body. The many parts of the human body where implants are used are shown in **Figure 2.1**. The most common areas where implants are used are in the hips, knees, elbows, and ears (Pandey *et al.*, 2020). The human body, however, is not the most hospitable environment for bioimplants due to the various ions that form part of the human body fluid. It is generally a warm, wet and chemically and biologically active

environment which is not conducive for a bioimplant (Dorozhkin, 2018). In addition to this, the human body environment is subject to changes in the pH due to various reasons such as a rise in an infection or inflammation which can in turn affect the implanted device. Various parts of the human body are subjected to different levels of loads and stress. Bones are typically subjected to loads of ~40 MPa while tendons and ligaments experience loads in the range of 40 – 80 MPa (Dorozhkin, 2018). The average load that hip joints are subjected to is approximately up to three times the body weight (3000N) which can go up to ten times the body weight during jumping action. Because of this, all implants must be able to sustain this aggressive environment that the human body poses. For this to be a possibility, the artificial or natural materials used in the making of bioimplants must possess the acceptable biomechanical and biological properties before they can be used in the manufacturing of the bioimplants (Geetha *et al.*, 2009).

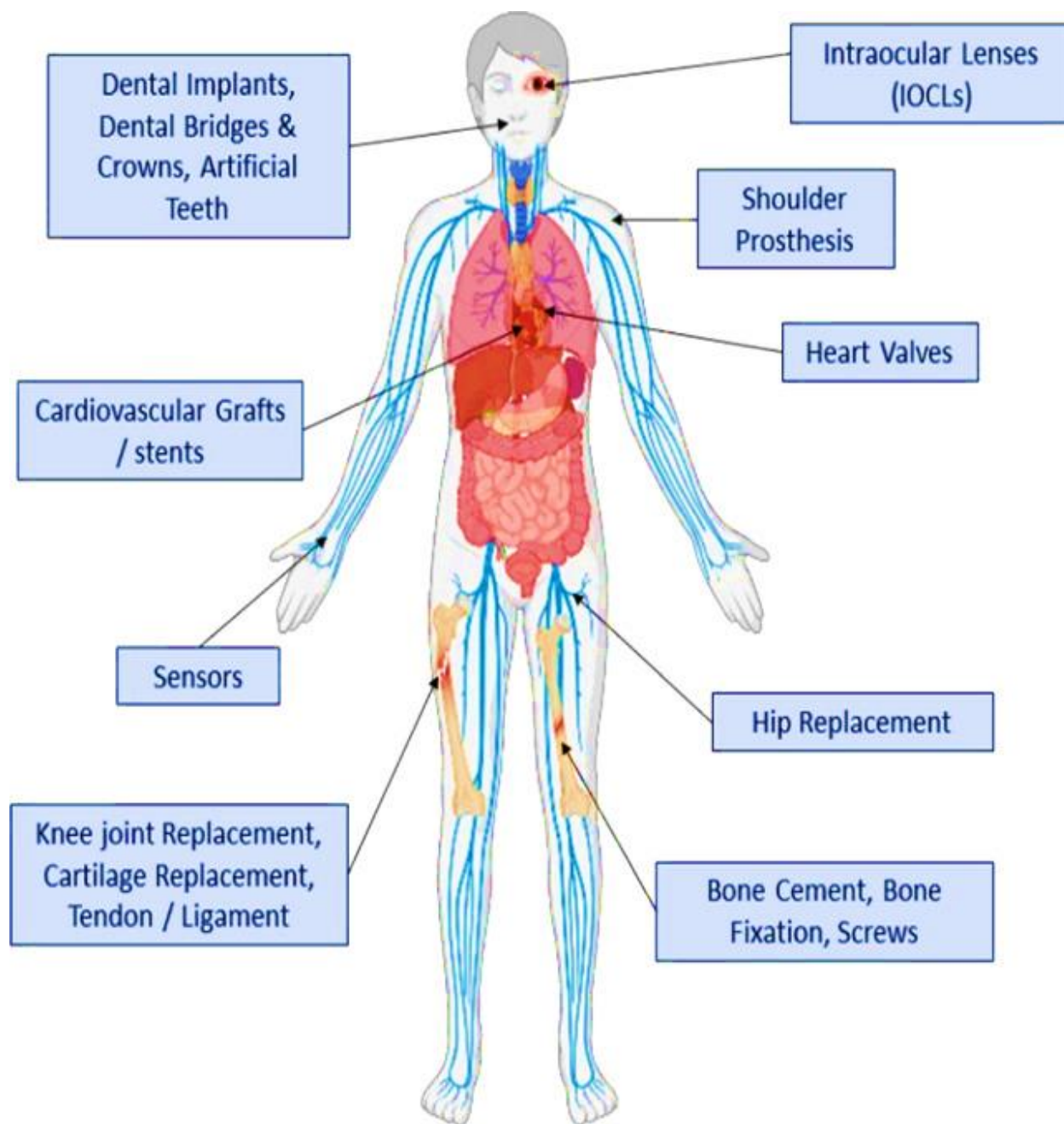


Figure 2.1: Various implants in the human body (Ajmal *et al.*, 2022)

2.1.2 Orthopaedic Joint Replacements

Biomaterials are used for various applications in the human body as seen in **Figure 2.1**. The application of biomaterials in orthopaedics is quite prominent because many people such as sportspersons, suffer from pain and loss of function and mobility from orthopaedic injuries (Fang, 2018). Joint replacement surgery is the most common orthopaedic surgery with total hip and knee

arthroplasties topping the charts. Total joint arthroplasties are essentially a medical procedure where the whole joint is replaced by a prosthesis (Neto and Rainforth, 2020). A total hip arthroplasty is shown in **Figure 2.2** below. The demand for total hip and knee replacement surgery is expected to increase by approximately 40% by the year 2060 (Matharu *et al.*, 2022). This will place great pressure on the bioimplant industry.

The first Total Hip Replacement (THR) surgery was performed by Gluck in 1891 in Berlin where he used a ball made from ivory in a socket (Neto and Rainforth, 2020). Replacing the mobile hips also represents the most challenging biomechanical application of biomaterials. Following this procedure, several more materials were tried and tested, but many failures occurred because of the significant amount of wear and corrosion the materials underwent after being placed in the human body. The failures were ascribed to variation in the pH of the human blood as well as other limitations associated with the material properties (Pandey *et al.*, 2020). Wear has been found to be one of the leading causes of the failures of these implants and subsequent revision surgeries (Manivasagam *et al.*, 2010). This also accelerates the corrosion rate of the material. In the case of hip prostheses, the implants are generally known to fail due to fatigue (Pandey *et al.*, 2020). This is the case because the materials are subjected to cyclic loading in this part of the body hence the material is required to have a high fatigue strength (Chen and Thouas, 2015; Pandey *et al.*, 2020). It is therefore imperative to utilise materials with excellent properties, especially an excellent resistance to abrasion and wear. Metal on metal (MOM), metal on polymer, and ceramic on ceramic prostheses have been developed. MOM devices are expected to last longer than other hip implants because of the durability associated with metals. However, MOM replacement devices accumulate wear debris that can create adverse effects linked to infections, loosening, inflammation, damaging of enzymes, and pain (Gain *et al.*, 2021). Polymers are utilised today because of their resistance to wear; however, the combination of metals and polymers has been linked to implant loosening (Neto and Rainforth, 2020). The various material combinations have been proven to last for approximately fifteen years or more. This is ideal for the older generation; however, young people are not favoured by this implant lifetime because they will need to replace the implant at least once during their lifetime. This is undesirable because of the pain associated with the surgery, the high costs and the success rate of the replacement is lower than that of the first implant surgery (Geetha *et al.*, 2009). Stainless steels are rarely used due to their poor fatigue, corrosion, and wear resistances and heavy metal toxicity issues. Currently, Orthinox, Co-based

alloys, titanium alloys, and/or ceramic materials are used in the making of these implants. These biomaterials amongst others will be discussed in greater detail in the following section 2.1.3.



Figure 2.2: Total hip arthroplasty for an arthritic hip
<https://orthoinfo.aaos.org/en/treatment/total-hip-replacement/>

2.1.3 Biomaterials

Biomaterials are defined as the natural/synthetic materials that are used in the manufacturing of bioimplants to replace the lost, damaged or diseased biological structure to restore form and function (Geetha *et al.*, 2009). The field of biomaterials is crucial and is rapidly increasing as these materials aid in improving the quality of life as well as extend human life expectancy (Geetha *et al.*, 2009). Biomedical implants are surrounded with the human body fluids which include blood, and they are integrated with the bones. This brings about certain chemical reactions which take place in the human body at the site of implantation (Gain *et al.*, 2021). These reactions are known to cause several health problems while also reducing the life of the implant. Therefore, to avoid health issues, and to ensure that the implant lasts a lifetime without rejection, the biomaterials have to possess certain characteristics which include excellent biocompatibility in terms of excellent corrosion and wear resistance, a low strength to young's modulus ratio, high fatigue and ductility, and they must be non-toxic (Gain *et al.*, 2021).

The biomaterials must possess specific mechanical properties which are also known as biomechanical properties. The biomechanical properties that are of prime importance include hardness, tensile strength, elastic modulus, elongation, and fatigue strength. The materials have to be hard enough and possess adequate strength in order to avoid implant fractures or failures caused by a mismatch in the mechanical properties between the implant and bone (Geetha *et al.*, 2009;

Hussein *et al.*, 2015). The response of the material to the repeated cyclic loads or strains is determined by the fatigue strength of the material and this property is crucial in determining the long-term success of the implant subjected to cyclic loading (Geetha *et al.*, 2009). The biomechanical incompatibility associated with the young's modulus of the implant is known as the stress shielding effect. This is a phenomenon which occurs when the implant material have a higher stiffness/higher elastic modulus than the human bone (4 to 30 GPa) which limits the needed stress being transferred to the adjacent bone thus resulting in the death of the bones cells (Geetha *et al.*, 2009; Hussein *et al.*, 2015). This ultimately results in the resorption of the bone around the implant and consequently to the loosening of the implant. Therefore, to avoid loosening of implants and consequent revision surgery, a material with an excellent combination of high strength and low Young's modulus must be used for bioimplant manufacturing (Neto and Rainforth, 2020). Fatigue strength (fatigue limit or endurance limit) which refers to the maximal amplitude of cyclic stress that can be applied to a material without causing fatigue failure, is a major concern for bioimplants because the mechanical working conditions within the human body are quite complex (Geetha *et al.*, 2009). Skeletal bone implants such as artificial hip joints, knee joints, spinal fixations, plates, and wires suffer from fatigue due to cyclic loading because of the several thousand steps a day normally walked by human beings at a rate of 1 Hz (Geetha *et al.*, 2009). Artificial hip joints suffer the most as the loading stress level on these joints is several times higher than that of the patients' body weight. This is due to most of the body weight pivoting on only one leg at a time when the hip joint is located out of perpendicular alignment during a step for example (Geetha *et al.*, 2009). This kind of cyclic stress is also known to occur in dental implants during chewing motion as well as in non-osseous tissue implants such as pacemaker electrodes in response to myocardial activity. Ultimately, materials subject to cyclic loading can fracture far below the yield strength of the material. Therefore, it is imperative to scrutinise the fatigue and fracture resistance of any bioimplant manufactured from any material if it is expected to survive millions of cyclic deformations over their lifetime as fatigue fracture is among the major causes of premature failure in biomedical implants (Geetha *et al.*, 2009).

Biocompatibility is a major concern for biomaterials. The success of biomaterials is primarily dependent on the reaction of the human body to the implant. Bioimplants are expected to be nontoxic and should not cause any inflammatory or allergic reaction in the human body. They should be neither genotoxic which results in altering the DNA of the genome, nor cytotoxic which

causes damage to individual cells (Niinomi *et al.*, 2012). Ideally, in the case of metallic bioimplants, nontoxic elements should be selected as alloying elements in developing a biomedical alloy. However, in reality, no metals are completely inert or nontoxic (Chen and Thouas, 2015). Therefore, the construction of metallic implants requires the use of virtually inert elements, or those that exist as trace elements in the body; or in the case of reactive alloys, the use of highly corrosion resistant elements (Chen and Thouas, 2015). Metallosis is the term for the problems brought on by metal toxicity. This causes a number of difficulties, including infection, heart problems, depression, anxiety, visual impairment, cognitive impairment, nerve problems, thyroid problems, hearing impairment, and implant loosening (Neto and Rainforth, 2020). Apart from toxicity, thrombosis, which entails blood coagulation and platelet adherence to the biomaterial surface, and the fibrous tissue encapsulation of biomaterials implanted in soft tissues are significant concerns for biocompatibility (Geetha *et al.*, 2009; Hussein *et al.*, 2015).

Excellent biocompatibility is also associated with a high resistance to corrosion and wear. A high corrosion resistance prevents the excessive release of metals from the implants thus reducing the risks of allergic reactions. The service period of a biomaterial is mainly determined by its abrasion and wear resistance. A low wear resistance results in implant loosening due to an accumulation of the wear debris which has also been found to cause several reactions in the tissues in which they are deposited as well as inflammation that is destructive to the bone supporting the implant (Geetha *et al.*, 2009; Hussein *et al.*, 2015). Corrosion and wear will be discussed in greater detail in the sections to follow. Implant loosening can also be caused by inadequate osseointegration due to micromotions. Osseointegration is the integration of the implant with the adjacent bone and other tissues. A fibrous tissue is therefore formed between the bone and the implant when it is not well integrated with the bone (Geetha *et al.*, 2009). Therefore, it is crucial for biomaterials to have appropriate surface properties which include surface chemistry, surface roughness, and surface topography as they are essential in the development of good osseointegration.

The biomaterials used in the medical field today can be classified into four main categories based on their material type, as shown in **Figure 2.3**. Ceramics are generally inorganic materials made up of a combination of ionic and covalent bonding (Dorozhkin, 2018). These materials have low thermal and electrical conductivities and they have a relatively high hardness and high compressive strength thus making them resistant to breakdowns and compression (Dorozhkin, 2018; Ajmal *et*

al., 2022). Bioceramics have traditionally been employed mainly in medical grafts (Ajmal *et al.*, 2022). In addition to this, they can have structural functions as joint or tissue replacements, they can be used as coatings, and can function as resorbable lattices which provide temporary structures and frameworks that are dissolved and/or replaced as the body rebuilds the damaged tissues (Dorozhkin, 2018). Ceramics for biological use are classified into three categories, namely, bioinert ceramics which include alumina (Al_2O_3), zirconia (ZrO_2), and glassy carbon (Hassan *et al.*, 2019). These are widely used to fabricate femoral heads as they possess high strength, excellent corrosion and wear resistances while being non-toxic and biocompatible (Dorozhkin, 2018). Absorbable ceramics with the common one being hydroxyapatite, are predominantly used in dental implants as they have a high stiffness (Ajmal *et al.*, 2022). Lastly are the bioactive ceramics which include bioglass. These have an increased adhesion to the human bone (Hussein *et al.*, 2019). The biomedical applications of bioceramics are however limited due to their poor mechanical properties which include low impact and fracture resistance. In addition to this, these materials are highly brittle which is associated with low crack resistance (Dorozhkin, 2018).

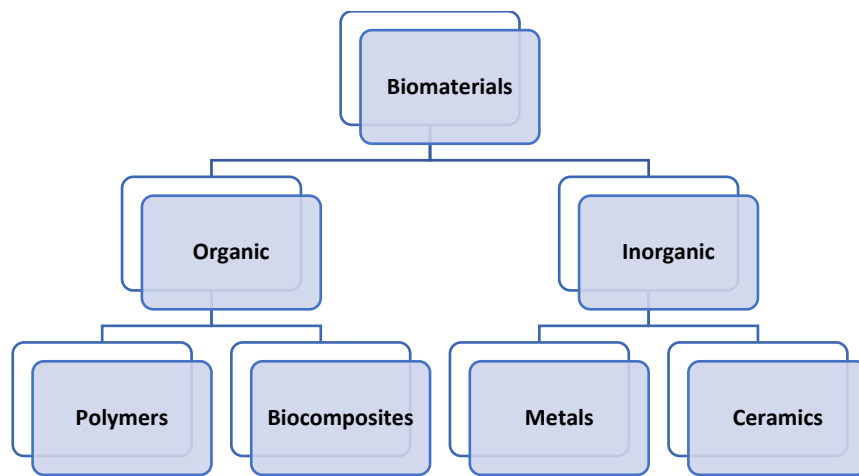


Figure 2.3: Classification of different types of biomaterials (Ajmal *et al.*, 2022)

Biopolymers are organic materials that are mainly used in drug delivery systems, disposable medical materials, prosthetics, bandages, dental materials, grafts, and skilled tissue products (Ajmal *et al.*, 2022). They have several benefits over bioceramics or metallic biomaterials which include the flexibility to generate diverse forms, easy secondary process steps, cost-effectiveness, and ease of obtaining particular mechanical capabilities (Hussein *et al.*, 2019; Ajmal *et al.*, 2022). These materials, however, possess poor mechanical properties like bioceramics and one of the

ways that have been sought to improve the reliability of both bioceramics and biopolymers is through the diverse reinforcement of ceramics, metals, or polymers to manufacture various biocomposites. Several biocomposites have recently been studied and verified for biomedical purposes. Some of these materials are already accessible in consumer markets due to the advantages over traditional materials (Ajmal *et al.*, 2022). However, all these materials fall short when compared to the inorganic metallic materials due to their lower strength, lower hardness and less biocompatibility (Hussein *et al.*, 2015). They have therefore gained less popularity in biomedical applications resulting in various types of metallic biomaterials being commonly utilised for the making of bioimplants today. Metals have an essential role as core structural materials in implants. These include stainless steels, cobalt alloys, magnesium, and titanium and its alloys (Hussein *et al.*, 2015).

Metals are used as implants in various parts of the body. They are specifically used for internal support and for the replacement of biological tissue, such as dental roots, joint replacements, orthopaedic fixation, and stents (Hussein *et al.*, 2015). The use of metallic materials in the making of bioimplants is not new and dates back to the 19th century leading up to the Industrial Revolution era where the metal industry began to expand (Chen and Thouas, 2015). The use of metals was mainly due to the demand for long bone fracture fixations. However, attempts made to implant devices such as bone pins and spinal wires made from metals such as iron, gold, or silver were completely unsuccessful until British surgeon known as Joseph Lister, implemented an aseptic surgical technique in the 1860s (Chen and Thouas, 2015). He essentially found a way to prevent infection in wounds during and after surgery. It was only after this discovery that metallic materials dominated as bioimplants, specifically in orthopaedic surgery playing a major role in both temporary implants (*e.g.* pins, screws, intramedullary nails, and bone plates) and permanent implants like total joint replacements (Chen and Thouas, 2015). An example of intramedullary nails can be seen in **Figure 2.4**. Metallic materials also found a space in dental and orthodontic practices during this time as well.



Figure 2.4: Intramedullary nails in (a) statically locked tibial nail; and (b) statically locked femoral nail (Glatt *et al.*, 2017).

Metallic biomaterials are widely used and are remarkably important for the reconstruction of failed hard tissue, to improve the quality of lives of patients. Elderly people have a higher risk of hard tissue failure and with the worlds ageing population rapidly increasing, there is a rapid increase in the demand for metallic biomaterials (Niinomi *et al.*, 2012). A variety of bioimplants made of stainless steel, cobalt based alloys, and titanium alloys have been approved for use by the United States Food and Drug Administration (FDA) and are commonly used in orthopaedic practice (Chen and Thouas, 2015). However, the biological and mechanical biocompatibility of metallic biomaterials require much improvement as there are many issues associated with the long-term maintenance of the implants integrity (Niinomi *et al.*, 2012; Chen and Thouas, 2015). In the beginning, implants were manufactured from pure metals when knowledge about the issue of corrosion was very limited. 4000 years ago the Egyptians and Romans used linen for sutures, gold and iron for dental applications and wood for toe replacement (Manivasagam *et al.*, 2010). These implants were problematic as they had very low mechanical strength and poor corrosion resistance. The introduction of steel then brought advancement into the bioimplant industry as this alloy enhanced the mechanical properties and corrosion resistance of the implants (Gain *et al.*, 2021).

The most used alloy of steel in the making of bioimplants is the austenitic stainless steel known as AISI 316L. This alloy is widely used in the making of temporary devices following bone trauma which are known as bone fixation implants such as bone plates, screws, hip nails, etc. It is also

used in spinal fixation as well as for cardiovascular applications (Niinomi *et al.*, 2012; Chen and Thouas, 2015). This alloy is highly accessible as it is relatively affordable compared to the other common alloys. However, there are several issues associated with using this alloy in implant making which has limited its use in the industry. Stainless steel is generally associated with/prone to localized corrosion such as crevice, stress corrosion, and pitting corrosion when exposed to a corrosive environment (Talha *et al.*, 2013; Gain *et al.*, 2021). It has been reported that more than 90% of the failure of 316L SS implants are due to pitting and crevice corrosion issues (Manivasagam *et al.*, 2010). In addition to this, AISI 316L stainless steel contains a large amount of nickel which can be quite toxic as the release of nickel in the human body causes some chemical reactions which cause irritation and allergies (Niinomi *et al.*, 2012; Talha *et al.*, 2013; Gain *et al.*, 2021). The released nickel has also been linked to a number of skin related diseases such as dermatitis (Geetha *et al.*, 2009). Currently, much attention is being placed on developing stainless steels with nitrogen in place of nickel to avoid these harmful effects. Nitrogen is known to be soluble in a relatively high content of austenitic stainless steel and it stabilizes the austenitic structure of iron (Chen and Thouas, 2015). Substituting nitrogen for nickel increases the mechanical strength as well as the resistance to pitting and crevice corrosion of the austenitic 316L stainless steel. However, stress corrosion cracking (SCC) which occurs in stainless steels that operate in a chloride-rich medium and is induced by the combined influence of tensile stress and a corrosive environment, cannot be prevented by making use of nitrogen so these nitrogen-rich alloys are not completely stain-proof (Chen and Thouas, 2015). The corrosion resistance of austenitic 316L stainless steel is not sufficient enough for long-term use as an implant material thus making their applications limited to temporary devices (Chen and Thouas, 2015). Currently, the high-nitrogen stainless steel, Orthinox, is a predominant stem material in the medical market of hip prosthesis. However, a challenge arises in producing final high – N stainless steels due to the difficulty in mechanically working them (Niinomi *et al.*, 2012; Gain *et al.*, 2021). In addition to this, this alloy has a much higher Young's modulus than human bone leading to the stress shielding effect which is the issue where insufficient stress is transferred to bone therefore leading to bone resorption and loosening of the implant after a few years of implantation (Geetha *et al.*, 2009). This is one of the leading causes of patients having to go for painful and expensive revision surgery after only a few years of implantation. This is undesirable as the goal is for biomaterials to remain intact for a longer period and not fail until the death of the person. This translates to

having a minimum service period of 15 to 20 years in older patients and more than 20 years for younger patients (Manivasagam *et al.*, 2010). The low cost of stainless steels has maintained their application in a large number of temporary devices, not only that, but high-nitrogen variants of 316L stainless steel have been developed primarily because of the low cost of stainless steel (Chen and Thouas, 2015).

Co based alloys exhibit better mechanical strength, abrasion resistance, and corrosion resistance compared to that of stainless steel so they are often employed for the manufacturing of artificial joints (Manivasagam *et al.*, 2010; Niinomi *et al.*, 2012). The excellent corrosion resistance of these alloys over stainless steel is governed by the presence of cobalt which contributes to the corrosion resistance of the alloys in addition to the chromium (Manivasagam *et al.*, 2010). Many Co-based alloys are used in biomedical applications such as artificial hip implants for better ductility and resistance to wearing in loading condition. They are dispersed with carbide to increase their wear resistance (Gain *et al.*, 2021). These alloys, however, just like stainless steel, contain nickel which is known to be toxic and the cause of adverse reactions when released into the human body. Ni-free Co – based alloys such as Co-Cr-Mo (ASTM F75) alloys have now been developed for biomedical applications in order to combat the issue of toxicity (Niinomi *et al.*, 2012). This has however not been very successful as the removal of nickel results in the formation of some unwanted constituent phases (ϵ phase and γ phase) which result in the poor cold workability of the alloys (Niinomi *et al.*, 2012). This has placed limitations on the use of Co – based alloys in the biomedical industry.

Compared to the 316L stainless steel and cobalt-based alloys, titanium and its alloys possess attractive properties that make them far superior in comparison. The attractive properties which include an excellent resistance to corrosion due to the matrix element, titanium, already having an excellent corrosion resistance by itself, drove the early introduction of commercially pure titanium (CP-Ti) and $\alpha+\beta$ Ti-6Al-4V alloys as well as the more recent development of metastable β alloys (Chen and Thouas, 2015). Titanium and its alloys are discussed in greater detail in the following sections.

2.2 Titanium and its alloys

2.2.1 Why Titanium?

The metal titanium was discovered in 1791 in Cornwall by a British mineralogist named William Gregor (Neto and Rainforth, 2020). This metal is hard and lustrous with a density that is approximately 60% that of iron and nearly half the density of cobalt (Chen and Thouas, 2015; Anene *et al.*, 2021). This gives it its superior strength-weight ratio which is highly desirable for bioimplant applications. This metal's properties such as its strength can be improved considerably by alloying and deformation processing (Chen and Thouas, 2015). Pure titanium has two allotropic forms namely, a hexagonal close-packed (HCP) crystal structure which is known as the α phase which undergoes an allotropic transformation at 885°C to a body centered cubic (BCC) crystal structure known as the β phase (Chen and Thouas, 2015). This transformation temperature known as the β -transus temperature can be modified by the presence of impurities as well as the types of alloying elements present (Anene *et al.*, 2021). Some elements are known to be α stabilizing elements (Al, O, N, and C) which essentially increase the β -transus temperature, while β stabilizing elements (Mo, V, Nb, Fe, Ta, Cr, Si, Ni, Co, and Mn) depress the β -transus temperature. In addition to this, zirconium and tin are neutral to the allotropic transformation as they do not have a marked effect on the stability of either of the phases but rather form solid solutions with titanium. The β transus temperature is important as heat treatments are carried out at some incremental temperature close to this temperature (Kaur and Singh, 2019a). After processing, titanium alloys are categorised into four classes based on their microstructure. These are α alloys, near- α alloys, $\alpha+\beta$ alloys, and β alloys. Most of the biomedical titanium alloys belong to the $\alpha+\beta$ or β class of titanium alloys.

In addition to their superior strength, titanium alloys lower elastic modulus, superior biocompatibility, and enhanced corrosion resistance has made them more suitable for biomedical implant applications in comparison to stainless steels and cobalt-based alloys and their use as biomaterials is continuously increasing (Pandey *et al.*, 2020). Before the use of titanium and its alloys in the biomedical industry, the development of the different types of alloys was mainly for aerospace applications due to their superior specific strength. Their use for implant fabrication was only then discovered in the late 1930s when it was found that titanium was well tolerated in cat femurs, like other implant materials such as stainless steel and vitallium, a CoCrMo alloy (Geetha *et al.*, 2009). The range of application of titanium and its alloys in the medical area is truly

astonishing as they are also used in used in healthcare goods such as wheelchairs, artificial limbs, artificial legs, etc. (Geetha *et al.*, 2009).

2.2.2 Classification of titanium and its alloys

2.2.2.1 α Titanium alloys

Alpha (α) titanium is essentially commercially pure titanium with a titanium composition of 98.9 – 99.6% (Chen and Thouas, 2015). These alloys have a relatively low strength and high ductility with their (Ultra high tensile strength) UTS and yield strength ranging from 240 to 550 MPa and 170 to 480 MPa respectively, as a result of the variations in the amount and levels of interstitials and impurities present (Chen and Thouas, 2015; Anene *et al.*, 2021). Increase in the oxygen content in these alloys is found to increase the tensile and fatigue strength of the alloys (Chen and Thouas, 2015). Small additions of β stabilizers in these α alloys further class them as super – α or near – α alloys, however, they still behave as CP titanium alloys rather than $\alpha+\beta$ alloys. α and near- α alloys contain aluminium as the most important alpha stabiliser (Peters *et al.*, 2003; Bodunrin *et al.*, 2021). An increase in the aluminium content leads to an increase in the alloy's creep and oxidation resistance. However, this increase can result in the degradation of the alloy's ductility and deformation capabilities (Peters *et al.*, 2003). Therefore, to prevent this degradation in ductility, the aluminium equivalent weight formula shown in equation 1 is used in the design of α alloy's. This allows for the alloying elements to be added within the acceptable limits (Peters *et al.*, 2003). This empirical formula is shown in the following equation (Peters *et al.*, 2003):

$$\text{Al eq.} = \text{wt. \%Al} + \frac{1}{3}\text{wt. \%Sn} + \frac{1}{6}\text{wt. \%Zr} + 10 \text{ wt. \% O} \quad (1)$$

To avoid the precipitation of the embrittling intermetallic compound, Ti_3Al , the Al eq. should not exceed 9 wt. % (Peters *et al.*, 2003). The elastic modulus of these alloy's ranges from 102 – 104 GPa which is lower than that of stainless steels, cobalt – based alloys, and the other titanium alloy classes, however, their low strength compared to $\alpha+\beta$ and β titanium alloys has placed limitations on their use in medical implants and medical devices. For non-load bearing applications which also require a high resistance to corrosion, the CP titanium grades are highly preferred.

2.2.2.2 $\alpha+\beta$ Titanium alloys

$\alpha+\beta$ titanium alloys contain β stabilizers which result in 10 – 30% of the β phase in the microstructure (Kaur and Singh, 2019a; Neto and Rainforth, 2021). Compared to the α titanium

alloys, these alloys possess good mechanical properties which include a high yield strength (795 – 1020 MPa), and a high ultimate tensile strength (UTS) which ranges between 715 and 1109 MPa (Anene *et al.*, 2021). These alloys can be adequately modified through alloying and heat treatment which alters the amount and distribution of the β phase thus controlling the properties of the alloys. The fatigue strength of these alloys is increased significantly by solution treatment and aging compared with that of the α alloys. Their fatigue strength is also higher than that of 316L stainless steels while being comparable to that of the cobalt-based alloys (Chen and Thouas, 2015). The $\alpha+\beta$ titanium alloys Ti-6Al-4V and Ti-6Al-4V (ELI) extra low interstitial are the most employed titanium alloys. They account for approximately 45% of all titanium production while unalloyed grades comprise approximately 30% of production, and all other alloys combined form the remaining 25% (Chen and Thouas, 2015). These $\alpha+\beta$ titanium alloys were initially developed for use in the aerospace industry, but later found use as a biomaterial due to their good mechanical properties, corrosion resistance, and good biocompatibility.

Nevertheless, the past decade has seen increased use of β -titanium alloys (second generation Ti alloys) for surgical implant applications. The increased use of β titanium alloys has been fuelled by the allergic reactions caused by the presence of vanadium and aluminium in the common commercial alloy, Ti-6Al-4V. Oral or inhalation exposure to vanadium and vanadium oxide compounds have been found to cause carcinogenicity and various adverse effects on the respiratory system, neurological system, and other organs (Chen and Thouas, 2015). The release of vanadium from biomedical implants has also been found to be toxic (Eliaz, 2019; Moghadasi *et al.*, 2022; Mosas *et al.*, 2022). This is because of the release of toxic ions of vanadium namely, oxidovanadium (IV) and vanadate (V) (Mosas *et al.*, 2022). Aluminium on the other hand, is associated with altered function of the blood-brain barrier and brain neurotoxicity. Aluminium has also been found to have the ability to bind to oestrogen receptors causing increased gene expression in human breast cancer cells in vitro (Chen and Thouas, 2015). Therefore, there are concerns that excessive exposure to aluminium may increase the risk of breast cancer and other neurological conditions, such as Alzheimer's disease (Chen and Thouas, 2015).

2.2.2.3 β Titanium alloys

These second-generation titanium alloys have been developed and investigated with great interest because of the issues of toxicity associated with the commercial $\alpha+\beta$ titanium alloys as non-toxic and relatively safe elements such as Mo, Ta, Nb, and Zr are used as alloying elements for the β -Ti

alloys. In addition to toxicity, another rationale behind the development of these second-generation titanium alloys is the issue of the stress shielding effect that is associated with the high Young's moduli of the implant. Compared to $\alpha+\beta$ titanium alloys, β -Ti alloys generally have a modulus closer to that of human bone and they exhibit almost no work hardening. Therefore, the risk of bone resorption and subsequent implant loosening is lowered when these alloys are employed as bioimplants (Geetha *et al.*, 2009; Kaur and Singh, 2019a). The lower modulus of the β -type titanium alloys compared to the α -type and $(\alpha+\beta)$ -type alloys is attributed to the crystal structure of the different phases. The β phase has a BCC crystal structure where the density of the atoms in this lattice is lower than the density in the α phase HCP crystal structure (Niinomi *et al.*, 2012). The non-toxic elements mentioned above also decrease the modulus of elasticity of these alloys without compromising their strength thus making them more suitable for implant applications.

The very first low modulus β titanium alloy developed for bioimplant fabrication was the Ti-13Nb-13Zr (TNZ) alloy (Niinomi *et al.*, 2012). This alloy was soon joined by the development of Ti-12Mo-6Zr-2Fe (TMZF), Ti-15Mo, Ti-16Nb-10Hf, Ti-35.3Nb-5.1Ta-7.2Zr (TNTZ), this alloy possess the lowest modulus of 55GPa, Ti-15Mo-5Zr-3Al, and Ti-29Nb-13Ta-4.6Zr (TNTZ) (Niinomi *et al.*, 2012; Neto and Rainforth, 2020). The effects of low modulus implants fabricated from β titanium alloys (TNTZ) on bone fracture healing, bone atrophy, and bone remodelling was investigated in rabbits. Bone plates and intramedullary rods were implanted into fracture models in the tibiae of these rabbits. The conventional $\alpha+\beta$ type Ti-6Al-4V ELI alloy and conventional AISI 316L stainless steel were also investigated for the sake of comparison. The Young's moduli of the TNTZ alloy were found to be the lowest compared to the conventional Ti-6Al-4V ELI alloy and the AISI 316L stainless steel. In the implantation of both the bone plates and intramedullary rods, it was found that bone atrophy and bone remodelling was the lowest and best for the β type TNTZ alloy (Niinomi *et al.*, 2012). In addition to a lower young's modulus and high specific strength, these alloys show better corrosion resistance in comparison to $\alpha+\beta$ titanium alloys and they exhibit better biocompatibility (Khorasani *et al.*, 2015).

The stability of the β phase which ultimately results in a stable β titanium alloy, is evaluated by using the parameter known as the molybdenum equivalent (Mo Eq) expressed in Equation 2:

$$\text{Mo Eq} = 1.0\text{Mo} + 0.67\text{V} + 0.44\text{W} + 0.28\text{Nb} + 0.22\text{Ta} + 1.6\text{Cr} + 1.0\text{Al} \quad (2)$$

As the Mo Eq. increases, the β transus temperature decreases thus allowing for the development of a stable alloy.

These alloys do, however, have some limitations. Although their elastic modulus is lower than that of the $\alpha+\beta$ titanium alloys, the commercial 316L stainless steel and cobalt-based alloys, there is still a gap when comparing it to the human bone as it is still significantly higher than the human bone. The main β stabilizers alloying elements, Ti, Ta, Mo, and Nb, are problematic to melt in a homogeneous way because of large differences in melting point and specific gravity. As a result, coarse grains and macro segregation are seen on the alloys produced by this traditional melting process, and this degrades the biocompatibility and mechanical properties of these alloys (Neto and Rainforth, 2021). The wear resistance of these alloys under loading conditions is very poor (Geetha *et al.*, 2009).

2.2.2.4 Biocompatible and low-cost titanium alloys

Due to the limitations posed by the commercial titanium alloy, Ti-6Al-4V, as well as the second generation titanium alloys as mentioned above, a lot of effort has been put into developing and investigating titanium alloys with a low toxicity and a young's modulus closer to that of the human bone while being inexpensive as the high cost of production for the various types of titanium alloys remain an impediment against their widespread applicability. These high production costs are approximately 6 times and 30 times higher, respectively, in comparison to those to obtain the same quantity of aluminium or steel (Bolzoni *et al.*, 2016). The Kroll process, which is the main titanium beneficiation technique, is a very complex process which involves several stages to produce a titanium sponge which undergoes several melting stages in order to produce a high quality metal (El Khalloufi *et al.*, 2021). The complexity of this process as well as the high energy expended in its production, gives titanium its high market price (El Khalloufi *et al.*, 2021). Beneficiation techniques that are low-cost and continuous such as the Armstrong process and the Fray, Farthing, and Chen (FFC) or Cambridge process, would reduce the cost of titanium (El Khalloufi *et al.*, 2021). However, the search for the most appropriate low-cost beneficiation process for titanium is still ongoing. Other pressing factors that contribute to the high cost of titanium alloys include the use of expensive and rare alloying elements, complex and multi-staged hot working, the use of special industrial processes to prevent the contamination of titanium from interstitials such as oxygen and nitrogen which degrade its ductility, and difficult machining as a result of its poor conductivity (Bolzoni *et al.*, 2016; Bodunrin *et al.*, 2021). To combat these issues, the expensive

alloying elements for titanium alloys need to be replaced by cheaper alternatives and the downstream processes (hot working and machining) need to be optimised to make cheaper titanium alloys.

β -type titanium alloys have been popular due to their low young's modulus however, the alloying elements used are very expensive. Low modulus β -type titanium alloys composed of low-cost elements such as Fe, Cr, Mn, Sn, and Al have therefore been developed in order to reduce the consumption of the original high-cost elements such as the rare metals Nb, Ta, Mo, and Zr (Niinomi *et al.*, 2012). The young's modulus of these alloys is however not close enough to the human bone and to achieve young's modulus values close to the human bone, these alloys would have to undergo solutionization. Solutionization however, compromises the strength and fatigue resistance of the β -type alloys and renders their properties poor in comparison to that of the (α + β)-type titanium alloys for biomedical applications (Niinomi *et al.*, 2012). The focus of this section is on the different cost reduction strategies for (α + β)-type titanium alloys.

In terms of the alloying elements, alpha stabilizing elements are affordable and relatively abundant compared to most of the beta stabilizers (Fujii and Takahashi, 2002; Bodunrin and Chown, 2021). Beta stabilizers are classed into isomorphous forming beta stabilizers and eutectoid forming beta stabilizers which are cheaper than the isomorphous forming beta stabilizers (Fujii and Takahashi, 2002; Bodunrin and Chown, 2021). To reduce the alloy costs, the expensive isomorphous beta stabilizers are usually replaced with the inexpensive or cheaper eutectoid forming beta stabilizers. The main isomorphous stabilizer in the commercial alloy Ti-6Al-4V, is vanadium. A lot of work and research has gone into completely replacing this element with an inexpensive eutectoid stabilizer as well as a non-toxic alternative as vanadium is known to cause unwanted chemical reactions in the human body as mentioned previously. Early in the development of vanadium free alloys for the biomedical industry alloys, Ti-6Al-7Nb and Ti-5Al-2.5Fe were developed as the toxicity of niobium and iron is relatively negligible compared to that of vanadium (Niinomi *et al.*, 2012; Lu *et al.*, 2016; Simsek and Ozyurek, 2019b). Ti-6Al-7Nb was promising as it showed similar strength to Ti-6Al-4V, it was found to be more ductile, and its resistance to corrosion was found to be better than that of the commercial alloy (Kaur and Singh, 2019b). However, the challenge of cost remains with this alloy as niobium is one of the expensive rare metals found today. Ti-5Al-2.5Fe, which was developed in the early 1980's also shows a high strength and yield

strength, however, the full substitution of vanadium or an isomorphous forming beta stabilizer with an eutectoid forming beta stabilizer such as iron is not very ideal as there is a risk of for the formation of Ti_2Fe and $TiFe$ intermetallic compounds as these are associated with using eutectoid beta stabilizers and these compounds are known to cause poor ductility and formability in titanium alloys (Fujii and Takahashi, 2002; Bodunrin *et al.*, 2021). Iron is however known as the most common beta stabilizing elements used to replace the isomorphous beta stabilizing elements as it is the cheapest beta stabilizing element with the strongest beta stabilizing factor compared to other eutectoid forming beta stabilizers (Bodunrin and Chown, 2021). In terms of alpha stabilizers, aluminium has been known as the most important and most common alpha stabilizer used in titanium alloys however, it has been reported to make the working and machining of titanium alloys difficult as the hot deformation resistance is increased whilst the hot workability is decreased, thus contributing to the high manufacturing cost of the alloys (Fujii *et al.*, 2002).

Attempts to replace the aluminium with interstitial elements nitrogen and oxygen, as these stabilize and strengthen the alpha phase just like aluminium, were therefore made while replacing vanadium with iron to retain the beta phase as a way to improve the hot workability thus reducing the cost of the alloys (Fujii *et al.*, 2002; Nochovnaya *et al.*, 2008). These Ti-Fe-O-N alloys were found to have good mechanical properties at room temperature, excellent grindability, good resistance to corrosion, and excellent formability (Fujii *et al.*, 2002). These alloys were therefore considered as potential metallic materials in the biomedical industry. Nochovnay *et al.* (2008) determined the optimum compositions of these Ti-Fe-O-N alloys initially investigated by Fujii *et al.* (2002) and found that the alloy, Ti-1.5Fe-0.49O-0.05N was the optimum as it had the best hot and cold deformation properties, it was highly corrosion resistant and biocompatible. The application of these alloys is however limited as segregation of iron challenges may arise and they are not suitable for high temperature applications as they do not contain aluminium which is responsible for promoting strength in high temperature regions (Fujii *et al.*, 2002). Other combinations not suitable for high temperature ($>400^{\circ}C$) applications include the use of aluminium as the alpha stabilizer and iron as the sole beta stabilizer. However, the mechanical properties of these alloys (Ti-3.5Al-1Fe and Ti-5.5Al-1Fe) were found to be superior to those of the commercially pure titanium while being comparable to those of Ti-6Al-4V (Fujii and Takahashi, 2002). Using iron as the sole beta stabilizer has however been unsuccessful in most cases due to the formation of $TiFe/Ti_2Fe$ intermetallic compounds and beta flecks which degrade the properties of the alloys (Bolzoni *et al.*,

2016). The partial substitution of isomorphous beta stabilizers with iron has therefore been explored as a means of combating the issue of the intermetallic compound formations.

It was reported that combining the cheap beta stabilizer iron with any of the isomorphous beta stabilizers (e.g., V, Mo, and Nb) could prevent the formation of intermetallic compounds in titanium alloys. Abdelrhman *et al.* (2019) developed and investigated the properties of two Ti-Mo-Fe alloys (Ti-2Mo-0.5Fe and Ti-3Mo-0.5Fe). These were designed as potential low-cost alloys for biomedical applications as Mo and Fe are low-cost elements. Molybdenum is known to improve the corrosion resistance in titanium alloys as well as reduce their young's modulus (Abdelrhman *et al.*, 2019). The hardness of the alloys was found to be higher than that of Ti-6Al-4V ELI alloy and their young's modulus (85-82 GPa) was found to be significantly lower than that of Ti-6Al-4V ELI (110 GPa). Their resistance to corrosion was also found to be better than that of the commercial alloy. While these alloys are promising as no intermetallic compounds were found in their microstructure, their potential application in the biomedical industry could be limited as the absence of aluminium in their composition limits the alloys from reaching their full-strength potentials as aluminium promotes strength in high temperature regions as mentioned previously.

Bodunrin *et al.*, (2020) also proved that the use of a cheap beta stabilizer in combination with an isomorphous beta stabilizer could prevent the formation of intermetallic compounds in titanium alloys when they developed a group of low-cost titanium alloys by partially substituting vanadium for iron. They found that no TiFe intermetallic phase formed in the alloys, instead, the beta phase proportion increased since iron is a strong beta stabilizer. The alloys developed are Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe. It has been reported that in order to produce iron-containing titanium alloys that are free of intermetallic compounds, the iron content should not exceed 2 wt.% (Nochovnaya *et al.*, 2008). However, Bodunrin and Chown. (2021) showed that it is possible to avoid intermetallic compound formation through the combination of an isomorphous beta stabilizer, vanadium, with up to 3% iron, a cheap eutectoid beta stabilizer. Their experimental alloys showed good mechanical properties that are comparable to Ti-6Al-4V. The addition and increase in the iron content resulted in a higher hardness in comparison to the commercial Ti-6Al-4V alloy. This is ascribed to the solid solution strengthening effect of iron caused by the difference in the atomic radii of iron and titanium. In addition to this, the basket-weave microstructure of the experimental alloys enables more resistance to dislocation movement which leads to the higher

hardness of the alloys (Bodunrin *et al.*, 2020). These alloys also showed superior resistance to corrosion in 3.5 wt.% NaCl and 3.5 M H₂SO₄ solutions compared to Ti-6Al-4V. These alloys have also been shown to have potential as use in the biomedical industry as for as corrosion resistance is compared as they show similar corrosion resistance to Ti-6Al-4V alloy in simulated body fluids (Leshetla *et al.*, 2022).

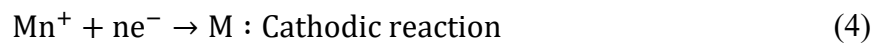
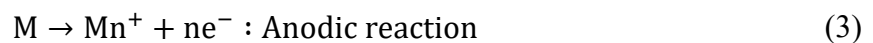
Processing the alloys is known to increase the cost of titanium alloys as well. The most suitable hot working parameters for these experimental were established as this can save about 40% of wasted materials during the forming process of the alloys (Bodunrin *et al.*, 2020). This reduces the contribution of complex and multi-stage forging processes to the high cost of titanium alloys production. These experimental alloys still need to undergo more tests to qualify as biomedical implants. This study is the basis of some of the tests considered in this study particularly corrosion, wear and tribocorrosion.

2.3 Theories of corrosion and tribology

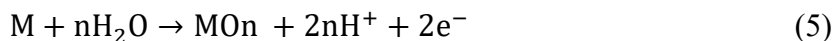
2.3.1 An overview on the fundamentals of corrosion

Corrosion is the gradual degradation of materials such as metals, ceramics, and polymers, by electrochemical reactions which occur between the material and its surrounding environment (Manivasagam *et al.*, 2010). The surrounding environment usually contains a liquid and/or a gas to facilitate the corrosion process. The tendency of a material to corrode is studied by electrochemistry where the free energy (ΔG) is used to get an understanding of the tendency of a particular chemical reaction to occur (Berradja, 2019). This essentially translates to the tendency of a material to corrode. A negative free energy indicates a high tendency of a material to corrode while a positive free energy indicates that a metal is a stable thus having a low tendency to corrode (Berradja, 2019).

The corrosion process of a metal is based on two reactions called the anodic reaction and cathodic reaction. The metal dissolves in an anodic reaction while it gets reduced in a cathodic reaction (Berradja, 2019). This is best illustrated by Equations 3 and 4:



For passive metals such as titanium, the anodic reaction of the metal results in the formation of an oxide (passive) film that is a few nm thin on the surface of the metal. This occurs according to the reaction shown in Equation 5:



The stable oxides formed on the surface of these metals are known to protect the metals from corrosion as they reduce the dissolution/the rate of oxidation of the metal (Berradja, 2019; Neto and Rainforth, 2020). When this occurs, the state of the metal under these conditions is known as passive state and it occurs in the passive potential region. The oxides contained in these passive films are generally made up of the alloying elements of the metal while the presence of oxygen or other oxidizing species is required for passivation to occur. The most common technique used to find the corrosion resistance of metals is called potentiodynamic polarization. This is a technique where the potential of the electrode is varied by applying a current through the electrolyte (ASTM International, 2014). In these conditions, the passive films on the metals and alloys may show a breakdown thus initiating corrosion. There are different types of corrosion which include uniform corrosion, crevice corrosion, hydrogen induced cracking, stress corrosion cracking, and microbial induced corrosion (Manivasagam *et al.*, 2010; Berradja, 2019).

2.3.2 Metallic biomaterials and corrosion

Metallic implants are generally expected to survive the conditions of the human body environment for as long as a lifetime. However, the environment inside the human body is both physically and chemically different from ambient conditions. As a result of this, a metal that is highly corrosion resistant in air may suffer severe corrosion in the human body. Metallic implants face the risk of severe corrosion as the human body environment is a very complex environment which consists of blood and other constituents of the body fluid which contain several constituents like water, sodium, chlorine, proteins, plasma, amino acids, and mucin as in the case of saliva (Manivasagam *et al.*, 2010; Chen and Thouas, 2015). These body fluids have a neutral pH value between 7.2 and 7.4 at 37°C and at a pressure of 1 atm (Chen and Thouas, 2015). These are the ideal body conditions; however, changes can occur at any time which drop the pH to 3 – 4. This usually occurs when there is inflammation caused by injury, surgery, or allergic reactions. In addition to this, an implant that performs well in one region of the body may suffer an unacceptable amount of corrosion in another part of the body due to acidic erosion and oxidation (Chen and Thouas, 2015).

These conditions render the human body an aggressive environment for any biomedical implant. The metals used to make these implants are therefore required to be corrosion resistant enough to be able to withstand severe conditions like these in the human body.

Ideally, the corrosion resistance of bioimplant materials should be such that the release of metal ions from a metallic implant will be minimized in the harsher and most severe conditions of the body and remain at a satisfactorily low level over a long service period (+30 years) (Chen and Thouas, 2015). Passive films play a major role in the corrosion behavior of metallic implants as they ensure that the corrosion of the implants when in service occur at a very slow, acceptable rate. Therefore, if the passive film formed is not as stable or if the corrosion resistant property of the material is low, ions are released into the blood thus destroying the surface of the metals as well. This leads to unwanted, sometimes life threatening allergic reactions in the human body as well as nervous system disorders which are undesirable (Pandey *et al.*, 2020).

The well-known austenitic 316L stainless steel is corrosion resistant as a result of the formation of a thin amorphous chromium oxide (Cr_2O_3) layer on its surface (Eliaz, 2019). This layer protects the alloy from electrochemical degradation due to the ionic bonding in the oxide. Chromium is the main element responsible for the high passivation ability of these alloys and an increase in the chromium content, as well as the molybdenum content, increases the resistance of the alloy against the localized breakdown of this passive film (Virtanen *et al.*, 2008). The low carbon content (<0.03%) of this alloy as indicated by the notation “L”, renders this alloy unsusceptible to intergranular corrosion due to the precipitation of Cr-carbides at the grain boundaries of the alloy (Virtanen *et al.*, 2008). However, the rate at which this alloy corrodes is not low enough to be used in the making of permanent bioimplants. Many researchers have shown that in comparison to cobalt-based alloys and titanium alloys, the corrosion potential of 316L stainless steel is typically more active and as a result, its corrosion rates are higher. This alloy also shows a higher susceptibility than Co and Ti-based alloys to pitting and crevice corrosion in halide solutions.

Pitting and crevice corrosion are some of the typical special modes of corrosion of implant alloys. Pitting corrosion is a common type of localised corrosion which is caused by the local dissolution of the passive layer and the formation of cavities surrounded by an intact passivated surface (Virtanen *et al.*, 2008). This type of corrosion thrives in halide containing solutions, of which the chloride ion is the most aggressive for most metal alloys. The resistance of this alloy to pitting

corrosion is typically dependent on the Cr and Mo content, as well as on the content of MnS inclusions where pit initiation takes place preferentially (Virtanen *et al.*, 2008). Crevice corrosion is also a type of localized corrosion which is closely related to pitting corrosion. This type of corrosion however, occurs in narrow crevices such as screw/plate interfaces or under deposits, these are shielded regions where mass transfer is limited on the metal surface (Geetha *et al.*, 2009). Additionally, the corrosion and wear of these alloys results in the release of toxic ions, nickel, and chromium, which cause unwanted issues in the human body. These alloys also lead to the stress shielding effect in the body as a result of its high modulus of elasticity which is about ten times that of the human bone (Eliaz, 2019). These issues have limited its use to temporary medical implants only such as plates, screws, medullary nails, pins, sutures and steel threads, and networks using in fixing fractures as permanent implants such as joint replacements, would not last a lifetime (Virtanen *et al.*, 2008; Eliaz, 2019).

Cobalt-based alloys are known to have good properties which include a good resistance to corrosion. Compared to 316L stainless steels, they are more resistant to chlorine-induced crevice corrosion as well as galvanic corrosion (Eliaz, 2019). Pitting corrosion is also seldom seen in these alloys as they typically fail by transpassive dissolution (Eliaz, 2019). It has been reported however, that when pitting corrosion occurs in these alloy implants, carcinogens are released into the body (Geetha *et al.*, 2009). Once again, the good resistance to corrosion is as a result of the chromium and molybdenum alloying elements. The two major types of cobalt-based alloys are the cast CoCrMo and wrought CoNiCrMo alloys. CoCrMo has been used in dentistry applications for years while the wrought CoNiCrMo alloy recently found favour in the making of hip stems and knee joints due to their excellent resistance to corrosion as well as their good mechanical properties. The transpassive dissolution of the CoCrMo alloy is however a concern as it leads to the activation of the surface due to oxidation of the insoluble Cr(III) oxide layer to soluble Cr(VI) species which drastically increases the metal ion release (Virtanen *et al.*, 2008). These alloys possess other drawbacks which have posed some limitations on their use in the making of bioimplants. Firstly, when subjected to wear processes, toxic chromium, cobalt, and nickel ions are released into the body. Secondly, their very high modulus of elasticity enhances the stress shielding compared to titanium-based alloys and stainless steel. Titanium alloys are considered the most corrosion resistant of the alloys described above. This is attributed to the high stability of the passive oxide film that forms spontaneously on the alloy surface. The dominant oxide making up this film is

TiO₂ which is thermodynamically stable in the pH range of 2 – 12. This film will only experience a substantial amount of dissolution when exposed to complex species like HF or H₂O₂. These alloys show good and stable passivation in neutral halide solutions which translates to having a good resistance to corrosion in these solutions. However, in acidic solutions, these alloys become more prone to corrosion. The corrosion of titanium and its alloys is described in Section 2.3.3.

In essence, the formation of a protective oxide layer on the surface of metal implants considerably reduces the corrosion of the said implant. Structural changes in the film or any variation in the ionic or electrical conductivity of the film may alter the films resistance against corrosion. It is important to note that the corrosion resistance of passive alloys is greatly dependent on the alloying elements and the oxides formed.

2.3.3 Titanium alloys and corrosion

As mentioned in Section 2.2 titanium and its alloys are greatly known as corrosion-resistant alloys in most corrosive solutions as a result of their chemically inert and tenacious oxide film that is formed spontaneously on their surface (Virtanen, 2012a). This film forms when titanium reacts aggressively with oxygen when exposed to air or an aqueous solution of any kind. This makes the use of these alloys in the chemical and biomedical industries so prominent. The oxides making up this film can either be anatase or rutile (Eliaz, 2019). Other oxides of the alloying elements accompany the titanium oxides. These include Al₂O₃ and V₂O₅ in the commercial alloy (Ti-6Al-4V) and Nb₂O₅ in Ti-6Al-7Nb in addition to the aluminium oxide. The corrosion resistance of Ti-6Al-7Nb has been found to be higher than that of Ti-6Al-4V. This is due to the chemically more stable, less soluble, and more biocompatible Nb₂O₅ compared to the V₂O₅ formed on the Ti-6Al-4V alloy (Geetha *et al.*, 2009). The level of stability of this film determines the alloy's resistance to corrosion. Because of the simplicity of the alloying elements in CP-Ti and near alpha titanium alloys, as well as the limited impurities found in these alloys, they are more resistant to corrosion compared to the $\alpha+\beta$ and β titanium alloys (Virtanen, 2012b; Anene *et al.*, 2021). This is due to the fact that elements and impurities modify the oxide film which can either improve or destroy the protectiveness of the oxide film of which it has been proven that in the common titanium alloys, the latter is observed. Manganese, vanadium, and aluminium have been found to reduce the protectiveness of the film, while the protectiveness of this film is improved when noble alloying elements such as palladium and ruthenium are utilized (Virtanen, 2012a).

In addition to the effect of the alloying elements on the corrosion resistance of titanium alloys, the environment to which they are exposed also influence their resistance to corrosion. In strong reducing environments such as hydrochloric acid, hydrofluoric acid, and sulphuric acid environments, the oxide film of titanium alloys readily dissolves thus activating the surface of the alloy making it prone to corrosion attack (Virtanen *et al.*, 2008; Khorasani *et al.*, 2015). There is however an upside to acidic environments. If the concentration of the acid is strong enough, it can induce the formation of a titanium hydride film on the surface of the alloy once the oxide film has dissolved (Owen *et al.*, 1972; Andijani *et al.*, 2000; Bodunrin *et al.*, 2020). This film does not form spontaneously but it does have the protective characteristics of the oxide film. The only environment known to render titanium and its alloys extremely susceptible to corrosion is a fluoride-containing environment. This puts titanium dental implants at risk and as a result, thorough investigations go into these alloys before their application in dental components. The repassivation behavior of a material after corroding also plays a vital role in determining the corrosion behavior of the material. Titanium alloys repassivate much faster and more spontaneously than stainless steel, cobalt-based alloys, and other biomedical alloys (Geetha *et al.*, 2009).

Titanium alloys are highly resistant to pitting and microbial-induced corrosion because of the spontaneous repassivation of the dissolved oxide layer (Manivasagam *et al.*, 2010; Eliaz, 2019; Anene *et al.*, 2021). However, like 316L stainless steel and cobalt-based alloys, titanium and its alloys are susceptible to crevice corrosion, hydrogen induced cracking and stress corrosion cracking (Eliaz, 2019). A review of the literature on commercial and newly developed alloys in different simulated body fluid environments is presented in Section 2.3.3.1.

2.3.3.1 Corrosion behavior in physiological solutions

2.3.3.1.1 Influence of surface passivation and temperature

The accumulation of titanium as well as its alloying elements in tissues adjacent to the implant has been reported and this has been attributed to both corrosion and wear amongst other things. This has led to a series of investigations into the properties of the passive film on titanium and the specific changes which occur in it upon exposure to the aggressive conditions present in a biological environment.

Hodgson *et al.*, (2002) studied the electrochemical characterisation of the passive films on Ti, Ti-6Al-4V, and Ti-6Al-7Nb under simulated physiological/biological conditions to specifically get an understanding of the interactions of the calcium- and phosphate-ions present in the biological solution with the titanium oxide surfaces. These ions have been proven to selectively interact with titanium oxide surfaces, causing a removal of the oxides. Electrochemical impedance spectroscopy and photo-electrochemistry were employed to monitor the evolution of the passive film on exposure to simulated body fluid environments. Large variations on the intensity of the generated photocurrent indicated the presence of adsorbed ions on the surface. Different behaviour between the three metals investigated was also observed. The evolution of the adsorption of the ions has been shown to take place already within the first hours of exposure to simulated biological environments at 37°C. This adsorption resulted in a thicker passive film formation.

Bai *et al.*, (2013) studied the corrosion behaviour of biomedical Ti-24Nb-4Zr-8Sn (Ti2448) alloy in SBF (HBSS, 0.9% NaCl solution, and artificial saliva) at the body temperature of 37°C. This is one of the works that have proved that a passive film containing oxides of beta alloying elements is more stable than that of alpha alloying elements as the authors found that the Ti2448 alloy exhibited good resistance to corrosion due to the formation of a protective passive film containing mainly TiO₂ and Nb₂O₅, and some oxides with neutral stabilisers (ZrO₂ and SnO₂). This was confirmed by the X-ray photoelectron spectroscopy (XPS) characterisation that was conducted. The XPS spectra is shown in **Figure 2.5**. This author also found that the calcium ions in both electrolytes absorbed onto the passive film layer. However, unlike Hodgson *et al.*, (2002), it was concluded that the calcium ions had a negative influence on the stability of the passive film thus having a negative effect on the corrosion resistance of the alloys. This confirms the work of Narayanan and Seshadri. (2008) who found that the presence of Ca in the oxide layer leads to a reduction in the corrosion resistance of titanium alloys. They explained further that the more the concentration of calcium in the passive film, the more the number of calcium ion vacancies present which leads to insufficient annihilation of these vacancies as well as those already present as a result of lower titanium oxidation states (The point defect model). This then results in the localized breakdown of the passive film which result in higher corrosion rates (Bai *et al.*, 2013).

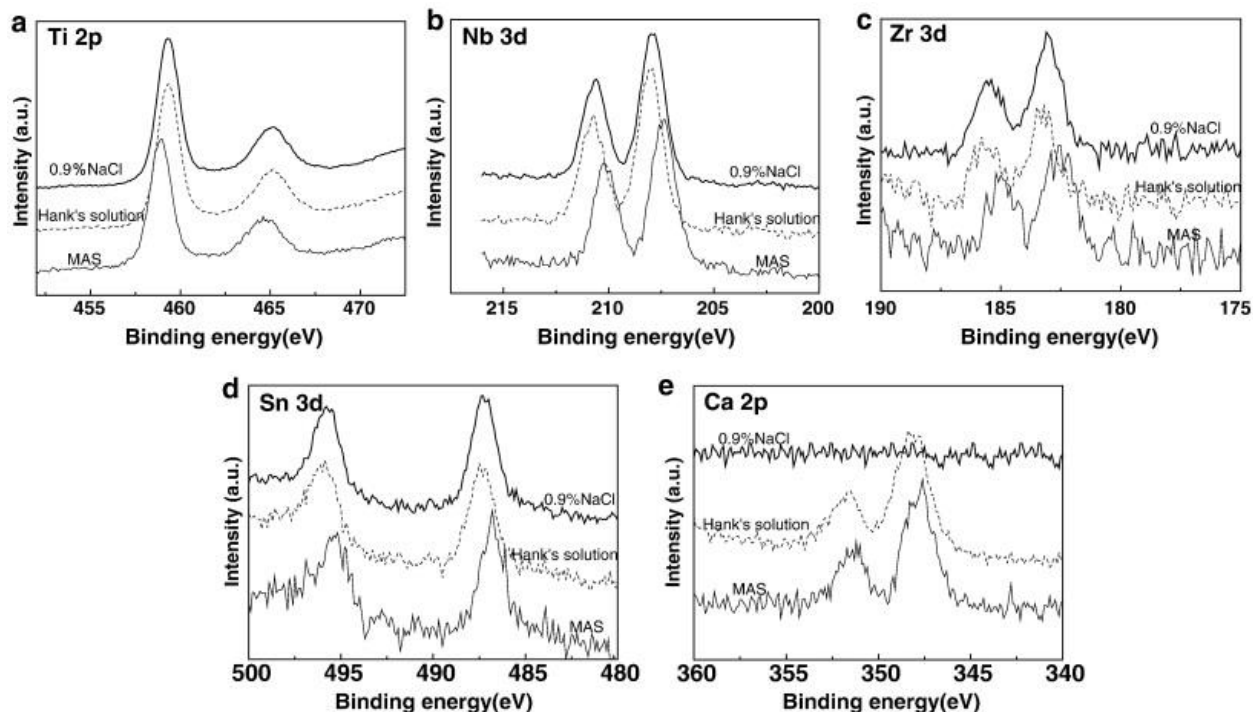


Figure 2.5: XPS spectra obtained for the passive oxide film of Ti2448 alloy in 0.9 wt. % NaCl, HBSS, and Fusayama–Meyer artificial saliva at 37 °C (a) Ti 2p, (b) Nb 3d, (c) Zr 3d, (d) Sn 3d and (e) Ca 2p (Bai et al., 2013).

Yi *et al.* (2021) studied the characteristics of the passive films formed on the commercial alloy, Ti-6Al-4V before and after transpassivation by electrochemical methods in HBSS. Based on the results, it was found that the stability of the passive film formed on the alloys was higher in the passive region than it was in the repassivation rate. This is because metastable pitting was observed in the repassivation range. The metastable pitting is attributed to the fact that the passive film absorbs more ingress ions (e.g., halide ions) at higher potentials regardless of the thicker passive film formation at these potentials. The ingress ions trigger the localized breakdown of the passive films according to the point defect model as reported by Narayanan and Seshadri. (2008). Electrochemical impedance spectroscopy (EIS) examinations determined the growth rates of the formed passive films before and after transpassivation and found that the growth rate was higher in the repassivation range than it was in the passivation range. According to this and the greater thickness in higher potential regions (repassivation range), it can be concluded that the passive film formed under high applied potential has better protective qualities. However, it is important to be aware of the potential of localized corrosion taking place due to the adsorption of aggressive ions.

Gurappa (2002) studied the corrosion resistance of Cp-Ti, Ti-6Al-4V and compared their properties to other common biomedical alloys, 316L stainless steel and a cobalt-based alloy (Co-35Ni-35Co-10Mo) under SBF conditions at a temperature of 37°C. The findings confirm that titanium alloys are superior to the 316L stainless steel and cobalt-based alloys. Ti-6Al-4V alloy was found to have the highest breakdown potential as well as the lowest corrosion rate. In addition, this alloy was found to have excellent resistance to pitting and crevice corrosion compared to 316L stainless steel. Tamilselvi *et al.* (2006) investigated the corrosion behavior of the commercial Ti-6Al-4V ELI alloy comparing it to its common, less toxic alternative, Ti-6Al-7Nb alloy in simulated body fluid conditions. Once again, the influence of niobium on the stability of the passive oxide film was demonstrated. Ti-6Al-7Nb alloy was found to show a lower current density and higher corrosion potential than the Ti-6Al-4V ELI alloy. This indicates that this alloy has better corrosion resistance overall. This is attributed to the fact that the niobium alloying element improved and stabilized the passive film on the alloy by decreasing the concentration of anion vacancies present on the titanium oxide film. The same result was reported by Takadoun *et al.* (2012) when they investigated the corrosion behavior of the commercial alloy including a beta alloy with niobium as one of the alloying elements, Ti-10Zr-10Nb-5Ta. They found that the beta titanium alloy presented a better resistance to corrosion as a result of the more stable passive oxide film compared to the commercial alloys. Tamilselvi *et al.* (2006) also reported that a bi-layered passive film formed on the surface of the alloys after being immersed for a long period (360 hours) in the electrolyte. This film consisted of an inner layer and an outer layer. This resulted in an increase in the resistance to corrosion of both alloys.

The effect of temperature on the electrochemical corrosion behavior of biomedical implants is of great importance as a human being operates at a temperature above room temperature, 37°C. Therefore, to get a more accurate characterisation, it is important to evaluate the alloys behavior at the specified body temperature. Alves *et al.* (2009) studied the effect of temperature (room and body temperature) on the corrosion behavior of CP-Ti and Ti-6Al-4V biomaterials. At body temperature, it was found that Ti is more resistant to corrosion compared to Ti-6Al-4V. The corrosion resistance of Ti-6Al-4V deteriorates at body temperature because of the increased dissolution of the passive film at increased temperature. Whereas the passive film morphology of CP-Ti was favoured at increased temperatures (body temperature) thus showed a better resistance

to corrosion. This once again supports the fact that the characteristics of the passive films formed on titanium alloys have a huge influence on the alloy's resistance to corrosion.

2.3.3.1.2 Influence of alloying elements on corrosion resistance

It is well known that surface sensitive properties like corrosion and high temperature oxidation are dependent on the chemical composition of the surface. The replacement of vanadium in Ti-6Al-4V alloys by cheaper and non-poisonous beta stabilizing elements such as iron and niobium have an influence on the mechanical properties of the alloys as well as their electrochemical behavior. Therefore, Choubey *et al.* (2004) studied the effects of the alloying elements Nb and Fe as a replacement for V on the electrochemical and corrosion behavior of Ti-6Al-4V alloy in HBSS at 37°C. The vanadium in Ti-6Al-4V was replaced with the same percentage of Nb and Fe to understand the role of chemical composition on the electrochemical and corrosion behavior. The alloys Ti-6Al-4Nb, Ti-6Al-4Fe, and Ti-5Al-2.5Fe were compared to the commercial alloy. The Ti-5Al-2.5Fe alloy was evaluated because it has been suggested as a candidate human body implant material. All alloys passivated immediately upon exposure to the electrolyte. The alloy containing niobium as the substitute showed a slightly significant difference in the passivation as its passivation was in a more noble region compared to the rest of the alloys. This can be seen in the potentiodynamic curves presented in **Figure 2.6**. This behavior is attributed to the niobium content as it has been found to positively modify the oxidation reaction on the surface of the alloy. Elements such as niobium are found to bring stability to the passive film due to the formation of niobium oxides. Overall, the corrosion characteristics of these alloys were found to be comparable to that of the commercial alloy which is an indication that the modification with the different low-cost elements did not significantly/negatively alter the properties of the alloy.

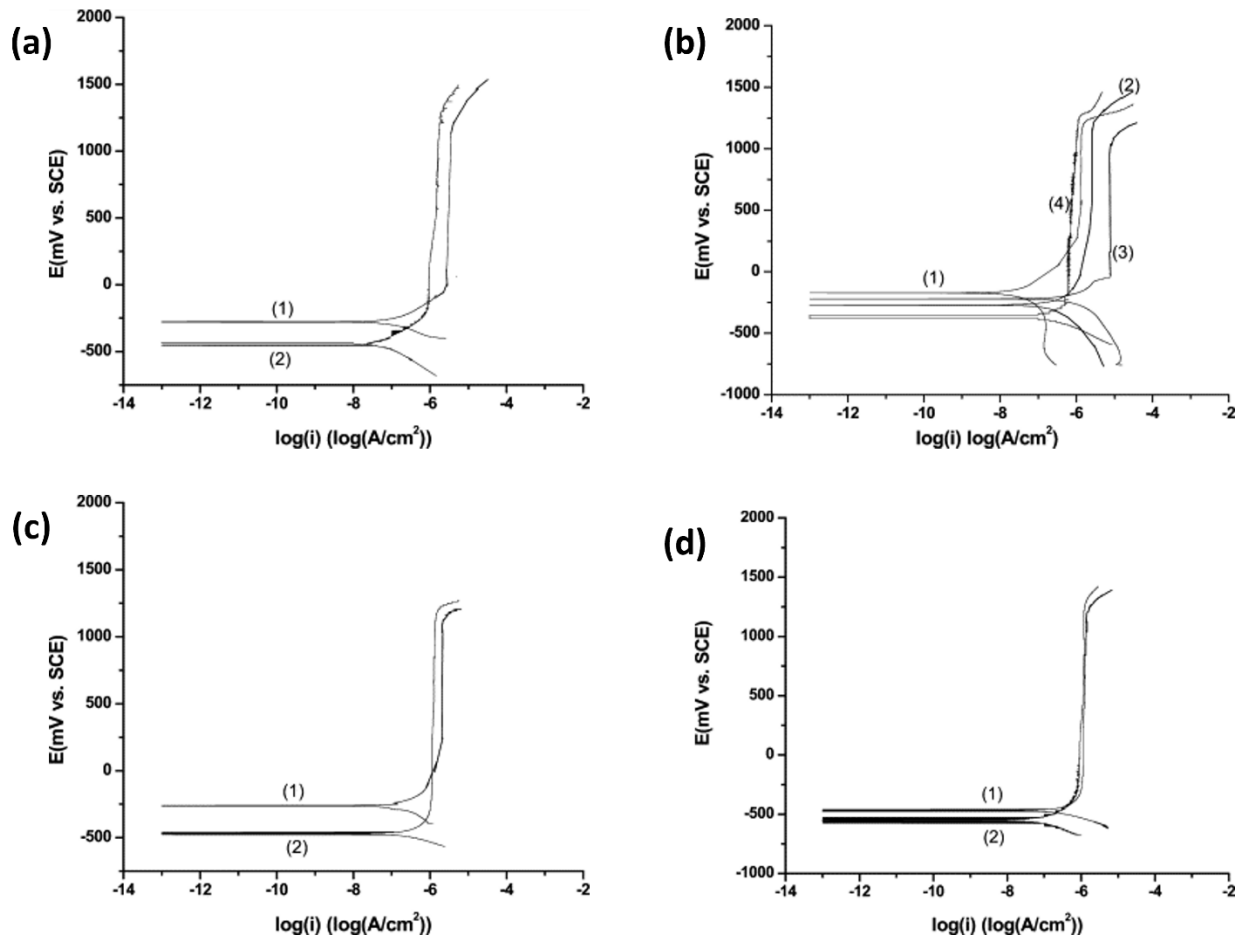


Figure 2.6: Potentiodynamic polarisation curves for (a) Ti-6Al-4V; (b) Ti-6Al-4Nb; (c) Ti-6Al-4Fe; and (d) Ti-5Al-2.5Fe in HBSS at 37°C and pH 7.4. The numbers within parentheses refer to results from the repeated experiments (Choubey *et al.*, 2004).

Pimenova and Starr (2006) focused on titanium alloys modified by fully replacing the toxic and expensive vanadium with iron. A series of Ti-xAl-yFe alloys were developed using a technique known as direct metal deposition (DMD). This allows for the fabrication of seven different compositions in one coupon thus making the production of Ti-xAl-yFe alloys time and cost effective. It was established that binary titanium alloys containing either Al or Fe performs poorly when the aluminium and iron content is increased beyond 3 wt.% and 9 wt.% respectively. In the case of the α Ti-xAl alloys, brittle Ti_3Al phases form in the Ti-based matrix thus degrading the corrosion resistance properties of these alloys. In the β Ti-xFe alloys, various compositions of brittle intermetallic Ti-Fe phases were found to form when the iron concentration was increased up to 25%. This degraded the corrosion resistance of these alloys as they damage the passive film. Out of all the tested $\alpha+\beta$ Ti-xAl-yFe compositions, Ti-7A-4Fe was found to perform well in the

HBSS as it had the highest OCP value and the lowest passive current density. Even though these alloys performed well in HBSS, when the concentration of either Al or Fe or both is increased significantly, localised corrosion becomes dominant. This has been attributed to the presence of a large number of beta grains and uneven distribution of the alloying elements in various phases. Corban *et al.* (2012) however, found that even a small concentration of iron deteriorated the corrosion resistance of the alloys as the alloys with less iron content (Ti-6Al-4V and Ti-6Al-7Nb) had superior corrosion performance over the Ti-5Al-2.5Fe alloy. However, Mareci *et al.* (2009) investigated the common Ti-5Al-2.5Fe alloy in artificial saliva among Ti-6Al-4V and Ti-6Al-7Nb and found that the alloys containing iron and niobium had better corrosion resistance than that of Ti-6Al-4V alloy.

Lu *et al.* (2016) also investigated a series of Ti-6Al-xFe alloys in simulated body fluids. The effect of Fe addition on the electrochemical corrosion behavior and elasticity properties of Ti-6Al alloys was investigated comparing to the commercial Ti-6Al-4V alloy. The iron containing alloys were once again found to perform well as they had OCP values more noble than that of the commercial alloy, Ti-6Al-4V. Overall, the use of iron in place of vanadium improved the alloys' resistance to corrosion. This was mainly attributed to the compact aluminium and iron oxide layer formed on the surface of the passive film because of the oxidation of the aluminium and iron. This inhibits the dissolution of the oxide film. The addition of Fe element in Ti-6Al alloy not only stabilises the β phase, but also improves the stability of passive film for the corrosion resistance due to the formation of Fe^{3+} and Fe^{2+} cations located in the crystal lattice of titanium oxide (Lu *et al.*, 2016; Zadorozhnyy *et al.*, 2017). Simsek and Ozyurek (2019) conducted a study on the corrosion behavior of Ti-5Al-2.5Fe, one of the alloys investigated by Choubey *et al.* (2004), and Ti-6Al-4V alloys in a simulated body fluid and found that the use of iron instead of vanadium increased the corrosion resistance of the alloy quite significantly. This was contrary to the results obtained by Choubey *et al.* (2004) which found that the corrosion behavior of the Ti-xAl-yFe alloys in simulated body fluids was not significantly affected by substituting vanadium with niobium and iron. This also contradicted the results reported by Corban *et al.* (2012) as they found iron to deteriorate the corrosion resistance of the alloys.

Another group of low-cost alloys that has been investigated is the Ti-Fe-Cu series where Fe is used in place of vanadium while copper is used in place of the aluminium in the commercial alloy, Ti-

6Al-4V. These elements were selected for use as they fall into the low-cost alloying elements category. The tensile properties of Ti-3.5Fe-3.9Cu produced by Zadorozhnyy *et al.* (2017) were found to be close to that of the commercial alloy containing vanadium. As mentioned previously, Fe is one of the most efficient β phase stabilizing elements for Ti alloys which can increase mechanical strength and improve the hot cracking resistance of Ti-based alloys. The addition of Cu was found to be beneficial as it is a β stabilizing element that can provide high hardness, high strength, and good wear resistance. Furthermore Ti-based alloys with small amount of Cu exhibit adequate cell biocompatibility and Cu content has no influence on the cell proliferation and differentiation. The corrosion tests in 0.9 wt.% NaCl revealed that this experimental alloy has comparable properties to those of the commercial alloy. Ti-3.5Fe-3.9Cu had the noblest corrosion potential and a slightly lower corrosion current density compared to that of Ti-6Al-4V. Lu *et al.* (2016) showed that the addition of iron in the right amounts (less than 15 wt. %) can improve the corrosion resistance of a Ti alloy. Zadorozhnyy *et al.* (2017) showed here that this is true, and that copper and iron oxidize and form a compact copper and iron oxide layer on the surface of the passive film, which improves the alloys corrosion resistance.

The full replacement of vanadium by niobium or iron in the conventional titanium alloys yields unsatisfactory results due to the formation of brittle intermetallic compounds within the alloys. Bodunrin *et al.* (2018) and Leshetla *et al.* (2022) therefore studied the effect of the partial replacement of vanadium with iron on the corrosion behavior of the Ti-Al-xV-yFe alloys. Bodunrin *et al.* (2018) tested the alloys in 3.5 wt.% NaCl and 3.5M H₂SO₄ solutions which are simulations of typical chemical, marine, and petrochemical industries. The partial substitution of V with 2-3 wt.% Fe was found to yield excellent corrosion resistance in both solutions compared to the Ti-6Al-4V alloy. However, in the H₂SO₄ solution, the experimental alloys oxide film was less stable than that of the Ti-6Al-4V alloy. This is because of the effect of iron on the modification of the oxide film and the fact that sulphate ions increase the dissolution rate of the TiO₂ formed on the surface. Leshetla *et al.* (2022) conducted corrosion tests in simulated body fluids (0.9 wt.% NaCl and HBSS) as the properties of these alloys have been found to be promising for use in the making of bioimplants. The experimental alloys were found to possess better corrosion resistance in both solutions compared to the Ti-6Al-4V alloy. The partial substitution of vanadium with iron is advantageous to the corrosion performance of the alloy. The exact mechanism by which iron improves the corrosion resistance of the alloys is still, however, unclear.

2.3.3.1.3 Effects of organic and inorganic species on corrosion of titanium alloys

The titanium alloys utilised in the construction of bioimplants (titanium alloy biomaterials) are exposed to harsh corrosive environments after implantation. This is due to the aggressive and complex nature of the human body as the human physiological fluid is an oxygenated saline solution with a high salt concentration of about 0.9% which has the ability to induce localised corrosion, at a pH of ~ 7.4 and temperature of $37 \pm 1^\circ\text{C}$ (Mudali *et al.*, 2003; Kocijan *et al.*, 2003; Virtanen *et al.*, 2008). Variation in pH levels has an impact on corrosion. The pH value of the human body is typically maintained at 7.0, however, this value can fluctuate between 3 and 9 as a result of various factors such as accidents and imbalances in the biological system that arise from diseases, infections, and other factors (Manivasagam *et al.*, 2010b). Additionally, the pH value near the implant site usually ranges from 5.3 to 5.6 after surgery (Manivasagam *et al.*, 2010b). The body temperature is known to accelerate the electrochemical reactions taking place at the implant interface (Virtanen *et al.*, 2008). In addition to the large amounts of sodium and chloride ions, the body fluid contains bicarbonate, some potassium, calcium, magnesium, phosphate, sulphate, and amino acids (Mudali *et al.*, 2003). In addition to these species, the physiological solution also contains inorganic species such as H_2O_2 or fluoride ions as well as organic species which include lipopolysaccharide (LPS), serum, proteins such as albumin as well as glucose (Mudali *et al.*, 2003; Manivasagam *et al.*, 2010a). There have been numerous studies investigating the influence of biomolecules on biomaterials.

Proteins are one of the primary constituents of the synovial fluid in joints along with other organic compounds such as hyaluronic acid and lubricin (Yan *et al.*, 2007; Virtanen *et al.*, 2008). Bovine serum albumin (BSA) is one of the most common proteins that is present in the physiological medium (Burgos-asperilla *et al.*, 2010). The presence of proteins is known to either inhibit or accelerate the corrosion behavior of some metals (Revathi *et al.*, 2016). Since their role in a corrosive environment is governed by several factors which include the surface chemistry of the metal, protein adsorption characteristics, interaction of protein molecules with other ions present in solution, and the transportation of anionic and cationic charges around and away from the local environment, their behavior is different with different metals (Khan *et al.*, 1999b). Proteins have the ability to attach to metal ions and move them away from the surface of an implant, disrupting the balance within the surface layer (Khan *et al.*, 1999b; Huang *et al.*, 2015). This layer is created by the presence of electrons on the implant surface and an excess of cations in the solution. This

disruption encourages further dissolution (Khan *et al.*, 1999b). Furthermore, proteins can adhere to the metal surface thus impeding the diffusion of oxygen in those specific areas. This increases the difficulty in repassivation on the alloy surface thus resulting in preferential corrosion in those regions (Khan *et al.*, 1999b; Manivasagam *et al.*, 2010a; Huang *et al.*, 2015). This was reported by Omanovic and Roscoe. (1999) when they studied the adsorption behavior of bovine serum albumin on stainless steel and found that the adsorption of the albumin on the stainless-steel surface resulted in an accelerated corrosion rate. The acceleration was found to be controlled by both the surface diffusion and charge transfer process. Protein interactions with the passive film on the metal surface are therefore of considerable interest as they may have a bearing on film breakdown, metal ion release, and film repair processes (Omanovic and Roscoe, 1999).

Khan *et al.* (1999b) investigated the influence of proteins on the repassivation process of biomedical titanium alloys (Ti-6Al-4V, Ti-6Al-7Nb, and Ti-13Nb-13Zr) in phosphate buffered saline (PBS) solution at different pH levels. The surface properties of the alloys were found to play a role as the corrosion processes in the different environments were found to have an influence of the surface hardness of the alloys. The addition of albumin to the PBS solution significantly reduced the hardness of Ti-6Al-4V and Ti-6Al-7Nb whilst that of Ti-13Nb-13Zr was only marginally reduced. Subsequently, the corrosion resistance of Ti-6Al-4V and Ti-6Al-7Nb decreased whilst that of Ti-13Nb-13Zr remained at the same level. This was said to be due to the level of solubility of the different alloying elements. Aluminium and Vanadium are more soluble in aqueous environments compared to niobium and zirconium. Khan *et al.* (1999b) essentially established that the proteins interacted with the surface layer and affected the repassivation process for Ti-6Al-4V and Ti-6Al-7Nb to a greater extent than Ti-13Nb-13Zr. Ti-13Nb-13Zr is a beta titanium alloy and this class of alloys is generally known to have superior mechanical properties and corrosion resistance to that of $\alpha+\beta$ type alloys. This is attributed to their stable and superior alloying elements. Karimi *et al.* (2011) also investigated the effects of protein (BSA) (concentration: 0 – 4 g L⁻¹) on the corrosion behavior of Ti-6Al-4V alloy in PBS solution at a neutral pH of 7.4. Their results were consistent with those of Khan *et al.*, (1999b) as they found that the BSA resulted in the acceleration of the corrosion rate of the titanium alloy. This occurred because of the negatively charged albumin at neutral pH reacting with the positively charged ions released from the metal alloy. These reactions could have either formed an adsorbed film on the alloy surface as mentioned previously or they could have resulted in the formation of

metal/protein/hydroxylated compounds (Karimi *et al.*, 2011). It was established that the detrimental effect of the protein was only observed at BSA concentrations of $0.2 - 2 \text{ g L}^{-1}$. At concentrations of 4 g L^{-1} or greater, the stability of the protective oxide layer was increased with minimal disruptions.

Huang *et al.* (2015) studied the corrosion behavior of a metastable beta titanium alloy (Ti-25Nb-3Mo-3Zr-2Sn) in a PBS solution with and without the addition of 10 g L^{-1} BSA. The results obtained did not agree with those of Karimi *et al.* (2011) who found that a concentration greater than 4 g L^{-1} would improve the corrosion resistance of the titanium alloy. In this case, the addition of 10 g L^{-1} of BSA was found to cause a drop in the corrosion potential of the titanium alloy thus increasing the alloys tendency to corrosion. The high affinity of proteins for adsorption onto metal alloy surfaces resulted in the transportation of metal ions away from the interface between the solution and passive film thus resulting in an accelerated corrosion rate of the titanium alloy. In contrast, Masdek *et al.* (2018) found that the commercially available alloy, Ti-6Al-4V, can perform well in the presence of proteins as they found that a stable passive film formed on the alloy surface when BSA was added to the simulated body fluid. The studies discussed thus far are not all in agreement as there are some contradictions. Most of the results, however, point to the detrimental effects of the BSA on the performance of the alloy in the human body environment. This however remains unclear and further studies are required to get clearer answers.

The different elements, ions and species found in the human body fluid influence the implant integrity. They can lead to the release of harmful species from the implant into the human body which results in unfavourable biological responses and the possibility of implant failure. It is therefore important to understand the corrosion behavior of the various biomedical materials in human body fluids. The blood glucose concentration is a crucial index to characterise the human body fluid (Liu and Wang, 2020). Given the significant prevalence of diabetes among a substantial population, it is imperative to gain insights into how implant materials behave when exposed to the body environment of typical diabetes patients. The corrosion of metallic alloys, particularly Ti alloys, cast iron, and mild steel, is significantly influenced by glucose. For instance, glucose inhibits the corrosion of cast iron and mild steel in acidic liquids through both physical and chemical interactions (Ostovari *et al.*, 2009; Rajeswari *et al.*, 2013; Zeng *et al.*, 2015). Titanium surfaces rapidly absorb glucose, and this facilitates the diffusion of oxygen ions to the electrode

(Burgos-asperilla *et al.*, 2010). Despite effective implant treatments in healthy individuals, people with medically precarious systemic illnesses, such as diabetes, are more prone to experience implant failures (Tamam and Turkyilmaz, 2014; Zeng *et al.*, 2015).

Zeng *et al.* (2015) investigated the corrosion behavior of pure magnesium in saline solution and HBSS with the addition of different glucose concentrations. In the normal saline solution, the corrosion rate of the magnesium was found to increase with an increase in the glucose concentration. This detrimental effect of glucose was attributed to the reaction of the glucose with the ions found in the saline solution as the glucose transformed into gluconic acid which attacked the metal oxides of the passive film and acidified the solution by decreasing its pH. Additionally, the glucose promoted the adsorption of chloride ions on the magnesium surface which accelerated the corrosion rate. In the HBSS, the glucose reacted with the calcium ions in the solution thus improving the formation of Ca-P compounds on the pure Mg surface which therefore inhibits the corrosion of the metal. This result essentially showed how the type and composition of the electrolyte has a role on the corrosion behavior as the glucose molecules bind to and react with different ions in solution differently, thus bringing about a unique response to the resistance to corrosion of the material under investigation. Because of the complexity of the HBSS compared to the NaCl solution, it is expected that it would have a negative response to the corrosion behavior of the alloys, however this is not the case. The positive effects of the other ions in the HBSS such as the calcium, suppress the negative effects of the chloride ions on the corrosion resistance of the alloys. This is due to the formation of calcium phosphate products on the alloy surface which improve corrosion resistance (Zeng *et al.*, 2015).

Liu and Wang (2020) investigated the corrosion behavior of a magnesium calcium alloy (containing 0.8 wt.% calcium and 99.2 wt.% magnesium) in HBSS with different glucose concentrations. Based on the results, it was found that the integrity of the passive film on the alloy was affected as the corrosion potential decreased with an increase in the glucose concentration from 0.7 g/L to 1.6 g/L (0.7 g/L, 0.8 g/L, 1.4 g/L, 1.6 g/L). In contrast, the corrosion current density decreased which is an indication that the corrosion rate of the alloy was inhibited by a high glucose concentration. Liu and Wang (2020) found that the corrosion resistance of the magnesium calcium alloy was based on the effect of glucose on the solution viscosity and diffusion of ions within the solution. HBSS with a higher glucose concentration is generally known to have a higher viscosity

which results in a stronger ion adsorption upon the tested alloy surface, but a lower ion diffusion rate thus resulting in a lower corrosion rate (Liu and Wang, 2020). The corrosion rate of the alloy was therefore found to be the lowest at the highest glucose concentration of 1.6 g/L. The corrosion of the magnesium calcium alloy was therefore inhibited effectively by high glucose concentrations. Nady *et al.* (2021a) investigated the effects of H₂O₂/albumin and glucose on the corrosion behavior of biomedical iron alloys (Fe-14Cr-8Mn and Fe-14Cr-8Ni). Albumin addition was found to accelerate the anodic degradation of the alloys while suppressing the cathodic reaction. Fe-14Cr-8Mn displayed the highest corrosion resistance in the presence of H₂O₂/albumin and when the glucose concentration was 100 ppm within the simulated body fluid. The results prove that the iron alloy, Fe-14Cr-8Mn, can perform effectively in body fluids with extremely low glucose levels because it displayed outstanding passivation capabilities at 100 ppm concentration of glucose which is also 2.5 times higher than that of Fe-14Cr-8Ni.

Messer *et al.* (2008) studied the effects of elevated glucose levels (2.7 g/L), common for a patient with uncontrolled diabetes or undiagnosed type II diabetes, on the corrosion resistance of commercially available titanium alloy dental implants. The results indicated that the alloys subjected to the dextrose solutions had a significantly higher corrosion rate compared to those tested in normal PBS solution. Tamam and Turkyilmaz. (2014) also studied the effects of pH and elevated glucose levels on the corrosion behavior of actual titanium alloy dental implants in Ringers simulated body fluid. They also performed tests in a 2.7 g/L glucose Ringers solution to simulate the body environment of a patient with uncontrolled or undiagnosed type II diabetes (extreme diabetic conditions). The corrosion rates of the titanium alloys were once again found to be significantly higher in the dextrose containing solution than the normal Ringer's solution. Hyperglycaemic conditions were therefore not found to be favourable for titanium dental implants. Faverani *et al.* (2014) studied the effects of different glucose concentrations (0.9 g/L (healthy patient), 1.35 g/L (initial stages of diabetes), and 2.7 g/L (uncontrolled diabetes or undiagnosed type II diabetes)) with the addition of lipopolysaccharide (LPS) on the corrosion behavior of the commercially available alloy, Ti-6Al-4V, with a smooth surface and one treated with double-acid-etching, in a simulated body fluid. LPS simulates the presence of an infection as diabetic patients are prone to infections which ultimately result in the production of LPS (Faverani *et al.* (2014)). Glucose alone was found to have no effect on the corrosion behavior of the smooth Ti-6Al-4V and the double-acid-etching treated alloy. In contrast, the addition of LPS to the glucose resulted in the

corrosion rate of the double-acid-etching treated alloy thus showing the deleterious effects of the LPS on the corrosion resistance of the surface treated alloy. The smooth alloy experienced a significant decrease in its corrosion potential when it was exposed to a combination of the glucose and LPS solution, thus suggesting that the solution altered the alloys surface properties making it less stable thus making the alloy more prone to corrosion. Ultimately, patients with a combination of hyperglycaemia and infections may be more prone to experience implant failures due to the reduced electrochemical stability of Ti-6Al-4V.

Liu *et al.* (2016) studied the effects of different glucose concentrations on the electrochemical corrosion behavior of pure titanium TA2 in HBSS. When the glucose concentration was less than 12 mmol/L (216 mg/dL), the titanium alloy displayed the best resistance to corrosion resistance. This is an indication that this alloy can play an effective role as an implant in the human body of an individual with normal and slightly elevated glucose concentrations. Comparatively, the corrosion of the titanium alloy is more probable when the glucose concentration is over 12 mmol/L due to the premature penetration of the solution through the passive film on the alloy surface thus acceleration the oxidation/corrosion rate of the alloy. Some published articles on the corrosion behavior of titanium alloys in different physiological solutions are summarised in **Table 2-1**.

Table 2-1: Previous studies on the corrosion behavior of titanium alloys immersed in various physiological solutions.

Author	Alloy type	Alloy name	Treatment/ Design	Testing parameters			Main Findings
				Solution	Temperature (°C)	Technique	
Kobayashi <i>et al.</i> (1998)	($\alpha+\beta$)	Ti-6Al-7Nb	Alloying with Nb	0.9% NaCl + 1.0% lactic acid	37	Potentiodynamic polarisation & OCP	Ti-6Al-4Nb showed superior corrosion resistance to Ti-6Al-4V due to a more stable passive oxide film.
Shukla, <i>et al.</i> (2005)	($\alpha+\beta$)	Ti-6Al-4Fe, Ti-6Al-4Nb	Alloying with Fe and Nb in place of V	HBSS	30	Potentiodynamic polarisation & EIS	Fe and Nb containing alloys exhibited superior corrosion resistance to Ti-6Al-4V. This was attributed to the positive effects of Fe and Nb in the passive film on the alloy surfaces as the alloys had greater passive film resistance. Nb has a stabilising effect on passive films.
Fujimoto <i>et al.</i> (2006)	($\alpha+\beta$) & β	Ti-6Al-7Nb, Ti-29Nb-13Ta-4.6Zr	-	HBSS & Eagles minimum essential medium (MEM) solution	37	Potentiodynamic polarisation & OCP	Because of the passive film stabilising effects of Nb, Ti-6Al-7Nb exhibited the best resistance to corrosion in the long-term tests. Deformation enhanced the corrosion resistance of the alloys. Ti-29Nb-13Ta-4.6Zr displayed superior corrosion resistance after deformation.
Bhola <i>et al.</i> (2011)	β	Ti-35.5Nb-7.5Zr-5.7Ta	-	Phosphate buffer saline (PBS) solution	37	Potentiodynamic polarisation, OCP, & EIS	The beta alloy had superior corrosion resistance compared to commercially pure (CP) Ti and Ti-6Al-4V. This was attributed to a bilayer passive oxide film compared to the single layer formed on Ti-6Al-4V and CP-Ti. The bilayer promotes osseointegration in bioimplant applications.

Wang <i>et al.</i> , (2015)	β	Ti-25Nb-3Mo-3Zr-2Sn	Alloying and heat treatment	0.9 wt.% NaCl, HBSS, and Ringer's solution	37	Potentiodynamic polarisation & current-time curves	The beta alloy had poor corrosion resistance in the HBSS due to the complex nature of the solution. After heat treatment, the alloys properties were enhanced thus improving its corrosion resistance. Overall, the beta alloy had poor resistance to corrosion in comparison to Ti-6Al-4V. The current-time curves of the beta alloy were more stable than those of Ti-6Al-4V. This was attributed to a greater content of oxides in its passive film compared to that of Ti-6Al-4V.
Hwang <i>et al.</i> (2015)	$(\alpha+\beta)$	Ti-Nb alloys (5, 10, 15, 20 wt.% Nb)	Alloying	0.9 wt.% NaCl	37	Potentiodynamic polarisation	The passive layer on the Nb containing alloys contained four layers as opposed to the 3 layers observed on the CP alloy. The thick 4-layer passive film on the Ti-Nb alloys enhanced the alloys corrosion resistance compared to the CP-Ti.
Xu <i>et al.</i> (2020)	β	Ti-35Zr-28Nb	Alloying Powder metallurgy fabrication	Simulated body fluid	37	Potentiodynamic polarisation, OCP, & EIS	The beta alloy had superior resistance to corrosion in comparison to the as-cast Ti-6Al-4V alloy and CP-Ti. This was attributed to the oxide rich (TiO_2 , Nb_2O_5 , and ZrO_2) protective passive film on the alloys surface.

2.3.4 Tribology: Wear

Tribology is defined as the field of science and technology concerned with interacting surfaces in sliding contact (Gahr, 1987). Lubrication, wear, and friction is part of tribology. Friction is the resistance to movement between two surfaces in contact. Lubricants are used to reduce friction by forming a thin film between surfaces. Low values of the coefficient of friction, such as 0.01, are created by the development of a thin film at the interface of movement between the materials in contact and act as a lubricant. If the film between the moving materials in the contact area is not homogeneous (in mixed lubrication), the coefficient of friction will be between 0.01 and 0.1. The surface oxide film that forms on metals, polymers and ceramics reduces the adhesion between the interfaces, resulting in a lower COF (Neto and Rainforth, 2020). Surface finish is also known to affect the COF. A smoother surface with fewer asperities can dramatically reduce the COF of a material (Gahr, 1987).

Wear is a complex process that happens when two bodies that are mating experience relative displacement as a result of the clamping force, whether there is cyclic load on either body or not. In the presence of cyclic load, it is known as fretting wear. Moreover, fretting action results in surface degradation that shortens a component's fatigue life or causes failure at a stress much below the fatigue strength of the material by causing premature initiation and propagation of fatigue fractures (Gahr, 1987; Magaziner *et al.*, 2009). Wear can result in the loss of material from the subsurface (Gahr, 1987). In most cases, material removal from a surface is due to mechanical methods exerted by the opposing surface. In this process, some materials are removed from the contact surfaces in the form of small particles (Gang *et al.*, 2018). Wear development occurs in the following steps: formation and detachment of debris by any wear mechanism (abrasion, adhesion, tribochemical reaction, or surface fatigue); change in surface morphology and composition due to the third-body effect; and finally, removal of these wear deposits/debris (Gahr, 1987; Neto and Rainforth, 2020). The different wear mechanisms are explained based on the different methods by which materials can be removed from bearing surfaces. In other words, the different wear mechanisms can be defined in terms of the mechanical methods of removing material from bearing surfaces, these are known as the wear sub-mechanisms (Gahr, 1987; Gang *et al.*, 2018).

Abrasive wear is a common wear mechanism where a hard material slides against a relatively soft material cutting and ploughing the softer materials surface (Balla and Das, 2017; Gang *et al.*,

2018). This action is because of the millions of asperities found on the harder surface (Gahr, 1987). The abrasive wear damage can occur via two-body or three-body wear mechanisms where the overall wear begins with the two-body wear which may lead to the three-body wear mechanism as the small and hard debris formed by the two-body wear act as a third body which produces many small visible scratches on the bearing surface (Gahr, 1987; Balla and Das, 2017). Abrasive wear can therefore be classified as either two-body abrasion or three-body abrasion. Interestingly, there is a substantial difference in the extent of wear between three-body abrasion and two-body abrasion, with wear being significantly lower by about one to two orders of magnitude in the former. This is because only a small fraction of the abrasive particles contributes to the wear process in three-body abrasion, primarily because of the varying angles at which the particles impact the alloy (Gahr, 1987). Abrasive particles that roll or slide freely cause minimal wear.

Adhesive wear occurs when the contact stress between two bearing surfaces is relatively high thus resulting in the asperities of the articulating materials fusing together (Gahr, 1987; Balla and Das, 2017). In this process, the fused areas on the materials rupture subsequently due to relative motion leading to transfer of small material from one surface to the other (Balla and Das, 2017). Material transfer of soft polymer onto hard surfaces, such as ceramic or metal alloys, is the result of adhesive wear (Gang *et al.*, 2018). To avoid or reduce adhesive wear, the articulating surfaces should be well lubricated by some protective film as this will prevent or limit the penetration of the asperities found on the hard surface into the soft materials surface (Balla and Das, 2017).

Corrosive wear, which falls under tribochemical reactions, is a wear mechanism that is induced by the simultaneous influence of wear and corrosion. The scientific name for this is tribocorrosion (Mischler *et al.*, 1999; Licausi *et al.*, 2013). During corrosion wear, the surface reacts chemically with the environment to form oxide layers that can easily detach from the surface under the influence of mechanical wear, resulting in pitting and third-body abrasive wear (Gahr, 1987). In general, the damage caused by corrosion wear is greater than that caused by corrosion and wear, which occur independently of each other. This is because friction removes the protective passive layer from the surface and prevents its reformation. Similarly, the oxide layers that form as a result of corrosion are brittle and are removed from the surface under the influence of the relative motion between articulating materials (Balla and Das, 2017). This will be discussed further in subsequent sections. Surface fatigue wear is localised, progressive structural damage that occurs when contact

surfaces are subjected to high, localised cyclic loads during articulation (Gahr, 1987; Balla and Das, 2017). Usually, the process begins with damage appearing at the material's surface, where there is a high level of friction. Subsequently, cracks develop, penetrate deeply into the material, and eventually merge resulting in the detachment of small fragments of material from the surface (Balla and Das, 2017).

One of the main requirements for biomaterials is to have a high resistance to wear as both wear and corrosion have been reported to be the primary reasons for the failure of bioimplants (Hussein *et al.*, 2015). The bioimplant should have high wear resistance and low coefficient of friction when sliding against body tissues. A great increase in the coefficient of friction or a decrease in the wear resistance may lead to loosening of the implant. In addition, the resulting wear particles can cause inflammation that destroys the bone supporting the implant (Hussein *et al.*, 2015). Wear is therefore an important factor in controlling and determining the long-term clinical performance of a metallic biomaterial. Therefore, it is important to understand the current knowledge of metallic biomaterial wear and the effects of material properties and conditions in terms of the types of alloys developed and experimental testing techniques on the wear of the biomaterials.

Wear is an inevitable issue in any joint replacement implant no matter the type of material used. Currently, clinically used joint prostheses are made of ceramic-on-ultra high molecular weight polyethylene (UHMWPE) or metal-on-UHMWPE which are categorized as HARD-ON-SOFT. They can also be made of ceramic-on-ceramic, CoCrMo-on-CoCrMo (metal-on-metal), or Al₂O₃-on-CoCrMo (ceramic-on-metal) which are categorised as HARD-ON-HARD (Chen and Thouas, 2015). The low wear resistance or high friction coefficient of these joint systems results in implant loosening (Jin and Wei, 2009; Hussein *et al.*, 2015). While joint replacements initially perform their intended biomechanical function very well, long-term wear and tear gradually produces more particles, which then attract immune system macrophages that recognise and engulf the particles as foreign bodies, much like bacteria or pyrogens. This is a natural defence mechanism; however, foreign synthetic particles tend to kill macrophages after ingestion. As a result, the dying macrophages release enzymes and metabolites that cause severe acidification in the surrounding microenvironment (Chen and Thouas, 2015). These enzymes, acidic chemicals, ions, and debris contribute to implant and bone erosion during aseptic loosening. In short, wear debris leads to serious adverse reactions that are likely to result in revision surgery. High fatigue strength,

excellent corrosion and wear resistance are therefore the key properties that determine the longevity of joint implants in the human body (Chen and Thouas, 2015).

Titanium alloys are used for the modular neck and femoral stem in joint prostheses, while using these alloys, the acetabular cup is avoided because of their poor wear resistance. Hip joint simulation tests have shown that the use of titanium alloys, particularly the commercial alloy, Ti-6Al-4V, is not advised as the wear rates of UHMWPE against Ti-6Al-4V are 35% greater than that against Co-Cr-Mo alloy (Pandey *et al.*, 2020). The high UHMWPE wear rates against Ti alloys have been related to the mechanical instability of the metal oxide layer. This layer is broken down easily by stresses applied externally. When the oxide layer is broken down, hard oxide debris which act as a third body abrasive body are formed, and lead to further surface damage. Titanium is therefore not used for articulation against any materials, but for components of modular constraints, whereby a titanium femoral stem with a cobalt-chromium or a ceramic ball to articulate against a UHMWPE line is used. The underlying factors contributing to the poor tribological properties of Ti and its alloys are enormous, including low work hardening, low resistance to shear from plastic deformation, and the effects of loosely bonded metal oxide layers contributing to a high wear rate (Molinari *et al.*, 1997; Geetha *et al.*, 2009; Philip *et al.*, 2019).

Compared to the other two popular metallic biomaterials, Co-based alloys (Co-Cr-Mo), and stainless steels (316 L stainless steel), titanium alloys have the poorest resistance to wear. This has been confirmed by several studies which include implant retrievals where different femoral heads made of Co-Cr-Mo, 316L stainless steel, and Ti-6Al-4V that were loosened by aseptic loosening were retrieved and analysed. From these studies and analysis, it was found that femoral heads made of the titanium alloy consistently had the highest wear averaging 74.3% against the UHMWPE acetabular component. The Co-Cr-Mo femoral heads were found to wear the least while the wear rate of the 316L stainless steel was between that of the titanium alloy and the cobalt-based alloy (Geetha *et al.*, 2009).

Some researchers performed experimental studies on the wear behavior of the common titanium alloys which includes the commercial alloy, Ti-6Al-4V. Molinari *et al.* (1997) found that the poor wear resistance of Ti-6Al-4V was as a result of the low resistance of the alloy to plastic deformation/delamination at both low and high loads. This is a sub-mechanism of the surface fatigue wear mechanism (Gahr, 1987). This wear mechanism has also been reported by a number

of other researchers (Mao *et al.*, 2013; Niu *et al.*, 2013; Sahoo *et al.*, 2014; Jothi and Ramanathan, 2015; Li *et al.*, 2015; Jozwik, 2018; Gain *et al.*, 2021; Du *et al.*, 2022; Enayati and Sayyed, 2022; Herrera *et al.*, 2023). In addition to this, they confirmed that the protection exerted by the surface oxide on the alloy surface is not sufficient enough to protect it against wear (Molinari *et al.*, 1997). Titanium alloys with niobium as the alloying element in place of vanadium, or titanium alloys with a high niobium content, have been found to possess good resistance to wear. This is because of the niobium oxide (Nb_2O_5) that forms on the surface of the alloys. This is due to the very good lubricating properties of (Geetha *et al.*, 2009). This good lubrication afforded by the Nb_2O_5 is attributed to the fast-repassivating capabilities of niobium. The passive film also adheres more strongly onto the surface of the niobium containing alloy and it is more stable (Geetha *et al.*, 2009). This was reported by Alam and Haseeb. (2002) when they performed a study on the wear behavior of Ti-6Al-4V and Ti-24Al-11Nb against hardened steel. It was found that the niobium containing alloy, Ti-24Al-11Nb, possessed a wear resistance that was about 48 times higher than Ti-6Al-4V. This is a significant difference and the poor wear resistance of Ti-6Al-4V was once again found to be a result of severe delamination. The protective layer formed by Ti-24Al-11Nb was found to be responsible for its much lower wear rate.

Although some of these titanium alloys, particularly the beta type titanium alloys, possess better resistance to wear compared to the $\alpha+\beta$ Ti-6Al-4V, all titanium alloys generally possess poorer resistance to wear in comparison to cobalt based alloys and stainless steels. To address this issue, some surface modifications techniques have been employed on the different titanium alloys. Molinari *et al.* (1997) modified the surface of the commercial alloy Ti-6Al-4V through plasma nitriding. This technique proved to improve the wear resistance of the titanium alloys as compared to the untreated Ti-6Al-4V alloy, the nitrided Ti-6Al-4V had lower wear volume loss under specific nitriding treating conditions which include load and nitriding temperature. This improvement is brought about by the deposited compound layer that provides a high resistance to oxidative wear. This compound layer, however, could be prone to adhesive wear if not formed at the right treating temperature (1073 K) (Molinari *et al.*, 1997). Borgioli *et al.* (2005) performed thermal oxidation treatments on Ti-6Al-4V disks to harden the alloy and subsequently improve their wear properties. This proved to be successful as the wear volumes of the treated samples was reduced from about 4 to 6 times in comparison with the untreated alloy.

2.3.5 Tribocorrosion

Titanium and its alloys are known as passive alloys as they spontaneously form a protective oxide layer on their surface when exposed to water (Dimah *et al.*, 2012; Bryant and Neville, 2016). The most common oxides formed by titanium alloys are anatase (TiO) and rutile (TiO₂) which are two forms of titanium dioxide. In the case of titanium alloys with other alloying elements apart from titanium, other oxides also tend to form on the surface of the alloy. In the case of the popular commercially available alloy, Ti-6Al-4V, it has been reported that vanadium is able to fuse to the surface of the alloy to oxidize into small amounts of vanadium oxides which are namely, V₂O₅, VO₂ and V₂O₃ at the outermost surface (Dimah *et al.*, 2012). These oxides are however not as protective as the titanium dioxides and can therefore result in the instability and deterioration of the passivity of Ti-6Al-4V (Dimah *et al.*, 2012). Because titanium alloys are commonly employed in the manufacturing of bioimplants, it is important to study all their properties including their passivation abilities as bioimplants are subjected to various processes in the human body that result in their deterioration and subsequent failure (Manhabosco *et al.*, 2011; Sharma and Sehgal, 2012; Doni *et al.*, 2013). These processes include corrosion due to the corrosive human body fluids, wear, and the simultaneous action of both, which is known as tribocorrosion (Mischler *et al.*, 1999; Licausi *et al.*, 2013). Tribocorrosion greatly influences the life of bioimplants as the simultaneous action of wear and corrosion occurring between the bioimplant and its articulating surface and the surrounding bones and/or tissues results in the removal of the protective oxide film on the surface of the implants thus exposing them to the corrosive body fluids (Khan *et al.*, 1999b). The passive film has an important role on mechanical degradation and friction can alter the corrosion behavior of metals (Mischler *et al.*, 1999; Okazaki, 2002). This can accelerate the corrosion of these implants thus reducing their lifecycle. Corrosion is also enhanced due to the galvanic coupling between worn and unworn surfaces.

The tribocorrosion behavior of metallic alloys is influenced by several factors, including material composition. The proportions of different elements in an alloy can significantly impact its mechanical properties and corrosion resistance (Mathew *et al.*, 2009). This also subsequently affects the passive film formation of the alloys as well as the characteristics, effectiveness, and stability of the formed passive film. Mechanical properties such as hardness and yield strength significantly affect the tribocorrosion behavior of the alloy. The hardness of a material is crucial as a high hardness enables the material to resist abrasion and deformation, particularly plastic

deformation, quite significantly (Mathew *et al.*, 2009; Bozic *et al.*, 2010; Runa *et al.*, 2015). Lubricants/coatings can reduce the friction and wear between the alloy and its surrounding environment thus minimising the detrimental effects of tribocorrosion (Moghadas *et al.*, 2022; Runa *et al.*, 2013; Zhang *et al.*, 2022). The corrosion resistance of the alloy as well as its microstructure also play a role in its ability to resist tribocorrosion. Lastly, environmental factors which includes the pH, temperature, and the presence of aggressive species such as acids and chlorides in the corrosive solution significantly impact tribocorrosion behavior (Mathew *et al.*, 2009; Dorozhkin, 2018; Pandey *et al.*, 2020). It is therefore important to subject bioimplant materials to tribocorrosion tests to understand how they perform under both mechanical and corrosive stresses to select or design materials that meet the specific tribocorrosion requirements of a given application.

Tribocorrosion can be characterised by its synergy resulting from the coupling of mechanical and environmental effects. This synergism often results in degradation and, hence, loss of material that often is much larger than the one which would be expected by simply summing up the degradation due to individual process. This synergism can have positive or negative effects depending upon the specific reaction products formed on the surface of the materials, which can protect the surface as in the case of self-lubricating and/or self-healing layers or can aggravate the material degradation process causing more material removal. The synergetic approach and mechanistic approach are two of the main methods used to quantitatively describe the synergistic effect between corrosion and wear. The synergistic approach which was developed by Watson *et al.* (1995) consists of measuring the individual contribution of corrosion (C_o) separately, it measures the individual contribution of wear (W_o) by applying a cathodic potential of 1V vs OCP to eliminate the corrosion contribution, and lastly, these individual components form the total material loss (T) which is the concurrence of wear and corrosion. The synergistic factor (S), which is the combined effect of wear and corrosion, also forms part of this approach. The total material loss due to tribocorrosion is therefore expressed using Equation 6 (Watson *et al.*, 1995; Landolt *et al.*, 2001; Mischler, 2008; Cao and Mischler, 2018):

$$T = C_o + W_o + S \quad (6)$$

Where T is the total material loss, Co is the material loss rate due to corrosion, Wo is the material loss rate due to wear, and S is the material loss rate due to corrosion and wear. The other important approach, which is the mechanistic approach, distinguishes two main contributions; the anodic dissolution (wear-accelerated corrosion) and the mechanical removal of metal particles (mechanical wear) (Mischler, 2008; Toh *et al.*, 2017; Toptan *et al.*, 2019). This approach is expressed by Equation 7 (Mischler, 2008):

$$V_t = V_{chem} + V_{mech} \quad (7)$$

Where V_t is the total material loss, V_{chem} is the material loss due to corrosion, and V_{mech} is the material loss due to mechanical wear in mm^3 . Using Faraday's law, the materials loss due to corrosion is found using Equation 8 (Mischler, 2008; Toh *et al.*, 2017; Toptan *et al.*, 2019):

$$V_{chem} = \frac{i \times t \times M}{n \times F \times \rho} \quad (8)$$

Where M is the molar mass of the metal (g/mol), t is the time duration of the sliding process (s), F is the Faraday constant (approximately 96,485 C/mol), ρ is the density of the metal (g/mm^3), i is the average current during rubbing for polarization tests (cathodic and anodic potentials).

More *et al.* (2011) investigated the tribocorrosion behavior of a group of beta type titanium alloys against an UHMWPE ball in HBSS with the addition of synovial components. The alloys were found to spontaneously repassivate after removal/damage of the passive film. Compared to the commercial alloy, Ti-6Al-4Fe, the beta titanium alloys OCP decreased and stabilised to a higher value. This was an indication that Ti-6Al-4Fe was not able to recover its passivity fully during this sliding compared to the beta titanium alloys. This was attributed to the presence of iron in the alloy (More *et al.*, 2011). The iron affects the passive film and the mechanical properties of the alloy. So, the passive film of the titanium alloys plays a very huge role in the tribocorrosion behavior and in the tribocorrosion resistance of the alloys. This is seen throughout many studies which show that once the passive film is destroyed by mechanical wear, there is a drop in the OCP as well as an increase in the current in the case of potentiostatic tests (Dimah *et al.*, 2012; Licausi *et al.*, 2013; Runa *et al.*, 2013; Silva *et al.*, 2016; Wang *et al.*, 2017). These observations are an indication of electrochemical activity/corrosion as the bare alloy surface becomes exposed to the corrosive

electrolyte. A passive film made up of good and stable oxides is required as they will ensure the stability and strong adherence of the passive film to the surface of the alloy.

Mechanical properties, particularly hardness, also have an effect on the tribocorrosion resistance of the titanium alloys. Yazdi *et al.* (2018) investigated the tribocorrosion behavior of Ti-6Al-4V that has undergone thermal oxidation treatment to enhance the properties of the alloy. A bio-tribofilm with a higher hardness and strength formed on the treated alloy in comparison to the untreated alloy. This higher hardness and strength resulted in a 95% decrease in the wear rate compared to the untreated Ti-6Al-4V alloy. A lower hardness and strength promote higher and easy deformation of the alloy during wear which results in heightened/severe wear (Yazdi *et al.* 2018). The wear mechanism that commonly dominates in such alloys is surface fatigue/plastic deformation. Buciumeanu *et al.* (2018) also found that hardness plays a critical role in the tribocorrosion behavior of titanium alloys when he compared the tribocorrosion resistance of an additively manufactured Ti-6Al-4V alloy to that of casted and hot-pressed Ti-6Al-4V alloys. The additive manufacturing produced an alloy with a higher hardness compared to the other manufacturing methods. This resulted in the alloy having the highest tribocorrosion and wear resistance. Although the hardness and other mechanical properties play a significant role in the tribocorrosion behavior, the surface properties of the alloys are equally important. Hacısalihoglu *et al.* (2014) found that an alloy with superior mechanical properties (Ti-15Mo), exhibited a high wear loss. This is attributed to the nature of the passive film of the alloy. The rate of depassivation and repassivation of this alloy influenced its wear rate as the rate of chemical reaction was higher compared to the other alloys (Ti-6Al-4V, Ti-13Nb-13Zr, Ti-45Nb). Manhabosco *et al.* (2011) investigated the effects of nitriding surface treatment on the tribocorrosion behavior of Ti-6Al-4V. Plasma nitriding is known to enhance the titanium properties by forming a hard compound layer composed of TiN and Ti₂N on the alloys surface (Manhabosco *et al.*, 2011). The nitrided alloy displayed a higher resistance to wear, corrosion, and tribocorrosion compared to the untreated alloy. Silva *et al.* (2016) investigated the surface treatment known as laser modification which also increases the surface hardness. They found that the laser modified alloy possessed a higher resistance to tribocorrosion compared to the untreated alloy.

The synergy which results from the coupling of mechanical and environmental effects can have positive or negative effects depending on the specific reaction products formed on the surface of

the materials, which can protect the surface as in the case of self-lubricating and/or self-healing layers or can aggravate the material degradation process causing more material removal (Ortega *et al.*, 2018). The wear of a beta alloy, Ti-12Mo-6Zr-2Fe, increased when it was subjected to tribocorrosion tests conducted by Yang and Hutchinson. (2016). This was due to the positive synergy which existed between wear and corrosion which leads to accelerated wear because of the corrosion imposed by the simulated body fluid/corrosive electrolyte. When simulated body fluid was introduced (tribocorrosion) for Ti-6Al-4V in comparison, the wear rate of the alloy decreased. This was an example of negative synergy where the effects of corrosion resulted in a deceleration of the wear. This was due to the simulated body fluid playing a predominant role as a liquid lubricant rather than a corrosive solution. A positive synergy rate is generally expected in tribocorrosion systems as the introduction of corrosion is usually expected to accelerate the wear process of the alloy thus decreasing its tribocorrosion resistance ability. Yazdi *et al.* (2020) found the presence of corrosion to cause 28% -245% increase in the wear rate of Ti-6Al-4V. This is a typical example of positive synergy where the alloy suffers from much more severe damage than wear alone Yazdi *et al.* (2020).

Tribocorrosion tests are usually conducted under potentiodynamic, electrochemical impedance spectroscopy (EIS), OCP, electrochemical noise (EN) analysis, and potentiostatic (applied passive potential) conditions (Ortega *et al.*, 2018). The commonly employed techniques in the tribocorrosion evaluation are the OCP and potentiostatic tests. The volume loss can be higher at either OCP or passive potential conditions depending on the alloy surface properties and the experimental conditions. At passive potential, a thicker passive oxide film forms compared to OCP conditions (Diomidis *et al.*, 2012). Diomidis *et al.* (2012) investigated the tribocorrosion behavior of Ti-29Nb-13Ta-4.6Zr. The material loss of this alloy was found to be higher at OCP than at passive potential. This was attributed to the greater thickness of the passive film at the higher potential (Diomidis *et al.*, 2012). In contrast to this, in the study conducted by Hacisalihoglu *et al.* (2014), the different α , $\alpha+\beta$, and β alloys material loss was more pronounced at tribocorrosion tests performed at passive potential than those performed under OCP conditions. This is because the material loss due to the corrosive effect under OCP conditions is negligible while that under anodic condition is more pronounced. Therefore, based off these two contrasting results, it is evident that the material loss of an alloy due to the tribocorrosion tests is attributed to both the passivity of the alloy and the rate of corrosion taking place during the tribocorrosion tests.

The predominant wear mechanism for titanium alloys during tribocorrosion is the abrasive wear mechanism shown by parallel scratches and grooves on the alloy surface. This was reported by Choubey *et al.* (2004) for the various titanium alloys tested in HBSS against bearing steel. Dimah *et al.* (2012) and Runa *et al.* (2013) who performed tribocorrosion investigations on Ti-6Al-4V sliding against an alumina ball found the predominant wear mechanism to be abrasive wear. Other wear mechanisms such as adhesive wear, tribochemical reactions, and surface fatigue have also been reported (Licausi *et al.*, 2013; Pina *et al.*, 2015; Toptan *et al.*, 2019; Namus *et al.*, 2021; Buciumeanu *et al.*, 2022). Scanning electron microscopy (SEM) images showing the surface of the wear tracks characterised by abrasive wear and adhesive wear mechanism are shown in **Figure 2.7**.

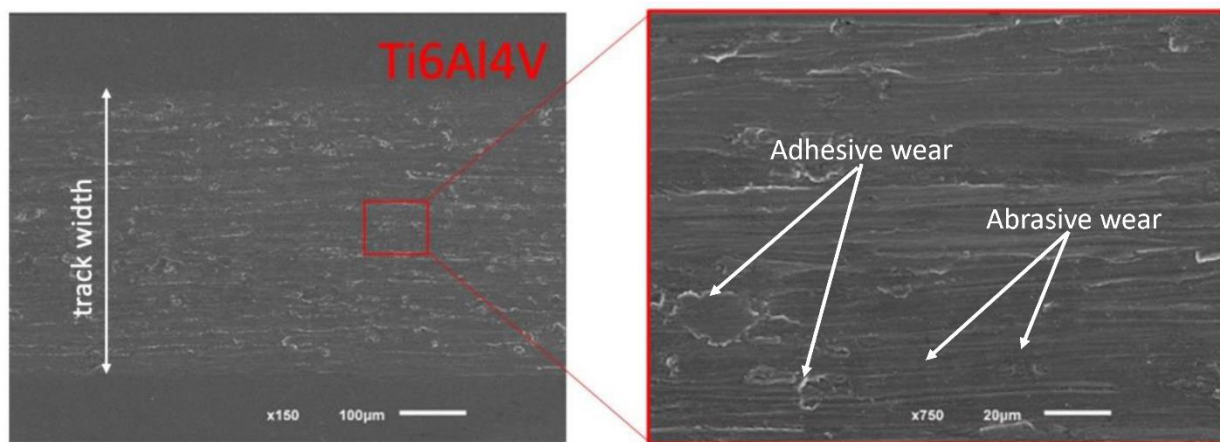


Figure 2.7: SEM image of the wear track of LB-DED Ti-6Al-4V alloy illustrating the abrasive vs adhesive wear mechanism (Buciumeanu *et al.*, 2022).

Table 2-2 presents some findings of tribocorrosion tests of titanium alloys in various simulated body fluids.

Table 2-2: Previous studies on the tribocorrosion behavior of titanium alloys immersed in various physiological solutions.

Author	Alloy type	Alloy	Treatment/Design	Experimental test technique	Testing parameters			Main Findings
					Temperature (°C)	Load (N)	Sliding speed (m/s)	
Galliano <i>et al.</i> (2001)	($\alpha+\beta$)	Ti-6Al-4V	Plasma nitriding	Ball-on-plate tribometer in 0.9 wt.% NaCl solution. Counterpart material: Alumina ball	25	20 – 60	0.26 – 1.0	The combination of a thick nitride layer and a hardened sublayer increases the wear resistance of the alloy and prevents the nucleation of cracking in the nitride layer.
Cvijović-Alagić <i>et al.</i> (2010)	β	Ti-13Nb-13Zr	Alloying	Block-on-disk tribometer in Ringer's solution. Counterpart material: Case-hardened 30CrNiMo8 steel disc	25	20 – 60	0.26 – 1.0	An increase in the load and the sliding speed resulted in an increase in the wear of the alloys. Ti-6Al-4V possessed a higher tribocorrosion resistance than Ti-13Nb-13Zr.
Pina <i>et al.</i> (2015)	β	Ti-30Nb, Ti-30Nb-2Sn, and Ti-30Nb-4Sn	Alloying. Powder metallurgy fabrication.	Ball-on-disk tribometer in phosphate buffered saline (PBS) solution. Counterpart material: Alumina ball	37	5	0.0188	The Sn content above 2 wt.% resulted in an increase in the wear of the alloys as it increased the rate of the active and passive dissolution of the alloys.
Chávez <i>et al.</i> (2020)	($\alpha+\beta$)	Ti-6Al-4V-xTa (x = 5, 15, and 30 vol%)	Alloying	Ball-on-disk reciprocating tribometer in SBF. Counterpart: Alumina ball.	37	2	-	Ti-6Al-4V-xTa formed a more stable passive film compared to Ti-6Al-4V thus promoting better passivation behavior in comparison. The wear rates of the alloys improved with a Ta addition up to 15 % but decreased beyond 15%.
Guan <i>et al.</i> (2021)	α	Pure titanium (TA1)	Electromagnetic induction nitriding	- In HBSS. Counterpart material: Alumina ball	37	2	0.0153	The thick nitriding layer on the alloys surface which increased the alloys hardness about 6 times, improved the tribocorrosion resistance of the alloy. The mass loss of the untreated sample was about 20 times that of the treated sample.

2.4 Summary of the literature review

The superiority of titanium and its alloys as biomaterials over other materials such as Co-based alloys and stainless steels (316L stainless steel) has been presented in this literature review. An overview of the different types of titanium alloys including their various advantages and disadvantages was detailed. It has been established that the use of the excellent β -type titanium alloys in the manufacturing of bioimplants is limited due to the high cost of these alloys which is mainly attributed to their expensive alloying elements such as Nb, Zr, and Ta. To address the concerns of cost, researchers have explored various modifications of the $\alpha+\beta$ type Ti-6Al-4V by the substitution of expensive alloying elements for low-cost alloying elements.

Some researchers have explored fully replacing the expensive and potentially toxic beta stabilising element, V, with a cheaper alternative such as Fe. This approach results in a decrease in the cost, and it produces less toxic alloys, however, such modifications face the risk of intermetallic compounds developing in the microstructure which have been proven to degrade the mechanical properties of the alloys thus making them inferior to the commercial alloys. In this chapter, it has been shown that the approach of partially substituting the expensive and potentially toxic vanadium with a cheaper alternative such as iron, was beneficial as it produced titanium alloys with mechanical properties closely comparable to those of the commercial alloy. Literature on the corrosion behavior of these alloys (Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe) in various environments such as marine and biomedical environments, has shown that these alloys have the potential to compete on a commercial scale.

Because these alloys are largely considered for use as biomaterials, it is imperative to perform screening tests such as wear, corrosion, and tribocorrosion tests to assess their suitability for use in the human body. This study therefore investigates the wear, corrosion, and tribocorrosion behavior of the alloys where the partial substitution of vanadium with iron was employed (Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe) as well as an alloy where the full replacement of V with Fe was employed (Ti-3Fe). The influence of these alloy compositions on the corrosion, wear, and tribocorrosion behavior must be established to gain more insight into their suitability for their use as biomaterials. The insights obtained from this study will take us one step closer to establishing whether these alloys can compete on a global commercial scale.

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Chapter 3: Experimental procedure

This chapter provides details on all the materials and consumables used as well as the experimental methods followed in this study.

3.1 Materials

The alloys under investigation in this study are shown in **Table 3-1**. These alloys were previously produced using vacuum induction melting and underwent hot isostatic pressing (Bodunrin *et al.*, 2018).

Table 3-1: Experimental alloy compositions

Titanium Alloys
Ti-3Fe
Ti-4.5Al-1V-3Fe
Ti-6Al-1V-3Fe
Ti-6Al-4V

3.2 Metallography

The preparation of the samples for the experimental tests is described in this section.

3.2.1 Machining

The alloys were cut into small 3 mm thick disks with a diameter of 14 mm using a Gold San computer numerical controls wire-cutting electrical discharge machine. Water was used as a coolant throughout the cutting of the samples to prevent the samples from heating up.

3.2.2 Mounting

The sectioned samples were then mounted in Struers Polyfast resin using a Struers hot mounting press machine at a temperature and pressure of 180°C and 250 bar respectively for 10 minutes including cooling time. Water was used as a coolant during the cooling stage of this process.

3.2.3 Grinding and Polishing

Grinding and polishing were employed to achieve a clean scratch free surface for the wear, corrosion and tribocorrosion tests. Manual grinding was conducted on an Imptech grinding machine using abrasive silicon carbide paper of different grit sizes (P120 – P4000) with water used

as a coolant. After grinding up to a grit size of P4000, the samples were polished using a Struers Tegramin-20 automatic polishing machine using MD-Chem polishing cloths both automatically and by hand at a speed of about 120 - 150 rpm. A non-crystallising colloidal silica suspension was used to aid the polishing process. For each sample, polishing took approximately 30 minutes.

3.3 Alloy Characterisation

The surface and microstructure of the samples that underwent dry sliding wear tests, corrosion tests, and tribocorrosion tests were examined using a high-resolution Zeiss Sigma Field Emission Scanning Electron Microscope (FEG-SEM) equipped with both back-scattered and Oxford energy dispersive X-ray (EDX) detectors. The FEG-SEM was operated in back-scattered electron imaging (BSE) mode at 20 kV and in secondary electron imaging (SEI) mode to show the surface morphology. EDX spot and area analyses were performed for all the samples to determine the composition of specific areas of interest. Stereoscopic images of the dry sliding wear test and tribocorrosion test samples were taken using the stereoscopic microscope to measure the area of the wear tracks of the surface of the alloys. The MarSurf PS 10 roughness measuring device was employed to measure the alloys' wear track profiles after the wear tests, as well as the maximum penetration depth of the wear tracks.

3.4 Sliding wear tests

Dry sliding wear tests were performed on the samples using a ball-on-disk configuration in order to determine the sliding wear resistance of the alloys using a CSM ball-on-disk tribometer. A 2N load was applied using a 6 mm diameter alumina ball for the sliding wear tests. The testing parameters are given in **Table 3-2**.

Table 3-2: Sliding wear test testing parameters

Testing parameters	Value
Sliding speed	0.08 m/s
Sliding distance	300 m
Nominal load	2.00 N
Acquisition radius	2 mm
Acquisition rate	4Hz
Humidity	40%
Testing temperature	20 ± 5°C

The wear volumes of the titanium alloys were calculated using the conventional method based on the average maximum penetration depth of the wear track (Bhushan, 1992). The average penetration depth method is a method based on the assumption that the wear track has an elliptic Hertzian profile. The data on the penetration depth of the wear tracks of the alloys was found by analysing the wear scar profiles of the alloys which were found by using a surface roughness tester (profilometer) to measure the cross-sectional area of the wear scars by moving the stylus across the wear scar from the edge. Equation (9) was used to calculate the worn volume (V_w) of the titanium alloys.

$$V_w = A_w Pd_{\max} \quad (9)$$

Where: V_w = wear volume (mm^3), A_w = worn surface area (mm^2), and $Pd_{\max}$ = average penetration depth (mm).

The specific wear rates (SWR) of the titanium alloys were calculated using Equation (10) (Archard, 1953; Kiefer, 2006).

$$\text{SWR} = \frac{V_w}{F \times s} \quad (10)$$

Where SWR = wear rate (mm^3/Nm), F = load (N), and s = sliding distance (m).

3.5 Corrosion tests

Electrochemical corrosion testing was performed on the samples with a surface area of 0.283 cm² exposed to the corrosive solutions. The electrolytes used were 0.9% NaCl solution, Hanks Balanced Salt solution (HBSS), prediabetic HBSS, and diabetic HBSS. The 0.9% NaCl was prepared with 9 g of NaCl in 1000 ml of distilled water. Prepared HBSS was purchased from Sigma Aldrich. For the diabetic HBSS, a 200 mg/dL solution was prepared by adding 2 g of glucose to 1000 ml of HBSS. For the prediabetic solution, a 100 mg/dL solution was prepared by adding 1 g of glucose to 1000 ml of HBSS. A conventional three-electrode electrochemical cell connected to a Gamry® potentiostat/galvanostat was used for the corrosion testing. A platinum wire was used as the counter electrode with Ag/AgCl saturated in 3 M KCl serving as the reference electrode. The open circuit potential (OCP) is the potential of the working electrode relative to the reference electrode without applied current. This was measured for 3600 s in all the environments. Linear potentiodynamic scans were then performed on the samples in all the environments from -0.5 V to 2.5 V at the standard scan rate of 0.1667 mV/s. Faster scan rates were found to cause a distortion in the data obtained because the sample (working electrode) was unable to remain relatively stable. The corrosion current density (i_{corr}) with the associated corrosion potential (E_{corr}) and the corrosion rate were determined using the polarization technique according to ASTM standard G59-97 (ASTM International, 2014). The corrosion rates (CR) were calculated using Equation (11).

$$\text{CR} = \frac{K i_{\text{corr}} \text{EW}}{\rho} \quad (11)$$

where: K = constant, EW = equivalent weight and ρ = calculated density.

3.6 Tribocorrosion tests

The tribocorrosion tests were conducted in different simulated body fluids. Normal Hanks Balanced Salt Solution (HBSS) was utilised. The next batch of samples were immersed in a solution of 100 mg/dL glucose HBSS to simulate the body environment of a pre-diabetic individual. The last batch of alloy samples was immersed in a 200 mg/dL glucose HBSS to simulate the body environment of a diabetic individual. The tribocorrosion tests were conducted

under room temperature ($\pm 25^{\circ}\text{C}$). The tests were conducted by using a tribo-electrochemical cell installed in a tribometer and connected to a potentiostat as shown in the schematic in **Figure 3.1**.

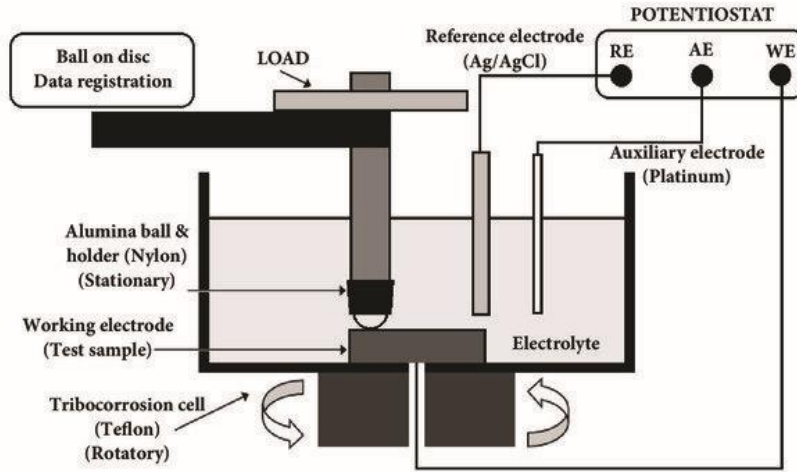


Figure 3.1: Schematic of the tribocorrosion ball-on-disk experimental setup (Ortega *et al.*, 2018)

The tribo-electrochemical cell was essentially set up as the conventional 3 electrode system where the counter electrode used was a platinum wire, a silver – silver chloride (Ag/AgCl) saturated in 3.5 M KCl solution served as the reference electrode and the alloy sample served as the working electrode. The tribocorrosion tests were performed according to a ball-on-disk configuration which conformed to the ASTM G133 standard and tribocorrosion mechanistic approach conformed to an ASTM G119.09 standard (ASTM International, 2021). The 6 mm diameter alumina ball was installed in the upper ball holder which is connected to a vertical linear motion system of the tribometer. The test specimen (alloy sample) was mounted in the tribocell. The tribocorrosion tests were performed under open circuit potential and anodic potential (+0.5 V vs OCP). In both cases a normal load of 2 N was employed. This load falls under low loading conditions (from ~1.8 N to 5 N) which have been investigated by various researchers (Li *et al.*, 2004; Chan *et al.*, 2011; Jozwik, 2018; Gain, Zhang and Lim, 2021). The loads exerted by the human body on the implant at any given moment vary greatly depending on the different activities of daily living. Therefore, a wide range of loads can be used for tribocorrosion tests. The tribocell is rotated at the chosen

speed by a precision spindle. A speed of 0.08 m/s was chosen for the tribocorrosion tests. Biomedical implants and their counterparts will move at various sliding speeds in application, low or high. 0.08 m/s lies in the low sliding speed range and was chosen mainly due to the testing constraints of the available tribometer. These parameters were chosen because this work aims to look at the worst-case scenario in the application of these alloys as bioimplants and it has been reported that local contact pressure in the hips could reach different expected values. The test duration differed for the open circuit potential and potentiostatic tests respectively.

3.6.1 Open circuit potential tribocorrosion tests

For the open circuit potential (OCP) tests, a cathodic potential of -1V was initially employed to clean and remove any oxides that might have formed on the alloy surface. This is also known as the electrochemical cleaning phase. The OCP was monitored thereafter. OCP tests best simulate real tribocorrosion situations, where the prevailing potential is controlled by the physio-chemical conditions at the metal–electrolyte interface and not by an external device such as a potentiostat. The tests were conducted for a total duration of 75 min where sliding was activated after every 15 minutes. The alloy samples were initially immersed in the electrolyte for 15 minutes to allow the alloy surface to passivate and stabilize before sliding commenced. After 15 minutes, sliding was initiated for 15 minutes before it was put to a stop for 15 minutes again. This static and dynamic process went on for 75 min. The change in OCP was measured as a function of time to evaluate the performance of the alloys before and after sliding. The friction coefficients during the sliding portions of the tests were also monitored and recorded. All the tests were performed on a fresh face of the alumina ball. Further, stereoscopic examination showed that the counterface was intact after all tests. Thus, the wear of the alumina ball is not considered in the wear rate analysis.

3.6.2 Potentiostatic (anodic potential) tribocorrosion tests

Potentiostatic tests were performed at an anodic potential of +0.5V vs OCP to study the properties of the passive surface films under controlled electrochemical conditions. +0.5V corresponds to the passive region of the alloys according to the previously obtained potentiodynamic corrosion results (Rundora *et al.*, 2023). In this case, the potentiostat ensures that the selected potential is maintained between the working electrode and the reference electrode by passing an appropriate current between the working and counter electrodes. The potentiostatic tests were conducted for a total duration of 1hr40min where the test comprised of three steps: 1. Initial surface stabilization – 20 min, 2. Sliding – 60 min, 3. Standby after sliding – 20 min. The evolution of current as a function

of time was recorded during the tests. The friction coefficients during the sliding portions of the tests were also recorded. Again, stereoscopic examination showed that the counterface was intact after all tests. Thus, the wear of the alumina ball is not considered in the wear rate analysis.

3.6.3 Specific Wear Rate and Coefficient of Friction (COF) Calculations

Using the stereoscopic microscope, the average cross-sectional wear track area, A , was calculated. The MarSurf PS 10 roughness measuring device was employed to assess the alloys' wear track profiles after the tribocorrosion tests, as well as the maximum penetration depth of the wear tracks. The total wear volume of the alloys was then calculated by multiplying the average wear track area by the maximum wear track penetration depth. The specific wear rates (SWR) of the alloys were then calculated according to Archard's theory for sliding wear of homogenous materials, where the wear volume is assumed to be proportional to the normal load and the sliding distance (Kiefer, 2006; Ortega *et al.*, 2018). This formula is depicted in Equation 12:

$$SWR(mm^3/Nm) = \frac{V_{tot}}{dL} \quad (12)$$

where V_{tot} is the total material loss in mm^3 , d is the total sliding distance in m, and L is the normal load in N.

The COF, which is the ratio of the tangential force and normal force, was measured by the CETR UMT software.

The mechanistic approach distinguishes between two main contributions: anodic dissolution (wear-accelerated corrosion) and mechanical removal of metal particles (mechanical wear). This approach is important because it has been found that the electrochemical material removal rate is strongly influenced by mechanical parameters and, on the other hand, that the mechanical material removal rate depends on the prevailing electrochemical conditions. This approach is expressed by Equation 7 and 8 depicted in the previous section. i in Faraday's Law depicted in Equation 8 is the average current during rubbing for polarization tests (cathodic and anodic potentials) as shown in Equation 13:

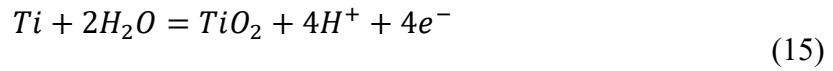
$$I_{measured} = \sum [I_{anodic} + I_{cathodic}] \quad (13)$$

At OCP, the measured current is 0 and the anodic and cathodic reactions occur at the same rate therefore there is no measured current (Mischler, 2008).

Therefore, at anodic potential:

$$I_{anodic\ charge\ (Ave\ I\ in\ wear\ track)} = AveI_{rubbing} - I_o \quad (14)$$

n is the charge number for the oxidation reaction. In most natural environments, titanium and its alloys are generally passive due to the spontaneous formation of a protective oxide film according to the reaction expressed in Equation 15:



In most natural environments titanium dissolves to Ti^{4+} therefore the oxidation number was taken as 4. However, it is important to note that other oxides besides the Ti-based oxides, such as Al_2O_3 , VO , V_2O_5 , Fe_2O_4 , and Fe_3O_4 may also form on the Ti alloy surface and contribute to the passive oxide film.

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Chapter 4: Dry sliding wear tests

Dry sliding wear behavior of experimental low-cost titanium alloys

This chapter gives insight into wear and how it affects biomedical implants in application. The different properties known to affect the wear resistance of titanium alloys are detailed. The dry sliding ball-on-disk wear test procedure performed on the titanium alloys under investigation is provided in this chapter. The results obtained address the first research objective which is to determine the wear behavior of the low-cost Ti-Al-V-Fe alloys and the dominant wear mechanisms in comparison with Ti-6Al-4V alloy. The graphical abstract provided in **Figure 4.1** gives a graphical overview of the dry sliding wear tests of the titanium alloys and it highlights the main results obtained in this chapter. This chapter was produced in paper form which was submitted to *Tribology Transactions* and is currently under review.

Graphical Abstract

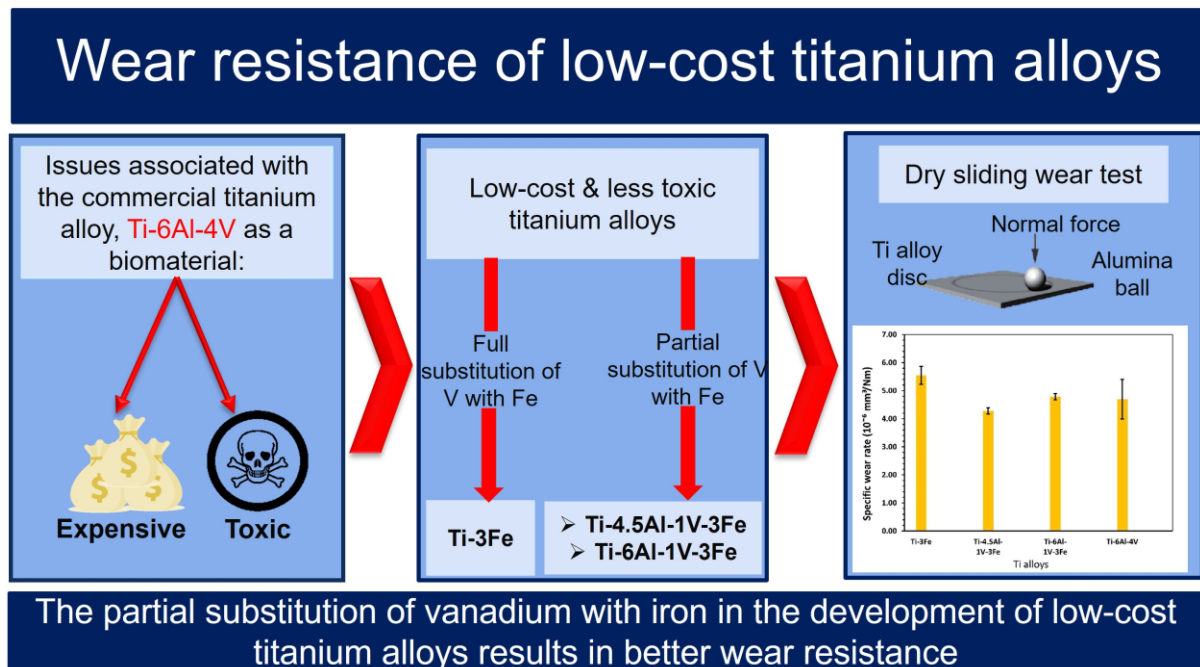


Figure 4.1: Dry sliding wear tests graphical abstract

4.1. Introduction

The attractive properties of titanium and its alloys have led to their extensive utilisation across various industries (Ahmed *et al.*, 2014; Gain *et al.*, 2021). The aerospace industry benefits from their low density, using them in making aircraft components such as airframes and engine parts (Ahmed *et al.*, 2014; Khalloufi *et al.*, 2021; Li *et al.*, 2021; Gupta *et al.*, 2022). The marine sector finds use for titanium alloys in ship equipment, as well as offshore structures, as they have exceptional resistance to corrosion in saltwater environment (Chen and Thouas, 2015; Bodunrin *et al.*, 2018). The sports industry mainly exploits the high specific strength of titanium alloys, incorporating them into manufacturing bicycles, golf clubs, and tennis rackets to enhance performance while minimizing weight (Nnamchi and Obayi, 2020). The automotive industry, one of the biggest industries using titanium alloys today, incorporates them in various components, such as valves and exhaust systems, because of their excellent specific strength, which improves fuel efficiency and reduces carbon dioxide emissions (Gupta *et al.*, 2022; Nyamekye *et al.*, 2023). Furthermore, the oil and gas industry, the desalination sector, and the jewellery industry also find significant benefits in utilising titanium and its alloys (Li *et al.*, 2021). Titanium alloys have gained significant importance in the biomedical field, commonly employed in joint replacements, dental implants, and surgical instruments due to their excellent biocompatibility and ability to integrate with the human bone (Sharma and Sehgal, 2012; Anene *et al.*, 2021; Gupta *et al.*, 2022).

Wear is an inevitable issue in any joint replacement implant, no matter the type of material used. Because wear has been identified as the leading cause of implant failure, one of the main requirements for biomaterials is to have high resistance to wear (Gain *et al.*, 2021). Wear leads to bioimplants' failure due to implant loosening (Gang *et al.*, 2018; Gain *et al.*, 2021). Additionally, the resulting wear particles can cause inflammation that destroys the bone supporting the implant, ultimately resulting in revision surgery (Hussein *et al.*, 2015). Despite the preference given to titanium alloys in the biomedical industry, their poor wear resistance pose significant challenges (Kumar *et al.*, 2018; Gupta *et al.*, 2022).

Poor wear resistance can be attributed to several factors. First is the low hardness of titanium and its alloys, particularly the commercially available titanium alloy, Ti-6Al-4V, compared to some cobalt-based alloys (CoCrMo alloys) (Chirico *et al.*, 2022; Gupta *et al.*, 2022). Hardness plays a crucial role in wear resistance as it determines the material's ability to resist plastic deformation

and surface damage. Therefore, the low hardness of titanium alloys contributes to their poor wear resistance as it makes them more susceptible to wear when subjected to abrasive and/or erosive forces (Borgioli *et al.*, 2005; Gupta *et al.*, 2022). Secondly, titanium and its alloys are also prone to adhesive wear due to their capacity to develop an oxide layer on their surface, which can promote adhesion between the titanium alloy and the mating surface, resulting in increased wear (Lepicka and Dahlke, 2016; Gupta *et al.*, 2022). Third, when compared to other materials, titanium alloys have relatively high coefficients of friction (Sharma and Sehgal, 2012). This increases frictional heat during sliding contact, and the resulting elevation in temperature promotes adhesion and material transfer, which accelerates wear (Gupta *et al.*, 2022). A few researchers have reported that the main reasons for titanium alloys' poor resistance to wear is their low resistance to plastic shearing and work hardening (Molinari *et al.*, 1997; Sahoo *et al.*, 2014; Weng *et al.*, 2020). The poor resistance to plastic shearing reduces thermal conductivity, bringing about poor tribological properties (Gupta *et al.*, 2022). Additionally, studies have indicated that the inadequate wear resistance of titanium alloys can be attributed to the minimal protection provided by the surface oxides that form due to the high flash temperatures generated by friction during dry sliding (Molinari *et al.*, 1997; Straffelini and Molinari, 1999; Alam and Haseeb, 2002; Sahoo *et al.*, 2014).

Several researchers have examined the wear behavior and characteristics of titanium alloys, particularly the commercial alloy, Ti-6Al-4V. Most of these investigations focused on the wear mechanisms of these alloys under different loads and sliding speeds to establish the wear behavior of Ti-6Al-4V in diverse operational conditions. Molinari *et al.* (1997) investigated the wear mechanisms of Ti-6Al-4V sliding against itself and found that the primary wear mechanisms were adhesion, abrasion, and tribochemical reactions (oxidative wear). Wear rates and wear mechanisms were sensitive to the applied load and sliding velocity. For example, oxidative wear dominated at low sliding speed. Oxides are protective, and the development of oxides within the tribo-layer generally improves the wear resistance of the alloy (Sharma and Sehgal, 2012). Molinari *et al.* (1997) observed that the tribo-oxides formed on the surface of Ti-6Al-4V were susceptible to spalling and micro-fragmentation. This therefore led to their easy removal thus exposing the bare metal to further damage. Moreover, increasing the load and sliding velocity decreased the wear resistance of Ti-6Al-4V. Oxidative wear was also observed in the study by Straffelini and Molinari (1999). According to reports, the effectiveness in providing protection is compromised when the oxides lack adequate support from the underlying material that has undergone strain hardening. In

addition, these tribo-layers do not sufficiently adhere to the substrate and can be brittle, thus leading to continuous fragmentation and spalling (Straffelini and Molinari, 1999). In contrast to the studies mentioned so far, Kumar *et al.*, (2018) found that a protective oxide layer formed under heavier loads and increased sliding velocities, improved the commercial alloy's wear resistance. This difference in results is due to the differences in the counter material used (alumina), as well as in the testing parameters employed (Gupta *et al.*, 2022). Higher sliding velocities have been reported to raise the sliding temperatures, resulting in the formation of oxides (Sharma and Sehgal, 2012).

A direct relationship between titanium alloy's hardness and wear resistance has been indicated in previous works. Alam and Haseeb (2002) demonstrated the influence of hardness on wear resistance. They discovered that Ti-24Al-11Nb exhibited significantly higher wear resistance (approximately 48 times higher) compared to Ti-6Al-4V, which is attributed to its superior hardness. In addition to the high hardness, a stable and protective oxide layer contributed to the good wear resistance of Ti-24Al-11Nb. Gain *et al.* (2021) confirmed the poor wear resistance of Ti-6Al-4V when they found severe loose fragments and delamination on the surface following the dry sliding wear tests, the severity of which escalated with higher applied loads.

Regardless of the variation in the applied loads and speed, titanium alloys ultimately have poor resistance to wear as they have much higher coefficients of friction compared to other materials on the market (Sharma and Sehgal, 2012). In most cases, the wear rates of titanium alloys, particularly Ti-6Al-4V, exceed the upper limit typically associated with mild wear of materials ($10^{-3} \text{ mm}^3/\text{Nm}$) (Venkatesan and Rigney, 1992; Straffelini and Molinari, 1999). This is concerning as titanium alloys have numerous advantageous and attractive properties that are beneficial for many industries, but the poor wear resistance makes it challenging to exploit them fully.

Researchers have explored various strategies to address and overcome the poor wear resistance of titanium alloys (Molinari *et al.*, 1997; Sharma and Sehgal, 2012; Sahoo *et al.*, 2014; Kumar *et al.*, 2018). These mainly include surface modifications, such as coatings, ion implantation, and surface treatments aiming to enhance the hardness and lubricity of the materials (Sharma and Sehgal, 2012; Sreesha *et al.*, 2021). Additionally, alloying elements and heat treatments can be employed to modify the microstructure and improve wear resistance (Yadav and Saxena, 2020). These approaches aim to improve the tribological performance of titanium alloys by reducing friction,

minimizing wear rates, and increasing the lifespan of bioimplants. The current research activities have focused on developing advanced titanium alloys and exploring novel surface engineering techniques to address the wear limitations and expand the range of applications for these materials.

The group of low-cost titanium alloys investigated in this study was developed by Bodunrin *et al.* (2018) as possible alternatives for the expensive and potentially toxic commercially available alloy, Ti-6Al-4V. To this point, these low-cost titanium alloys have proven to compete with the commercial alloy as they exhibit higher hardness than the commercial alloy (Bodunrin and Chown, 2021). In addition, the corrosion resistance of these alloys in various environments, including acidic and simulated marine environments, as well as simulated body fluids, is comparable to that of the commercial alloy and is, in some cases, better (Bodunrin *et al.*, 2018; Leshetla *et al.*, 2022). Because these alloys have potential applicability in the bioimplant industry, it is imperative to understand their wear properties and compare them to the commercial Ti-6Al-4V alloy.

A huge number of joint replacement revision surgeries are required yearly due to the failure and destruction of the artificial implant caused by loosening, which leads to osteolysis (Bozic *et al.*, 2010). This implant loosening, as mentioned previously, is highly attributed to the wear taking place between the bioimplant and its articulating materials, as well as the bones in contact (Moghadasli, Mohd Isa, *et al.*, 2022). Understanding the wear mechanisms of these low-cost titanium alloys is, therefore, a major requirement for their possible application in making artificial implants. By overcoming the limitations related to wear resistance, the full potential of titanium and its alloys can be realized across a broader range of industries, particularly in the biomedical field where durability and longevity are critical for successful bioimplant applications. This study examined the dry sliding wear properties of these alloys by looking at their coefficient of friction (COF), wear volume, wear rates and analysing their wear mechanisms by studying their respective wear scars.

4.2. Materials and methods

4.2.1. Materials

Refer to Section 3.1 and Section 3.2 for the materials used as well as the sample preparation procedure.

4.2.2. Sliding wear tests

Dry sliding wear tests were conducted using a CSM ball-on-disk tribometer operating under the following conditions: ambient temperature of 25°C, normal load of 2 N, sliding velocity of 0.08 m/s, and a sliding distance of 300 m. The normal load of 2 N which was employed falls under low loading conditions (from ~1.8 N to 5 N) which have been investigated by several researchers (Li *et al.*, 2004; Chan *et al.*, 2015; Jozwik, 2018 and Gain *et al.*, 2021) . The loads exerted by the human body on the implant at any given moment vary greatly depending on the activities of daily living. Therefore, a wide range of loads can be used for dry sliding wear tests (D'Angeli *et al.*, 2013; Damm *et al.*, 2013 and Stenlund *et al.*, 2017). The sliding speed of 0.08 m/s lies in the low sliding speed range and was chosen mainly due to the testing constraints of the available tribometer. During the duration of the sliding test, the normal force of 2 N was constantly exerted on the titanium surface with an alumina ball. Alumina (Al_2O_3) ceramic balls with a 6 mm diameter and a hardness of around 780.4 HV were used as the articulating counter material. Alumina was used since it has a much higher hardness than the titanium alloys, so it was expected that the deformation process during sliding would primarily occur within the titanium alloys. Additionally, using a much harder material than the titanium alloy itself allows the performance of the experimental titanium alloys to be assessed under extreme conditions. The duration of each test was one hour and two minutes. The tests were performed at least twice to check for reproducibility of the results. Friction coefficients were recorded during the tests. The penetration depth of the alloys' wear tracks was found by analysing their wear scar profiles, using a surface roughness tester (profilometer) to measure the cross-sectional area of the wear scars by moving the stylus across the wear scar from the edge. The wear rates of the alloys were then calculated according to Archard's theory for sliding wear of homogenous materials, where the wear volume is assumed to be proportional to the normal load and the sliding distance (Archard, 1953; Kiefer, 2006).

4.2.3. Microstructural characterization

Refer to Section 3.3 for the details of the alloy characterisation employed to analyse the wear scars of the alloys after the dry sliding wear tests.

4.3. Results

4.3.1. Coefficient of friction of the tested alloys under dry sliding

The COF versus sliding distance curve is presented in **Figure 4.2**. The COF varied with sliding distance for all the alloys. A running-in/break-in phase was observed for about 35 m from the beginning of the test for Ti-6Al-1V-3Fe and about 20 m for the rest of the alloys. In this region, the COF of all the alloys was between 0.18 and 0.43. After the running-in phase, a gradual increase in the alloys' COF was observed. The highest COF was attained by Ti-3Fe from the initial point until the completion of the 300 m sliding distance. The highest COF reached by this alloy was approximately 0.62. Ti-6Al-1V-3Fe had the lowest COF from the initial point until the completion of the 300 m sliding distance. The highest COF reached by this alloy was approximately 0.35, which is much lower than that of Ti-3Fe. The COF of all the alloys reached a plateau (steady state) at about 50 m, where the COF began fluctuating within a close range. The fluctuation or oscillations in the COF can be explained by the third body effect (Sharma and Sehgal, 2012); the stick-slip behavior that occurs under applied load leading to the periodic accumulation and removal of wear debris between the alumina ball and the titanium alloy surface (Kiefer, 2006; Doni *et al.*, 2013). **Table 4-1** displays the average COF. The COF of Ti-4.5Al-1V-3Fe and the common commercial alloy Ti-6Al-4V were quite close to each other and not too far off from that of Ti-3Fe. The average COF of Ti-4.5Al-1V-3Fe was 0.51, while that of Ti-6Al-4V was 0.49. This result correlates with a study conducted by Jozwik. (2018), who performed a similar dry wear test on Ti-6Al-4V alloy with alumina as the counter material under a load of 5 N and found the COF of the commercial alloy to be 0.52 at room temperature. The higher load of 5N had a slightly negative impact on the wear of the alloy as its COF was slightly higher than that of the Ti-6Al-4V alloy tested under a lower load of 2N.

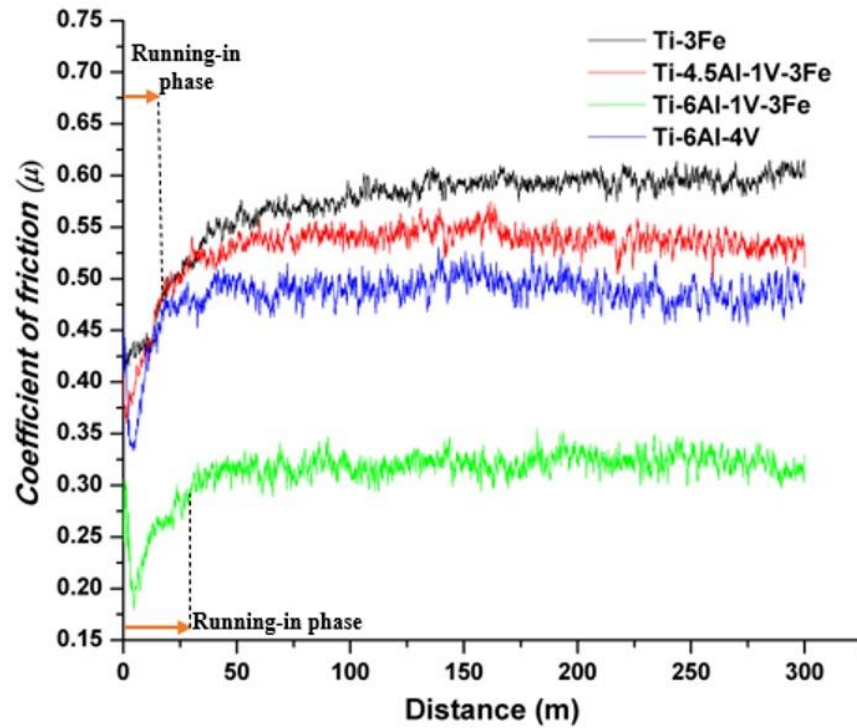


Figure 4.2: Coefficient of friction behavior of experimental and commercial (Ti-6Al-4V) titanium alloys against an alumina ball over a 300 m sliding distance

Table 4-1: Average coefficient of friction of experimental and commercial titanium alloys

Titanium alloys	Coefficient of friction (μ)
Ti-3Fe	0.55 ± 0.035
Ti-4.5Al-1V-3Fe	0.51 ± 0.029
Ti-6Al-1V-3Fe	0.37 ± 0.078
Ti-6Al-4V (commercial)	0.49 ± 0.00002

4.3.2. Worn wear volume and wear rates

Four areas of the wear track were analysed and recorded using the profilometer. These four profile measurements were then averaged and plotted as a single profile (Penetration depth versus wear track width; **Figure 4.3**). The alloys had similar wear tracks, suggesting their wear mechanism

could be comparable. Ti-3Fe displayed a deeper wear scar than the rest of the alloys. This supports its high COF as a deeper wear track indicates a strong resistance to motion between the alloy and the alumina ball, which resulted in more abrasion between the two surfaces, thus deepening the wear scar on this alloy. This suggests that a greater level of wear took place (Chirico *et al.*, 2022). Although it had the deepest wear scar, the maximum penetration depth values in **Table 4.2** show that the penetration depths of the alloys were quite similar as the values lie in a very similar and close range (between -0.11 and -0.09). In addition to the deepest wear track, Ti-3Fe displayed the widest wear track among all alloys, while Ti-4.5Al-1V-3Fe had the narrowest and shallowest wear track compared to the rest of the alloys. The penetration depth and the track width of Ti-6Al-4V were very close to that of Ti-4.5Al-1V-3Fe.

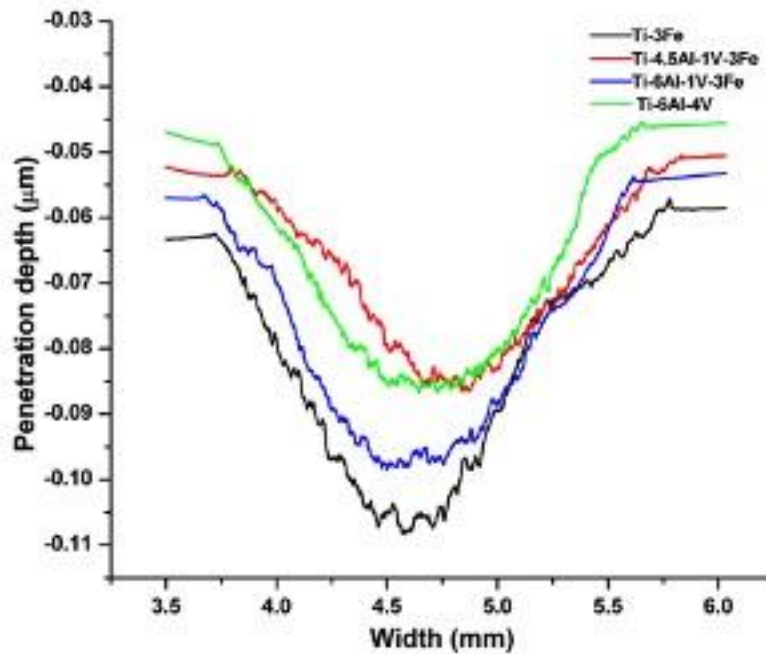


Figure 4.3: Penetration depth versus wear track width of experimental and commercial (Ti-6Al-4V) titanium alloys

The worn wear volume graph shown in **Figure 4.4**, supported by the data in **Table 4.2**, shows that Ti-3Fe experienced the most material loss of 0.0033 mm^3 compared to the rest of the alloys, while Ti-4.5Al-1V-3Fe had the least amount of material loss of 0.0026 mm^3 for the entire duration of the wear tests. Once again, the alloys' material losses were within a very similar range, further supporting the observation that these alloys have very similar wear resistance.

It is quite important to note that the third body concept plays a role in this tribosystem as the two solids sliding against each other resulted in the generation of a third body. This third body was composed of particles detached from the alloy and alumina surfaces and it possesses several functions. Firstly, the third body somewhat releases the pressure from the alloy surface as it supports the load, it accommodates the sliding velocity, and lastly, it separates the sliding surfaces thus avoiding direct interactions (Fillot *et al.*, 2007). All of this leads to a reduction in all of the stresses and displacements imposed by the system in contact. The third body has the ability to act as a solid lubricant that ultimately protects the materials rubbing against each other from further degradation (Fillot *et al.*, 2007). Ideally, the ejection of the third body from the contact has to be prevented as much as possible to maintain the lubrication role of the third body thus avoiding the detachment of further particles (Fillot *et al.*, 2007). Wear is generally one to two orders of magnitude smaller in three body abrasion than in two body abrasion as a result of the lubrication provided by the third body particles (Fischer *et al.*, 2018). Therefore, based on this lubrication role, the worn wear volume should rather be considered as the loss of the third body particles from the contact as opposed to the whole area of the wear scar. In this study however, because the alumina ball experienced negligible wear, the third body phenomena was not necessarily considered. It would however be of interest to explore it in further studies.

Finally, the wear rates of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and the commercial alloy Ti-6Al-4V were in a similar range, with the experimental alloy Ti-3Fe having the highest wear rate (**Table 4.2**). This high wear rate is supported by a combination of different parameters: deeper maximum penetration depth, greater worn volume, and higher COF. Despite Ti-4.5Al-1V-3Fe having a COF value quite close to that of Ti-3Fe, it had the lowest wear rate, which is supported by its shallow and narrow wear track, as well as its minimal worn volume. This shows that this alloy has the best resistance to wear compared to the commercial alloy and the other alloys under investigation (Chirico *et al.*, 2022). A clearer representation of the wear rates is presented in **Figure 4.5**.

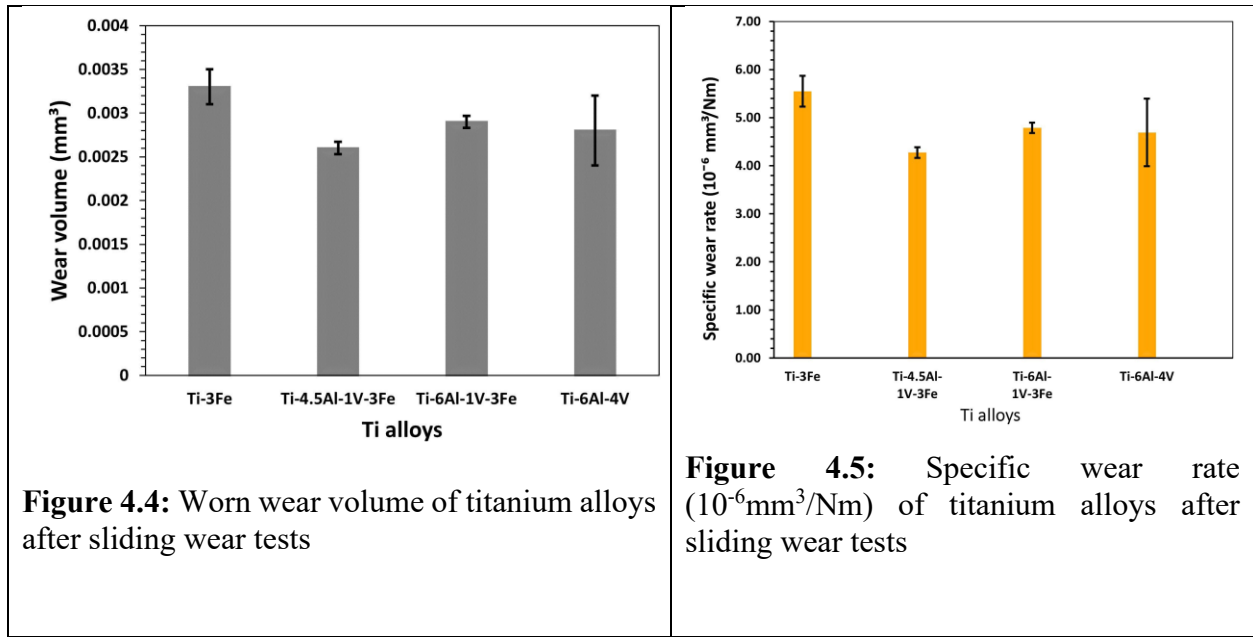


Table 4.2: Sliding wear parameters of experimental and commercial titanium alloys

Ti alloy	Worn surface area (mm ²)	Penetration depth (μm)	Worn volume (mm ³)	Wear rate (10 ⁻⁶ mm ³ /Nm)	Wear track width (mm)
Ti-3Fe	29.3	-0.11 ± 0.0075	0.0033 ± 0.0002	5.55 ± 0.32	1.98 ± 0.10
Ti-4.5Al-1V-3Fe	29.7	-0.09 ± 0.0003	0.0026 ± 0.0001	4.27 ± 0.11	1.80 ± 0.34
Ti-6Al-1V-3Fe	29.4	-0.10 ± 0.0013	0.0029 ± 0.0001	4.79 ± 0.11	1.86 ± 0.20
Ti-6Al-4V (commercial)	29.6	-0.09 ± 0.0117	0.0028 ± 0.0004	4.69 ± 0.70	1.90 ± 0.02

4.3.3. Surface morphology: Wear tracks and sliding wear mechanisms.

The scanning electron images of the wear tracks of the commercial and experimental alloys under investigation are presented in **Figure 4.6**. In sliding contact, wear can occur due to any of the four main wear mechanisms which include abrasion, adhesion, surface fatigue, and tribochemical

reactions, together with their respective sub mechanisms (Gahr, 1987). To understand the tribological behavior of a particular material, it is important to understand its exact acting wear mechanisms and their sub-mechanisms (Fischer *et al.*, 2018). Insight into the acting wear mechanisms can be given through the determination of the sub-mechanisms. In this study, all the alloys' wear tracks were made of parallel wear scars caused by the ploughing and crushing action of the hard alumina ball sliding against the alloys. These parallel wear scars are indicative of micro ploughing which is a sub-mechanism of abrasion. Therefore abrasion is one of the main acting wear mechanisms for these alloys (Chirico *et al.*, 2022). Very minimal differences are observed in the wear tracks of these alloys, which indicates that their wear mechanisms were the same, with slight differences in the intensity of the wear. The depth of the wear grooves on the wear tracks was quite shallow, suggesting that the abrasive wear taking place was quite mild (Enayati and Sayyedan, 2022). The depth of the wear grooves on the commercial alloy Ti-6Al-4V was slightly deeper than those on the rest of the alloys, indicating higher abrasive wear in the commercial alloy.

Plastic deformation is not considered a wear mechanism but it plays a very important role in many wear processes (Gahr, 1987). Plastic deformation generally occurs as a result of the surface fatigue wear mechanism. A few researchers have reported having observed plastic deformation on the titanium alloys after dry sliding wear tests (Straffelini and Molinari, 1999; Jozwik, 2018). Plastic deformation is generally characterized by smooth compacted layers lying on top of many abrasive grooves aligned in the sliding direction (Straffelini and Molinari, 1999; Jozwik, 2018). Plastic deformation, usually accompanied by delamination, indicates severe wear and is thus undesirable for biomaterials (Qiu *et al.*, 2007). After analyses of the experimental alloys under investigation, it was found that the alloys did not display any plastic deformation. However, sub-surface plastic deformation could have occurred, and this would have to be confirmed by performing an analysis of longitudinal cross-sections of the alloys in order to obtain information on the sub-surface damage. No distinct grey or dark (black) patches were found on these wear tracks. This suggests there was possibly no active tribo-oxidation (tribochemical reactions wear mechanism) in this tribosystem. So, the tribochemical reactions wear mechanism did not form part of the alloys' wear mechanisms, as it is possible not to have the formation of an oxide layer (Venkatesan and Rigney, 1992). The EDS (energy dispersive X-ray spectroscopy) images in **Figure 4.7** confirm this, as no oxygen peaks were observed in the EDS spectra of any of the alloys. Analysis of the wear debris using X-ray diffraction was not performed as the debris was too small for this analysis. Only the

EDS spectra of the Ti-3Fe and Ti-4.5Al-1V-3Fe alloys are shown here as all the alloys displayed metallic peaks but no oxygen peaks.

The wear scars on the alumina balls were analysed using the stereoscope. These are presented in **Figure 4.8**. The wear scar on all the balls is almost round in shape. A more irregular and elliptical shape would be observed if the wear was severe (Jozwik, 2018). This was not the case, as the scars are more circular, which is evidence of mild wear. Evidence of material transfer from the alloys to the alumina ball (counterbody) can be seen through the black/metallic marks on the wear scar of the alumina balls seen in **Figure 4.8**. This is a sub-mechanism of adhesive wear. Therefore, adhesion was one of the acting wear mechanisms of this tribosystem. The wear rate of the counterbody was assumed to be negligible due to the very small wear scar observed on their surface. According to the ASTM G133-05 standard, if the ball tip remains significantly round with only light abrasion, a few scratches, and/or an adherent deposit of wear debris, after the wear tests, this is an indication that the flat alloy sample experienced the greatest amount of wear, therefore the ball (counterbody) exhibited no measurable wear (Standard, 2010). Therefore, no measure of wear shall be reported. The evolution of the 3D surface topographies can be seen in **Figure 4.9**. Upon analysis of the 3D images, it was observed that the valley or scar of Ti-3Fe was deeper than that of the other alloys under investigation. The scar of Ti-4.5Al-1V-3Fe was closely comparable to that of the commercial alloy, Ti-6Al-4V.

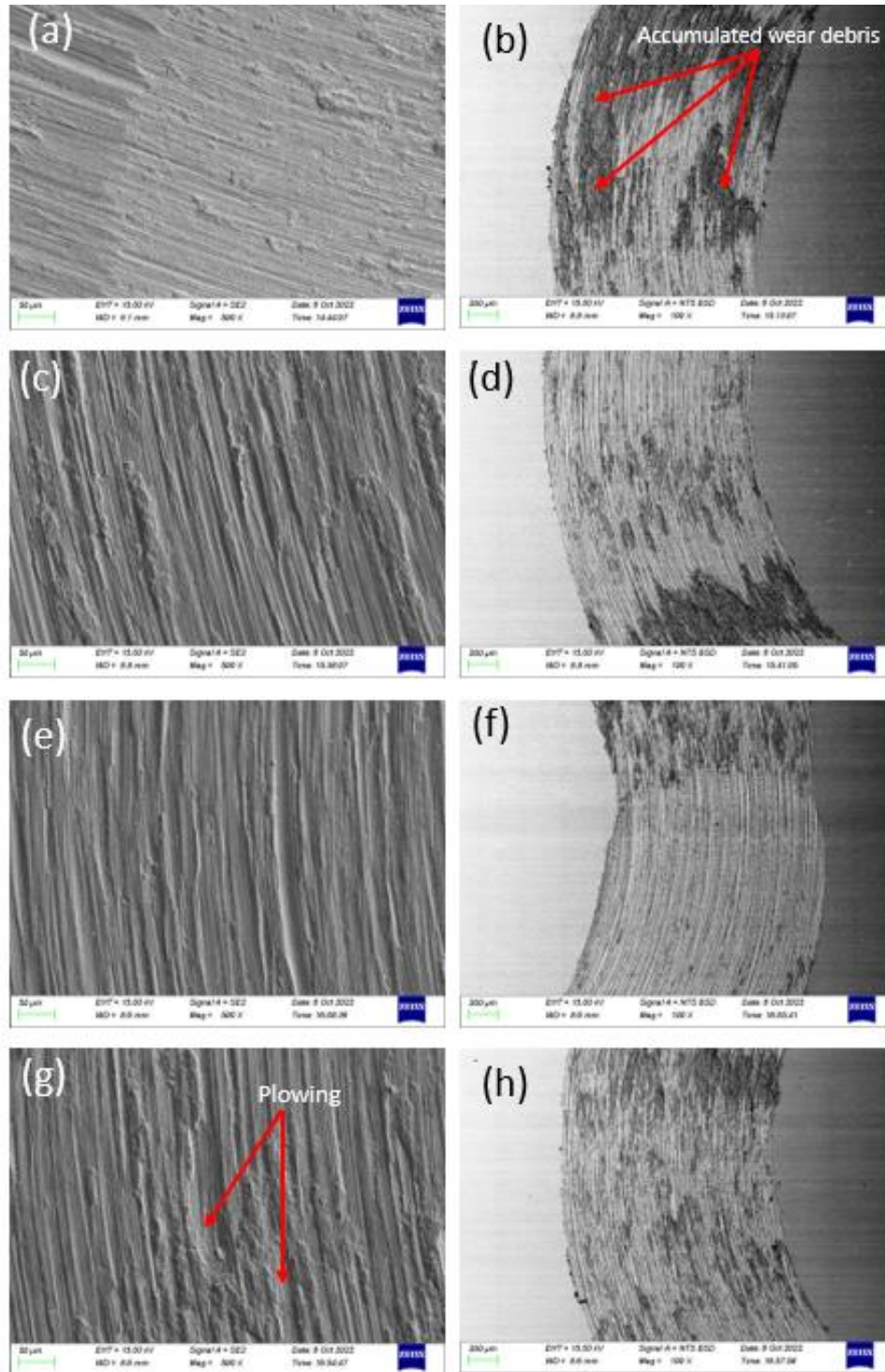


Figure 4.6: Secondary electron (a, c, e, and g) and back-scattered electron (b, d, f, and h) scanning electron micrographs of experimental and commercial titanium alloys' wear tracks after dry sliding: (a) and (b) Ti-3Fe; (c) and (d) Ti-4.5Al-1V-3Fe; (e) and (f) Ti-6Al-1V-3Fe; (g) and (h) Ti-6Al-4V

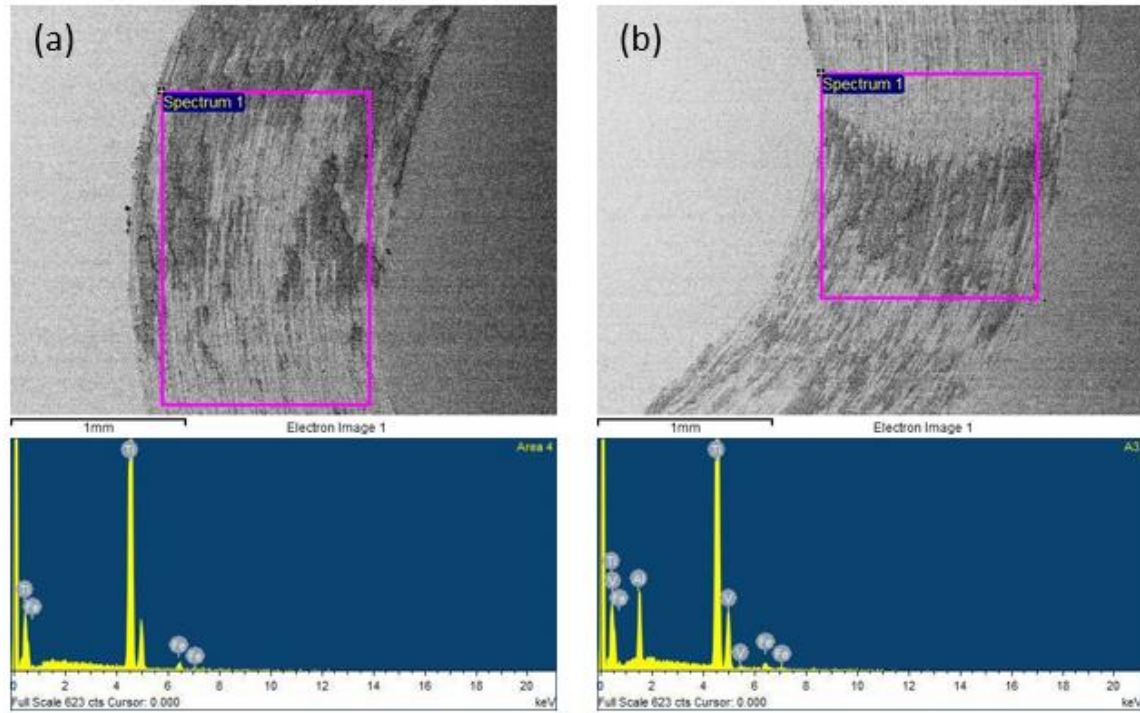


Figure 4.7: Energy dispersive X-ray images of the area analysis of experimental and commercial titanium alloy wear tracks: (a) Ti-3Fe and (b) Ti-4.5Al-1V-3Fe

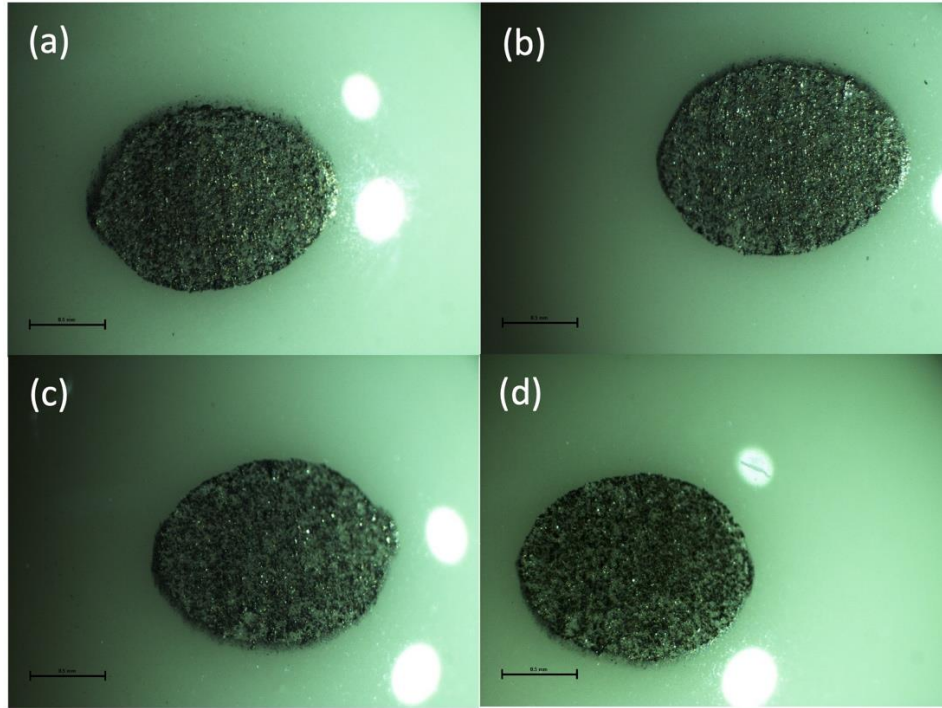


Figure 4.8: Stereoscope images of the alumina balls after the dry sliding wear tests with experimental and commercial titanium alloys (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V (commercial alloy)

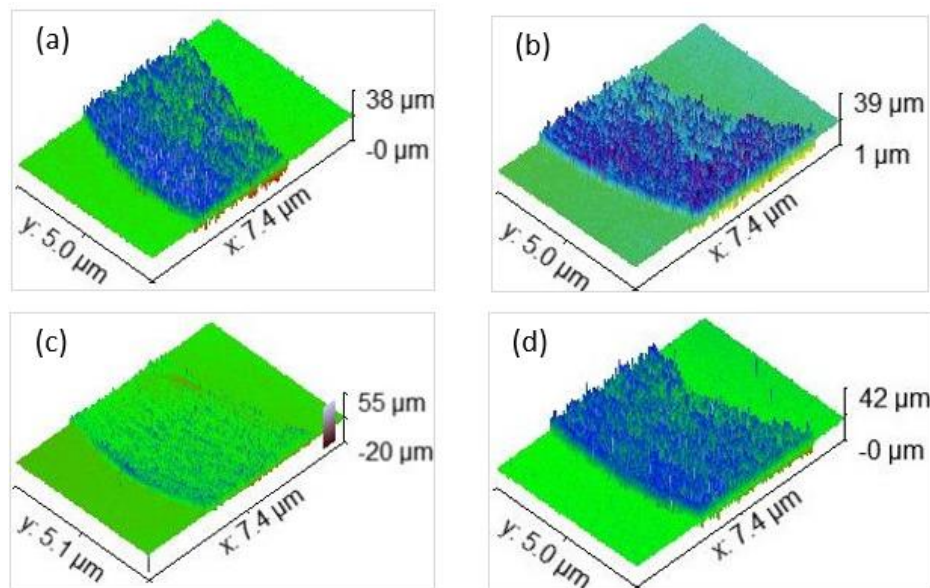


Figure 4.9: 3D surface topography images of the experimental and commercial titanium alloys' wear tracks: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V (commercial alloy)

4.4. Discussion

A material's wear characteristics are determined by a vast number of factors, including the material composition, hardness, friction coefficient, and elastic modulus (Hutchings, 1994; Kato, 2000; Sharma and Sehgal, 2012; Gupta *et al.*, 2022). The hardness of a material is crucial as a high hardness enables the material to resist abrasion and deformation, particularly plastic deformation, quite significantly (Chirico *et al.*, 2022; Gupta *et al.*, 2022). High resistance to plastic deformation will ultimately reduce the risk of delamination, which is a wear type commonly seen in metallic alloys with very poor wear resistance and quite detrimental to the material's life (Gain *et al.*, 2021). The importance of hardness can also be seen through the tribo-layers that form on the alloys' surface during the dry sliding test. A compacted, continuous, and hard tribo-layer has high load-bearing capabilities, inhibiting the applied force from being transferred to the matrix underneath the tribo-layer, potentially damaging the alloy (Li *et al.*, 2015). The material's frictional property is also of utmost importance as it plays a role in the alloy's wear behavior. A high COF can be beneficial or detrimental to a system depending on the material's field of application. For example, for braking systems or tyres where increased friction is desired to enhance grip and control, a high COF is advantageous (Kumar and Suman, 2017). On the other hand, it can lead to wear in mechanical systems as it requires more energy to overcome resistance and can generate heat or cause unwanted abrasion between surfaces (Seidlitz and Kip, 2018; Gupta *et al.*, 2022). The latter applies to bioimplants and bioimplant materials. A very high COF is not desirable, as the friction between a biomedical implant and the bones and bone tissues in the human body should be minimized for various reasons. Excessive friction can cause inflammation, severe discomfort, and restricted mobility for the individual with the implant (Hussein *et al.*, 2015; Seidlitz and Kip, 2018; Moghadasi *et al.*, 2022; Zhang *et al.*, 2022). In addition, friction generates wear and tear on both the implant and the bone tissue, gradually leading to the implant material's degradation and potential damage to the surrounding bone (Moghadasi *et al.*, 2022). Minimising friction would help to reduce the risk of implant failure and ensure its long-term durability, thus reducing the need for expensive and painful revision surgery (Moghadasi *et al.*, 2022; Zhang *et al.*, 2022). It is important to note, however, that a considerable amount of friction, enough to bring about safe resistance against motion between the bone and implant, has been reported to be desirable (de Vries *et al.*, 2022). This promotes bone ingrowth, reducing the risks of fibrous tissue formation at the implant interface, which results in implant loosening (de Vries *et al.*, 2022). It is, therefore,

important to have a COF that is high enough to reduce excessive relative motions but low enough to minimise material volume loss and wear rate.

The analysis of friction alone cannot determine a material's wear resistance. Often a combination of multiple parameters, including friction behavior, worn volume, penetration depth, and wear rate, should be considered to determine and optimise the material's wear resistance. According to Kato. (2000), it should not be assumed that there is always a straightforward, conventional correlation between friction and wear, as the COF and wear are not inherent material properties but rather two types of responses within a tribosystem. Their relationship is reasonably established when the tribosystems' essential functions are adequately considered (Kato, 2000).

In this chapter, the wear resistance of the low-cost titanium alloys with partial or full substitution of V with Fe under dry conditions with alumina as the counterpart material was evaluated. The objective was to understand how these alloys would behave when exposed to environments characterised by high levels of friction and wear, such as the human body. When biomedical implants such as joint replacement implants are inserted into the human body, they experience a combination of corrosion and wear because of the corrosive body fluids in the environment, and the various daily movement activities of the individual ultimately result in scratching against the implant. This does not only apply to the biomedical industry, applications in the aerospace and automotive industries also cause wear to metallic materials. It was, therefore, important to study the wear characteristics of these alloys as it will give valuable insights into their performance when subjected to tribocorrosion conditions. The friction behavior during the dry sliding wear test was quite different. Ti-3Fe had the highest average COF of 0.55, while Ti-6Al-1V-3Fe had the lowest average COF (0.37). The high COF indicates a high amount of friction between the surface of the alloy and the counterpart alumina ball. This friction is attributed to a strong resistance of motion between the two surfaces, which could result from the differences in the material compositions. As mentioned previously, hardness influences the wear properties of a material. In this case, alumina is a ceramic with a greater hardness than the titanium alloys, allowing this material to dig into the titanium alloys with relative ease, thus generating great resistance to motion. As mentioned previously, this high friction is detrimental for bioimplant applications because of the discomfort and mobility restrictions experienced by the individual due to possible aseptic loosening caused by released wear debris (Li *et al.*, 2015; Moghadasi *et al.*, 2022). The low COF of the Ti-6Al-1V-

3Fe alloy enables smooth motion between this alloy and its counterpart. The lower COF and smoother motion, in this case, could be attributed to the hardness of the Ti-6Al-1V-3Fe alloy. This alloy was reported to have a hardness of approximately 405 VHN, higher than that of the commercial alloy and the rest of the experimental alloys (Bodunrin and Chown, 2021). From the frictional behavior of these alloys, it is quite clear that differences in material composition influence their wear resistance differently.

Ti-3Fe also displayed the deepest maximum penetration depth, as well as the widest wear track width, compared to the rest of the alloys. This further indicates that there was a greater amount of frictional force between this alloy and the alumina ball. The largest worn volume displayed by this alloy compared to the rest of the alloys under investigation further justifies the highest wear rate of this alloy ($5.55\text{E-}06 \text{ mm}^3/\text{Nm}$) as it indicates that it was unable to resist wear adequately and subsequently resist material loss as much as the rest of the alloys. Ti-4.5Al-1V-3Fe had a high COF as well. It was the closest to that of Ti-3Fe. This suggests that the material exhibits a high frictional force. The ease of motion between its surface and the alumina ball was minimal compared to that of Ti-6Al-4V and Ti-6Al-1V-3Fe. However, this alloy displayed the shallowest and narrowest wear track with the smallest amount of worn volume. This suggests a great amount of friction between the two surfaces, but it can withstand and resist wear and material loss effectively. So, this alloy can essentially withstand mechanical forces and abrasion wear, minimizing its wear loss and wear rate ($4.27\text{E-}06 \text{ mm}^3/\text{Nm}$). This alloy is quite resilient and can withstand friction despite the frictional forces involved compared to the other titanium alloys investigated. It is however important to note that the wear behavior of all the alloys was not too different from each other. The wear rates of all the alloys under the specifically applied load were well below $10^{-5} \text{ mm}^3/\text{Nm}$, which is the proposed wear rate limit for the mild wear of metallic materials (Venkatesan and Rigney, 1992). Additionally, the wear rates of the experimental alloys are very close to that of the commercial alloy ($4.69\text{E-}06 \text{ mm}^3/\text{Nm}$), with Ti-4.5Al-1V-3Fe having a wear rate lower than the commercial alloy. Some researchers studied the wear behavior of Ti-6Al-4V against various material counter bodies which include 304 stainless steel and GCr 15 steel, and they also found that the wear rate lies in the range of $10^{-6} \text{ mm}^3/\text{Nm}$ (Mao *et al.*, 2013). Gain *et al.* (2021) however, found the wear rate of Ti-6Al-4V alloy against 304 stainless steel to lie in the range of $10^{-5} \text{ mm}^3/\text{Nm}$. This indicates severe wear behavior and describes catastrophic behavior (Venkatesan and Rigney, 1992). Jozwik. (2018) also found the wear rate of the commercial alloy to be in the

region of severe wear ($4.51\text{E-}04 \text{ mm}^3/\text{Nm}$). This gives insight into how the testing conditions play a role in the wear rate of a material since the load and sliding speed employed by Jozwik. (2018) was higher (5 N and 0.3 m/s) than the ones used in this study (2 N and 0.08 m/s). Straffelini and Molinari. (1999) also found the wear rates of the alloys tested under 50N, 100N, and 200N to lie within the severe wear region as they were higher than $10^{-3} \text{ mm}^3/\text{Nm}$. Load was also a factor in the wear of these alloys as an increase in the load resulted in an increase in the wear rates of the alloys. Raj and Kailas. (2020) also reported wear rates in the range of $10^{-5} \text{ mm}^3/\text{Nm}$. Although the wear rates of the titanium alloys under investigation in this study lie in the mild wear region, hip joints perform well under wear rates in the ultra-mild wear region ($\leq 10^{-9} \text{ mm}^3/\text{Nm}$) (Fischer *et al.*, 2018). So, wear rates in the mild wear region are not sufficient enough for biomedical use and are considered high, however, the experimental alloys are promising as their wear rates are lower than that of the commercially available alloy Ti-6Al-4V. To improve the wear rates of these alloys to bring them down to the ultra-mild wear region, alloy composition optimization will be considered for future works.

The process of sliding wear in metals and alloys can be characterized by the progression of the following phenomena: surface and sub-surface plastic deformation, generation of debris and material transfer, reaction with the surrounding environment, and mechanical mixing. These cumulative effects ultimately lead to the formation of a mechanically mixed layer, also referred to as the tribo-layer, on the alloy's surface (Venkatesan and Rigney, 1992). In this case, plastic deformation could not be detected when the wear scars of the alloys under investigation was analysed. According to several researchers, one of the factors influencing wear resistance is plastic deformation and delamination (Straffelini and Molinari, 1999; Alam and Haseeb, 2002; Farokhzadeh and Edrisy, 2016; Kumar and Suman, 2017; Seidlitz and Kip, 2018; Gain *et al.*, 2021; Nyamekye *et al.*, 2023). They also found that the applied load plays an important role in the wear and the subsequent wear mechanism. Mild wear will be observed at low loads, and severe wear, which is associated with plastic deformation, will be observed at higher loads. Our study and other similar investigations (Li *et al.*, 2004; Chan *et al.*, 2011; Jozwik, 2018; Gain, Zhang and Lim, 2021) conducted wear tests under low loading conditions (from $\sim 1.8 \text{ N}$ to 5 N) while the investigations mentioned above operated at high loading conditions (15 N to 250 N). Noticeable plastic deformation and delamination were reported mostly for very high loading conditions. A wide range of loading can be used to investigate the wear resistance of biomaterials because the

loads exerted by the human body on the implant at any given moment vary greatly depending on the different activities of daily living such as walking, walking upstairs or downstairs, sitting, lying, running, and exercising (D'Angeli *et al.*, 2013; Damm *et al.*, 2013; Stenlund *et al.*, 2017). In addition, the loads applied on the implants vary significantly as different locations in the human bone apply different pressure levels on the implant, which all ultimately depend on the type of movement taking place (Brown and Shaw, 1983; Stenlund *et al.*, 2017; de Vries *et al.*, 2022). Although abrasive wear was the main wear mechanism observed for the alloys in this study, some adhesive wear also occurred, as upon analysis of the alumina balls in **Figure 4.8**, some of the alloy material, the dark grey/black metallic patches, and agglomerated debris, was transferred onto the scar of the alumina balls. No grey or black patches, which are usually an indication of oxides, were observed on the wear scars. No oxygen was detected from the EDS analysis as well.

Efforts to develop titanium alloys with reduced toxicity and cost have involved completely substituting vanadium, the expensive beta-stabilizing element in the commercial Ti-6Al-4V alloy, with iron, a less expensive eutectoid beta-stabilizing element. These substitutions enhanced resistance to corrosion compared to Ti-6Al-4V (Li *et al.*, 2004; Chan *et al.*, 2011; Mao *et al.*, 2013). However, the alloy's mechanical properties are often compromised due to the potential formation of brittle intermetallic phases (Fujii and Takahashi, 2002). In this investigation, Ti-3Fe exhibited the poorest wear resistance, which could be attributed to the weakened properties brought about by the complete substitution of vanadium with iron (Fujii and Takahashi, 2002; Fujii *et al.*, 2002). In contrast, alloys employing partial substitution of vanadium with iron, such as Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe, demonstrated superior wear resistance when compared to both Ti-6Al-4V and Ti-3Fe. Furthermore, reports indicate that these alloys (Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe) exhibit improved hardness (370 VHN and 405 VHN respectively) and corrosion resistance (Bodunrin *et al.*, 2018, 2020)(Bodunrin *et al.*, 2018, 2020) . Based on these findings, it is evident that incorporating both vanadium and iron as beta-stabilizing elements by retaining 1 wt.% of vanadium in Ti-6Al-4V and replacing the remaining portion with iron proves more advantageous than completely substituting with iron alone. This combined approach not only enhances corrosion resistance and hardness but also improves wear resistance, as observed in these alloys.

4.5. Conclusions

The findings of this study indicate that the low-cost experimental alloys are quite comparable to the commercially available alloy as far as their dry wear properties are concerned. According to the COF, wear volume, and wear, Ti-3Fe displayed the least resistance to wear compared to other alloys. Another experimental alloy, Ti-4.5Al-1V-3Fe, displayed the best resistance to wear, performing better than the commercial alloy under the testing conditions. Although the wear rate of commercial alloy was higher than that of Ti-6Al-1V-3Fe, it was only by a very small margin, so the wear properties are comparable. Overall, the wear rates lie within the mild wear region. However, effort should be made to get the wear rates of the titanium alloys in the ultra-mild wear region ($\leq 10^{-9}$ mm³/Nm) as biomedical implants, particularly hip joints, work well in this region. To achieve such wear rates, the typical acting wear mechanisms should be tribochemical reactions and surface fatigue. The commercial alloy, as well as the experimental alloys, displayed the same wear mechanism of abrasive wear and adhesive wear. The grooves within the wear scar were quite shallow, further reinforcing that the alloys displayed mild wear. This observation further confirms the superiority of the partial substitution of vanadium with iron over the complete substitution of vanadium with iron when developing low-cost and less toxic titanium alloys, as Ti-3Fe had poor wear resistance, whereas Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe displayed the best resistance to wear. These alloys could, therefore, potentially compete with Ti-6Al-4V for commercial applications in implant applications.

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Chapter 5: Corrosion tests

Enhanced corrosion performance of low-cost titanium alloys in a simulated diabetic environment

This chapter provides insight into the importance of titanium and its alloys for the biomedical industry. The importance of the simulated diabetic environment is discussed. The results from the corrosion tests of the titanium alloys under investigation in this research, which address the second and third objectives are provided in this chapter. The results of these corrosion tests are discussed in detail in this chapter. A general overview of this chapter is graphically presented in **Figure 5.1**. This chapter has been written in paper form and has been published in the journal of *Materials and Corrosion*: N. R. Rundora, J. W. Van der Merwe, D. E. P. Klenam, and M. O. Bodunrin, “Enhanced corrosion performance of low-cost titanium alloys in a simulated diabetic environment,” *Mater. Corros.*, no. May, pp. 1–13, 2023, doi: 10.1002/maco.202313927.

Graphical Abstract

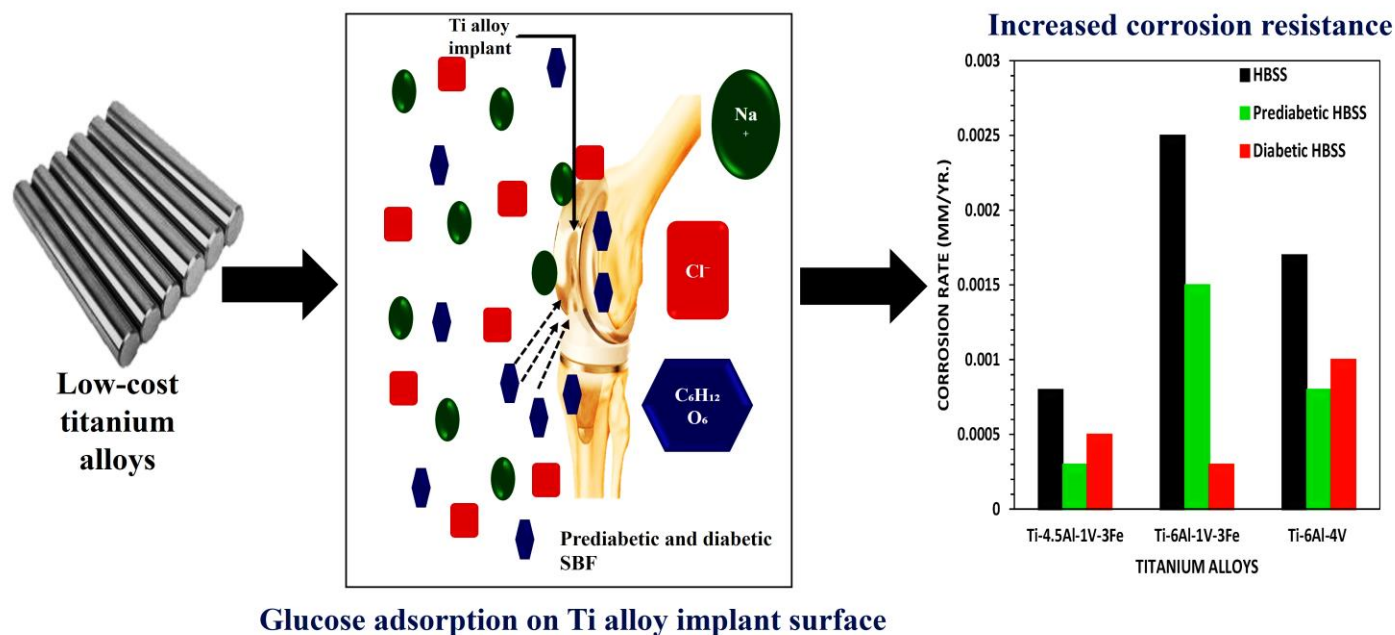


Figure 5.1: Corrosion tests graphical abstract

5.1. Introduction

Since 1910, titanium and its alloys have been widely regarded as the benchmark material for use in various industries (Ahmed *et al.*, 2014). The primary reason for this is the array of appealing properties that these materials exhibit, including high specific strength, outstanding high-temperature properties, remarkable toughness, good resistance to corrosion in diverse corrosive environments, and high biocompatibility (Chen and Thouas, 2015; Bodunrin *et al.*, 2018; Pandey *et al.*, 2020). Industries such as aerospace, sports, marine, electrical, desalination, oil and gas, automotive, chemical and jewellery use these alloys due to their attractive properties (Ahmed *et al.*, 2014; El Khalloufi *et al.*, 2021; Li *et al.*, 2021). Titanium and its alloys are widely utilized in reconstructive surgery, particularly in orthopaedics and dentistry, and are favoured over stainless steels and cobalt-based alloys because of their exceptional biocompatibility, resistance to corrosion, and mechanical properties (Anene *et al.*, 2021). Demand for titanium alloys in this field is growing rapidly, partly due to the increasing aging population, which is known to be at higher risk of hard tissue failure for various reasons, including bone weakening, commonly referred to as osteoporosis, trauma and osteoarthritis, which is simply inflammation in bone joints (Niinomi *et al.*, 2012; Pandey *et al.*, 2020).

One of the key factors driving the demand for bioimplants is the rapidly increasing prevalence of diabetes, considered one of the most significant health emergencies of the 21st century (International Diabetes Federation, 2021). Diabetes has become a critical health concern, with an estimated 537 million individuals affected by the disease worldwide as of the year 2021 (International Diabetes Federation, 2021). Projections indicate that this number will likely climb to 643 million by 2030 and could rapidly increase to 783 million by 2045 (International Diabetes Federation, 2021). Due to the growing occurrence of obesity, there has been a yearly rise in the incidence of type 2 diabetes among children and adolescents (up to 19 years old). This is a worrisome trend (International Diabetes Federation, 2021). Both type 1 and type 2 diabetes can lead to detrimental effects on multiple organs in the body, giving rise to severe, disabling, and potentially life-threatening health complications (Patoulas *et al.*, 2020; International Diabetes Federation, 2021). Some of these complications include neuropathy, kidney disease, peripheral artery disease, and cardiovascular diseases (Patoulas *et al.*, 2020; International Diabetes Federation, 2021). Diabetics also risk developing bone and joint diseases, such as osteoporosis and

osteoarthritis (International Diabetes Federation, 2021). In extreme cases, they face the risk of leg and foot amputation, ultimately leading to the need for bioimplants (International Diabetes Federation, 2021). There is, therefore, a huge need for good biomaterials that are also affordable as their affordability will come under more scrutiny as more and more people will need them in the future.

Although titanium and its alloys possess desirable characteristics, their high cost has significantly limited their use in many industries, including the biomedical industry, restricting their use to applications where they are the sole option to meet specified operational needs (Prozesky *et al.*, 2017). The expensive nature of titanium is attributed to the complex extraction process required to obtain the element from its ores, as well as the intricate processing methods involved in converting it into finished goods (Froes *et al.*, 2004; Wang *et al.*, 2012). Additionally, the use of costly alloying elements contributes to the high cost of the alloys (Kolli and Devaraj, 2018). Commercially pure α -type titanium and $\alpha+\beta$ type Ti-6Al-4V and Ti-6Al-4V ELI (extra low interstitials) are the common alloys being employed in the biomedical industry today (Kolli and Devaraj, 2018). However, the high cost and toxicity of the $\alpha+\beta$ type alloys resulting from the aluminium and vanadium alloying elements have made the inexpensive 316L stainless steel seemingly attractive. However, the drawbacks associated with 316L stainless steel, such as its heightened vulnerability to localized corrosion and its high density, almost twice that of titanium, are concerning. Additionally, the high elastic modulus of 316L stainless steel results in bone resorption and implant loosening (Talha *et al.*, 2013; Gain *et al.*, 2021).

Several research efforts have been geared toward combating the toxicity and high cost associated with titanium alloys. Some researchers replaced aluminium with oxygen and nitrogen in Ti-Fe-O-N $\alpha+\beta$ alloy (Fujii *et al.*, 2002; Nochovnaya *et al.*, 2008). Fujii and Takahashi. (2002) substituted iron for the costly beta stabilizer, vanadium, in Ti-Al-Fe $\alpha+\beta$ alloys. These were all modifications of the commercial alloy. Instead of fully replacing vanadium with other beta stabilizers like iron, chromium and manganese, Bodunrin *et al.* (2018) developed a group of low-cost alloys by partially replacing vanadium with iron, a less expensive eutectoid β -stabilizing element. The retention of 1% vanadium inhibited the formation of brittle and degrading intermetallic phases (titanium-iron). Bodunrin *et al.* (2018) found that this improved the alloy's mechanical properties, as well as its

resistance to corrosion when compared to the commercial alloy. The objective of this chapter is to further investigate the biocompatibility of these alloys by studying their corrosion behavior in simulated body fluids with various concentrations of glucose.

The blood glucose concentration is a significant measure for describing the bodily fluid environment. Glucose, like other organic molecules in the body, plays a vital role in the corrosion behavior of various metal alloys, including titanium alloys, cast iron, and mild steel (Manivasagam *et al.*, 2010). Investigating the properties of biomaterials in simple body fluids fails to accurately represent the human body environment because they lack the additions of essential proteins, bacteria, and other biomolecules, such as glucose, that are naturally found in the human body (Yu, 2015). The human body environment is quite intricate, and knowing exactly how bioimplants will behave in such an environment is important. Glucose inhibits the corrosion of mild steel and cast iron in acidic environments through a combination of physical and chemical interactions (Nady *et al.*, 2021). Understanding the corrosion characteristics of implant materials in the body environment of typical diabetic patients is crucial, given the prevalence of diabetes. The experimental titanium alloys underwent corrosion testing in glucose-containing solutions representing diabetic and prediabetic patients to see how the alloys will perform when used in such environments. Prediabetic conditions were considered as these are conditions of elevated blood glucose concentrations above normal levels, which may also ultimately alter the corrosion properties of the metal implants. Although patients are treated to lower blood glucose concentrations, it is important to perform these investigations as almost one in two adults living with diabetes are undiagnosed and thus unaware of their status (International Diabetes Federation, 2021).

5.2. Materials and methods

5.2.1. Materials

Refer to Section 3.1 and Section 3.2 for the materials used as well as the sample preparation procedure.

5.2.2. Corrosion testing

Refer to Section 3.5 for the detailed corrosion testing procedure in the various environments.

5.2.3. Microstructural characterization

Refer to Section 3.3 for the details of the alloy characterisation employed to analyse the corroded surfaces of the alloys after the corrosion tests.

5.3. Results

5.3.1. Sodium chloride and Hanks Balanced Salt Solution

The tested alloys are typically composed of two phases: the dark lamellae α -phase and the light β -phase, which form at the interfaces of the α - α lamellae. The SEM images captured after exposure to the various electrolytes show this. To evaluate the stability of the passive film on the surface of the experimental alloys compared to the commercial alloy in commonly used simulated body fluids (0.9 wt.% sodium chloride and HBSS), the OCP was analysed for 3600 seconds. **Figure 5.2** illustrates the OCP-time plots for the commercial and experimental alloys when submerged in 0.9 wt.% sodium chloride solution and HBSS. The OCP behavior of the alloys was similar in both solutions, ranging between -0.6 V and 0 V. All the alloys showed a gradual rise in OCP, shifting toward more positive values with increasing exposure time. This is the typical behavior of passive alloys as OCP indicates a protective passive titanium dioxide film is forming and thickening on the surface of the alloys (Virtanen, 2012). The experimental alloys displayed a slightly higher fluctuation in OCP when exposed to 0.9 wt.% sodium chloride solution compared to HBSS. This fluctuation can be explained by the dissolution and re-passivation of the titanium dioxide film formed on the alloys, which can be attributed to the instability caused by anions like chloride ions in the corrosion media (Khorasani *et al.*, 2015). The high diffusivity of chloride ions makes them easily penetrate the passive film (Talha *et al.*, 2019).

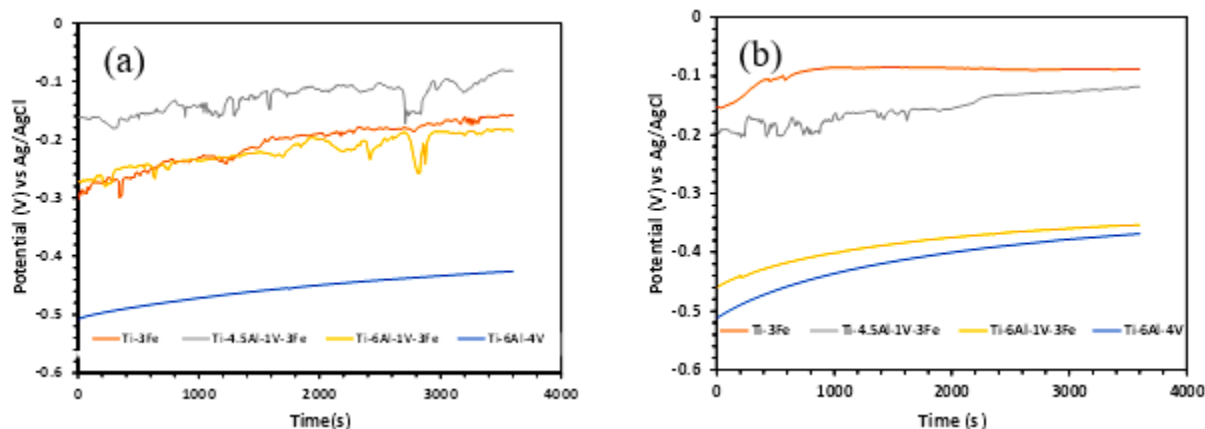


Figure 5.2: Open circuit potential (OCP)-time curve of titanium alloys in (a) 0.9 wt.% sodium chloride; (b) Hanks Balanced Salt Solution (reference electrode is silver/silver chloride).

Ti-4.5Al-1V-3Fe and Ti-3Fe alloys had the highest OCP values in both solutions. This indicates that these alloys have the least tendencies to corrode, with the Ti-3Fe alloy exhibiting the greatest OCP when immersed in HBSS. However, the OCP curve of Ti-4.5Al-1V-3Fe showed many fluctuations indicative of localized depassivation and repassivation of the passive film on its surface (More *et al.*, 2011). Ti-6Al-4V had the lowest OCP in both solutions meaning that it has the highest tendency to corrode; however, its oxide film is more stable as it had a relatively smooth curve. These findings align with previous studies by Leshetla *et al.* (2022) and Bodunrin *et al.* (2018). The composition of titanium alloys influences the stability and integrity of the titanium dioxide film that forms on their surface (Geetha *et al.*, 2009). According to previous reports, oxide compounds of alloying elements such as aluminium and vanadium have been identified on titanium alloy surfaces (Geetha *et al.*, 2009). It has also been reported that because of the relatively simple composition and microstructure of commercially pure titanium and α titanium alloys, as well as the limited impurities found in these alloys, they are more resistant to corrosion than the $\alpha+\beta$ and β titanium alloys (Virtanen, 2012). This is because elements and impurities modify the oxide film, which can either improve or destroy the protective characteristics of the passive oxide film. The latter is observed in most commercial titanium alloys. Studies have shown that manganese, vanadium, and aluminium decrease the protective nature of the oxide film (Virtanen, 2012). The protectiveness of this film is enhanced when noble alloying elements, such as palladium and ruthenium, are utilized (Virtanen, 2012).

Figure 5.3 exhibits the linear polarization curves of the experimental and commercial titanium alloys obtained after the OCP tests. The corrosion performance of the commercial and experimental alloys in both corrosive environments is comparable, as seen by the similarities in the alloys' passivation current densities. None of the alloys exhibited a distinct transition region from an active state to a passive state up to a stop potential of 2.5 V, indicating that they all underwent spontaneous passivation.

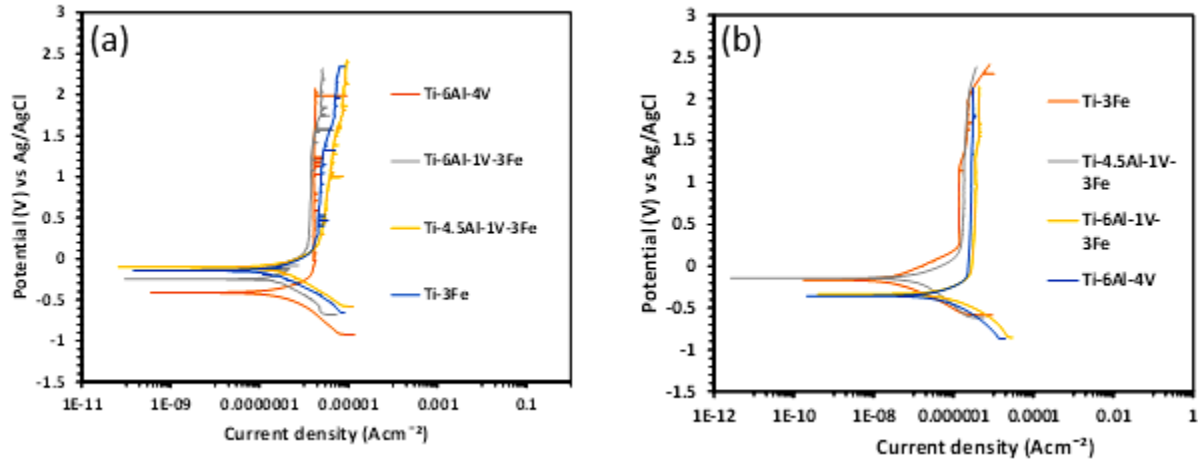


Figure 5.3: Polarization curves for titanium alloys in (a) 0.9 wt.% sodium chloride; (b) Hanks Balanced Salt Solution (reference electrode is silver/silver chloride)

Transient currents were observed in the passive region of all the alloys in the sodium chloride environment. This is again due to the instability of the oxide film caused by the chloride ions in the solution. No transient currents were observed in the more complex HBSS, suggesting that these alloys can build up relatively stable anodic passive films in this environment. The corrosion parameters obtained during the linear polarization tests in the sodium chloride solution are displayed in **Table 5-1**. The corrosion potentials of the low-cost experimental alloys were similar while significantly different from that of the commercial alloy. The corrosion current densities and corrosion rates of the alloys were generally similar, except for the low-cost Ti-6Al-1V-3Fe alloy, which exhibited some differences in its corrosion behavior. The Ti-6Al-1V-3Fe alloy, in particular, demonstrated the highest I_{corr} , indicating lower resistance to corrosion than the other alloys. This is further supported by its higher corrosion rate, indicating the alloy's faster degradation in the given solution.

The electrochemical parameters obtained when the samples were immersed in the HBSS (**Table 5-2**) are comparable to those obtained in the 0.9 wt.% sodium chloride solution. It is important to highlight that apart from the commercial alloy, the titanium alloys under investigation are more susceptible to corrosion in HBSS than in 0.9 wt.% sodium chloride solution. This is seen through the higher corrosion potential values obtained in the HBSS. This observation is attributed to the difference in the complexity of the two solutions. The 0.9 wt.% sodium chloride solution has mainly one active anion, the chloride anion, while the HBSS consists of more than one active anion (chloride, carbonate, sulphate, and phosphate) (Bodunrin *et al.*, 2020). This renders the HBSS environment more hostile than the sodium chloride solution environment, so it ultimately dissolves the passive layer on the alloys more readily (Fujii and Takahashi, 2002; Khorasani *et al.*, 2015; Bodunrin *et al.*, 2018). Once again, despite the commercial alloy being more prone to corrosion, the low-cost Ti-6Al-1V-3Fe alloy showed the highest corrosion rate. Therefore, this alloy can be characterized as having the poorest corrosion characteristics in both simulated body fluids. This finding was documented by Leshetla *et al.* (2022) The low-cost Ti-3Fe alloy once again shows the lowest corrosion rate, comparable to Ti-4.5Al-1V-3Fe.

The alloys' secondary electron images after the potentiodynamic tests are shown in **Figure 5.4** and **Figure 5.5**. From these images, it is evident that no significant amount of corrosion took place. Most importantly, there was no sign of localized corrosion, such as pitting corrosion, indicating that uniform corrosion is the dominant form of corrosion in these alloys. This finding aligns with the observations reported by Leshetla *et al.* (2022). Some of the tested alloys in the HBSS exhibited a few notable chunks of corrosion product on their surfaces. However, overall, the amount of corrosion product observed on the alloy surfaces in 0.9 wt.% sodium chloride and HBSS was minimal, indicating that these alloys have favourable corrosion resistance in these environments.

Table 5-1: Electrochemical parameters obtained after potentiodynamic tests in 0.9 wt.% sodium chloride.

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm yr^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.14	0.08	0.0007	341364
Ti-4.5Al-1V-3Fe	11.93	-0.10	0.14	0.0012	191904
Ti-6Al-1V-3Fe	11.83	-0.25	0.28	0.0024	94500
Ti-6Al-4V	11.82	-0.41	0.15	0.0014	168793

Table 5-2: Electrochemical parameters obtained after potentiodynamic tests in Hanks Balanced Salt Solution

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm yr^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.17	0.07	0.0006	369438
Ti-4.5Al-1V-3Fe	11.93	-0.14	0.09	0.0008	278180
Ti-6Al-1V-3Fe	11.83	-0.33	0.29	0.0025	90472
Ti-6Al-4V	11.82	-0.36	0.20	0.0017	132990

5.3.2. Prediabetic and diabetic Hanks Balanced Salt Solution

Figure 5.6 displays the OCP curves of the alloys when submerged in HBSS containing varying concentrations of glucose. In the 100 mg dL^{-1} and 200 mg dL^{-1} glucose solutions, the experimental Ti-4.5Al-1V-3Fe alloy exhibited a consistent and stable OCP from the initial period. In the 100 mg dL^{-1} solution, the OCP of the Ti-6Al-1V, Ti-3Fe, and Ti-6Al-1V-3Fe alloys stabilized after about 2800 seconds. This similarity in OCP stability suggests that these alloys achieve a favourable balance between material dissolution and ion adsorption on their surfaces (Liu and Wang, 2020). In the 200 mg dL^{-1} solution, the OCP of Ti-3Fe became stable shortly after the initial period, displaying a similar behavior to the Ti-4.5Al-1V-3Fe alloy in this solution, while the commercial alloy stabilized at around 3300 seconds. Although the Ti-6Al-1V-3Fe alloy had the highest OCP in the diabetic (200 mg dL^{-1} glucose) environment, the passive film developed

on its surface was very unstable. As observed from the breakdowns in the OCP, the downward trend suggests that this alloy struggles to build up its protective barrier in this solution (Liu and Wang, 2020). Similar to the observation in the sodium chloride and normal HBSS environments, Ti-6Al-4V had the lowest OCP in both glucose environments, suggesting its high tendency to corrode compared to the experimental alloys. According to the corrosion potential values in **Table 5-3** and **Table 5-4**, the E_{corr} of all the alloys except for Ti-3Fe was slightly higher at the diabetic glucose concentration of 200 mg dL^{-1} than the pre-diabetic glucose concentration of 100 mg dL^{-1} . This indicates that the corrosion resistance of the alloys seems to be higher at higher glucose concentrations. **Figure 5.7** illustrates the potentiodynamic polarization curves of the titanium alloys when immersed in HBSS with varying glucose concentrations.

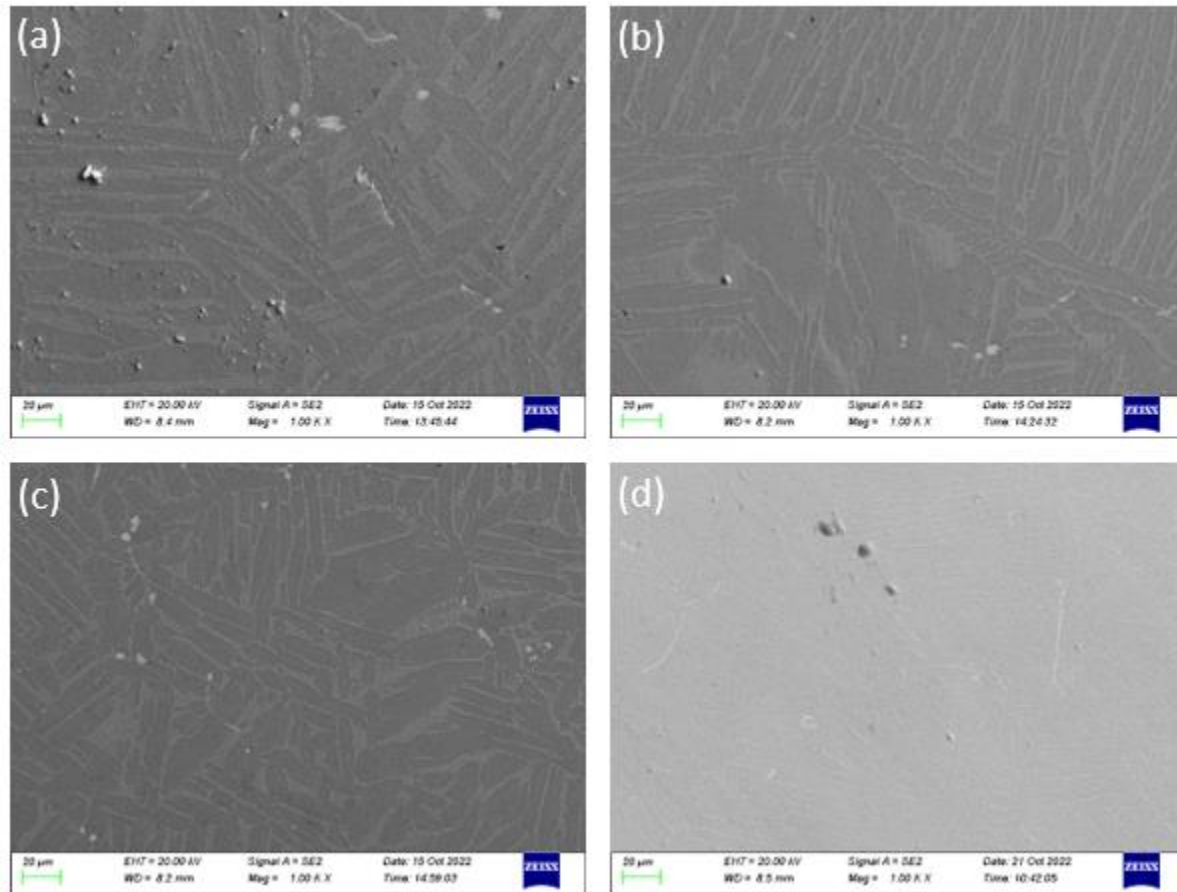


Figure 5.4: Scanning electron images of corroded titanium samples exposed to 0.9 wt.% sodium chloride solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V

The corrosion behaviours of these alloys exhibit a similar trend, as the curves show close resemblance in both media. In the pre-diabetic medium, transient currents were observed only in

the commercial alloy. All the alloys displayed comparable passivation current values. In the diabetic environment, transient currents were observed in the commercial alloy, as well as in the Ti-4.5Al-1V-3Fe alloy. The measured corrosion potentials of the alloys in both solutions, as seen in **Table 5-3** and **Table 5-4**, were very similar. Apart from Ti-3Fe, the corrosion potentials in the diabetic solution are slightly higher than those in the prediabetic solution. The corrosion current densities were quite different from each other in both solutions. In the pre-diabetic environment, it is quite clear that the alloys have similar corrosion resistance as their corrosion rates lie within a similar range. Among these alloys, the Ti-4.5Al-1V-3Fe alloy has a reduced susceptibility to corrosion due to its higher corrosion potential, and it demonstrated the lowest corrosion rate in this particular solution. In the diabetic solution (200 mg/dL⁻¹ glucose), the commercial alloy, with the highest tendency to corrode, had the poorest resistance to corrosion as it also had the highest corrosion rate. The Ti-6Al-1V-3Fe and Ti-4.5Al-1V-3Fe alloys exhibit the lowest corrosion rates, the least susceptible to corrosion in this solution.

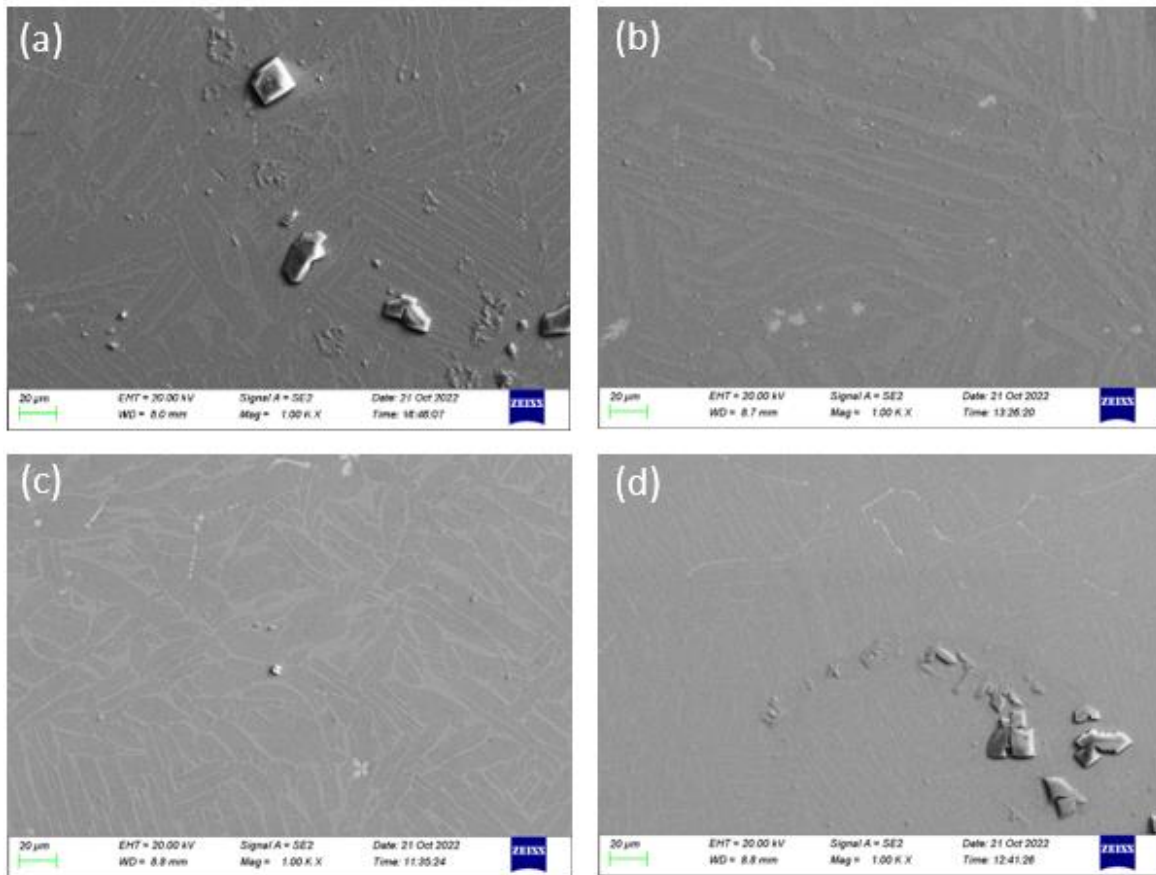


Figure 5.5: Scanning electron images of corroded titanium samples exposed to Hanks Balanced Salt Solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V

The SEM images after the potentiodynamic tests in the glucose solutions are displayed in **Figure 5.8** and **Figure 5.9**. It is evident from the images that no form of localized corrosion, such as pitting corrosion, was observed. The dominant corrosion mode for these alloys at both glucose concentrations was uniform corrosion. This can be seen as the alloys have relatively no defects on their surfaces, apart from the deposits of corrosion products on their surfaces. The quantity of corrosion product on the surface of the alloys does not directly impact their corrosion resistance, as all the alloys exhibited low corrosion rates within a similar range.

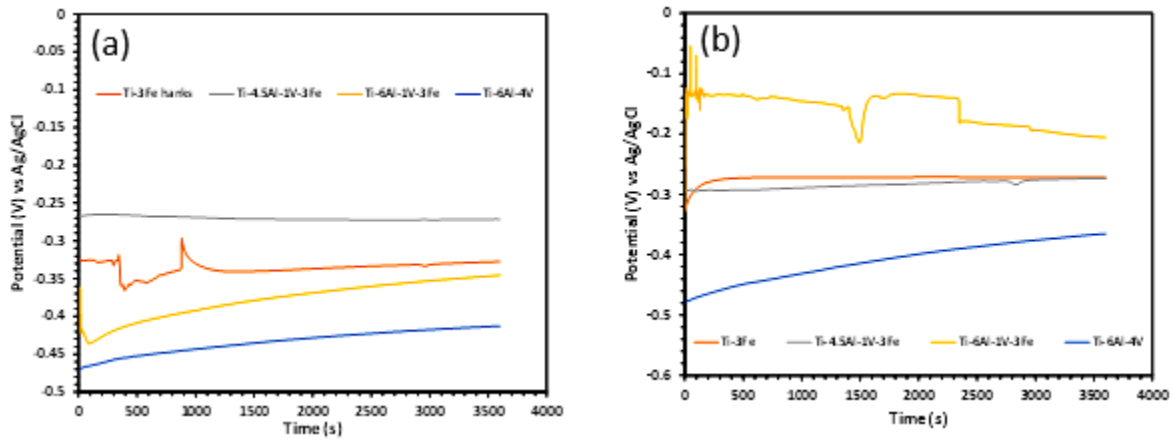


Figure 5.6: Open circuit potential (OCP) of the titanium alloys in (a) Hanks Balanced Salt Solution (HBSS) + 100 mg dL⁻¹ glucose; (b) HBSS + 200 mg dL⁻¹ glucose.

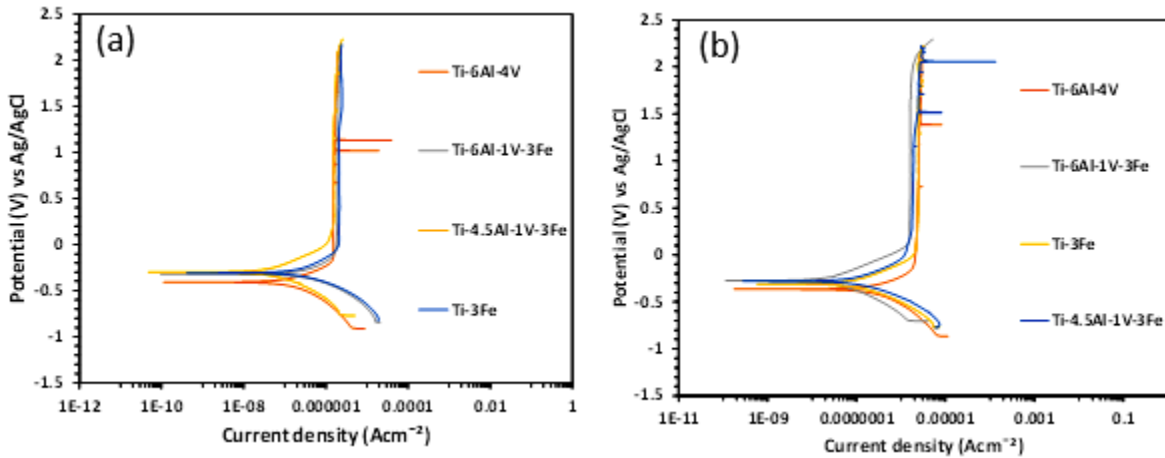


Figure 5.7: Potentiodynamic curves of the titanium alloys in (a) Hanks Balanced Salt Solution (HBSS) + 100 mg/dL⁻¹ glucose; (b) HBSS + 200 mg dL⁻¹ glucose.

Table 5-3: Electrochemical parameters obtained after potentiodynamic tests in Hanks Balanced Salt Solution+ 100 mg/dL glucose

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm yr^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.31	0.15	0.0013	169971
Ti-4.5Al-1V-3Fe	11.93	-0.30	0.04	0.0003	706713
Ti-6Al-1V-3Fe	11.83	-0.32	0.17	0.0015	152595
Ti-6Al-4V	11.82	-0.41	0.09	0.0008	281152

Table 5-4: Electrochemical parameters obtained after potentiodynamic tests in Hanks Balanced Salt Solution + 200 mg/dL glucose

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm yr^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.31	0.08	0.0007	344045
Ti-4.5Al-1V-3Fe	11.93	-0.28	0.06	0.0005	457269
Ti-6Al-1V-3Fe	11.83	-0.27	0.04	0.0003	696238
Ti-6Al-4V	11.82	-0.37	0.12	0.001	219179

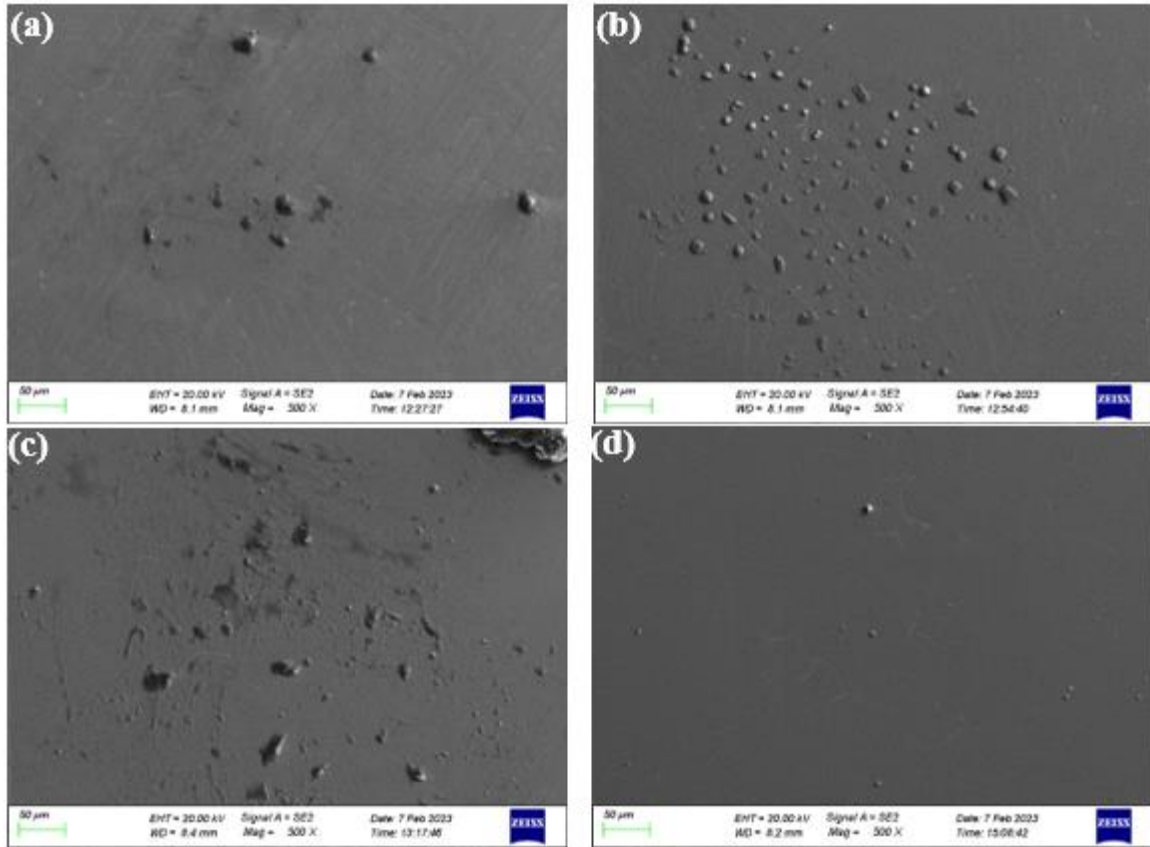


Figure 5.8: Scanning electron images of corroded titanium samples in 100 mg dL⁻¹ Hanks Balanced Salt Solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V

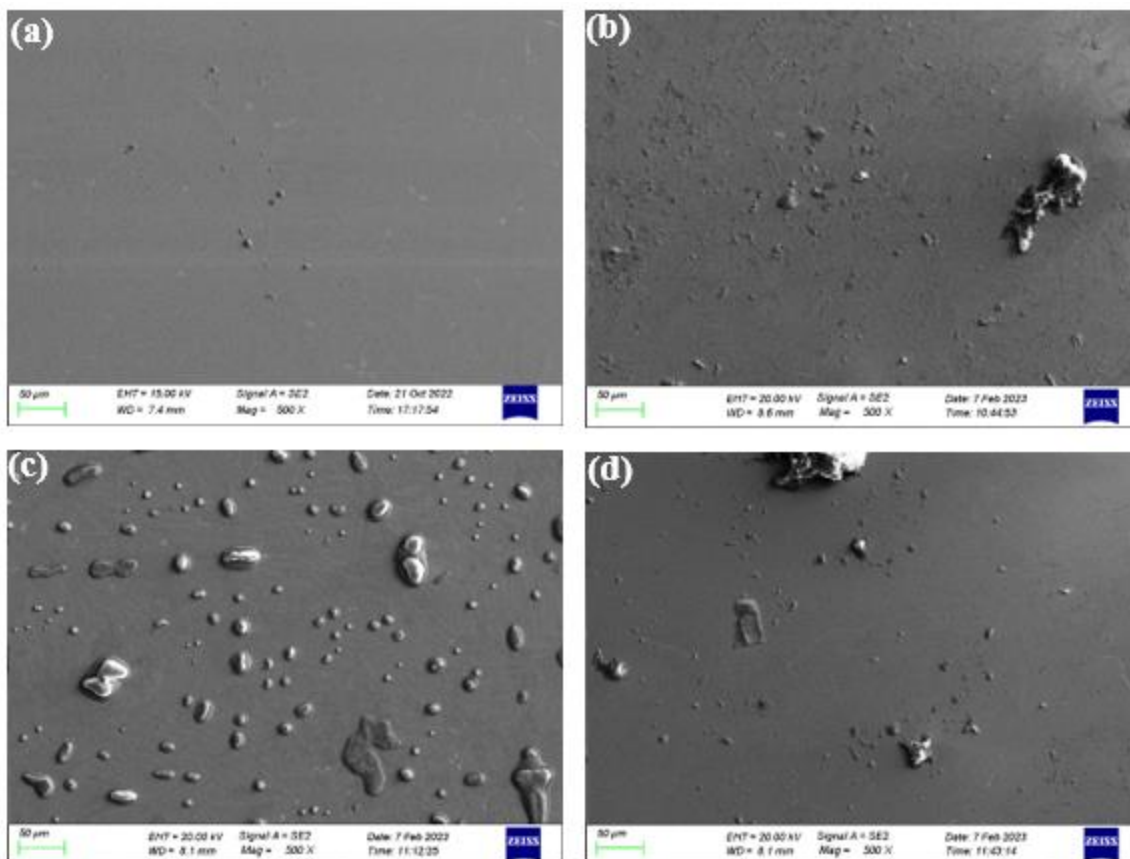


Figure 5.9: Scanning electron micrographs of corroded titanium samples in 200 mg dL⁻¹ HBSS: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V

5.4. Discussion

The outstanding resistance to corrosion of titanium alloys can be primarily attributed to the development of a stable and adherent passive film on their surface upon exposure to corrosive environments. This passive film typically consists of two layers composed of stable oxide compounds. These oxides are anatase, which serves as the inner layer, and rutile, which serves as the outer layer of the passive film (Geetha *et al.*, 2009; Pandey *et al.*, 2020). The formation of the hard titanium dioxide layers is a result of the diffusion of oxygen through the following reaction: $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^-$ (Pandey *et al.*, 2020). The presence or addition of other elements to titanium can potentially modify the double-layered passive film. These modifications can either be beneficial or detrimental to the alloy's resistance to corrosion. Leshetla *et al.* (2022) reported that the vanadium and aluminium oxides formed in the passive film of the commercial alloy were detrimental to the corrosion behavior of titanium alloys. This is because they render the oxide film

unstable while elements like ruthenium and palladium, which are predominantly found in β titanium alloys, promote excellent corrosion resistance. Also, they improve the protectiveness of the titanium oxide layer (Leshetla *et al.*, 2022). In addition to this, the constituents, severity of the electrolyte, its temperature, the complexity of the ions in solution, and the immersion time have all been reported to influence the corrosion behavior of metallic alloys (Bodunrin *et al.*, 2018).

The corrosion performance of the inexpensive experimental titanium alloys was therefore evaluated in simulated body fluids to understand the effect of their compositions and the electrolyte's ion complexity on their resistance to corrosion. Similar corrosion behavior trends were observed for these alloys in 0.9 wt.% sodium chloride solution and HBSS. The transient currents observed in some of the alloys were due to the chloride ions in the 0.9 wt.% sodium chloride solution. These currents indicate disruption in the development and stability of the passive films on the alloys' surfaces (Aragon, 1972). Although there was no significant variation in the corrosion rates of the alloys in both solutions, the corrosion potentials of the experimental alloys are slightly higher in the 0.9 wt.% sodium chloride solution than in HBSS. This suggests that the surface of the alloys is more activated in HBSS (Leshetla *et al.*, 2022). In the 0.9 wt.% sodium chloride solution, the chloride ion is the main attacking anion on the surface of the alloys, while in HBSS, the anions responsible for corrosion include phosphate, chloride, sulphate, and carbonate (Bodunrin *et al.*, 2018). It has been reported that corrosive media with multiple anions can more easily dissolve the passive layer than electrolytes with a single anion (Bodunrin *et al.*, 2018).

The OCP and polarization results and the electrochemical parameters show that the experimental alloys have better resistance to corrosion due to their higher corrosion potentials. Ti-3Fe exhibits superior corrosion resistance compared to the other alloys in the sodium chloride solution and HBSS. This superior corrosion resistance can be attributed to its low corrosion rate, as evidenced by its high corrosion potential and low corrosion current density. Alloying titanium with iron as the sole beta stabilizer, however, has been found to degrade the mechanical properties of the alloy. This is due to the formation of some intermetallic compounds, such as titanium-iron phases, which make the alloys brittle, thus reducing their toughness (Hideki Fujii, 2014; Bolzoni *et al.*, 2016). Some studies, however, found that it enhances the alloy's resistance to corrosion (More *et al.*, 2011; Talha *et al.*, 2019). This is evident in the results obtained from the current study, as Ti-3Fe

has the lowest corrosion rate when exposed to both solutions. The precise mechanism by which iron enhances the stability and protectiveness of the titanium oxide passive film is still not completely understood. To acquire a more profound comprehension of the role of iron in the corrosion behavior of these alloys and the mechanisms underlying their superior performance, further tests and investigations are required. Despite the experimental Ti-6Al-1V-3Fe alloy having the highest corrosion rate among the examined alloys in both solutions, it displays a lower inclination to undergo corrosion than the commercial alloy. The corrosion rate is, however, well below the maximum acceptable corrosion rate for bioimplant materials (0.13 mm per year), just like the rest of the alloys (Pimenova and Starr, 2006). Additionally, while the corrosion rate may be higher for Ti-6Al-1V-3Fe, its overall corrosion resistance may still be superior to that of the commercial alloy, indicating that other factors, such as composition and microstructure, play a role in determining the alloy's overall resistance to corrosion. These results are consistent with the observations made by Leshetla *et al.* (2022) who tested these alloys in the same simulated body fluids. The SEM images of the alloys in this chapter confirm that the corrosion behavior is predominantly uniform corrosion, without any indication of localized corrosion such as pitting or crevice corrosion. The absence of localized corrosion further supports the low corrosion rates observed for these alloys in both solutions, indicating their good overall corrosion resistance.

Biomolecules in the human body environment play a role in an implant material's resistance to corrosion. Biomolecules such as proteins have been found to either enhance or degrade the corrosion resistance of implant materials (Choubey *et al.*, 2004; Pimenova and Starr, 2006; Bhola *et al.*, 2011; Takadoun *et al.*, 2012). Because of the bone and joint disorders developed by diabetic people, it was important to understand the effects of glucose on the corrosion behavior of these titanium alloys. The corrosion rates of the alloys at both glucose concentrations are quite like each other, and they are well below the accepted 0.13 mm per year. In the pre-diabetic environment, the Ti-4.5Al-1V-3Fe alloy exhibits superior corrosion resistance compared to the other alloys. It demonstrated the lowest corrosion rate and corrosion current density, indicating its ability to withstand corrosion and maintain its integrity in this environment. Similarly, in the diabetic HBSS, the experimental Ti-6Al-1V-3Fe alloy outperforms the other alloys, showing the lowest corrosion rate and the least susceptibility to corrosion. The alloys tested in the pre-diabetic solution exhibit a higher tendency to corrode than those in the diabetic solution, indicated by their lower corrosion

potential, suggesting a greater susceptibility to corrosion in the pre-diabetic environment. From this, we deduce that a high glucose concentration is more effective in inhibiting the corrosion of the alloys. The corrosion rates are, however, quite similar to each other. The glucose concentration in HBSS primarily affects the viscosity of the solution and the diffusion of ions within it (Liu and Wang, 2020). Higher glucose concentrations in HBSS increase its viscosity, leading to stronger ion adsorption on the surface of the titanium alloys but a slower rate of ion diffusion (Liu and Wang, 2020). This ion diffusion rate becomes lower in HBSS with higher glucose concentrations, thereby reducing the corrosion rate of the material surface (Liu and Wang, 2020). Consequently, higher glucose concentrations contribute to an increase in corrosion potential and a decrease in corrosion current density, ultimately resulting in a lower corrosion rate.

Apart from Ti-3Fe, the titanium alloys' corrosion rates are lower than those of the alloys tested in 0.9 wt.% sodium chloride solution and normal HBSS. In addition, the corrosion rates are well below the maximum acceptable corrosion rate for bioimplants. From these results, we conclude that the experimental alloys, as well as the commercial alloy, would perform well in the body environment of a normal person, as well as the body environment of pre-diabetic and diabetic patients. Liu *et al.* (2016) investigated the influence of different glucose concentrations in HBSS on the corrosion behavior of a pure titanium alloy (TA2). The glucose concentrations under investigation included concentrations that mimicked a healthy person before and after eating, as well as a diabetic person before and after eating. The results showed that the alloy was suitable for use by a diabetic patient as the glucose concentration before eating (180 mg dL^{-1}) provided an environment in which the alloy could perform well. They concluded that the alloy could perform well at normal (90 mg dL^{-1} to 126 mg dL^{-1}) and slightly high glucose concentrations (180 mg dL^{-1} to 216 mg dL^{-1}). However, the alloy would not be suitable for diabetic patients with a blood glucose concentration exceeding 216 mg dL^{-1} . These results correlate with our findings, as a glucose concentration of 200 mg dL^{-1} , which lies within the range reported by Liu *et al.* (2016), was found to lower the titanium alloys' corrosion rate. However, our study did not consider glucose concentrations above 200 mg dL^{-1} , so there is no evidence of how the alloys would perform at higher glucose concentrations, such as 216 mg dL^{-1} . Faverani *et al.* (2014) investigated the influence of glucose and lipopolysaccharide on the corrosion behavior of the commercial Ti-6Al-4V alloy. They concluded that glucose alone did not substantially impact the corrosion

behavior of the alloy. Although the alloy's corrosion potential decreased, the overall corrosion properties were not altered. This does not fully correlate with our results and that of Liu *et al.* (2016). The results in this chapter show that a glucose concentration of up to 200 mg dL⁻¹ improved the corrosion resistance of the titanium alloys, while the investigation by Liu *et al.* (2016) showed that a glucose concentration of up to 216 mg dL⁻¹ improved the corrosion properties of TA2 and a glucose concentration beyond 216 mg dL⁻¹ was detrimental to the properties of TA2.

It is worth noting that the results in these investigations, including ours, will not be entirely the same mainly because the alloys under investigation are different, which play a crucial role in the results obtained. The alloying elements and types of protective film formed would alter the corrosion properties of the different alloys. In addition, some inconsistencies in the results are also due to the differences in the electrolytes used and the conditions under which they were used. Faverani *et al.* (2014) used a simulated body fluid at 37°C and a pH of 7.4. Liu *et al.* (2016) used HBSS but conducted their potentiodynamic tests with different testing parameters (scanning range ± 200 mV and scanning speed = 10 mV s⁻¹) to ours. The scanning rate of 10 mV s⁻¹ is significantly higher than the recommended standard scanning rate (0.1667 mV s⁻¹) used in our study, which may render the testing system unstable, thus altering the results obtained.

5.5. Conclusion

From the results obtained in this chapter, it can be inferred that the experimental alloys exhibited favourable corrosion resistance when exposed to simulated body fluid conditions. The corrosion resistance of these alloys was comparable, and even superior in certain instances, to that of the commercial alloy. In 0.9 wt.% sodium chloride solution and HBSS, the Ti-4.5Al-1V-3Fe and Ti-3Fe alloys display superior resistance to corrosion compared to the commercial alloy. The experimental alloys, which incorporated iron as a β -stabilizing element, exhibit reduced susceptibility to corrosion compared to the commercial alloy. This was evident from their higher corrosion potential values compared to the commercial alloy. Therefore, these alloys could serve as a suitable alternative to the toxic and expensive Ti-6Al-4V alloy in making biomedical implants. The experimental alloys perform better in glucose environments. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe show superior resistance to corrosion compared to the other alloys in the 100 mg dL⁻¹ and

200 mg dL⁻¹ glucose HBSS, respectively. Overall, the experimental alloys, including the commercial alloy, perform better at a slightly elevated glucose concentration of 200 mg dL⁻¹. Therefore, these alloys could be utilized by a person with a normal blood glucose concentration, as well as those living with diabetes. Notably, diabetic conditions are not the only cause of high blood glucose. Other disorders, such as pancreatitis, pancreatic cancer, Cushing's syndrome, Addison's disease, and other alterations of the adrenal glands, also cause elevated blood glucose levels Faverani *et al.* (2014). It is, therefore, important to conduct more investigations on the effect of glucose concentrations on the properties of titanium alloy biomaterials.

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Chapter 6: Tribocorrosion Evaluation

Tribocorrosion behavior of low-cost experimental titanium alloys in simulated body fluids

In this chapter, a brief introduction into tribocorrosion and the need to subject various biomaterials, particularly titanium alloys to tribocorrosion tests is given. The results of the tribocorrosion tests that were conducted in the various simulated body fluids (normal Hanks balanced salt solution (HBSS), pre-diabetic HBSS, and diabetic HBSS) are presented. These results are also discussed in detail. This chapter follows a manuscript format that will be submitted to the journal of *Mechanical Behavior of Biomedical Materials*.

6.1. Introduction

The biomedical industry, particularly the bioimplant industry, has seen tremendous growth over the past few years and continues to grow as a result of the increased need for bioimplants across all age groups across the world (Geetha *et al.*, 2009). The main driving force for this growth is the aging population and associated issues of osteoporosis and osteoarthritis. It has been reported that approximately 90% of people over 40 years old suffer from degenerative and inflammatory diseases, which results in difficult mobility and subsequent unbearable pain (Fang, 2018). Apart from the aging population, road accidents contribute tremendously to the bioimplant industry. According to the World Health Organisation, as of 2018, approximately 50 million people suffer non-fatal injuries as a result of road accidents, with many incurring a disability as a result of their injury (World Health Organization, 2018). These non-fatal injuries are related to bone fractures which result in the need for bone/joint replacement surgery. Young and active people such as athletes are also likely to face bioimplant surgery due to the fracture and excessive strain they may experience during their various physical activities (Fang, 2018). In addition to this, diabetes, a chronic disease that occurs either when the pancreas does not produce enough insulin or when the body cannot effectively use the insulin it produces, results in various disabling and life-threatening health issues which include heart attacks, strokes, and kidney failures (nephropathy) (International Diabetes Federation, 2021). In addition to this, diabetes can cause nerve damage (neuropathy) and

poor blood flow in the feet thus leading to foot ulcers and ultimately foot amputation (International Diabetes Federation, 2021). It is becoming increasingly important to factor in diabetic patients in the manufacturing of bioimplants because as of 2021, it has been estimated that 537 million people are living with diabetes and this number is set to increase to 783 million by the year 2045 (International Diabetes Federation, 2021).

The field of bioimplant manufacturing is closely linked to the development of biomaterials (Fang, 2018). The field of biomaterials has been receiving substantial attention since the year 1969 when the world's first summit about biomaterials was held at Clemson University (Fang, 2018). Since then, the study of biomaterials has grown and expanded tremendously. The selection of the right and appropriate biomaterials for the manufacturing of a bioimplant, that is to perform a specific function in a specific part of the human body, is dependent on the knowledge of the various properties of the material. Proper selection of the biomaterials is critical for the long-term success of the manufactured bioimplants. Suitable and acceptable biomaterials must meet several requirements before their selection. Firstly, and most importantly, the material must be highly biocompatible which relates to it being non-toxic so as to avoid inflammatory and/or allergic reactions post implantation (Gain *et al.*, 2021). The longevity of bioimplants is governed by the biomaterial's corrosion and wear resistance (Geetha *et al.*, 2009; Pande and Dhattrak, 2021). The human body's environment is naturally corrosive due to the biological fluids found in the body. The interaction of the implant in the body with its counterparts and various other parts of the body (e.g., bones) inevitably results in wear. This is undesirable as it may lead to accumulation of the wear debris at the implant location which, apart from the potential toxicity, can result in implant loosening also known as osteolysis which is extremely painful and results in revision surgery thus cutting the implants life short (Geetha *et al.*, 2009; Hussein *et al.*, 2015). It is therefore important for the material to possess a high corrosion and wear resistance. Orthopaedic implants such as hip and knee joint replacement implants are subjected to the weight of the patient's body. Therefore, acceptable mechanical properties are a crucial requirement in order to prevent or minimise fatigue failure of the implant after the inevitable millions of cyclic loading (Fang, 2018). Lastly but equally important, the manufacturing processes of bioimplants are expected to be economically viable to allow for the bioimplants accessibility to the greater population.

The common biomaterials in use today are ceramics, polymers, and metallic alloys. Ceramics have been exploited since the 1970s mainly due to their excellent biocompatibility, high hardness, and excellent corrosion resistance (Dorozhkin, 2018; Ajmal *et al.*, 2022). However, the use of ceramics as biomaterials has been limited due to some of their poor mechanical properties (Dorozhkin, 2018). Polymers are now frequently applied in bioimplant manufacturing, commonly as acetabular cups, due to their ease of manufacturability, adequate mechanical properties, and low cost (Hussein *et al.*, 2019; Ajmal *et al.*, 2022). However, their relatively low strength hinders their application in hard tissues thus placing a limitation on their use in the bioimplant industry. Metallic alloys are currently the biomaterials of choice for the manufacturing of bioimplants today. The commonly employed metallic alloys in the manufacturing of bioimplants today are stainless steels, cobalt-based alloys, and titanium alloys (Hussein *et al.*, 2015). However, titanium and its alloys are the most favoured and most promising metallic biomaterials today due to a vast number of reasons. The combinations of excellent biocompatibility, high strength, low density, and good mechanical properties has resulted in the continued demand of these alloys in the biomedical industry (Chen and Thouas, 2015; Pandey *et al.*, 2020; Anene *et al.*, 2021). Ti-6Al-4V is the most commonly employed titanium-based alloy and takes up about 45% of the total titanium alloy production (Chen and Thouas, 2015). This alloy was initially developed for the aerospace industry, but it later found its way to the biomedical industry due to its good biocompatibility. Although titanium has been proven to be non-toxic and totally inert to the human body, Ti-6Al-4V alloy implants have been reported to cause health issues such as osteomalacia, allergic reactions, and peripheral neuropathy which are possibly related to the release of aluminium and vanadium from the alloy (Chen and Thouas, 2015). This led to the development of new titanium alloys. One option has been to develop titanium alloys by replacing aluminium and vanadium with relatively safer elements such as Zr, Ta, Mo, and Nb. This led to the development of β titanium alloys (Geetha *et al.*, 2009; Kaur and Singh, 2019). These alloys are however very expensive compared to the normal $\alpha+\beta$ titanium alloys. A huge number of researchers focus today on developing new inexpensive and less toxic $\alpha+\beta$ titanium alloys. Bodunrin *et al.* (2018) developed a new series of low-cost titanium alloys by modifying the commercial alloys (Ti-6Al-4V) composition. They found that the partial substitution of vanadium with an inexpensive beta stabilizing element, iron, produced alloys with good mechanical properties comparable to that of the commercial alloy and in some cases better. These alloys are namely Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-3Fe. The corrosion behavior of

these alloys in various environments which include 3.5% NaCl, 0.5M H₂SO₄, and simulated body fluids (0.9% NaCl solution, and Hanks Balanced Salt Solution) was evaluated. In all environments, the alloys performed well with a corrosion resistance comparable to that of the commercial alloy and in some cases better. Because of the combined effects of corrosion and wear on the biomedical implants in application, it is imperative to study the tribocorrosion behavior of these alloys in simulated body fluids.

Tribocorrosion can be described as the deterioration of a material caused by a dual process involving both wear and corrosion. It encompasses a wide range of interactions between mechanical actions and chemical or electrochemical occurrences (Licausi *et al.*, 2013). The concurrent mechanical and electrochemical processes occurring at the contact interface are not isolated from each other; rather, they intricately influence one another. To elaborate, the mechanical disruption of the protective surface oxide layers on passive materials can accelerate the corrosion rate of the exposed metal (Mathew *et al.*, 2009). Yazdi *et al.* (2020) conducted a study on the tribocorrosion behavior of Ti-6Al-4V in a simulated body fluid under various loads. They found that the mechanical disruption of the passive oxide film resulted in an increase in corrosion of the alloy as the corrosion current density acquired from the polarization results increased by three orders of magnitude and the OCP experienced a cathodic shift. Additionally, the presence of these protective oxide surface layers can impact the mechanical characteristics of the material's surface and the behavior of third body particles in contact with it (Licausi *et al.*, 2013). Dimah *et al.* (2012) studied the tribocorrosion behavior of commercially pure titanium and Ti-6Al-4V in phosphate buffered saline solution (PBS). It was concluded that the characteristics of the passive film on the alloy surface has a significant influence on the tribocorrosion resistance of the alloys. The oxide rich layer formed on Ti-6Al-4V was more protective than the CP-Ti. This was attributed to the TiO/Ti₂O₃ passive film which is enriched with Al₂O₃ and other vanadium oxides. This led to an increased protection compared to the simple TiO passive film formed on the CP-Ti. Plastic deformation is also known to alter the mechanical properties of the alloys which has a direct impact on the tribocorrosion behavior of the alloys. In the study by Yazdi *et al.* (2020), the alloys experienced higher plastic deformation at higher loads (30N) which resulted in the alloys possessing a higher hardness. This was beneficial as it resulted in the alloy having lower wear rates. Implants typically undergo tribocorrosion as they must withstand significant loads within corrosive settings, such as exposure to saliva or synovial fluid (Pina *et al.*, 2015). Apart from loads,

implants and their counterparts will move against each other at various speeds in application and this is expected have an influence on the wear and tribocorrosion of the implant material. Namus *et al.* (2021) studied the influence of various sliding speeds on the tribocorrosion behavior of Ti-6Al-4V in a simulated body fluid. They found that higher sliding speeds had a negative influence on the tribocorrosion behavior of the alloy as they led to higher wear rates. This was attributed to the alloy repassivating during the sliding at the lower sliding speeds whereas it struggled to repassivate during sliding at the higher sliding speeds. The discharge of metallic ions resulting from both corrosion and wear is of utmost significance as it has the potential to negatively impact the compatibility of these implants with the human body and compromise their mechanical strength (Dimah *et al.*, 2012; Licausi *et al.*, 2013). It is therefore imperative to evaluate the resistance of biomaterials to corrosion and corrosive wear to ensure their safety within the corrosive environment of the human body. Enhancing wear resistance and the ability to rapidly repassivate can help reduce the vulnerability of alloys to tribocorrosion. To ensure the biological suitability of metallic implants, it is essential to gain a deeper understanding of how metals behave in biological conditions affected by both wear and corrosion. Consequently, there is a necessity for an approach that integrates electrochemistry and tribology to investigate these intricate processes and evaluate potential biomaterials effectively.

In this chapter, the tribocorrosion behavior of low-cost experimental titanium alloys (Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe) was investigated under open circuit potential (OCP) and potentiostatic conditions in normal Hanks Balanced Salt Solution (HBSS), 100 mg/dL glucose HBSS, and 200 mg/dL glucose HBSS which simulates the human body environment of a diabetic individual.

6.2. Materials and methods

6.2.1. Materials

Refer to Section 3.1 and Section 3.2 for the materials used as well as the sample preparation procedure.

6.2.2. Tribocorrosion testing methodology

Refer to Section 3.6 for the tribocorrosion test procedure and wear rate calculations.

6.2.3. Characterisation

Refer to Section 3.3 for the details of the alloy characterisation employed to analyse the alloys after the tribocorrosion tests.

6.3. Results

6.3.1. Tribocorrosion behavior in normal HBSS

6.3.1.1. *Evolution of open circuit potential (OCP) during tribocorrosion*

The evolution of the OCP as a function of testing time in normal HBSS of the titanium alloys that was monitored before, during and after sliding is shown in **Figure 6.1**. During the first 900 s before sliding was initiated, the OCP represents the presence and buildup of the passive oxide film on the surface of the titanium alloys in contact with the HBSS. Immediately after the initiation of sliding at about 900 s, a cathodic drop in the potential was observed for all the alloys under investigation. This is expected to happen and is typical of passive alloys as the passive film is destroyed when the alumina ball rubs against the alloy, thus exposing the bare alloy to the corrosive solution. This initiates electrochemical activity thus causing a drop in the potential (Bryant and Neville, 2016). The fluctuations in the potential observed during sliding are an indication of dynamic depassivation and repassivation of the passive film on the surface of the alloys (Berradja *et al.*, 2006; Sivakumar *et al.*, 2011).

Before the first stage of sliding commenced, Ti-3Fe was the noblest alloy with a potential of -0.42V. The potential of this alloy dropped to -1.03V when sliding commenced. This resulted in a potential drop (ΔE) of -0.61V. Very slight fluctuations in the potential are observed during the first 15 minutes of sliding. After 15 min of rubbing, the potential experienced an anodic shift within the anodic domain to a maximum of -0.54V. This is an indication of spontaneous repassivation. Greater fluctuations in this second stage of sliding are observed and this indicates that there is greater dynamic depassivation and repassivation in this stage. There is once again an abrupt shift in the potential within the anodic domain to a potential of -0.57 V at the end of the test. This indicates that the alloy has the ability to regain the passive state. This alloy experienced the smallest potential fluctuations in both the first and second stage of sliding which is an indication that compared to the rest of the alloys, this alloy struggled to regain its passive state after disruption in its passive film. A similar observation was reported by More *et al.* (2011) where they found that the OCP of the alloy containing iron, Ti-6Al-4Fe, decreased and stabilised to a lower value

compared to the other alloys under investigation with iron. This was an indication that no full recovery of the passivity took place during sliding and that it struggled to regain the passive state.

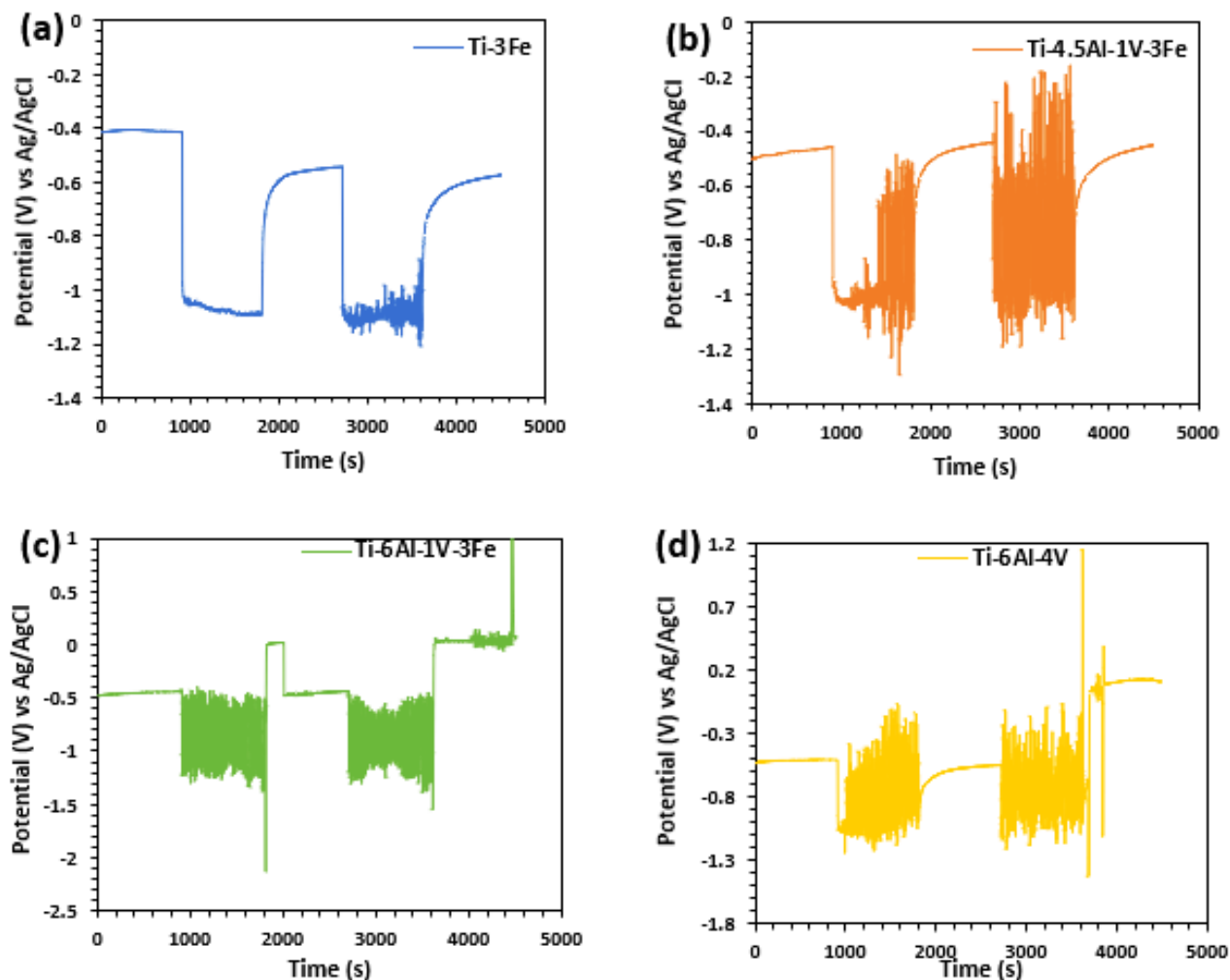


Figure 6.1: Evolution of OCP with time during sliding of an alumina ball against titanium alloys during OCP tribocorrosion for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe and (d) Ti-6Al-4V.

For Ti-4.5Al-1V-3Fe, very slight fluctuations in the potential are observed until around 1080 s. After this point, more aggressive fluctuations are observed which are an indication of abrupt local depassivation and repassivation of the passive film. After the sliding, the alloy repassivated spontaneously as a shift in the potential within the anodic domain was observed. Greater fluctuations are observed in the second stage of sliding. The fluctuating potential exceeded the

starting potential, and this indicates that there is greater dynamic depassivation and repassivation in this stage. The passive film rebuilt itself much quicker in the second stage of rubbing. This could be attributed to the greater electrochemical activity of the alloy surface in this stage. There is an abrupt shift in the potential within the anodic domain at the end of the test. This is higher than the initial OCP and this is the ideal situation as it indicates that the newly formed passive film, grown after the removal of the original passive film during the sliding, has similar properties to the naturally formed film present on titanium before the mechanical action (Licausi *et al.*, 2013). This observation was reported by Licausi *et al.* (2013) during a study conducted on the tribocorrosion behavior of a cast and sintered Ti-6Al-4V against an alumina ball in artificial saliva.

Looking at the Ti-6Al-1V-3Fe and Ti-6Al-4V alloys, abrupt fluctuations in the potential are seen in both the first and the second stage of sliding from the very beginning until the sliding is stopped. This indicates that the alloys can repassivate spontaneously throughout the sliding. The potential fluctuations during sliding came close to the initial potential while surpassing it at some points. At the end of the second stage of sliding, Ti-6Al-1V-3Fe passivated to a potential much higher than its starting potential in the positive domain. Therefore, this alloy can regain its passive state more spontaneously than the rest of the alloys under investigation. **Table 6-1** presents the OCP values of the titanium alloys before, during, and after sliding. This gives a clearer view of the repassivation capabilities of the alloys during the OCP tribocorrosion tests. As mentioned previously, Ti-3Fe had the noblest potential compared to the rest of the alloys before sliding commenced. During the first and second stage of sliding, the commercial alloy had the highest average OCP indicating its greater ability to repassivate. At the end of the tribocorrosion OCP tribocorrosion tests (stage 2), both the commercial Ti-6Al-4V alloy and Ti-6Al-1V-3Fe repassivated to potentials of 0.095 V and 0.059 V respectively. These were quite higher than the initial potentials recorded during the experiment. Ti-3Fe and Ti-4.5Al-1V-3Fe repassivated to potentials below the initial/starting potentials. This is an indication that the passive films formed at the end of the tests for these alloys were slightly weaker/poorer than the starting passive films, This is consistent with the observation reported in previous work (Licausi *et al.*, 2013).

Table 6-1: Average values of the potential measured before (OCP_0), during ($OCP_{sliding}$) and after sliding (OCP_{final}) of the Ti6Al4V alloy sliding against an alumina ball

<i>Alloys</i>	<i>OCP₀ (V)</i>		<i>OCP_{sliding} (V)</i>		<i>OCP_{final} (V)</i>	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
<i>Ti-3Fe</i>	-0.409 ± 0.003	-0.582 ± 0.066	-1.07 ± 0.016	-1.085 ± 0.044	-0.582 ± 0.066	-0.625 ± 0.060
<i>Ti-4.5Al-1V-3Fe</i>	-0.481 ± 0.012	-0.494 ± 0.065	-0.956 ± 0.131	-0.774 ± 0.209	-0.494 ± 0.065	-0.517 ± 0.057
<i>Ti-6Al-1V-3Fe</i>	-0.456 ± 0.011	-0.365 ± 0.207	-0.889 ± 0.236	-0.914 ± 0.204	-0.365 ± 0.207	0.059 ± 0.300
<i>Ti-6Al-4V</i>	-0.505 ± 0.006	-0.587 ± 0.051	-0.790 ± 0.230	-0.709 ± 0.198	-0.587 ± 0.051	0.095 ± 0.130

The evolution of the coefficient of friction (COF) as a function of time during the tribocorrosion tests is presented in **Figure 6.2**. For the alloys Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-4V, there is a clear run-in period for a few seconds at the commencement of each stage of sliding. This run-in period corresponds to the initial sliding process between the two surfaces and it's also an indication of the initial adherence of the two surfaces to each other (Manhabosco *et al.*, 2011). Thereafter, a steady state is established until the end of the sliding periods. Ti-6Al-1V-3Fe does not display a clear run-in period before the commencement of the two stages of sliding. The COF values of these alloys lie below 0.45. This is typical of metal-ceramic contact (Runa *et al.*, 2013). Ti-3Fe showed the highest COF compared to the rest of the alloys. A high COF is attributed to a lower hardness as well as a large amount of third body particles entrapped in the contact region because of poorer wear resistance/higher wear rates. These particles have also been said to contribute to the great oscillations in the COF (Manhabosco *et al.*, 2011; Wang *et al.*, 2017). The commercial alloy, Ti-6Al-4V, displayed the lowest COF in the negative range (-0.035). This is an indication that this alloy had better tribocorrosion resistance under these conditions compared to the rest of the alloys (Manhabosco *et al.*, 2011). However, it is worthy to note that a negative COF means that there is no friction between the two surfaces so the motion between the two surfaces is accelerated (Kumar and Suman, 2017). This is not ideal for biomedical implants as some friction is required between the two surfaces in order to allow for the stability of the bioimplant in application (Hussein *et al.*, 2015; Seidlitz and Kip, 2018; Moghadasi *et al.*, 2022; Zhang *et al.*, 2022). The fluctuations in the COF of Ti-6Al-1V-3Fe can also be attributed to a larger amount of third body particles generated between the contact region during the tribocorrosion tests (Manhabosco *et al.*, 2011; Wang *et al.*, 2017).

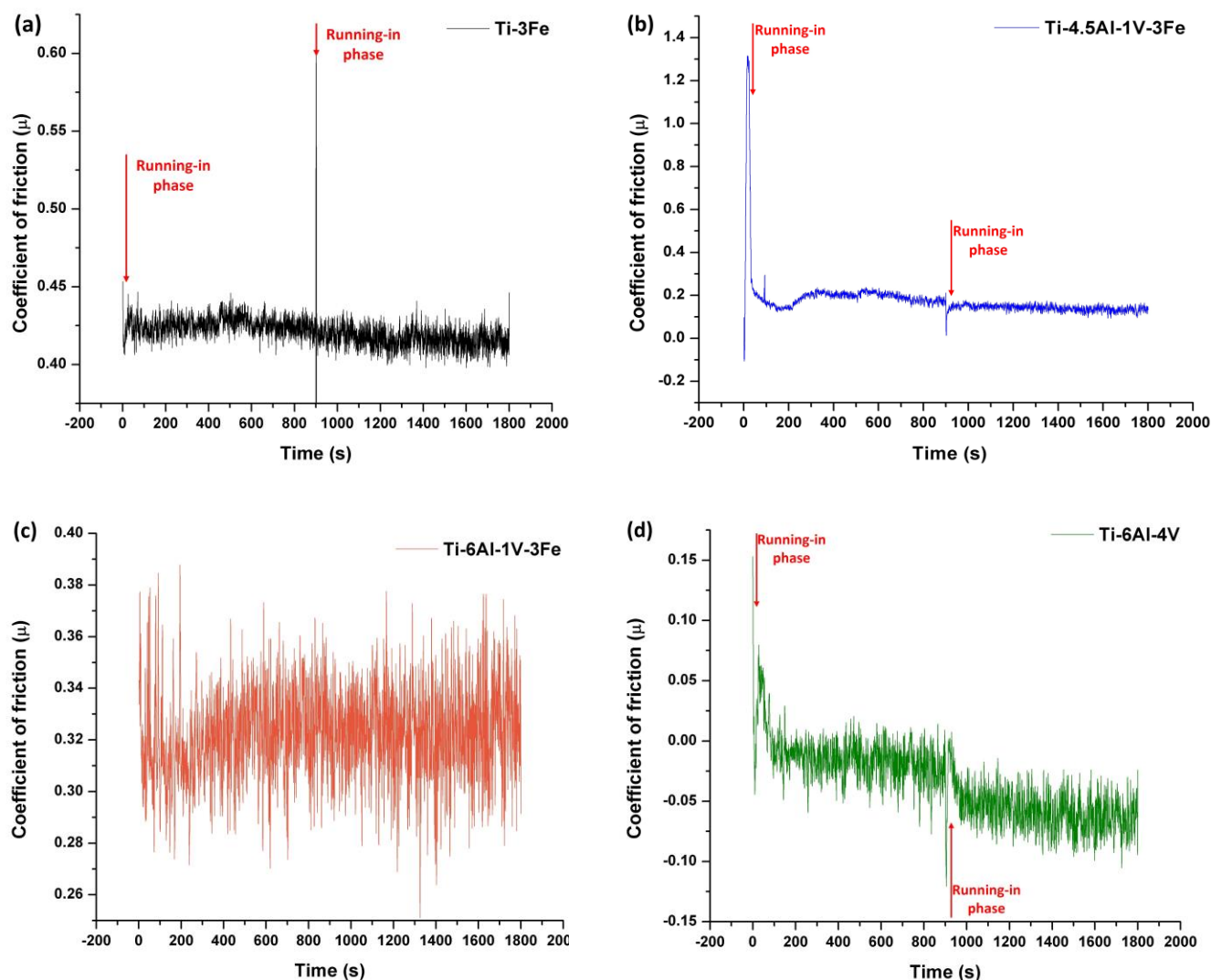


Figure 6.2: Evolution of coefficient of friction as a function of testing time during OCP tribocorrosion for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V

6.3.1.2. Evolution of anodic current (Potentiostatic) during tribocorrosion

Tribocorrosion tests were conducted under an imposed passive potential of +0.5V to study the properties of the passive surface films under controlled electrochemical conditions. The current vs time curves for the alloys tested in normal HBSS are presented in **Figure 6.3**. For the first 300 s, cathodic cleaning was employed on all of the alloys, thereafter, a disturbance in the form of the applied anodic potential was imposed, hence the little spike seen at the 300 s mark. The alloys were allowed to stabilise in the solution for 1200 s before sliding commenced. When sliding was initiated, an abrupt anodic increase in the current of all the alloys was observed.

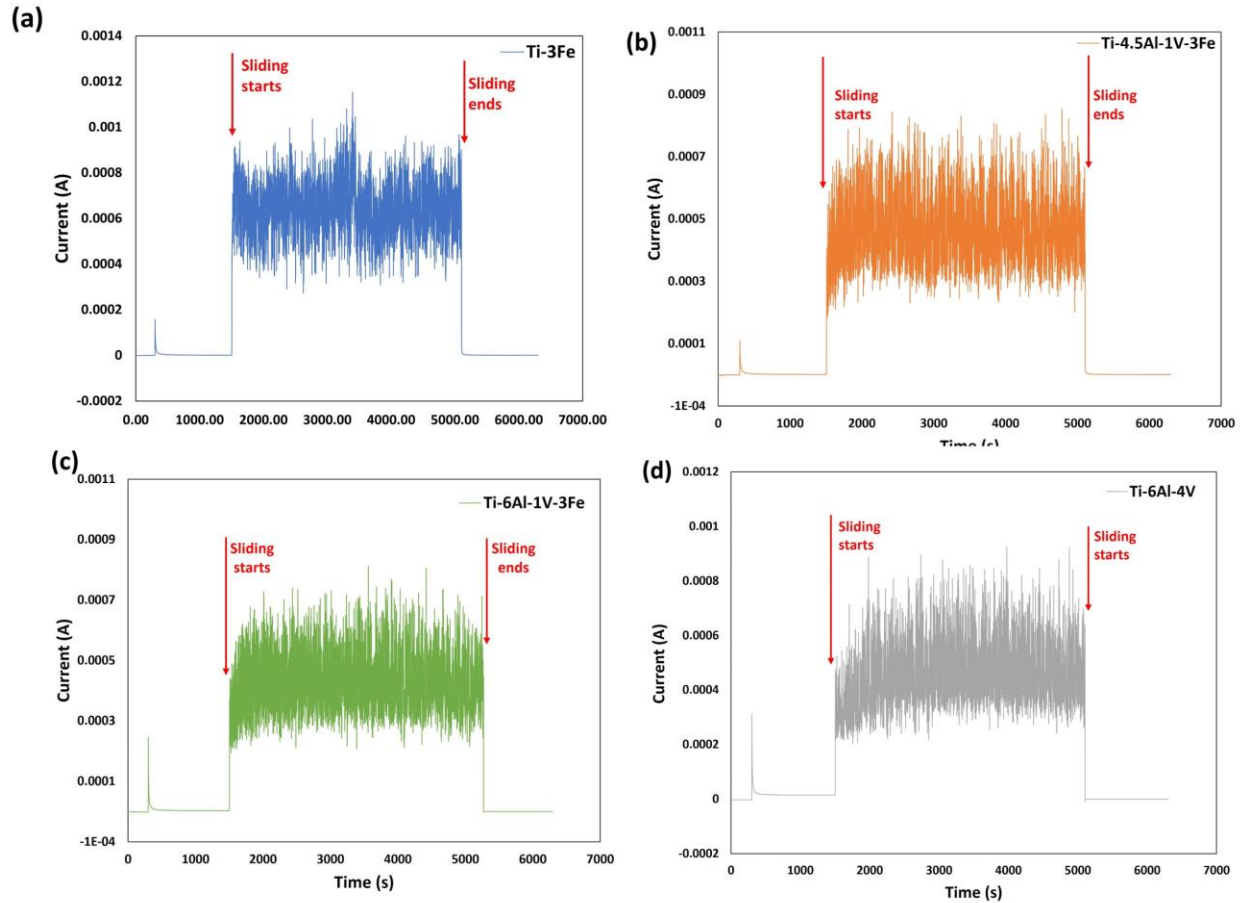


Figure 6.3: Evolution of current as a function of testing time in normal HBSS for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V.

This was expected as the depassivation of passive metallic alloys leads to anodic metal oxidation and higher dissolution rate of the alloys as the bare metal becomes exposed to the electrolyte (More *et al.*, 2011). During sliding, the current fluctuated in the case of all the alloys. This fluctuation is due to the depassivation and repassivation of the passive oxide film on the alloy surface and it is maintained around a constant value. The fluctuations indicate that the passive film is continuously being destroyed and reformed, indicating that the alloys have the ability to regain their passive state under sliding at anodic potentials. However, they are unable to recover and repassivate fully and completely throughout the mechanical action (Runa *et al.*, 2013). The isolated current peaks represent local repassivation points that rapidly depassivated (Mischler, 2008; Bryant and Neville, 2016). Ti-3Fe shows larger spikes in the current during sliding compared to the rest of the alloys. This is an indication that this alloy has poorer repassivation capabilities compared to the other alloys under investigation as higher current values are indicative of higher oxidation/dissolution

rates (Runa *et al.*, 2013). **Table 6-2** presents the average values of current before (I_0), during ($I_{sliding}$), and after sliding (I_{final}) during the potentiostatic tribocorrosion tests in normal HBSS.

Table 6-2: Average values of the current measured before (I_0), during ($I_{sliding}$), and after sliding (I_{final}) of the titanium alloys sliding against an alumina ball.

<i>Alloys</i>	<i>I_0 (A)</i>	<i>$I_{sliding}$ (A)</i>	<i>I_{final} (A)</i>
<i>Ti-3Fe</i>	2.75E-06 ± 9.0E-06	6.40E-04 ± 1.00E-04	1.05E-06 ± 4.1E-06
<i>Ti-4.5Al-1V-3Fe</i>	2.29E-06 ± 6.5E-06	4.60E-04 ± 1.00E-04	7.13E-07 ± 1.4E-06
<i>Ti-6Al-1V-3Fe</i>	5.12E-06 ± 1.2E-05	4.22E-04 ± 1.00E-04	-6.72E-10 ± 5.0E-08
<i>Ti-6Al-4V</i>	1.78E-05 ± 1.5E-05	4.32E-04 ± 1.00E-04	-6.99E-09 ± 2.4E-07

Ti-3Fe exhibited the highest average current (6.40E-04 A) during sliding. In contrast, Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V displayed average current values within a closely clustered range. Notably, Ti-6Al-1V-3Fe demonstrated the lowest average current (4.22E-04 A) during sliding. This observation suggests that Ti-6Al-1V-3Fe exhibited the lowest dissolution/oxidation rate throughout the sliding process. After 3600 s of sliding, a notable decrease in the current was observed for all the alloys. This reduction was attributed to the anodic repassivation of the alloy surfaces. It is worth noting that the post-sliding current values were consistently lower than those measured before the commencement of sliding. This phenomenon can be attributed to the modification of the alloy surface, as the passive film was found to continue growing in areas not subjected to rubbing, thereby reducing the current below the initial levels, a phenomenon documented in references (Archard, 1953; Berradja *et al.*, 2006; Bryant and Neville, 2016). Therefore, Ti-6Al-1V-3Fe and Ti-6Al-4V demonstrated a significant decrease in current after sliding, surpassing the other alloys in achieving notably lower post-sliding current values. This outcome is indicative of a more stable and adherent passive film in these alloys.

The evolution of coefficient of friction as a function of time for the titanium alloys during the potentiostatic tribocorrosion tests is shown in **Figure 6.4**. All the alloys under investigation experienced a running-in phase for a few seconds when sliding was initiated which corresponds to the initial sliding process between two surfaces (Manhabosco *et al.*, 2011). A steady state is

established after the running-in phase for all the titanium alloys after about 1500 s. A few sharp spikes are seen in the COF of Ti-3Fe throughout the duration of the test which was due to the entrapment of third body particles which increases the COF (Manhabosco *et al.*, 2011). The lower hardness of Ti-3Fe compared to the rest of the alloys results in it producing a larger amount of third body particles that become entrapped between the two surfaces during sliding (Manhabosco *et al.*, 2011). Throughout the sliding, fluctuations in the COF around a similar range are observed for all the alloys under investigation. These fluctuations or oscillations can be explained by the third body effect (Sharma and Sehgal, 2012); the stick-slip behavior that occurs under applied load leading to the periodic accumulation and removal of wear debris between the alumina ball and the titanium alloy surface (Sivakumar *et al.*, 2011; Runa *et al.*, 2013b; Ortega *et al.*, 2018). The frictional behavior of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe and the commercial alloy, Ti-6Al-4V, was quite similar as the average COF values attained for these alloys was quite similar (0.26, 0.23, and 0.18 respectively). Ti-3Fe showed the lowest average COF of 0.12. This contrasted with the results obtained during the OCP tests in the same normal HBSS environment as the OCP tests resulted in Ti-3Fe having the highest COF compared to the rest of the titanium alloys.

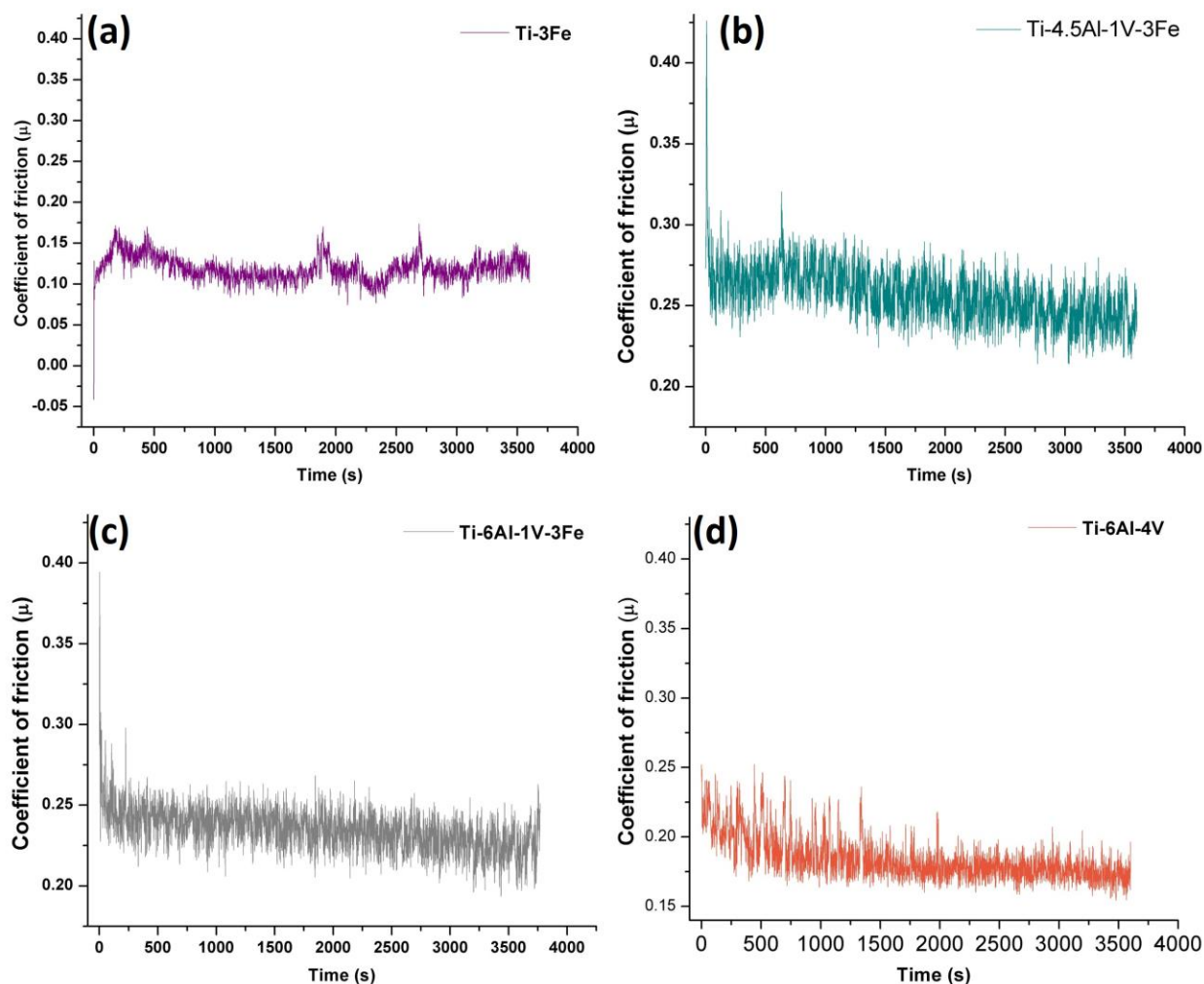


Figure 6.4: Evolution of coefficient of friction as a function of testing time during potentiostatic tribocorrosion tests for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V

6.3.1.3. *Wear volume loss under OCP conditions*

Four areas of the wear track were analysed and recorded using the profilometer. These four profile measurements were then averaged and plotted as a single profile. These profiles represent the penetration depth versus the wear track width of the wear track on the alloy surface. **Figure 6.5** presents the wear track profiles for the titanium alloys after the tribocorrosion tests at open circuit potential. The wear profiles of the alloys, particularly Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V were quite comparable to each other and this is an indication that their wear/tribocorrosion mechanisms could be quite similar. Ti-6Al-1V-3Fe had the deepest wear track compared to the rest of the alloys as its maximum penetration depth (P_{dmax}) was $-0.0835 \mu\text{m}$ followed by Ti-3Fe with a maximum penetration depth of $-0.0763 \mu\text{m}$.

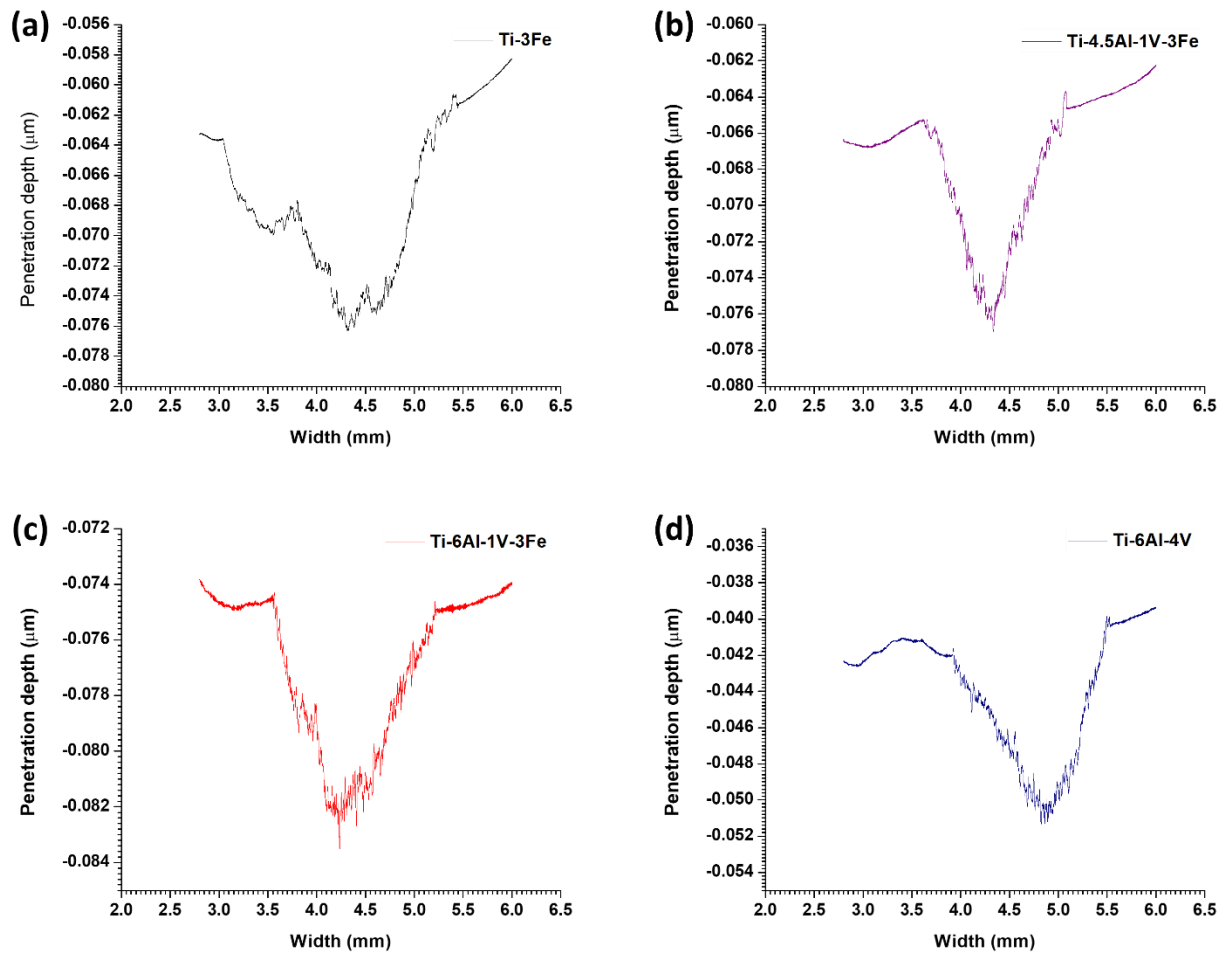


Figure 6.5: Penetration depth versus wear track width profiles for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under OCP conditions in normal HBSS

The commercial alloys, (Ti-6Al-4V) wear scar was the shallowest with a maximum penetration depth of $-0.515 \mu\text{m}$. The depth of Ti-3Fe and Ti-4.5Al-Fe were quite comparable to each other. Ti-3Fe had the widest wear track as its wear track width was the highest (2.43 mm) compared to the other alloys. The wear track width of the experimental alloy Ti-6Al-1V-3Fe was the same as that of Ti-6Al-4V (1.6 mm). The wear track width data is shown in Table A-1 in Appendix A. This data was used to calculate the total worn volume of the titanium alloys. The worn volume as well as the wear rates of the alloys tested in the normal HBSS is shown in **Table 6-3**. The total worn volume under OCP conditions corresponds to the wear volume as a result of the mechanical action (Licausi *et al.*, 2013). Ti-3Fe experienced the greatest material loss of $2.10\text{E-}03 \text{ mm}^3$, while the commercial alloy lost the least amount of material throughout the entire duration of the

tribocorrosion tests ($1.01\text{E-}03\text{ mm}^3$). The material loss experienced by the experimental Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe was found to be closely comparable to that of the commercial alloy supporting the initial observation that these alloys have similar tribocorrosion behavior. Although Ti-6Al-1V-3Fe had the deepest wear track, its wear rate was not the highest. This can be attributed to its smaller worn surface area in comparison to Ti-3Fe which contributed to it having a lower total wear volume. Ti-3Fe had the greatest wear rate compared to the rest of the alloys. This is supported by the alloys greater worn surface area, total worn volume as well as its deep wear track. All of this could be attributed to the weaker mechanical properties of this alloy, such as its hardness, compared to the rest of the alloys under investigation.

Table 6-3: OCP tribocorrosion parameters of experimental and commercial titanium alloys in normal HBSS

<i>Ti alloys</i>	<i>Worn surface area (mm²)</i>	<i>Max penetration depth (mm)</i>	<i>Total wear volume (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	27.48	-7.63E-05	2.10E-03	3.49454E-06
<i>Ti-4.5Al-1V-3Fe</i>	17.25	-7.70E-05	1.33E-03	2.21375E-06
<i>Ti-6Al-1V-3Fe</i>	18.24	-8.35E-05	1.52E-03	2.5384E-06
<i>Ti-6Al-4V</i>	19.6	-5.15E-05	1.01E-03	1.68233E-06

6.3.1.4. Wear volume loss under Potentiostatic conditions

Figure 6.6 presents the wear track profiles of the titanium alloys tested under potentiostatic conditions in normal HBSS. The profiles of all the titanium alloys look quite similar, while that of Ti-3Fe presents a much wider looking profile compared to the rest of the alloys. The wear track width of all the alloys is shown in Table A-1 in Appendix A. Ti-3Fe also presents a deeper looking profile. This is corroborated by the data presented in **Table 6-4** below which shows Ti-3Fe to have the biggest maximum penetration depth value ($1.22\text{E-}04\text{ mm}$). This is followed by the commercial alloy Ti-6Al-4V having a maximum penetration depth of $9.28\text{E-}05\text{ mm}$. Ti-4.5Al-1V-3Fe displays the shallowest wear track as it had the small maximum penetration depth. These results are

different to those obtained under OCP conditions as the commercial alloy displayed the shallowest wear track in that case. Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V do however display very similar parameters like in the OCP tests, thus indicating that they have similar tribocorrosion behavior in the normal HBSS.

The wear track area, P_{dmax} , and total wear volume values of the titanium alloys tested under potentiostatic conditions are greater than for the alloys tested under OCP conditions. The greater wear volume loss is expected as under OCP conditions, no significant amount of active corrosion is taking place whereas the volume loss under potentiostatic conditions is comprised of the volume loss due to mechanical action as well as the volume loss due to corrosion (Mischler, 2008; Toptan *et al.*, 2019; Mehkri *et al.*, 2021). Again, the wear track area as well as the penetration depth of the alloys under potentiostatic conditions is larger, which indicates a larger weight loss in comparison to the alloys tested under OCP conditions. This corresponds to studies by many other researchers including Barão *et al.* (2021) who studied the tribocorrosion behavior of Ti-based dental implants in 0.9% NaCl solution. They found that the alloy that had the biggest and deepest wear scar (Ti-10Zr) showed a significantly higher worn volume loss compared to the rest of the alloys. In this study, as expected, Ti-3Fe had the greatest volume loss of $3.90E-03 \text{ mm}^3$. This then resulted in this alloy having the highest wear rate in comparison to the rest of the alloys. The lowest total volume loss was experienced by Ti-6Al-1V-3Fe. This alloy also had the lowest specific wear rate of $3.02E-06 \text{ mm}^3/\text{Nm}$. This can be attributed to the alloys mechanical properties such as its high hardness as well as its good repassivation abilities and possibly strong and stable passive film (Barão *et al.*, 2021; Bodunrin and Chown, 2021).

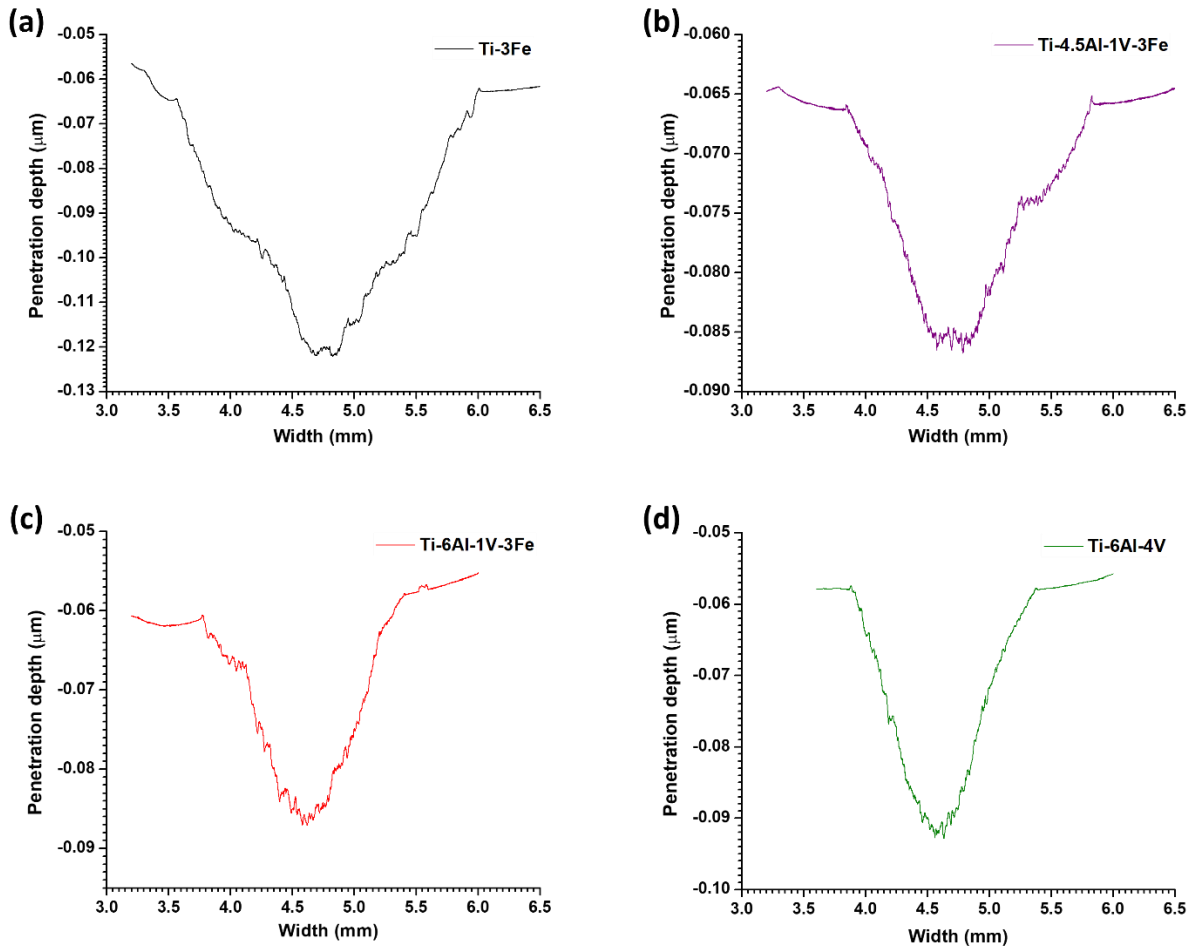


Figure 6.6: Penetration depth versus wear track width of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under potentiostatic conditions in normal HBSS

The volume loss as well as the specific wear rate of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V was once again similar in this case thus corroborating the comparable profiles and further substantiating the fact that these alloys may have very similar tribocorrosion mechanisms. The individual components of the total wear volume loss (V_{chem} (volume loss as a result of chemical wear or corrosion) and V_{mech} (volume loss as a result of mechanical wear)) are also presented in **Table 6-4**. V_{chem} for all alloys is bigger than the overall volume loss. This is attributed to the uncertainties in the actual valence number for the oxidation reactions taking place during the tribocorrosion tests.

Table 6-4: Tribocorrosion parameters of experimental and commercial alloys in normal HBSS tested under potentiostatic conditions

<i>Alloys</i>	<i>Area (mm²)</i>	<i>Maximum penetration depth (mm)</i>	<i>Total wear volume (mm³)</i>	<i>V_{chem} (mm³)</i>	<i>V_{mech} (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	31.91	-1.22E-04	3.90E-03	6.35E-02	-5.96E-02	6.50E-06
<i>Ti-4.5Al-1V-3Fe</i>	21.69	-8.68E-05	1.88E-03	4.56E-02	-4.38E-02	3.14E-06
<i>Ti-6Al-1V-3Fe</i>	20.79	-8.71E-05	1.81E-03	4.19E-02	-4.01E-02	3.02E-06
<i>Ti-6Al-4V</i>	21.83	-9.29E-05	2.03E-03	4.29E-02	-4.08E-02	3.38E-06

6.3.1.5. *Wear Morphology*

The morphology of the wear tracks on the titanium alloys that were tested in normal HBSS under OCP conditions and potentiostatic conditions are shown in **Figure 6.7** and **Figure 6.8** respectively. In both solutions, all the alloy wear tracks display visible scratches, grooves, and micro-ploughing which are parallel to the sliding movement. These are known as sub-mechanisms of the abrasive wear mechanism (Gahr, 1987; Fischer *et al.*, 2018; Chirico *et al.*, 2022). Therefore, abrasive wear is the predominant wear mechanism for these titanium alloys. The mechanical damage appears to be more prominent and severe in the alloys tested under anodic potential as opposed to those tested under OCP conditions. Although a more stable passive film is expected to form under anodic potential, the simultaneous effect of mechanical wear and corrosion at anodic potential results in the alloys experiencing a greater level of damage compared to OCP conditions where only mechanical wear is responsible for the material degradation.

Signs of surface plastic deformation which is indicated by the extruded material in the wear track as well as toward the edge of the wear track were also observed in all the alloys. Some of this is shown by the arrows in **Figure 6.7** (b) and **Figure 6.8** (d). Tiny, isolated and clumped up debris was observed on the wear track of the alloys. According to the EDX analysis, this debris consists of the bulk alloy elements as well as elements making up the electrolytes such as Na, Cl, P, K, and Ca. In the case of the alloys containing aluminium, elevated levels of aluminium were observed in the debris. This is said to be from the loss of material on the alumina surface (Licausi *et al.*, 2013). The alumina balls wear scars also showed many platelets of transferred titanium alloy material. The wear scars of the alumina balls tested under OCP conditions are shown in Figure B-1 in Appendix B. This is therefore an indication that adhesive wear is also a wear mechanism that was responsible for the degradation of the titanium alloys (Gahr, 1987; Fischer *et al.*, 2018). The darker/black wear debris as well as the grey patches seen on the Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V wear tracks are an indication of the tribochemical reactions wear mechanism as EDX analysis showed the presence of oxygen in these regions. The EDX spectra of Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe tested under OCP conditions showing the oxygen peaks are shown in Appendix C in Figure C-1.1 and Figure C-1.2 respectively. The EDX spectra of Ti-6Al-4V tested under potentiostatic conditions is shown in Figure C-2.1 in Appendix C. This oxygen could be an indication of the formation of oxide films on the surface of the alloys which is expected as titanium alloys are passive alloys which spontaneously form oxide films on their surface. This same

observation has been reported by other researchers (Hacisalihoglu *et al.*, 2015; Yazdi *et al.*, 2018a; Toptan *et al.*, 2019) which include Barão *et al.* (2021) where they found that the darker regions on the alloy surface were indicative of a thin passivation layer formed to protect the surface from tribocorrosion damage. This passive film was said to be made of the common TiO_2 and ZrO_2 which makes the passive film quite thick and stable enough to protect the alloys against tribocorrosion. Yazdi *et al.* (2018) found that the passive film formed on the Ti-6Al-4V surface was made up of oxides of the alloy elements such as TiO_2 and Al_2O_3 as well as phosphorous (titanium phosphates) and sodium from the saline electrolyte.

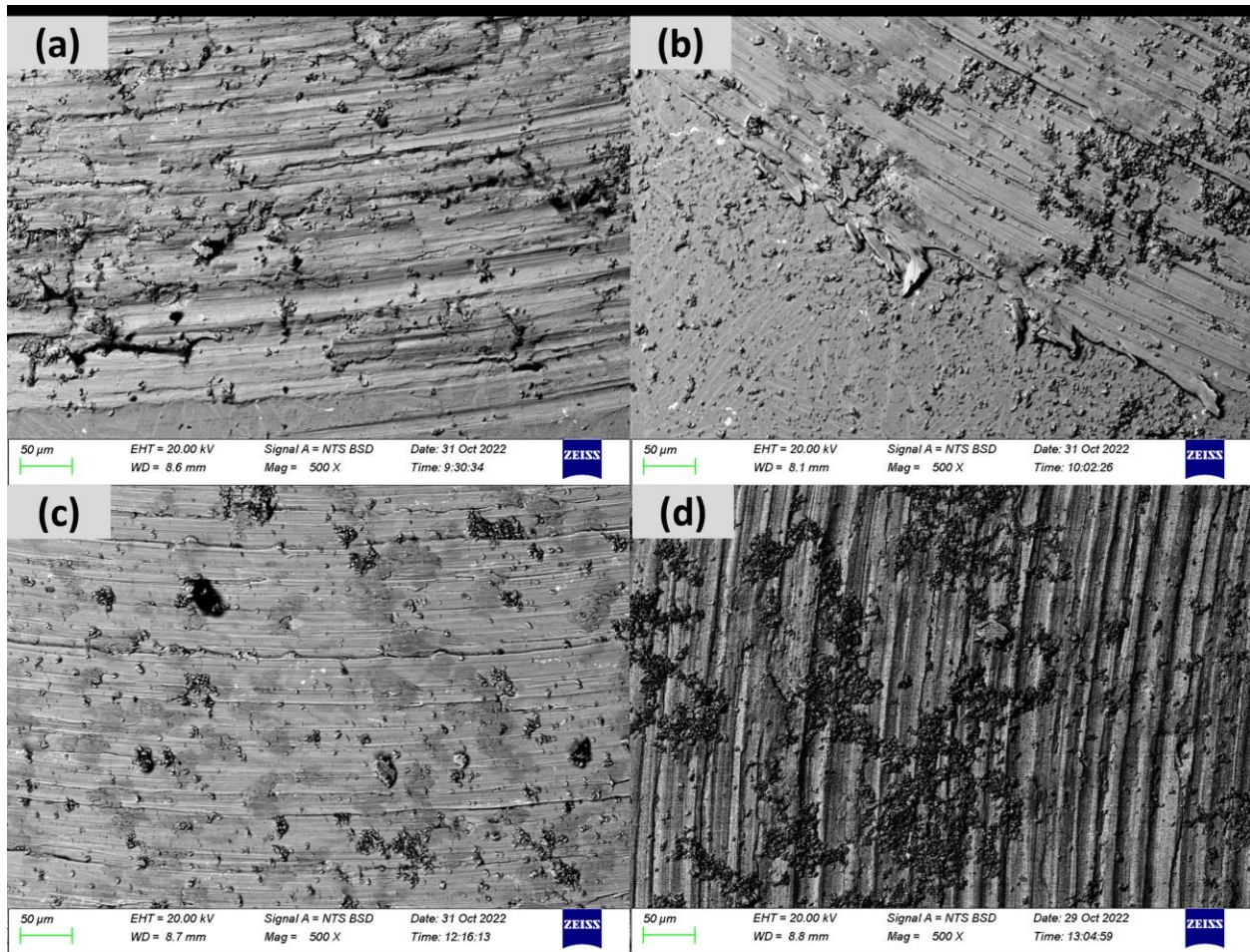


Figure 6.7: SEM images of the wear tracks for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under OCP conditions in normal HBSS.

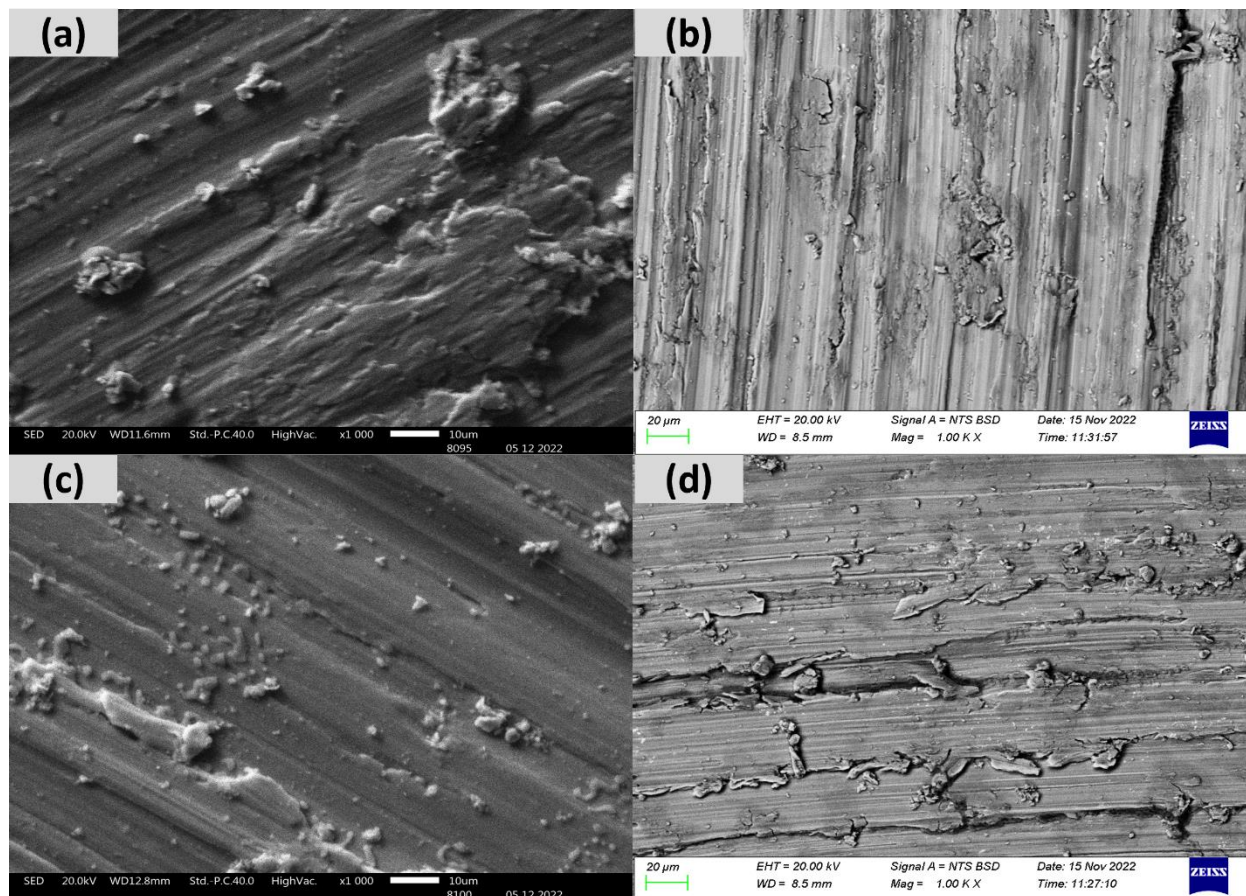


Figure 6.8: SEM images of the wear tracks for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under Potentiostatic conditions in normal HBSS.

6.3.2. Tribocorrosion behavior of titanium alloys in pre-diabetic HBSS

6.3.2.1. Evolution of open circuit potential (OCP) during tribocorrosion tests

The graphs representing the evolution of OCP as a function of testing time during the tribocorrosion tests under OCP conditions in the prediabetic (100 mg/dL glucose) HBSS are shown in **Figure 6.9**. At the onset of sliding, an abrupt drop in the potential is observed for all the alloys under investigation. This is the same observation seen in the normal HBSS and it indicates the removal of the passive film from the alloy surface thus exposing the bare alloy surface to the corrosive solution. Greater potential fluctuations are seen during the first and second stages of sliding for Ti-3Fe in this solution in comparison to the normal HBSS. This is an indication that the glucose in this solution is contributing to better repassivation capabilities of this alloy. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe once again display great potential fluctuations indicating their good

ability to repassivate during the mechanical action. These great fluctuations are also evident in both sliding stages for the commercial alloy, Ti-6Al-4V. Ti-6Al-1V-3Fe had the noblest potential before sliding was initiated. This indicates that this alloy had the greatest ability to form the most stable passive film on its surface in comparison to the other alloys. The potential fluctuations of this alloy together with those of Ti-4.5Al-1V-3Fe and Ti-6Al-4V reached the initial potential and even surpassed it. This is an indication of a greater rate of dynamic depassivation and repassivation which is desirable specifically for biomaterials as they are subjected to such movements when in use as bioimplants. When sliding was ceased, the alloys repassivated spontaneously as there was an abrupt increase in the potential. From the data shown in **Table 6-5**, it is clear that although the alloys repassivated spontaneously, none of the alloys apart from Ti-3Fe repassivated to their initial potential or greater when the second stage of sliding had ceased. Although Ti-3Fe repassivated to a potential greater than the initial potential, it had not attained equilibrium during the last stable 900 s in comparison to the other alloys. This indicates that its repassivation was slow and steady in comparison to the other alloys. These results are in contrast with the outcomes obtained in the normal (non-diabetic) HBSS as Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V repassivated to potentials greater than the starting potential when sliding had ceased. This is an indication that the glucose in this environment plays a role on the stability of the passive film on the surfaces of the alloys.

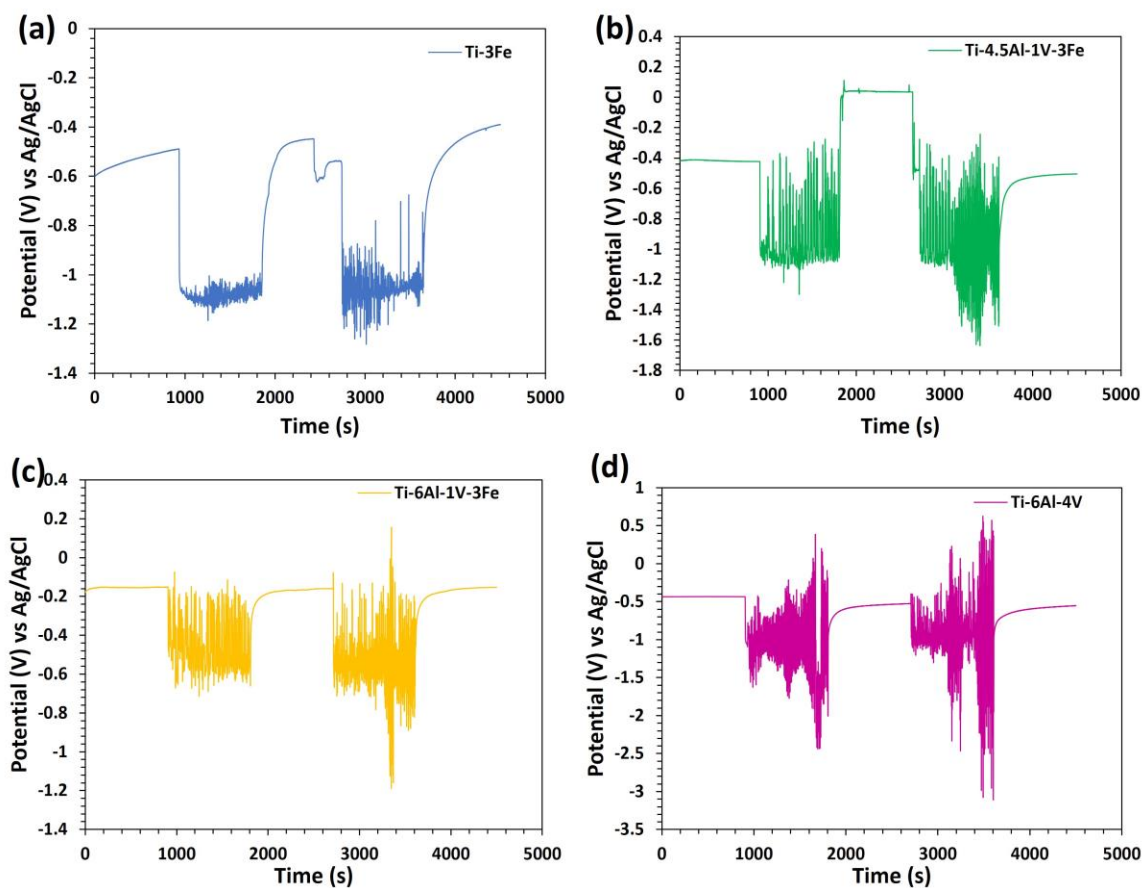


Figure 6.9: Evolution of OCP with time during sliding of an alumina ball against titanium alloys during OCP tribocorrosion tests in pre-diabetic HBSS for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe and (d) Ti-6Al-4V.

Table 6-5: Average values of the potential measured before (OCP_0), during ($OCP_{sliding}$) and after sliding (OCP_{final}) of the Ti alloys sliding against an alumina ball in the pre-diabetic HBSS.

<i>Alloys</i>	<i>OCP_o (V)</i>		<i>OCP_{sliding} (V)</i>		<i>OCP_{final} (V)</i>	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
<i>Ti-3Fe</i>	-0.532 ± 0.030	-0.536 ± 0.091	-1.08 ± 0.024	-1.046 ± 0.084	-0.536 ± 0.091	-0.482 ± 0.1
<i>Ti-4.5Al-1V-3Fe</i>	-0.418 ± 0.004	0.014 ± 0.162	-0.921 ± 0.202	-0.967 ± 0.224	0.014 ± 0.162	-0.548 ± 0.073
<i>Ti-6Al-1V-3Fe</i>	-0.154 ± 0.004	-0.181 ± 0.044	-0.458 ± 0.126	-0.529 ± 0.134	-0.181 ± 0.044	-0.177 ± 0.035
<i>Ti-6Al-4V</i>	-0.435 ± 0.001	-0.579 ± 0.084	-1.059 ± 0.389	-0.948 ± 0.432	-0.579 ± 0.084	-0.613 ± 0.064

Figure 6.10 presents the graphs of evolution of COF as a function of testing time for the alloys tested under OCP conditions. A clear run-in period which indicates the initial adherence of the two surfaces in contact to each other was observed for Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V for a few seconds (Manhabosco *et al.*, 2011). The run-in period for Ti-3Fe was less evident. Sharp spikes in the COF throughout the test for Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe were observed. These spikes can be attributed to the third body effect where the alumina ball makes contact with the loose particles on the alloy surface and these particles become entrapped between the titanium alloy and alumina ball thus causing sharp changes in the COF throughout the duration of the test (Wang *et al.*, 2017; Cao and Mischler, 2018; Fang *et al.*, 2019; Toptan *et al.*, 2019; Buciumeanu *et al.*, 2022). Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V attained a steady state in their COF after a few seconds of sliding during both sliding stages until the completion of the test. Ti-3Fe on the other hand struggled to attain steady state during both sliding stages. The average COF of all the alloys were below 0.45 similar to the normal HBSS which is typical of metal-ceramic contacts (Runa *et al.*, 2013). In this solution, Ti-6Al-4V showed the highest COF (0.4) compared to other alloys. This was different to the normal HBSS as Ti-3Fe had the highest COF in that solution.

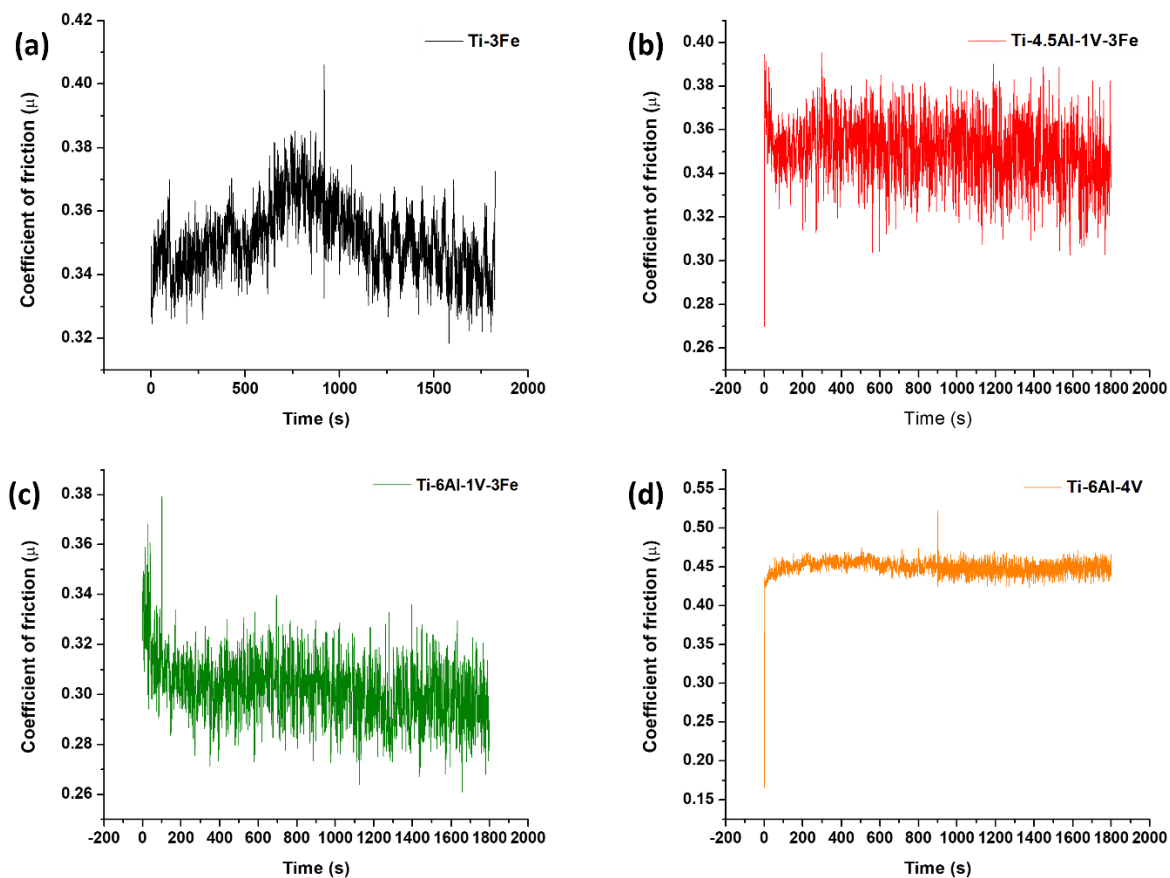


Figure 6.10: Evolution of COF as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested in pre-diabetic HBSS under OCP conditions

6.3.2.2. *Evolution of anodic current (Potentiostatic) during tribocorrosion*

The graphs representing the evolution of current as a function of testing time which were obtained during the potentiostatic tests in the pre-diabetic HBSS are shown in **Figure 6.11**. Once again, all the alloys experienced an abrupt increase in the current at the commencement of sliding which is an indication of the removal of the passive film on the alloy surfaces. Great fluctuations in the current during the 3600 s of sliding were observed in this environment as well. These are an indication of dynamic depassivation and repassivation of the passive film. The isolated current peaks once again represent local repassivation points that rapidly depassivated (Mischler, 2008; Bryant and Neville, 2016). The data in **Table 6-6** show that Ti-3Fe attained the highest average current during sliding. This is consistent with the results obtained in the normal HBSS. This high average current values are indicative of higher oxidation/dissolution rates which is an indication

of poorer resistance to tribocorrosion (Runa *et al.*, 2013). Similar to the normal HBSS, Ti-6Al-1V-3Fe had the lowest average current during sliding indicating that this alloy could potentially be more resistant to tribocorrosion compared to the rest of the alloys. When sliding had ceased, the current of all the alloys dropped to values lower than the starting potential which is an indication of spontaneous repassivation. Ti-6Al-1V-3Fe repassivated to the lowest current value compared to the rest of the alloys which further supports the idea that this alloy has better tribocorrosion resistance.

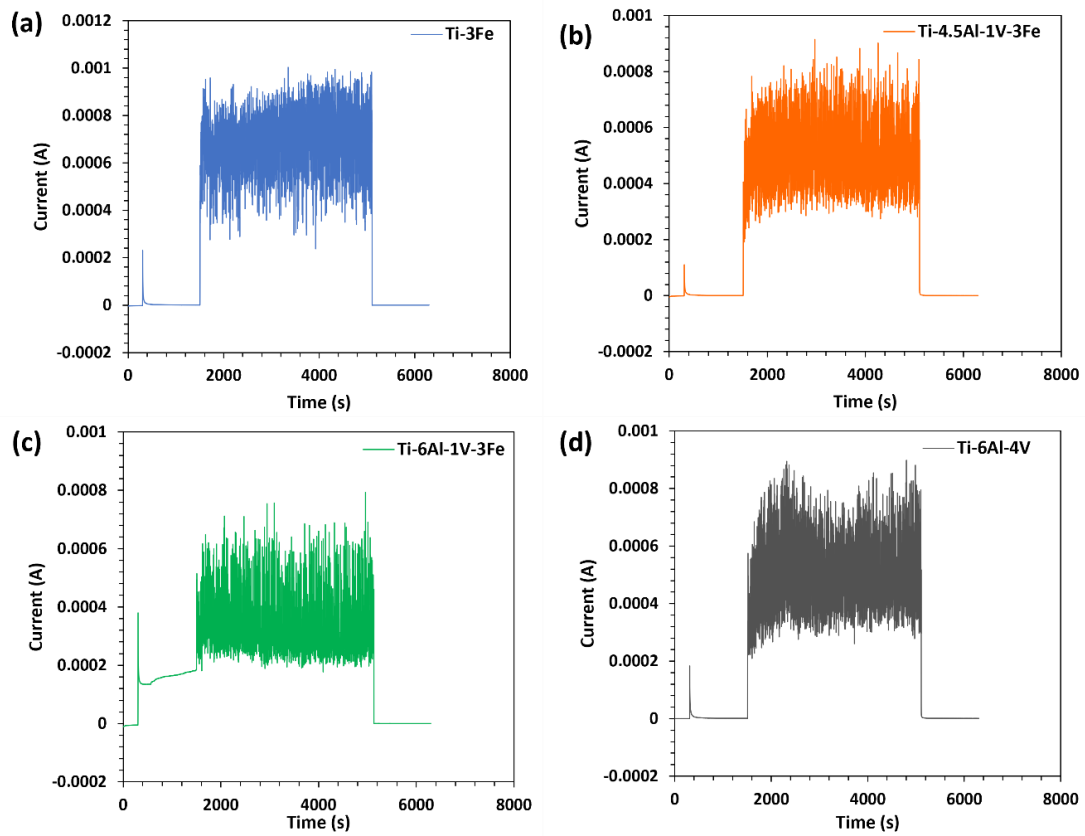


Figure 6.11: Evolution of anodic current as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V during potentiostatic tribocorrosion tests in pre-diabetic HBSS

Table 6-6: Average values of the current measured before (I_0), during ($I_{sliding}$), and after sliding (I_{final}) of the titanium alloys sliding against an alumina ball in pre-diabetic HBSS.

<i>Alloys</i>	<i>I₀ (A)</i>	<i>I_{sliding} (A)</i>	<i>I_{final} (A)</i>
<i>Ti-3Fe</i>	3.23E-06 ± 1.20E-05	6.91E-04 ± 1.23E-04	5.01E-10 ± 2.29E-08
<i>Ti-4.5Al-1V-3Fe</i>	2.34E-06 ± 6.78E-06	5.00E-04 ± 1.17E-04	6.96E-07 ± 1.59E-06
<i>Ti-6Al-1V-3Fe</i>	1.60E-04 ± 1.81E-05	3.27E-04 ± 9.52E-05	4.11E-10 ± 1.4E-08
<i>Ti-6Al-4V</i>	3.16E-06 ± 1.07E-05	4.92E-04 ± 1.25E-04	7.53E-07 ± 1.89E-06

The graphs representing the evolution of COF as a function of testing time for the alloys during the potentiostatic tests are shown in **Figure 6.12**. Once again, a clear run-in period which lasted for a few seconds is observed for all the alloys. Soon after, the COF of all the alloys reached a steady state until the end of the tribocorrosion tests. Greater fluctuations in the COF are seen for Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe. This can be attributed to a larger amount of third body particles generated between the contact region during the tribocorrosion tests (Manhabosco *et al.*, 2011; Wang *et al.*, 2017). Ti-3Fe attains the highest COF (0.62) which even exceeds the typical 0.45 which has been reported for metal-ceramic contacts. This is an indication that this alloy behaves poorly in this environment in comparison to the other alloys under investigation. The lowest COF was attained by Ti-6Al-4V (0.03) while the COF of Ti-4.5Al-1V-3Fe (0.32) was closely comparable to that of Ti-6Al-1V-3Fe (0.30).

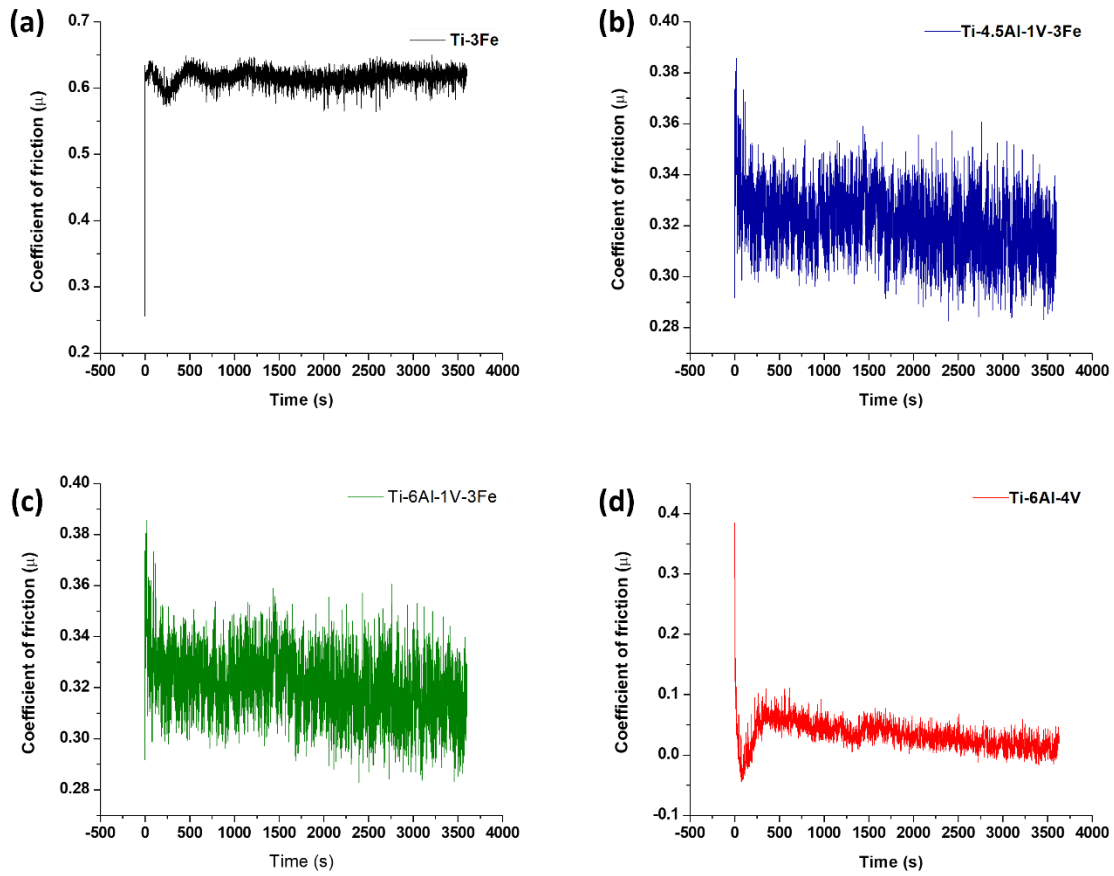


Figure 6.12: Evolution of COF as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V in pre-diabetic HBSS under potentiostatic tribocorrosion.

6.3.2.3. Wear volume loss under OCP conditions in pre-diabetic HBSS

The wear track profiles representing the penetration depth vs the wear track width of the alloys is shown in **Figure 6.13**. Judging by these profiles, Ti-6Al-4V had the deepest wear track in comparison to the other alloys. The depth of this alloys wear scar was closely comparable to that of Ti-3Fe. The wear track width of Ti-3Fe was however bigger than that of Ti-6Al-4V. The wear track width of these alloys is presented in Table A-2 in Appendix A. The wear track profiles of Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe are very similar to each other and their penetration depths are shallower than that of Ti-3Fe and Ti-6Al-4V. These observations are supported by the data in **Table 6-7** as Ti-6Al-4V had the greatest maximum penetration depth of $-8.09\text{E-}05$ mm while Ti-6Al-1V-3Fe had the shallowest wear track as its maximum penetration depth was $-5.98\text{E-}05$ mm. Because of the deeper wear track of Ti-6Al-4V, this alloy experienced the greatest total worn

volume which led to it having the highest specific wear rate ($2.78\text{E-}06 \text{ mm}^3/\text{N.m}$). This high wear rate was closely comparable to that of Ti-3Fe ($2.71\text{E-}06 \text{ mm}^3/\text{N.m}$). This is an indication that these alloys had the poorest resistance to tribocorrosion in comparison to the other experimental alloys in this solution under OCP conditions. Because of its shallower wear track and smallest worn surface area, Ti-6Al-1V-3Fe experienced the least worn volume loss which resulted in the alloy having the lowest specific wear rate. These results are different to those obtained in the normal HBSS as Ti-3Fe had the highest specific wear rate in that environment and Ti-6Al-4V had the lowest specific wear rate. It is interesting to note, however, that the worn surface area, maximum penetration depth, total wear volume, and the specific wear rate for majority of the alloys (Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe) in the normal HBSS under OCP conditions was greater than those obtained in the pre-diabetic environment. This is an indication that the 100 mg/dL glucose concentration in this environment had a positive effect on the tribocorrosion behavior of the alloys.

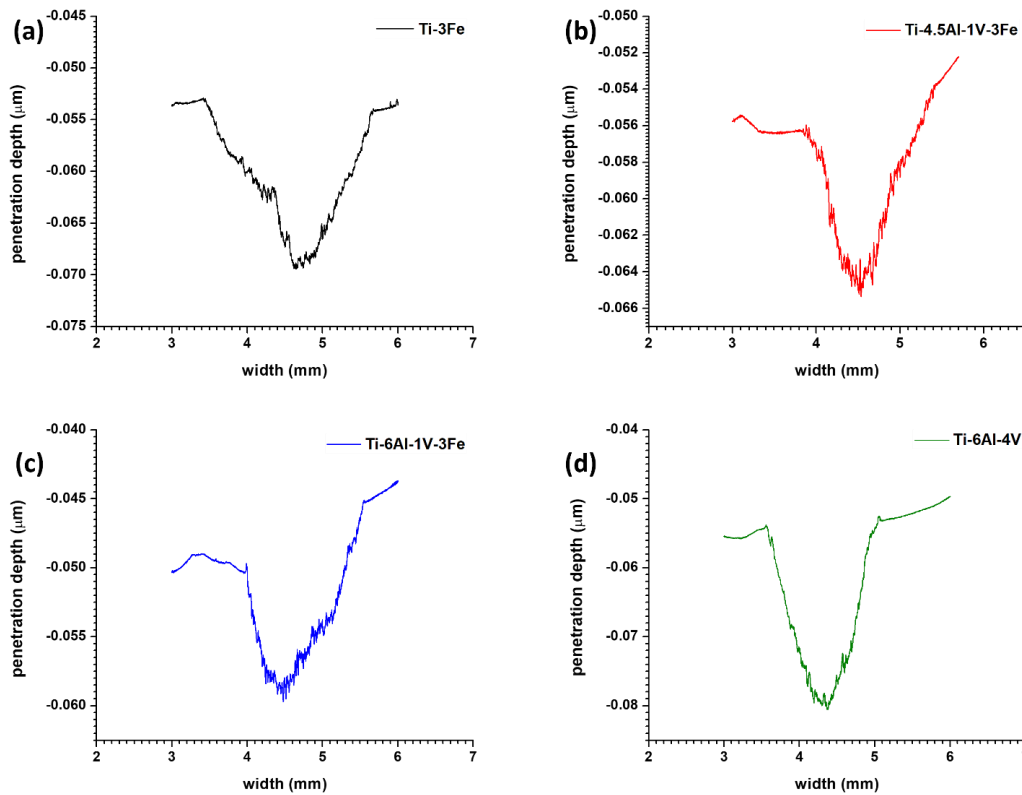


Figure 6.13: Penetration depth versus wear track width profiles of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under OCP conditions in pre-diabetic HBSS

Table 6-7: OCP tribocorrosion parameters of experimental and commercial titanium alloys in pre-diabetic HBSS

<i>Ti Alloys</i>	<i>Worn surface area (mm²)</i>	<i>Max penetration depth (mm)</i>	<i>Total wear volume (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	23.41	-6.95E-05	1.63E-03	2.71E-06
<i>Ti-4.5Al-1V-3Fe</i>	17.74	-6.54E-05	1.16E-03	1.93E-06
<i>Ti-6Al-1V-3Fe</i>	16.51	-5.98E-05	9.87E-04	1.65E-06
<i>Ti-6Al-4V</i>	20.61	-8.09E-05	1.67E-03	2.78E-06

6.3.2.4. *Wear volume loss under potentiostatic conditions in pre-diabetic HBSS*

Figure 6.14 represents the wear track profiles of the alloys tested under potentiostatic conditions. From these profiles, it is evident that Ti-3Fe presents the deeper and wider wear track in comparison to the other alloys under investigation. The wear track width of these alloys is presented in Table A-2 in Appendix A. The depth of the wear track for Ti-6Al-4V is closely comparable to that of Ti-3Fe. This deep wear track is an indication of these alloys potentially having the poorest resistance to tribocorrosion under these conditions. This observation similar to the one seen under OCP conditions as Ti-3Fe and Ti-6Al-4V also had the deeper wear scars under that condition. Once again, Ti-6Al-1V-3Fe has the shallowest wear track in comparison to the other alloys. This is supported by the data in **Table 6-8** as this alloy had a maximum penetration depth of -7.23E-05 mm in contrast to Ti-3Fe with a maximum penetration depth of -1.19E-04 mm. Ti-3Fe had the greatest total wear volume and largest specific wear rate. This is also supported by its higher COF which exceeded 0.45. This is an indication that the alloy has poor resistance to wear and tribocorrosion. Although Ti-6Al-1V-3Fe had a shallower wear track in comparison to Ti-4.5Al-1V-3Fe, its worn surface area was bigger than that of Ti-4.5Al-1V-3Fe. This resulted in the alloy having a slightly higher specific wear rate (2.49E-06 mm³/N.m) in comparison to that of Ti-4.5Al-1V-3Fe (2.32E-06 mm³/N.m). Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe wear rates were

lower than that of Ti-3Fe and Ti-6Al-4V indicating their superior resistance to tribocorrosion under these conditions.

Once again, the worn surface area, maximum penetration depth, total wear volume, and specific wear rates of the alloys tested under potentiostatic conditions is greater than those tested under OCP conditions. This is attributed to the negligible active corrosion taking place under OCP conditions in comparison to the potentiostatic conditions where the volume loss is made up of both mechanical action and a considerable amount of volume loss due to corrosion (Mischler, 2008; Toptan *et al.*, 2019; Mehkri *et al.*, 2021).

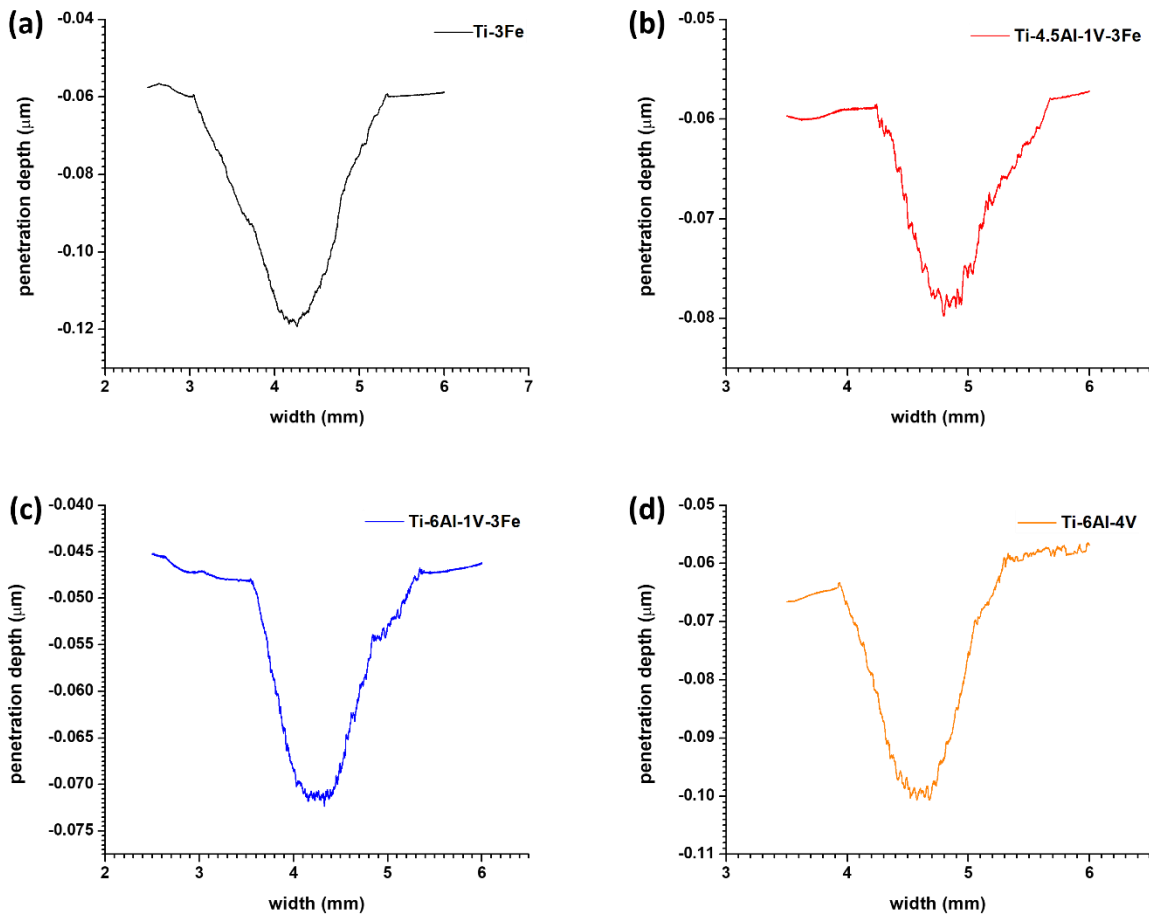


Figure 6.14: Penetration depth versus wear track width profiles of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under potentiostatic conditions in pre-diabetic HBSS

The individual components of the total wear volume loss (V_{chem} and V_{mech}) are also presented in **Table 6-8**. V_{chem} for all alloys is once again greater than the overall volume loss thus leaving V_{mech} in the negative range. This is also attributed to the uncertainties in the actual valence number for the oxidation reactions taking place during the tribocorrosion tests.

Table 6-8: Potentiostatic tribocorrosion parameters of experimental and commercial titanium alloys in pre-diabetic HBSS.

<i>Alloys</i>	<i>Area (mm²)</i>	<i>Pdmax (mm)</i>	<i>Total wear volume (mm³)</i>	<i>Vchem (mm³)</i>	<i>Vmech (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	27.53	-1.19E-04	3.28E-03	3.35E-01	-3.32E-01	5.47E-06
<i>Ti-4.5Al-1V-3Fe</i>	17.45	-7.97E-05	1.39E-03	4.58E-01	-4.57E-01	2.32E-06
<i>Ti-6Al-1V-3Fe</i>	20.64	-7.23E-05	1.49E-03	2.81E-01	-2.80E-01	2.49E-06
<i>Ti-6Al-4V</i>	20.67	-1.01E-04	2.09E-03	4.42E-01	-4.40E-01	3.48E-06

6.3.2.5. *Wear Morphology*

The morphology of the wear tracks on the titanium alloys that were tested in the pre-diabetic HBSS under OCP and potentiostatic conditions are shown in **Figure 6.15** and **Figure 6.16** respectively. Abrasive wear was once again found to be one of the predominant wear mechanisms of all the titanium alloys under investigation under both OCP and potentiostatic conditions. This was due to the evidence of abrasive wear on their wear scars. This is seen through the visible scratches, grooves, and micro-ploughing which are parallel to the sliding movement. These are sub-mechanisms of the abrasive wear mechanism (Gahr, 1987; Fischer *et al.*, 2018; Chirico *et al.*, 2022). In this environment, plastic deformation was not one of the predominant wear mechanisms of these alloys as there was no sign of any extruded material on the alloy wear scars. Deeper and more prominent wear grooves were observed on some areas of the wear tracks of the titanium alloys specifically the wear scar of Ti-3Fe tested under OCP. These deep grooves are an indication of higher abrasive wear (Enayati and Sayyedan, 2022).

According to the EDX analysis, the tiny wear debris seen all over the wear scars of the titanium alloys consisted mainly of the bulk alloying elements as well as the elements making up the electrolyte such as Na, Cl, P, K, and Ca. This was observed in the normal HBSS as well. Once again, the alloys containing aluminium as an alloying element showed elevated levels of aluminium in their wear debris. This was due to the loss of material from the alumina ball. The wear scars of the alumina balls tested against the titanium alloys under OCP conditions are shown in Figure B-2 in Appendix B. These wear scars also show many platelets of transferred titanium alloy material. This is therefore an indication that adhesive wear was also an acting wear mechanism that was responsible for the degradation of the titanium alloys similar to the alloys tested in the normal HBSS (Gahr, 1987; Fischer *et al.*, 2018). Wear debris that contained oxygen was also observed in these alloys. The EDX spectra of Ti-6Al-4V and Ti-4.5Al-1V-3Fe tested under OCP conditions is shown in Appendix C in Figure C-3.1 and Figure C-3.2 respectively. The EDX spectra for Ti-4.5Al-1V-3Fe tested under potentiostatic conditions is shown in Figure C-4.1 in Appendix C. The presence of oxygen was once again an indication of the formation of passive oxide films and an indication of the tribochemical reactions wear mechanism.

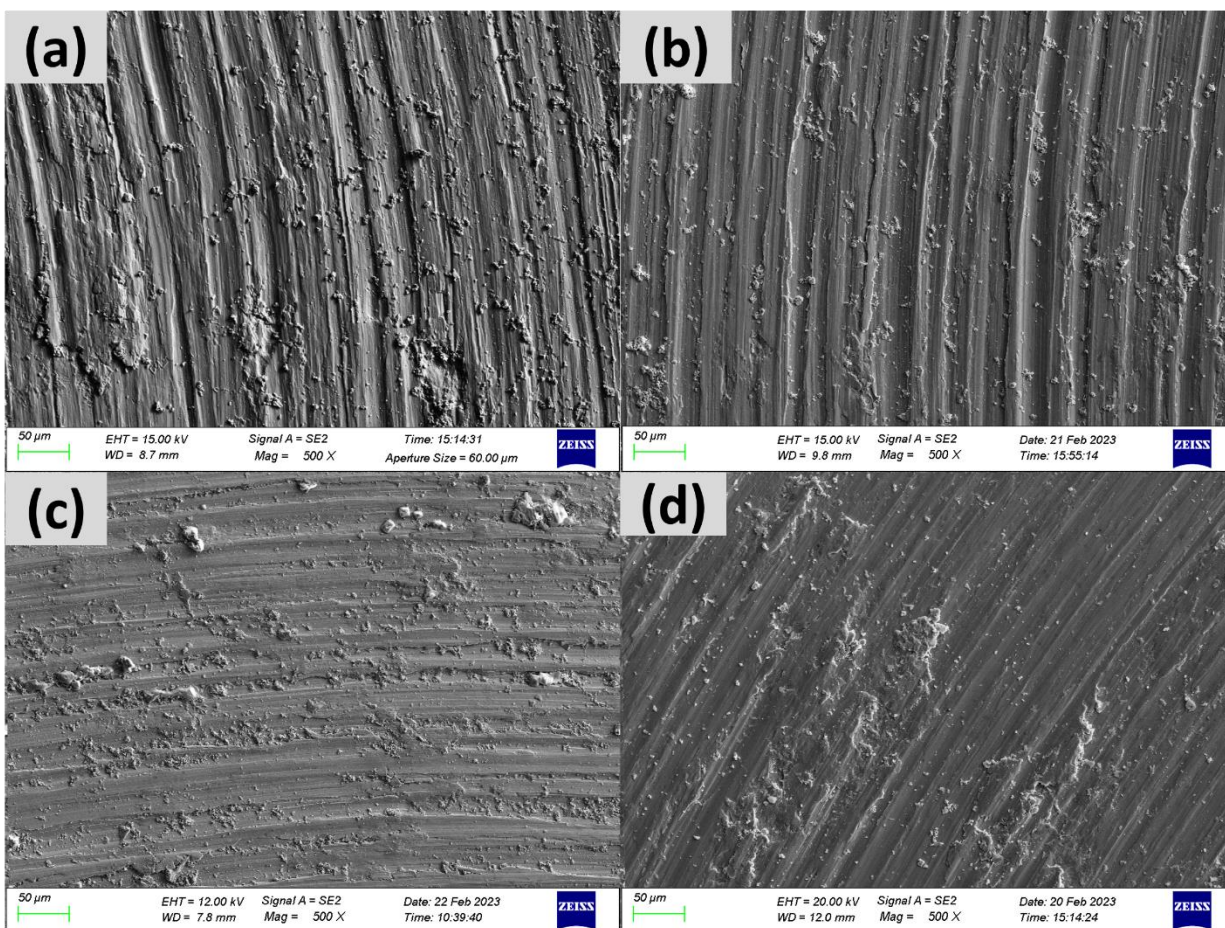


Figure 6.15: SEM images of the wear tracks for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under OCP conditions in pre-diabetic HBSS

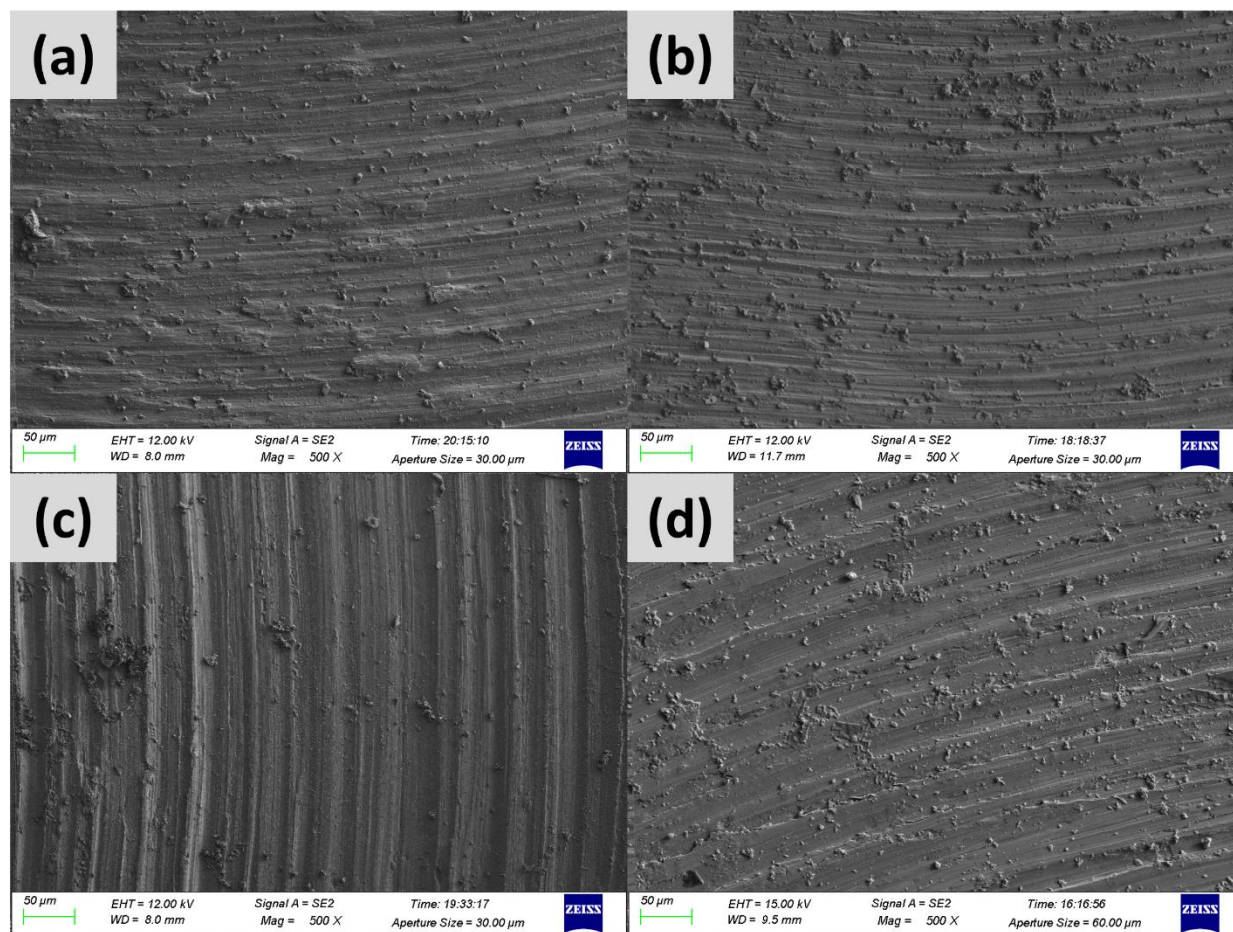


Figure 6.16: SEM images of the wear tracks for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under Potentiostatic conditions in pre-diabetic HBSS

6.3.3. Tribocorrosion behavior of titanium alloys in diabetic HBSS

6.3.3.1. Evolution of open circuit potential (OCP) during tribocorrosion

The graphs displaying the evolution of OCP as a function of testing time during the OCP tribocorrosion tests in diabetic HBSS are shown in **Figure 6.17**. The behavior of the titanium alloys in this solution is similar to the behavior in the normal HBSS and the pre-diabetic HBSS as an abrupt drop in the OCP is observed when sliding is initiated after the stable 900 s. During the first stage of sliding, Ti-3Fe once again struggles to regain its passive state as very few fluctuations are seen in its OCP during the 900 s of sliding. Greater fluctuations in the OCP are seen in the other alloys which is an indication of a greater rate of dynamic depassivation and repassivation of the passive film which is desirable as it is a direct indication of the alloys capabilities to repassivate during wear action/mechanical action on the alloy surface (Landolt *et al.*, 2001; Manhabosco *et*

al., 2011; More *et al.*, 2011; Licausi *et al.*, 2013; Runa *et al.*, 2013b; Ortega *et al.*, 2018). When sliding was stopped in the case of Ti-3Fe, the formation of the passive film during the static 900 s was not stable as a drop in the OCP is seen during this stage after both stages of sliding had been initiated and ceased. Ti-6Al-1V-3Fe, similar to the pre-diabetic HBSS, had the noblest OCP in the beginning of the test before the first stage of sliding was initiated. Great OCP fluctuations are seen during both stages of sliding for this alloy. However, the fluctuations were not as great as those observed in the normal HBSS and the prediabetic HBSS. The fluctuations could not reach the starting potential. When sliding had ceased, the alloys repassivated spontaneously but unlike the tests conducted in the normal HBSS, the initial/starting potential was not attained by this alloy. Ti-4.5Al-1V-3Fe and Ti-6Al-4V also struggled to regain their initial passive state in the diabetic environment. The was also observed in the pre-diabetic HBSS. The behavior of the commercial alloy in this environment is completely different from the normal HBSS environment as the potential remains in the negative range even after sliding had stopped whereas in the normal HBSS, the alloy reached and surpassed its starting potential when sliding had ceased.

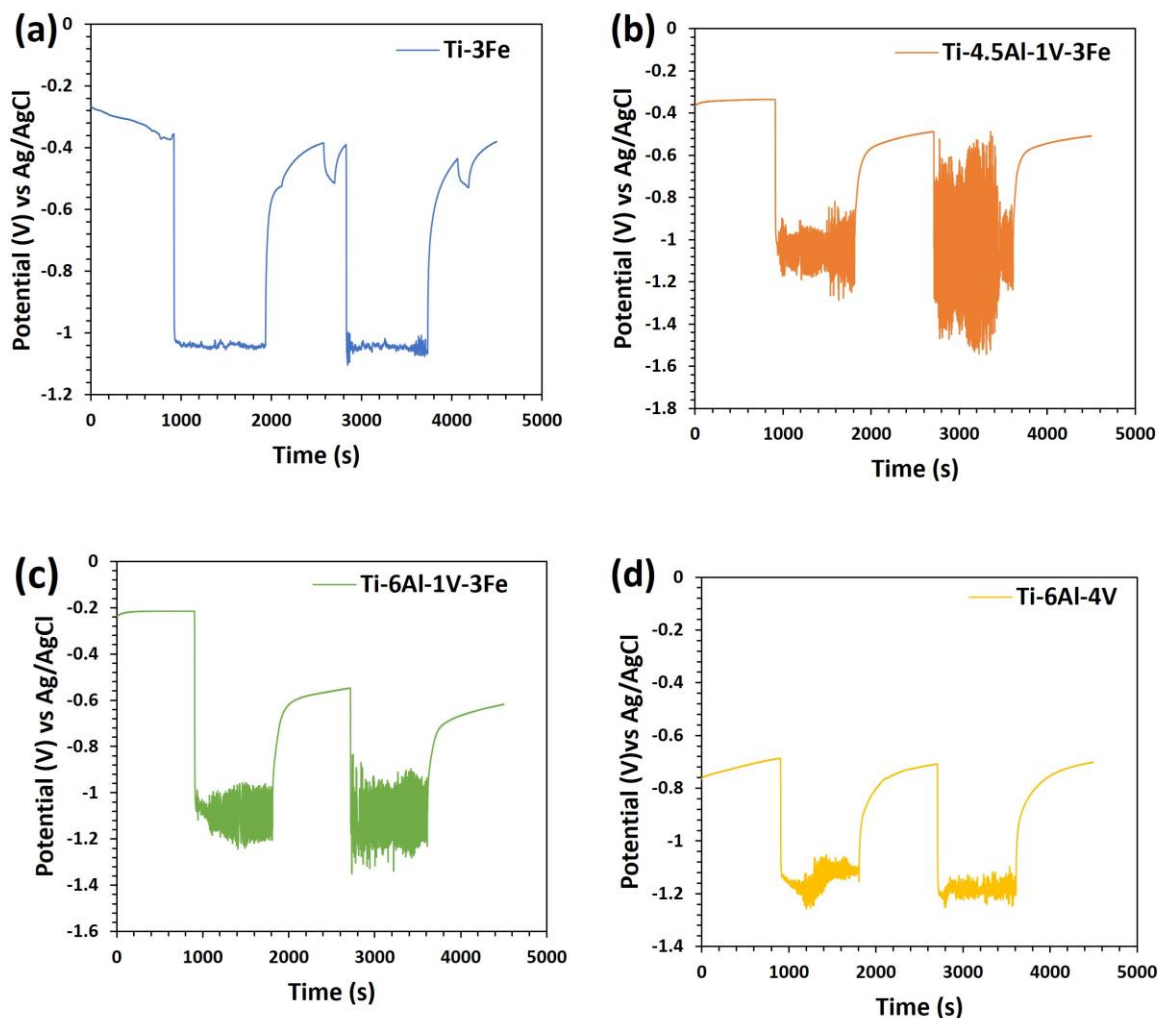


Figure 6.17: Evolution of OCP with time during sliding of an alumina ball against titanium alloys during OCP tribocorrosion tests in diabetic HBSS for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe and (d) Ti-6Al-4V.

Table 6-9 presents the OCP values of the titanium alloys before, during, and after sliding. This gives a clearer view of the repassivation capabilities of the alloys during the OCP tribocorrosion tests. In this environment, Ti-6Al-1V-3Fe had the noblest starting potential before sliding was initiated. Compared to the alloys tested in the normal HBSS, these alloys experienced great drops in potential reaching OCP values much lower than those observed in the normal HBSS. This is an indication that the glucose in this solution plays a big role in the stability of the passive film on the alloy surfaces. When the second stage of sliding ceased, none of the alloys repassivated to the starting potentials. The final potentials reached were below the starting potentials which indicates

that the addition of glucose to the HBSS resulted in the modification film of the passive film as the passive films did not possess the same characteristics as the starting films.

Table 6-9: Average values of the potential measured before (OCP_0), during ($OCP_{sliding}$) and after sliding (OCP_{final}) of the Ti alloys sliding against an alumina ball in the diabetic HBSS

<i>Alloys</i>	<i>OCP₀ (V)</i>		<i>OCP_{sliding} (V)</i>		<i>OCP_{final} (V)</i>	
	Stage 1	Stage 2	Stage 1	Stage 2	Stage 1	Stage 2
<i>Ti-3Fe</i>	-0.319 ± 0.031	-0.474 ± 0.083	-1.038 ± 0.043	-0.967 ± 0.207	-0.474 ± 0.083	-0.486 ± 0.089
<i>Ti-4.5Al-1V-3Fe</i>	-0.341 ± 0.006	-0.548 ± 0.076	-1.047 ± 0.090	-1.042 ± 0.238	-0.548 ± 0.076	-0.559 ± 0.068
<i>Ti-6Al-1V-3Fe</i>	-0.218 ± 0.004	-0.605 ± 0.077	-1.084 ± 0.089	-1.098 ± 0.104	-0.605 ± 0.077	-0.679 ± 0.065
<i>Ti-6Al-4V</i>	-0.72 ± 0.02	-0.76 ± 0.06	-1.14 ± 0.05	-1.18 ± 0.04	-0.76 ± 0.06	-0.77 ± 0.06

Figure 6.18 represents the evolution of COF as a function of testing time for the titanium alloys tested in diabetic HBSS. Similar to the alloys tested in the normal HBSS and pre-diabetic HBSS, a run-in phase is observed at the beginning of each stage of sliding for Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe while there is no distinct run-in phase observed for Ti-6Al-4V. Similar to the pre-diabetic HBSS, greater spikes in the COF of Ti-3Fe were observed and a steady state was not reached for this alloy in comparison to the normal HBSS. These spikes could once again be because of the third body effect. Ti-6Al-1V-3Fe attains a steady state after a few seconds during both stages of sliding while Ti-6Al-4V only attains a steady state in the COF during the second stage of sliding. Ti-3Fe possesses the highest COF of 0.41 while Ti-6Al-1V-3Fe possesses the lowest COF of 0.18. Again, the COF values of all the titanium alloys lie below 0.45 which is typical of metal-ceramic contact (Runa *et al.*, 2015).

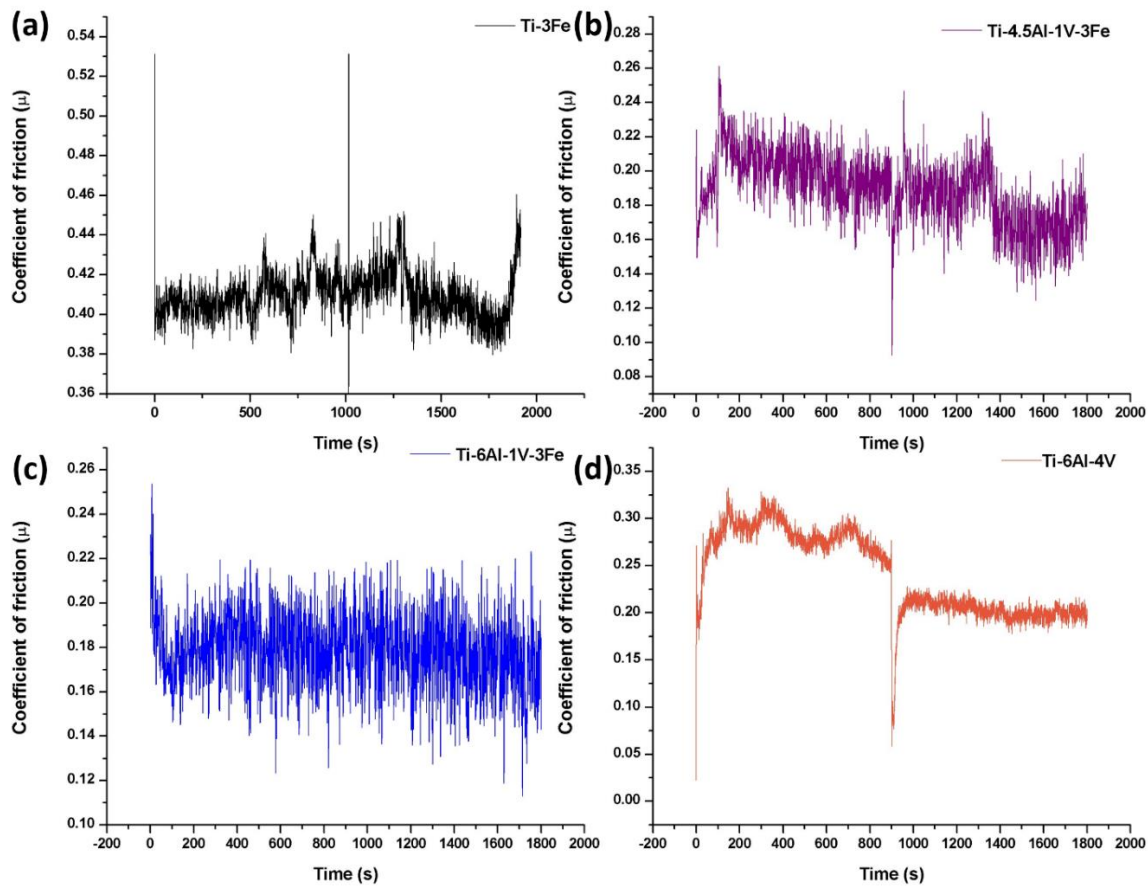


Figure 6.18: Evolution of COF as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested in diabetic HBSS under OCP conditions.

6.3.3.2. *Evolution of anodic current (Potentiostatic) during tribocorrosion*

Tribocorrosion tests were once again conducted under an imposed passive potential of +0.5V to study the properties of the passive surface films under controlled electrochemical conditions. The current vs time curves for the alloys tested in diabetic HBSS are presented in **Figure 6.19**. Once again, an abrupt shift in the current to more positive/noble values is observed when sliding is initiated at the 900 s mark. This is because of the surface being more active and more susceptible to corrosion when the passive film is broken and removed by the wear action of the ball on the alloy surface. The current fluctuates around a constant value for the entire duration of the sliding which indicates the action of dynamic depassivation and repassivation of the passive oxide film on the alloy surface. The effect of the 200 mg/dL HBSS compared to the normal HBSS and pre-diabetic HBSS is once again observed here as the average current during the sliding of these alloys in this solution is higher than those observed in the normal HBSS and pre-diabetic HBSS. This can be seen from the graphs as well as from the data recorded in **Table 6-10**. These higher average currents during sliding are indicative of higher oxidation/dissolution rates (Runa *et al.*, 2013). The average current during the 3600 s of sliding for all the alloys was in a very close range so the alloys behavior during the tribocorrosion tests in the diabetic HBSS appears to be quite similar to each other. Ti-3Fe once again reached the highest current during the sliding process as it had the highest I_{sliding} of 0.0007 A compared to the other alloys. Ti-6Al-1V-3Fe had the lowest average current during sliding. This result was observed in the potentiostatic tests performed in the normal HBSS and the pre-diabetic HBSS as well. This shows that the alloys behave in a similar way in these solutions with the 200 mg/dL glucose solution resulting in a more active alloy surface hence the higher current values. The alloys once again stabilize to current values lower than the initial current after the sliding stage. Just like in the pre-diabetic HBSS, Ti-6Al-1V-3Fe displays the lowest final current which lies in the negative range. This is an indication that this alloy possesses tribocorrosion resistance that is superior to that of the other alloys under investigation as the lower current is indicative of a more stable and adherent passive film.

The evolution of coefficient of friction as a function of time for the titanium alloys during the potentiostatic tribocorrosion tests is shown in **Figure 6.20**.

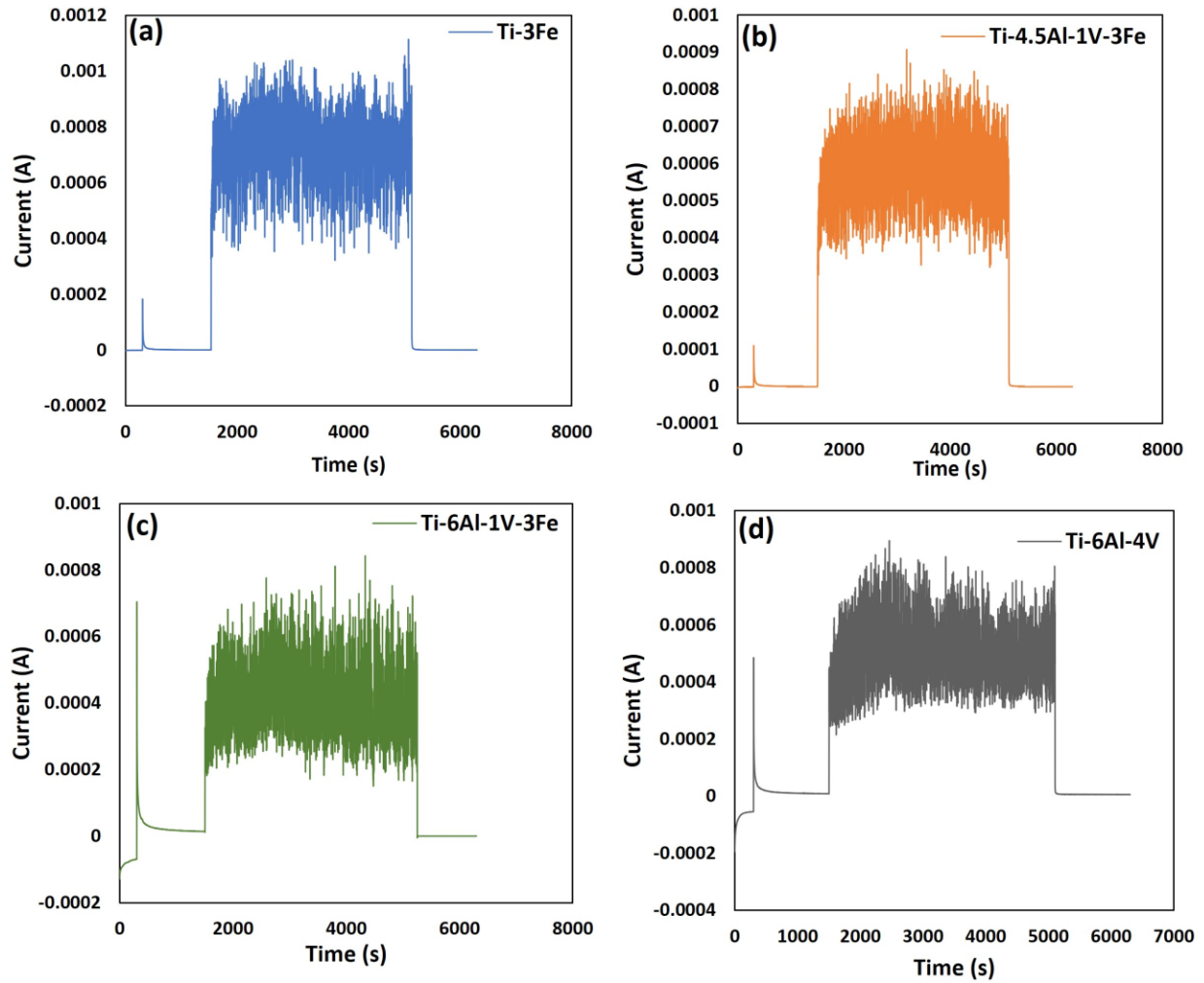


Figure 6.19: Evolution of anodic current as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V during tribocorrosion tests in diabetic HBSS under potentiostatic conditions.

Table 6-10: Average values of the current measured before (I_0), during ($I_{sliding}$), and after sliding (I_{final}) of the titanium alloys sliding against an alumina ball in diabetic HBSS.

<i>Alloys</i>	<i>I_0 (A)</i>	<i>$I_{sliding}$ (A)</i>	<i>I_{final} (A)</i>
<i>Ti-3Fe</i>	3.08E-06 ± 1.05E-05	0.0007 ± 0.0001	9.78E-07 ± 3.29E-06
<i>Ti-4.5Al-1V-3Fe</i>	2.29E-06 ± 7.17E-06	0.0006 ± 9.18E-05	5.7E-07 ± 1.24E-06
<i>Ti-6Al-1V-3Fe</i>	2.71E-05 ± 3.63E-05	0.0004 ± 0.0001	-3.85E-09 ± 1.45E-07
<i>Ti-6Al-4V</i>	1.70E-05 ± 2.52E-05	0.0005 ± 0.0001	6.28E-06 ± 2.05E-06

A running-in phase was experienced for all the alloys for approximately the first 100 – 150 s of sliding the alumina ball against the titanium alloys surface. After the run-in phase, Ti-3Fe experiences an increase in the COF for about 500 s, thereafter, a steady decrease in the COF is observed until the end of the sliding at 3600 s. After approximately 500 or 700 s, a steady state in the COF of the experimental alloys, Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe was observed. These alloys also displayed the lowest average COF values (0.22 and 0.31 respectively) compared to Ti-3Fe and the commercial alloy. In this solution, continuous sharp changes in the COF of the commercial alloy were observed. This alloy also had the highest average COF of 0.47.

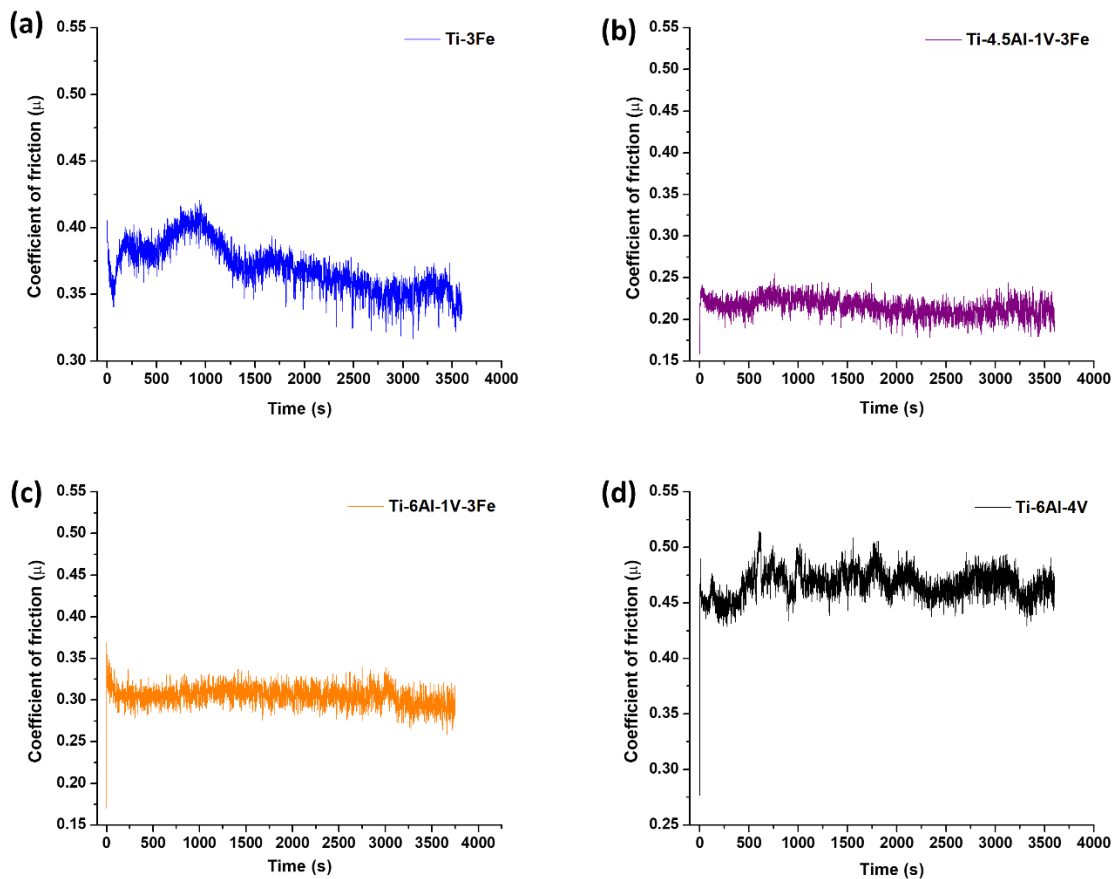


Figure 6.20: Evolution of COF as a function of testing time for (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V tested in diabetic HBSS under potentiostatic conditions.

6.3.3.3. *Wear volume loss under OCP conditions in diabetic HBSS*

The wear track profiles of the alloys which represent the wear track penetration depth vs the wear track width on the alloys tested in diabetic HBSS under OCP conditions are shown in **Figure 6.21**. The wear track profiles were once again quite comparable to each other. This is in line with the previous results discussed such as the current evolution as well as the COF evolution of these alloys during the tribocorrosion tests. The results obtained were very similar thus suggesting that the alloys could potentially have the same tribocorrosion mechanisms. Looking at these profiles, Ti-3Fe appears to have the deepest wear track followed by Ti-6Al-1V-3Fe. This is confirmed by the actual maximum penetration depth values seen in **Table 6-11**. Ti-3Fe displays a maximum penetration depth of $-8.85\text{E-}05$ mm while Ti-6Al-1V-3Fe had a maximum penetration depth of $-8.16\text{E-}05$ mm. This is also supported by their bigger worn surface areas compared to the other

alloys showing that a significant amount of alloy material was removed during the tribocorrosion tests. The commercial alloy Ti-6Al-4V and Ti-4.5Al-1V-3Fe had the shallowest wear tracks with maximum penetration depths of $-7.10\text{E-}05$ mm and $-7.20\text{E-}05$ mm respectively. These alloys also had the smallest worn surface areas which is an indication that they experienced the least amount of wear volume loss during the tribocorrosion tests (Licausi *et al.*, 2013). The total worn volume under OCP conditions in the diabetic HBSS as well as the specific wear rates of the alloys are shown in **Table 6-11** as well. The greatest material loss was experienced by Ti-3Fe as it had the highest worn volume of $2.19\text{E-}03$ mm³. This corresponds to its big worn surface area and its deeper wear track compared to the rest of the alloys under investigation (Licausi *et al.*, 2013). This alloy also possesses the highest specific wear rate ($3.65\text{-}06$ mm³/N.m) compared to the other alloys. A high worn volume corresponds to a high specific wear rate. This alloy also showed the highest specific wear rate when tested in the normal HBSS which is confirmation that this alloy possesses poor tribocorrosion properties compared to the other alloys which can be attributed to the weaker mechanical properties of this alloy compared to the other alloys as mentioned previously in section 3.1.3. Ti-6Al-4V experienced the least amount of material loss as it had the lowest total worn volume value ($1.28\text{E-}03$ mm³). This was closely comparable to the total wear volume loss of Ti-4.5Al-1V-3Fe as well as Ti-6Al-1V-3Fe. These alloys had very similar specific wear rates with the commercial alloy displaying the lowest specific wear rate.

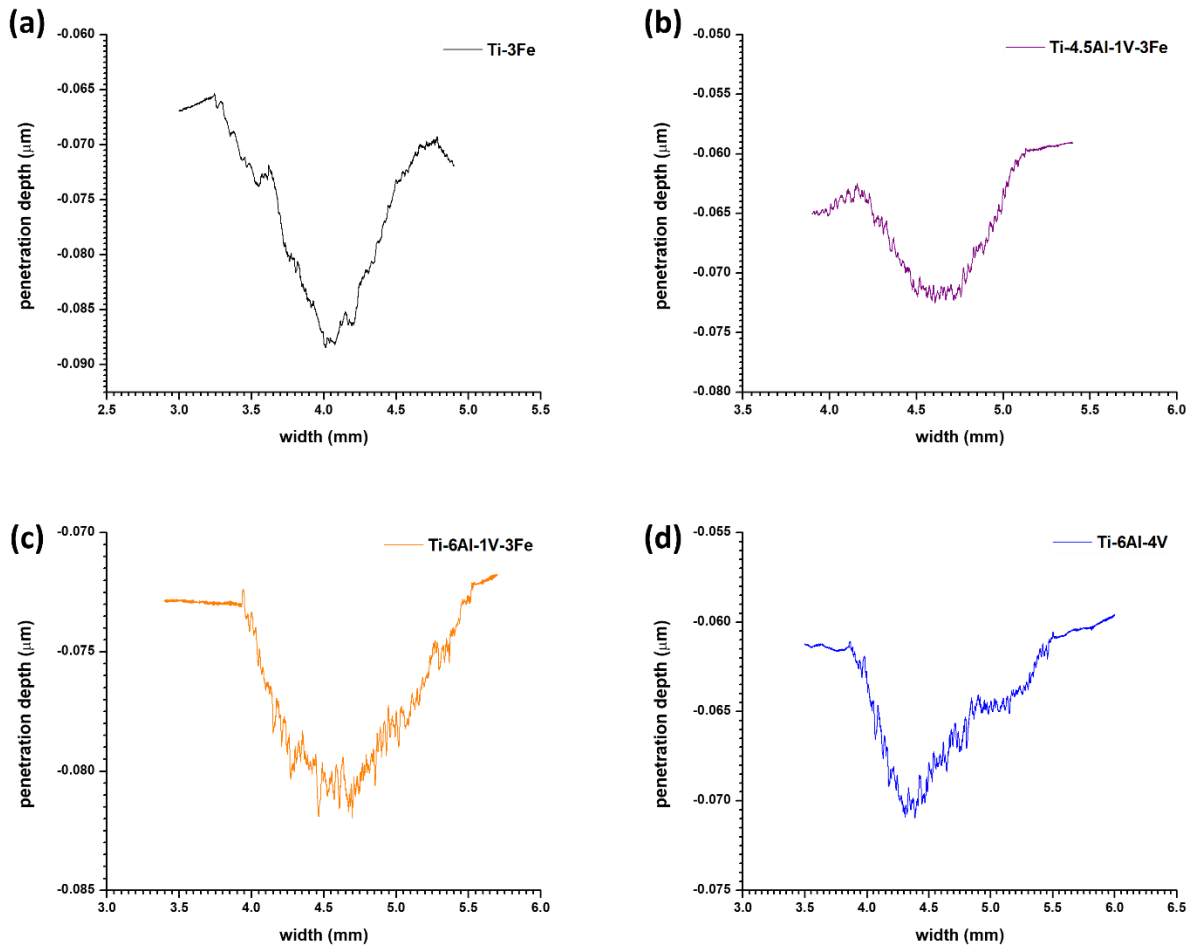


Figure 6.21: Penetration depth versus wear track width profiles of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under OCP conditions in diabetic HBSS

Table 6-11: OCP tribocorrosion parameters of experimental and commercial titanium alloys in diabetic HBSS

<i>Ti Alloys</i>	<i>Worn surface area (mm²)</i>	<i>Max penetration depth (mm)</i>	<i>Total wear volume (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	24.74	-8.85E-05	2.19E-03	3.65E-06
<i>Ti-4.5Al-1V-3Fe</i>	18.72	-7.20E-05	1.35E-03	2.25E-06
<i>Ti-6Al-1V-3Fe</i>	19.74	-8.16E-05	1.61E-03	2.68E-06
<i>Ti-6Al-4V</i>	18.08	-7.10E-05	1.28E-03	2.14E-06

6.3.3.4. *Wear volume loss under Potentiostatic conditions in diabetic HBSS*

Figure 6.22 presents the wear track profiles of the titanium alloys wear tracks obtained after the potentiostatic tests in the diabetic HBSS. The wear track profile of Ti-3Fe appears smoother than the rest of the alloys wear tracks. This alloy together with the commercial alloy Ti-6Al-4V present deeper looking wear tracks in comparison to the rest of the titanium alloys under investigation. The data in **Table 6-12** shows that Ti-3Fe indeed has the deepest wear track as it shows the greatest maximum penetration depth (-1.34E-04 mm) compared to the rest of the alloys. This is followed by the commercial alloy with a maximum penetration depth of -9.36E-05 mm. These deeper wear tracks correspond to a greater total volume loss as well as higher specific wear rates. Ti-3Fe had the highest specific wear rate of 6.22E-06 mm³/N.m followed by the commercial alloy with a specific wear rate of 2.99E-06 mm³/N.m. The specific wear rates as well as the total volume loss of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-1V are very similar to each thus once again confirming their similar resistance to tribocorrosion. These values are closely related to those obtained in the normal HBSS and pre-diabetic HBSS potentiostatic tests. However, the ones obtained in this solution are slightly higher which indicates that the 200 mg/dL glucose addition had a slightly negative effect on the tribocorrosion resistance of the alloys. Just like in the other solutions, the wear track area, Pdmax, total wear volume, and the specific wear rates of the alloys

tested under potentiostatic conditions were found to be greater than the alloys tested under OCP conditions. This is due to the synergistic effect of the mechanical action as well as the corrosion action which contributes to the overall volume loss of the alloys under potentiostatic conditions compared to only mechanical action making up the total wear volume of the alloys tested under OCP conditions. This same observation was reported by Manhabosco *et al.* (2011).

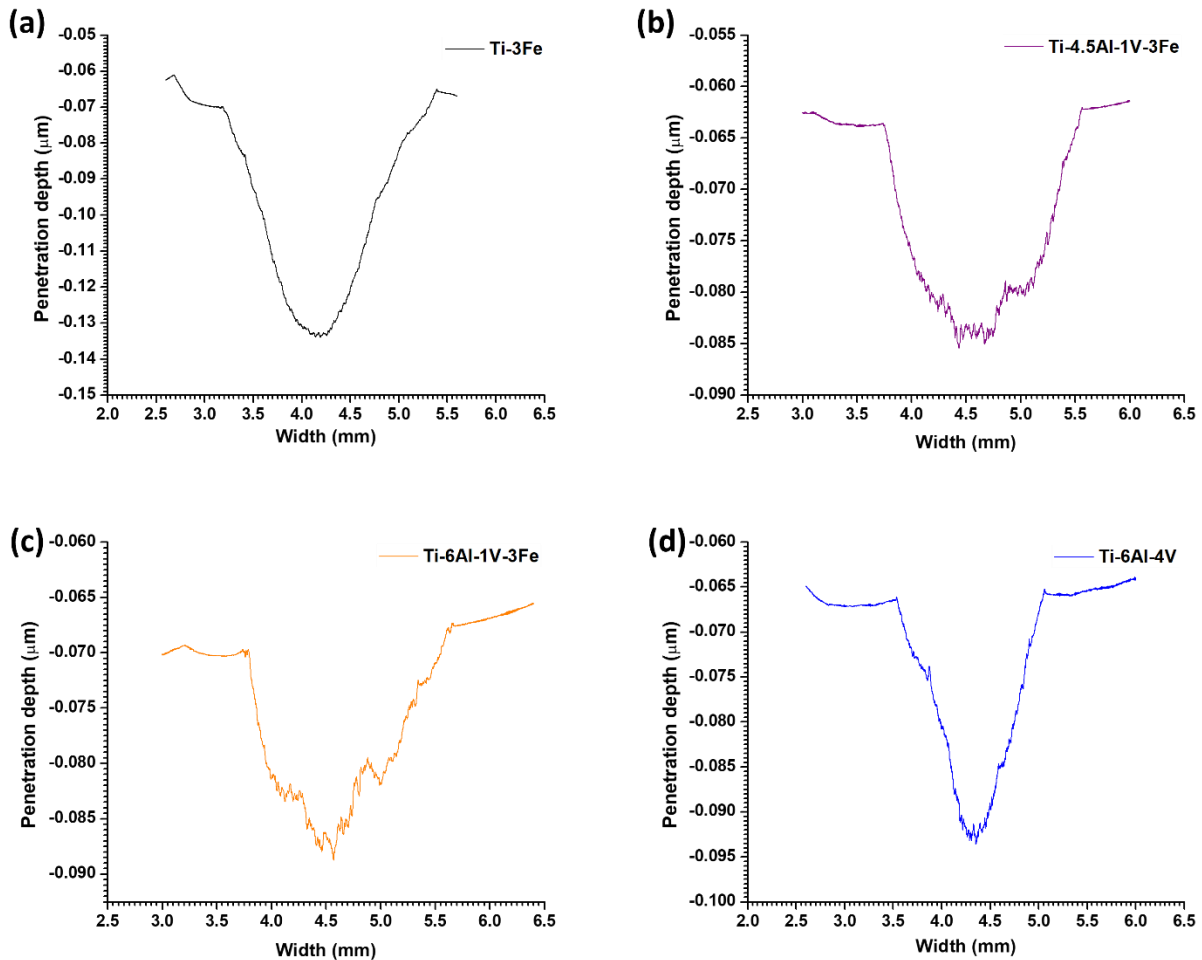


Figure 6.22: Penetration depth versus wear track width of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V tested under potentiostatic conditions in diabetic HBSS

Table 6-12: Potentiostatic tribocorrosion parameters of experimental and commercial titanium alloys in diabetic HBSS.

<i>Alloys</i>	<i>Area (mm²)</i>	<i>Pdmax (mm)</i>	<i>Total wear volume (mm³)</i>	<i>Vchem (mm³)</i>	<i>Vmech (mm³)</i>	<i>Specific wear rate (mm³/N.m)</i>
<i>Ti-3Fe</i>	27.84	-1.34E-04	3.73E-03	3.56E-01	-3.52E-01	6.22E-06
<i>Ti-4.5Al-1V-3Fe</i>	20.91	-8.54E-05	1.79E-03	5.25E-01	-5.23E-01	2.98E-06
<i>Ti-6Al-1V-3Fe</i>	21.4	-8.87E-05	1.90E-03	3.49E-01	-3.47E-01	3.16E-06
<i>Ti-6Al-4V</i>	19.17	-9.36E-05	1.79E-03	4.39E-01	-4.37E-01	2.99E-06

6.3.3.5. *Wear Morphology*

The morphology of the wear tracks on the titanium alloys that were tested in 200 mg/dL glucose HBSS (diabetic) under OCP conditions and potentiostatic conditions are shown in **Figure 6.23** and **Figure 6.24** respectively.

Just like in the normal HBSS and pre-diabetic HBSS, the titanium alloys wear tracks are made up of scratches and grooves which represent abrasive wear (Chirico *et al.*, 2022; Enayati and Sayyedani, 2022). Abrasive wear is therefore one of the main acting wear mechanisms taking place in this solution. Deeper and more prominent wear grooves are observed on some areas of the wear tracks of the titanium alloys tested under anodic potential. These deep grooves are an indication of higher abrasive wear (Enayati and Sayyedani, 2022). This is usually formed during two-body wear where the hard surface cuts and removes the soft material thus forming deep grooves (Balla and Das, 2017). This same wear mechanism was observed by Wang *et al.* (Z. Wang *et al.*, 2017) for the biomedical Ti-25Nb-3Mo-3Zr-2Sn tested in Ringers solution under tribocorrosion conditions. The removed material then result in the three-body wear (Balla and Das, 2017). Extruded material which is an indication of plastic deformation/surface fatigue is once again seen in Ti-4.5Al-1V-3Fe. Wear debris that contained oxygen was also observed in these alloys. Oxygen peaks were also observed in the EDX analysis of the grey patches found on the alloys wear scar surface. The EDX spectra of Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe tested under OCP conditions is shown in Appendix C in Figure C-5.1 and C-5.2 respectively. The EDX spectra of Ti-6Al-1V-3Fe tested under potentiostatic conditions is shown in Appendix C in Figure C-6.1. This is all once again an indication of the formation of passive oxide films. It is important to note that these were found in patches and isolated wear debris as opposed to uniformly covering the wear scars due to the continuous mechanical wearing action of the alumina ball on the titanium alloy surfaces which resulted in continuous depassivation and repassivation of the passive film. The wear debris found on the wear tracks acted as third body material which contributed to the sharp fluctuations in the COF as well as the OCP and current in the OCP and potentiostatic tests respectively.

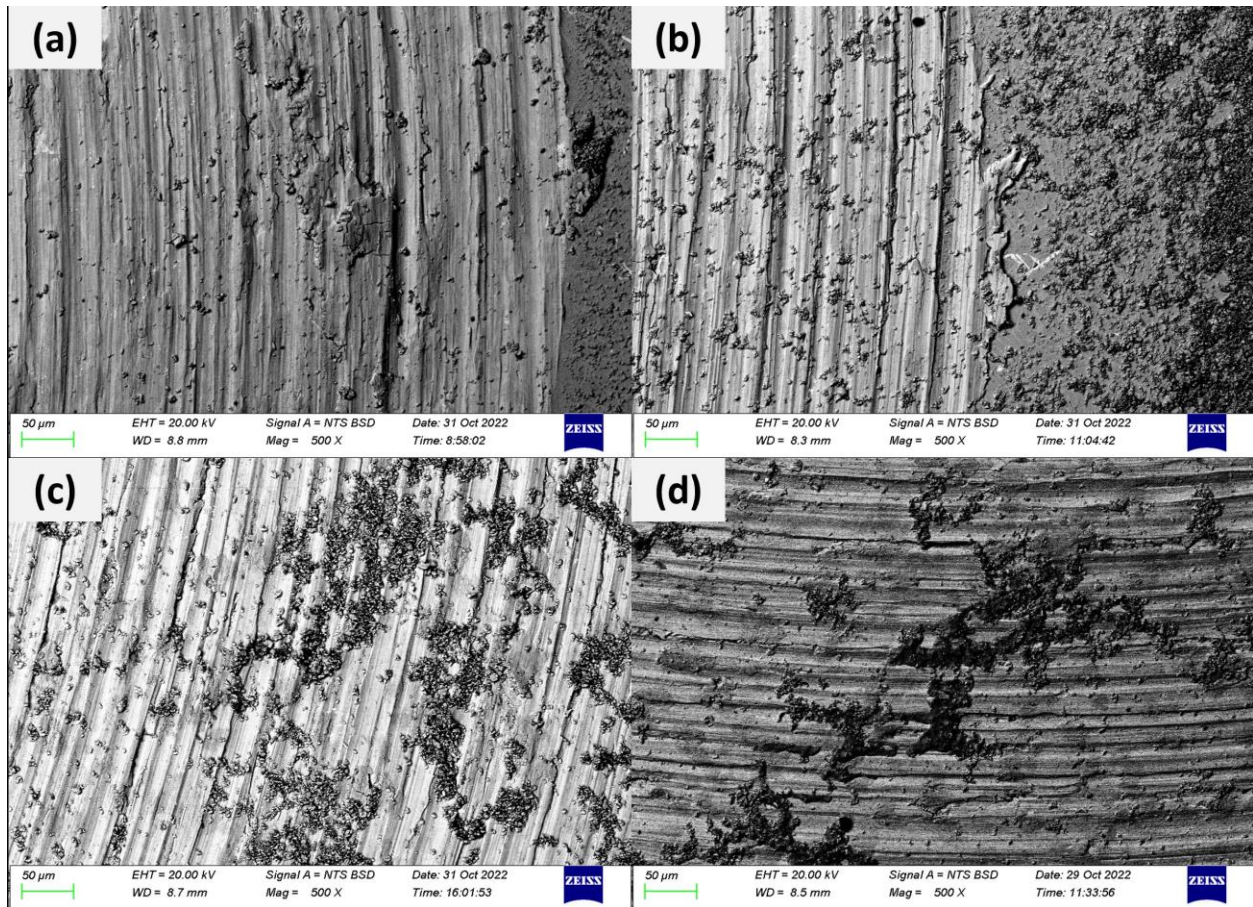


Figure 6.23: SEM images of (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V wear scars tested under OCP conditions in diabetic HBSS

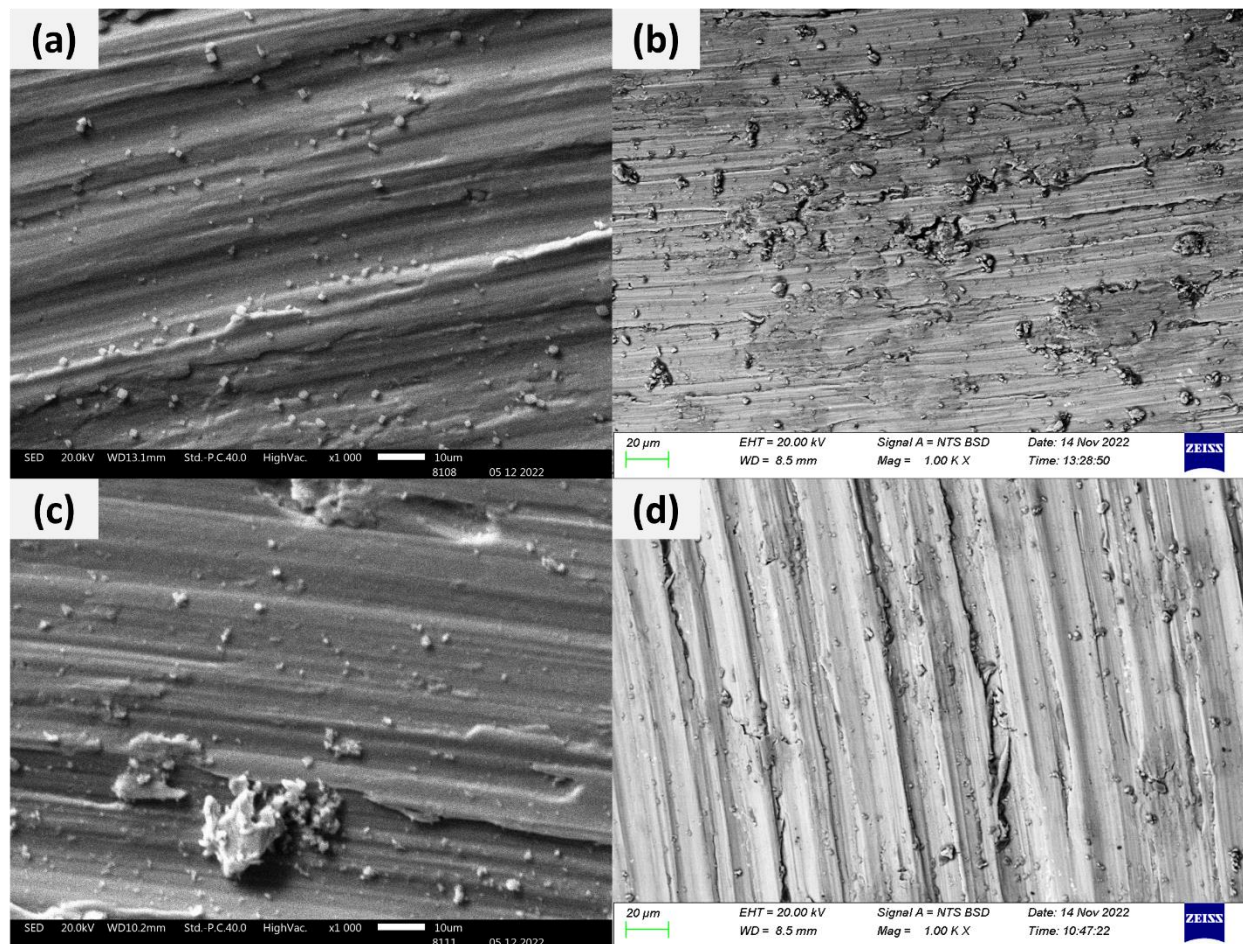


Figure 6.24: SEM images showing the wear scars of Ti (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V alloys tested under potentiostatic conditions in diabetic HBSS

6.4. Discussion

The tribocorrosion behavior of metallic alloys is influenced by several factors, including material composition. The proportions of different elements in an alloy can significantly impact its mechanical properties and corrosion resistance (Mathew *et al.*, 2009). This also subsequently affects the passive film formation of the alloys as well as the characteristics, effectiveness, and stability of the formed passive film. Mechanical properties such as hardness and yield strength significantly affect the tribocorrosion behavior of the alloy. The hardness of a material is crucial as a high hardness enables the material to resist abrasion and deformation, particularly plastic deformation, quite significantly (Mathew *et al.*, 2009; Doni *et al.*, 2013; Toptan *et al.*, 2019). Lubricants/coatings can reduce the friction and wear between the alloy and its surrounding

environment thus minimising the detrimental effects of tribocorrosion (More *et al.*, 2011; Barão *et al.*, 2021; Mehkri *et al.*, 2021). The corrosion resistance of the alloy as well as its microstructure also play a role in its ability to resist tribocorrosion. Lastly, environmental factors which includes the pH, temperature, and the presence of aggressive species such as acids and chlorides in the corrosive solution significantly impact tribocorrosion behavior (Mathew *et al.*, 2009; Dorozhkin, 2018; Pandey *et al.*, 2020)(Mathew *et al.*, 2009; Dorozhkin, 2018; Pandey, Awasthi and Saxena, 2020). It is therefore important to subject bioimplant materials to tribocorrosion tests to understand how they perform under both mechanical and corrosive stresses to select or design materials that meet the specific tribocorrosion requirements of a given application.

In this chapter, the low-cost experimental titanium alloys with either partial or full substitution of V with Fe were subjected to tribocorrosion testing in simulated body fluids under two different conditions. Firstly, the alloys were subjected to tribocorrosion testing under OCP and secondly, they were subjected to tribocorrosion testing under potentiostatic conditions at an anodic potential of +0.5V. This potential corresponds to the passive region of the titanium alloys under investigation. Under OCP conditions, the evolution of the open circuit potential during sliding was evaluated. During sliding, the OCP is expected to drop to lower/more negative values than the starting potential because the sliding action results in the removal of the protective passive film on the alloys surface thus making the alloys more active and exposed to the electrolyte. In the normal HBSS, the experimental alloys containing two beta stabilising elements, V and Fe, as well as the commercial alloy experienced great fluctuations in their potential which resulted in high average OCP during the sliding stages. These changes in the OCP represent the dynamic depassivation and repassivation rate of the passive films. The repassivation rate of the alloys depends on the chemical composition of the surface and the electrochemical conditions prevailing in the contact (More *et al.*, 2011). The composition of the passive film formed on the surface of Ti-3Fe seems to lack adequate properties that allows it to immediately rebuild when damaged hence the minimal OCP fluctuations observed for it. However, a previous study on the corrosion behavior of this alloy showed that the alloy had superior resistance to corrosion compared to that of Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe (Rundora *et al.*, 2023). This shows that the passive film of this alloy was good enough to adequately protect the alloy against corrosion alone, however, when subjected to both corrosion and wear, the passive film struggled to rebuild. The kinetics/rate of passivation needs to be understood better.

The impact of porosity of the alloys on the surface chemistry during corrosion and tribocorrosion was not investigated in this study. However, porosity is known to render the protective oxide layer of metallic alloys less resistant to corrosion attack (Makena and Shongwe, 2024). The introduction of pores in an alloy used for bioimplant manufacturing is beneficial in that it drastically reduces the elastic modulus of the alloy bringing it very close to that of the host bone (Makena and Shongwe, 2024). This is an attractive property as the stress shielding effect is reduced thus reducing the chances of revision surgery. However, the pores increase the surface area available for contact with the corrosive solution thus rendering the alloy susceptible to corrosion attack (Makena and Shongwe, 2024). Therefore, it is crucial to carefully determine the pore sizes in alloys manufactured by powder metallurgy techniques.

Some studies have reported that alloying titanium with iron as the sole beta stabilizer degrades the mechanical properties of the alloy due to the formation of some TiFe intermetallic compounds which reduces the alloys toughness and hardness (Fujii, 2014; Bolzoni *et al.*, 2016). The passive film potentially struggles to adhere to the damaged surface after the wear tests. This could explain the poor tribocorrosion behavior of Ti-3Fe. Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V were able to recover their initial potential and even exceed it when sliding was ceased during the first and the second stages of sliding indicating their superior repassivation capabilities compared to Ti-3Fe which managed to repassivate when sliding had ceased, but only to values lower than the starting potential.

The addition of glucose to HBSS has been previously reported to have an effect on the solution viscosity and subsequent ion diffusion within it (Liu and Wang, 2020). This ion diffusion rate becomes lower in HBSS with higher glucose concentrations, thereby reducing the corrosion of the material surface (Liu and Wang, 2020). Consequently, this translates to a higher corrosion potential and a lower corrosion rate. This positive effect of glucose was seen in the tribocorrosion tests conducted in the 100 mg/dL glucose HBSS (prediabetic) as the wear rates of the alloys in this solution were lower than those of the alloy samples tested in the normal HBSS. However, when the glucose concentration was increased beyond 100 mg/dL to 200 mg/dL, the wear rates of the alloys increased indicating the alloys poorer resistance to tribocorrosion in that solution. This is an indication that there is a limit at which the glucose affects the alloys positively. Liu *et al.* (2016) reported that a glucose concentration exceeding 216 mg/dL had a detrimental effect on the

corrosion resistance of the titanium alloys tested in that solution. The exact mechanism by which this takes place is still not fully understood.

During the sliding/wear action under tribocorrosion testing conditions in the diabetic HBSS, the dynamic depassivation and repassivation rates in this solution were not as great as those observed in the normal and pre-diabetic HBSS. The average OCP recorded during sliding was lower for all the alloys in the diabetic HBSS than in the normal HBSS and pre-diabetic HBSS. This shows that the passive oxide film can protect the alloys quite adequately against corrosion in the 200 mg/dL glucose HBSS, however, when mechanical wear is introduced to the system, the alloy's passive film struggles to protect the alloys against tribocorrosion. The alloys do however behave in a similar way to the alloys tested in the normal HBSS and 100 mg/dL glucose HBSS as Ti-3Fe still struggled to regain the passive state compared to the rest of the alloys. Ti-3Fe also exhibited the highest COF in all the solutions which is not always desirable, particularly when it comes to bioimplant materials as excessive friction between a biomedical implant and the bones and bone tissues in the human can cause inflammation, severe discomfort, and restricted mobility for the individual with the implant (Sharma and Sehgal, 2012; Chirico *et al.*, 2022). Iron acting as the single beta stabilising element in Ti-3Fe seems to have a negative effect on its tribocorrosion behavior. It has been reported that the mechanical properties of such alloys can be compromised due to the possible formation of detrimental intermetallic TiFe compounds forming in the structure of this alloy (Gahr, 1987; Fischer *et al.*, 2018). In addition to this, the absence of Al, could be a contributing factor to the poorer properties of Ti-3Fe in comparison to the alloys containing Al. This is because Al is a known alpha stabiliser, and this phase enhances and contributes to the overall hardness of the alloy (Bodunrin and Chown, 2021). Therefore, with the complete absence of aluminium in Ti-3Fe, this alloy becomes more susceptible to wear and tribocorrosion due to the lower hardness. The combined effect of V and Fe as beta stabilizers in Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe suppresses the formation of intermetallic compounds within the alloys thus improving the mechanical properties of the alloys which in turn has a positive effect on the alloys wear and tribocorrosion resistance (Bodunrin and Chown, 2021).

At applied anodic potential, the effects of sliding are seen through the evolution of current which occurs when the passive film is disturbed by the alumina counterbody. When sliding started during the potentiostatic tests in both solutions, the alloys experienced an abrupt shift in the current in the

anodic domain (to higher values). This was expected as the passive film depassivated thus exposing the bare alloy sample to the corrosive electrolyte. Just like in the OCP tests, the current fluctuated in the case of all the alloys indicating dynamic depassivation and repassivation of the passive film. Large current values are an indication of high oxidation/dissolution rates (Runa *et al.*, 2013). Ti-3Fe displayed the highest average current during sliding in both solutions thus further showing that its poorer tribocorrosion resistance in comparison to the other titanium alloys. Ti-6Al-1V-3Fe reached the lowest average current during sliding and it, together with Ti-6Al-4V, attained significantly lower values in current when the sliding had ceased compared to the rest of the alloys. This is an indication that these alloys surface properties allow for the spontaneous repassivation of the passive film. The effect of the 200 mg/dL glucose addition in the HBSS is also seen during the potentiostatic tests as the average currents obtained during and after sliding were much higher than those obtained in the normal HBSS and 100 mg/dL glucose HBSS thus cementing the fact that this higher glucose concentration has a slightly negative effect on the effectiveness and stability of the passive film during the sliding processes.

Various biomolecules found in the human body including glucose have been reported to have either a negative or a positive effect on the corrosion behavior of the alloys. Dimah *et al.* (2012) studied the tribocorrosion behavior of Ti-6Al-4V and commercially pure titanium in HBSS with the addition of protein (Bovine serum albumin (BSA)). The influence of the BSA on the corrosion behavior of the alloys was found to be negligible while it had a slightly greater effect when mechanical wear (tribocorrosion) was introduced. Because of the adsorption of the BSA on the alloy surfaces, there was a reduction in the oxide growth kinetics which resulted in an increase in the mechanical volume loss as there was no adequate passive oxide film to actively protect the surface from mechanical damage (Dimah *et al.*, 2012). Runa *et al.* (2013) found the BSA to have both a positive and negative effect on the tribocorrosion resistance of the titanium alloy (Ti-6Al-4V). The proteins were found to integrate the passive film reacting with the metal ions thus forming metal/protein complexes which absorb onto the alloy surface. This layer is then known as a tribolayer (Wimmer *et al.*, 2003, 2010; Mathew *et al.*, 2009; Runa *et al.*, 2013b). This tribolayer generally protective, however, it only forms after some time of sliding so in the initial moment of sliding/mechanical wear, the bare alloy surface is exposed to the electrolyte and albumin which can be detrimental to the alloys (Runa *et al.*, 2013). When repassivation occurs where the protein containing tribolayer forms on top of the wear scar, the initial damage is diminished due to the

protective nature of the tribolayer in comparison to the initial normal passive oxide layer. This favourable behavior of the formation of a tribolayer is not only dependent on the existence of the proteins/organic species in solution, but it also greatly depends on the characteristics of the normal passive film formed; how it interacts with the organic species (Runa *et al.*, 2013).

In this chapter, the different glucose concentrations (100 mg/dL and 200 mg/dL) also had both positive and negative effects on the tribocorrosion resistance of the titanium alloys. A lower glucose concentration (100 mg/dL glucose HBSS/prediabetic) resulted in the titanium alloys being more resistant to tribocorrosion in comparison to the normal HBSS. The diabetic/200 mg/dL glucose HBSS had a slightly negative effect on the tribocorrosion resistance of the titanium alloys as these alloys generally had a higher wear rate in this solution in comparison to the normal HBSS and the prediabetic HBSS. More studies, however, still need to be performed on the effects of various organic species, especially glucose, on the tribocorrosion behavior of various titanium alloys to gain better and clearer understanding on exactly how they affect the tribocorrosion resistance of the titanium alloys.

Tribocorrosion systems generally have two mechanisms which contribute to the materials degradation. These are namely mechanical wear as well as wear accelerated corrosion. Wear accelerated corrosion of passive alloys occurs as a result of the periodic removal of the passive film by mechanical action/wear followed by metal oxidation until repassivation occurs (Mischler, 2008). Mechanical wear consists of the detachment and elimination of metal particles during sliding (Mischler, 2008). In the case of the OCP tests, the corrosion measured is assumed to be negligible hence the wear volume loss occurs only as a result of the mechanical wear whereas in the potentiostatic tests, the wear volume loss is a combination of mechanical wear as well as corrosion wear (Licausi *et al.*, 2013). This is known as the synergistic approach of tribocorrosion systems. As expected, Ti-3Fe experienced the greatest volume loss in almost all the environments under the different testing conditions. Under both OCP conditions and potentiostatic conditions in both the normal HBSS and the 200 mg/dL glucose HBSS, it had the highest worn volume. In the prediabetic environment on the other hand, Ti-3Fe had the greatest volume loss under potentiostatic conditions only. This resulted in this alloy having the highest specific wear rate under those conditions. The poor tribocorrosion resistance of this alloy is because of its passive film properties which are yet to be established accurately using XPS. In addition to this, the poorer

mechanical properties of this alloy such as its hardness allowed for the alumina ball to abrade the alloy more compared to the other alloys thus removing more material from its surface.

The partial substitution of V with Fe seems to be beneficial as Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe displayed low worn volume loss and specific wear rates in both solutions during both tests. Their total worn volume and specific wear rates were closely comparable to that of the commercially available alloy. The wear rates of all the alloys under the specifically applied load in the normal HBSS, the 100 mg/dL glucose HBSS, and the 200 mg/dL glucose HBSS were well below 10^{-5} mm³/Nm, which is the proposed wear rate limit for the mild wear of metallic materials (Venkatesan and Rigney, 1992). While the wear rates observed in this study for the titanium alloys under examination fall within the category of mild wear, it's worth noting that hip joints typically exhibit optimal performance under wear rates categorised in the ultra-mild wear region (Fischer *et al.*, 2018). Therefore, wear rates in the mild wear range are deemed insufficient for biomedical applications and are, in fact, considered relatively high. However, the experimental alloys show promise because their wear rates are comparable to those of the commercially available Ti-6Al-4V alloy. To further enhance the wear characteristics of these alloys and bring them into the ultra-mild wear category, future research will explore surface modifications involving coatings and/or heat treatment (Obadele *et al.*, 2015).

In the case of the tests conducted under anodic potential, the total worn volume is made up of the volume loss as a result of the wear accelerated corrosion (V_{chem}) and the volume loss resulting from the mechanical wear (V_{mech}) (Mischler, 2008). In the normal HBSS and the glucose containing solutions, V_{chem} was found to be greater than the total volume loss which led to a negative V_{mech} . This is attributed to the uncertainties in the actual valence number for the oxidation reactions taking place during the tribocorrosion tests. V_{chem} is obtained through the integration of the current measured in the electrochemical potentiostatic experiments, provided that the valence of dissolution is known, and the secondary reactions are negligible. The transient coexistence of an active and passive state renders it difficult to estimate the valence of dissolution for metals such as Cr, Fe or Ti which present different valences for active dissolution (2 for Cr, Fe and Ti) and for the passive state (3 for Cr and Fe, 4 for Ti) (Mischler, 2008). This yields uncertainties on the relative contribution of the corrosion reaction to the overall material loss (Mischler, 2008). Because dissolution conditions in the wear scar are not known precisely and

anodic metal dissolution under active and passive conditions may occur with different valences, the values used in the calculation are subject to some uncertainty. This should not fundamentally alter the conclusions of the present study concerning the interactions of mechanical and electrochemical phenomena. A further uncertainty in the calculation of the results stems from the fact that possible corrosion reactions involving reduction of protons or oxygen are not taken into consideration when applying Faraday's law. It is assumed that when applying an anodic potential in the passive region the influence of corrosion can be neglected (Mischler *et al.*, 1999). In addition to this, the common assumption that TiO₂ is the only relevant oxide that forms on the titanium alloy surface and therefore the only relevant reaction to take into consideration when determining the valence number of the chemical reaction also yields uncertainties to the material loss resulting from the corrosion. Oxides of vanadium and/or aluminium could have formed part of the passive films of the titanium alloys under investigation in this study (Geetha *et al.*, 2009; Dimah *et al.*, 2012). However, establishing the exact oxides that formed and the valence numbers of the reactions would have to be determined using a specialized analysis such as XPS which was not conducted in this study, but is being considered for future studies.

The sliding wear behavior in metals and alloys can be defined by a sequence of events that includes surface and sub-surface plastic deformation, the creation of debris and material transfer, interactions with the surrounding environment, and mechanical blending (Venkatesan and Rigney, 1992). These combined processes ultimately result in the development of a mechanically mixed layer, often called the tribo-layer, on the surface of the alloy (Venkatesan and Rigney, 1992). Plastic deformation and delamination have been identified as key factors affecting the wear resistance of commercial alloys, as highlighted by various researchers (Runa *et al.*, 2015; Balla and Das, 2017; Cao and Mischler, 2018; Cui *et al.*, 2019; Gain *et al.*, 2021; Buciumeanu *et al.*, 2022; Enayati and Sayyedani, 2022). This was observed for Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V. However, the plastic deformation was not severe and was only observed in a few areas within the wear track as well as towards the edge of the track. Abrasive wear was one of the main acting wear mechanisms observed for the alloys in this study. This wear mechanism was reported by a vast number of researchers who conducted tribocorrosion studies on various types of titanium alloys (Dimah *et al.*, 2012; Licausi *et al.*, 2013; Bryant and Neville, 2016; Neto and Rainforth, 2020). In addition to this, adhesive wear also played a role in the tribocorrosion process as material transfer from the alloy to the ball and from the ball to the alloy occurred (Runa *et al.* 2013).

Tribochemical reactions were also a prominent wear mechanism for these alloys, particularly Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V as grey or black patches, which are usually an indication of oxides, were observed on the titanium alloys' wear scars. Oxygen was detected from the EDS analysis as well further cementing the idea of the formation of oxides.

The efforts to reduce the cost and toxicity associated with the popular commercially available alloy, Ti-6Al-4V, by partially substituting the expensive vanadium alloying element with a cheaper alternative, Fe, in order to develop new alloys with the desired properties and reduced cost, proved to improve the corrosion behavior of the alloys compared to Ti-6Al-4V (Bozic *et al.*, 2010; Bodunrin *et al.*, 2018; Rundora *et al.*, 2023). In this chapter, it has also been proven that this approach maintains good resistance to tribocorrosion that is closely comparable to that of the commercially available Ti-6Al-4V alloy.

6.5. Conclusion

This chapter clearly shows that the experimental titanium alloys where the partial substitution of V with Fe is employed possess tribocorrosion resistance that is comparable to the commercially available Ti-6Al-4V alloy. Ti-6Al-1V-3Fe displayed the best resistance to tribocorrosion compared to the other experimental alloys under OCP and potentiostatic conditions in all the environments. This alloy displayed very similar tribocorrosion behavior, worn volume loss, and specific wear rates to the commercial alloy and was in some cases better. Overall, the total worn volume loss, wear track surface area, maximum penetration, and specific wear rates of Ti-4.5Al-1V-3Fe, Ti-6Al-1V-3Fe, and Ti-6Al-4V were very similar as the values were found to be in a very close range. This is an indication that these alloys tribocorrosion resistance was very similar. The SEM images also showed that the alloys had very similar wear mechanism driving their tribocorrosion behavior. Overall, the alloys' wear rates lie within the mild wear region ($\leq 10^{-5}$ mm³/Nm). However, effort should be put in to get the wear rates of the titanium alloys in the ultra-mild wear region ($\leq 10^{-9}$ mm³/Nm) as biomedical implants, particularly hip joints, work well in this region. The alloys tribocorrosion behavior was found to be similar in the normal HBSS, pre-diabetic HBSS, and the diabetic HBSS, therefore, these alloys could potentially compete for commercial use where healthy patients as well as diabetic patients could utilize these alloys.

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Chapter 7: Conclusions and Recommendations

7.1. Conclusions

In this study, the suitability of low-cost and less toxic titanium alloys (Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe) for use as biomaterials was assessed by investigating their wear, corrosion, and tribocorrosion behavior. The corrosion and tribocorrosion behavior of these alloys were assessed in various simulated body fluids. The suitability of these alloys for use by diabetic people was also assessed by investigating the effects of various glucose concentrations on the corrosion and tribocorrosion behavior of the alloys. The following conclusions were drawn from the results:

- **The influence of alloy composition on the wear resistance of the alloys**

The full substitution of V with Fe was found to have detrimental effects on the wear behaviour of the alloys as Ti-3Fe had the highest COF, highest worn volume, and highest specific wear rate. This was attributed to the possibility of intermetallic TiFe compounds in the microstructure of the alloy which are known to degrade the alloy's mechanical properties such as its hardness. The partial substitution of V with Fe as in the case of Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe was advantageous as the worn volumes wear rates of these alloys were lower than that of Ti-3Fe and closely comparable to that of the commercial alloy, Ti-6Al-4V. Ti-4.5Al-1V-3Fe had the overall superior wear resistance as it had the lowest worn volume loss and lowest wear rate.

- **The influence of alloy composition and glucose addition on the corrosion resistance of the titanium alloys**

The experimental alloys all displayed good resistance to corrosion in the different simulated body fluids. Their corrosion rates were all acceptable for bioimplant application as they were well below the maximum acceptable limit of 0.13 mm/year. The corrosion resistance of the experimental alloys was closely comparable to that of the commercial alloy and was in some instances better. In the 0.9 wt.% sodium chloride solution and normal HBSS, Ti-4.5Al-1V-3Fe and Ti-3Fe displayed superior resistance to corrosion compared to the commercial alloy as they had lower corrosion rates in comparison. Ti-3Fe had the lowest corrosion rate in these two solutions and this was attributed to the properties of its passive film. However, detailed analysis into its passive film needs to be conducted

to get better insights into the composition of the film and its interaction with the corrosive environments. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe showed superior resistance to corrosion compared to the other alloys in the 100 mg dL⁻¹ and 200 mg dL⁻¹ glucose HBSS. These results showed that the experimental alloys can potentially find use in normal human body environments as well as diabetic environments and they can potentially compete with Ti-6Al-4V on a commercial scale.

- **The influence of alloy composition and glucose addition on the tribocorrosion resistance of the titanium alloys**

The partial substitution of V with Fe over the full replacement was once again found to be beneficial. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe were found to possess tribocorrosion resistance that was closely comparable to that of the commercial alloy in the normal HBSS as well as in the prediabetic and diabetic HBSS. Therefore, both healthy and diabetic patients could potentially utilise bioimplants made from these alloys. The wear mechanisms of these alloys are also comparable to those of the commercial alloy. Ti-3Fe on the other hand was found to possess the greatest worn volume loss and the highest wear rate amongst all the alloys under both the OCP and Potentiostatic conditions. This was once again attributed to its poorer mechanical properties compared to the other titanium alloys under investigation. The experimental and commercial alloys wear rates were found to lie in the mild wear region but for these alloys to be confidently accepted for long-term bioimplant use, their wear behavior should lie in the ultra-mild wear region.

7.2. Recommendations

- The exact mechanisms influencing the corrosion behavior of the experimental alloys, particularly Ti-3Fe, need to be investigated further. This should be done by investigating the properties of the passive oxide films formed on the alloy surfaces using XPS.
- Besides hardness, other mechanical properties such as toughness and fatigue should be studied to further assess the suitability of these alloys for biomedical use.
- The effects of surface modification such as nitriding on the wear and tribocorrosion behavior of these alloys should be investigated as a means to optimise the wear and tribocorrosion resistance of these alloys and to lower the wear rates to the ultra-mild wear region.

Appendix A: Titanium alloys wear track width

A-1: The following table presents the wear track widths of the titanium alloys tested in the normal HBSS under OCP and Potentiostatic conditions.

Titanium alloys	Wear track width (mm)	
	Open circuit potential	Potentiostatic
Ti-3Fe	2.43	2.43
Ti-4.5Al-1V-3Fe	1.49	2.00
Ti-6Al-1V-3Fe	1.61	1.63
Ti-6Al-4V	1.60	1.45

A-2: The following table presents the wear track widths of the titanium alloys tested in the pre-diabetic HBSS under OCP and Potentiostatic conditions.

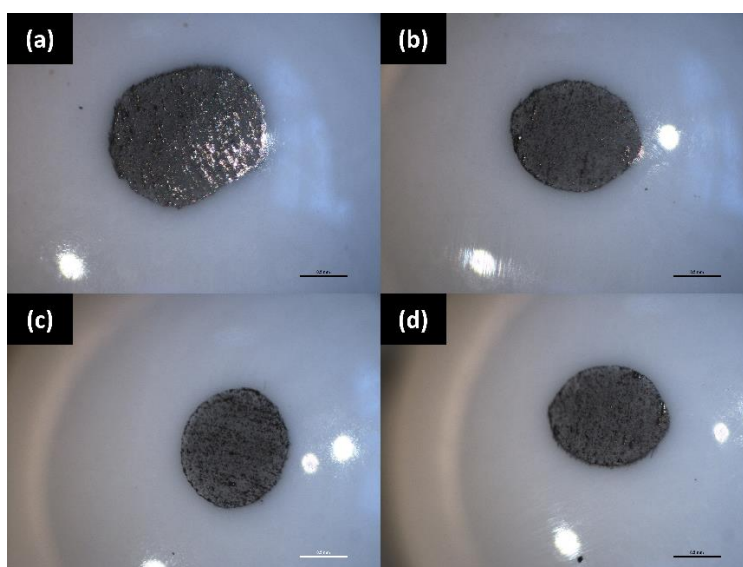
Titanium alloys	Wear track width (mm)	
	Open circuit potential	Potentiostatic
Ti-3Fe	2.29	2.24
Ti-4.5Al-1V-3Fe	1.53	1.47
Ti-6Al-1V-3Fe	1.58	1.81
Ti-6Al-4V	1.53	1.38

A-3: The following table presents the wear track widths of the titanium alloys tested in the diabetic HBSS under OCP and Potentiostatic conditions.

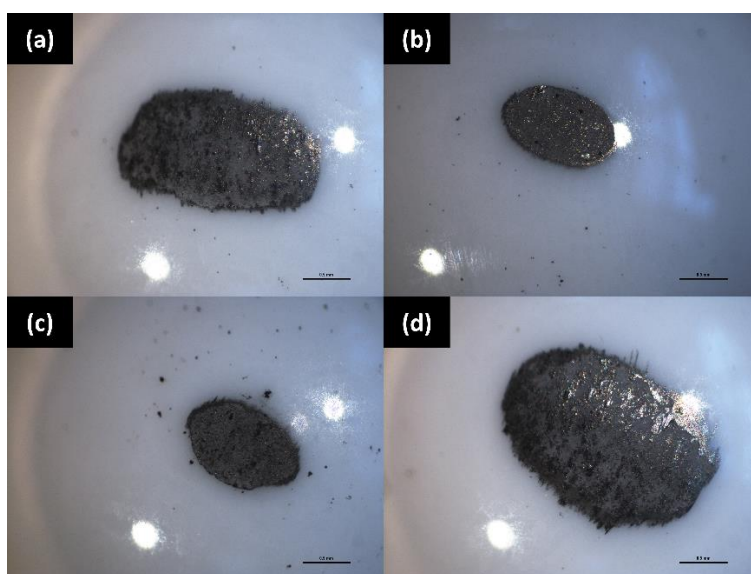
Titanium alloys	Wear track width (mm)	
	Open circuit potential	Potentiostatic
Ti-3Fe	1.54	2.20
Ti-4.5Al-1V-3Fe	0.99	1.80
Ti-6Al-1V-3Fe	1.61	1.37
Ti-6Al-4V	1.64	1.51

Appendix B: Alumina ball wear scars in tribocorrosion tests

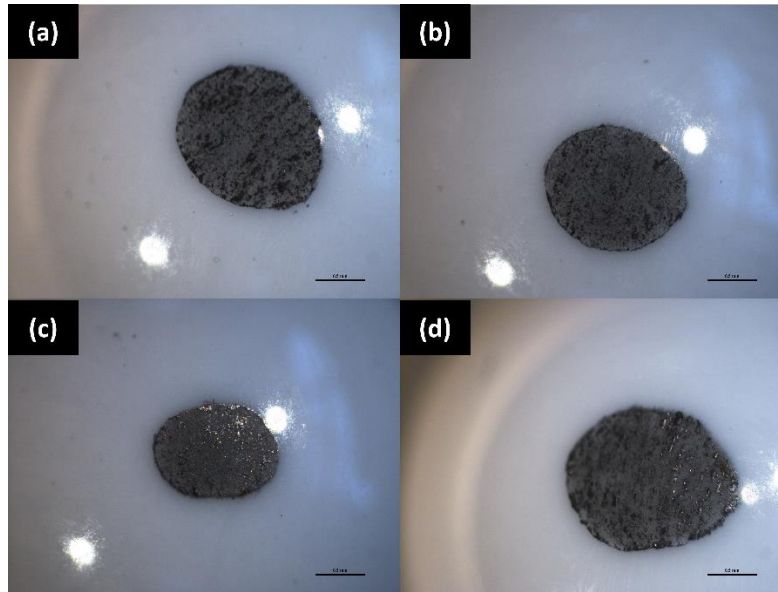
The following figures represents the wear scars on the alumina balls at the completion of the tribocorrosion tests in the various simulated body fluids.



B-1: The following figure presents the alumina ball wear scars for the tribocorrosion tests in the normal HBSS under OCP conditions against (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V



B-2: The following figure presents the alumina ball wear scars for the tribocorrosion tests in the pre-diabetic HBSS under OCP conditions against (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V



B-3: The following figure presents the alumina ball wear scars for the tribocorrosion tests in the diabetic HBSS under OCP conditions against (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V

Appendix C: Tribocorrosion tests EDX spectra

C-1: EDX spectra for titanium alloys in normal HBSS tested under OCP conditions

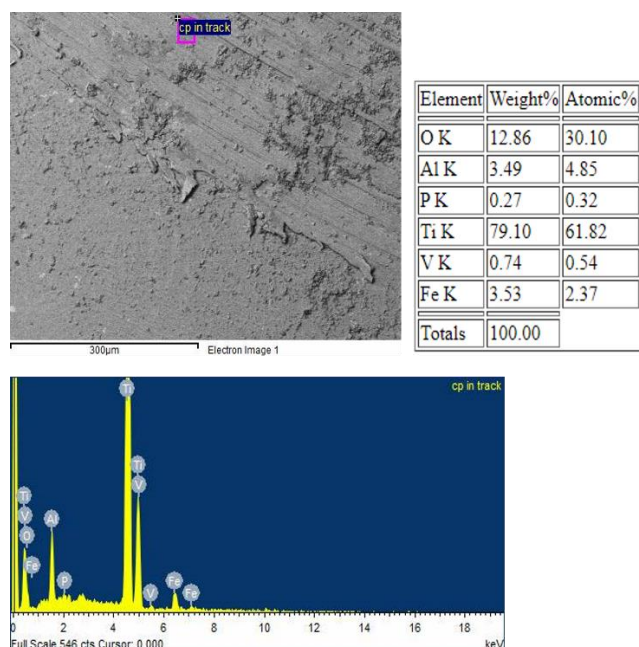


Figure C-1.1: Ti-4.5Al-1V-3Fe

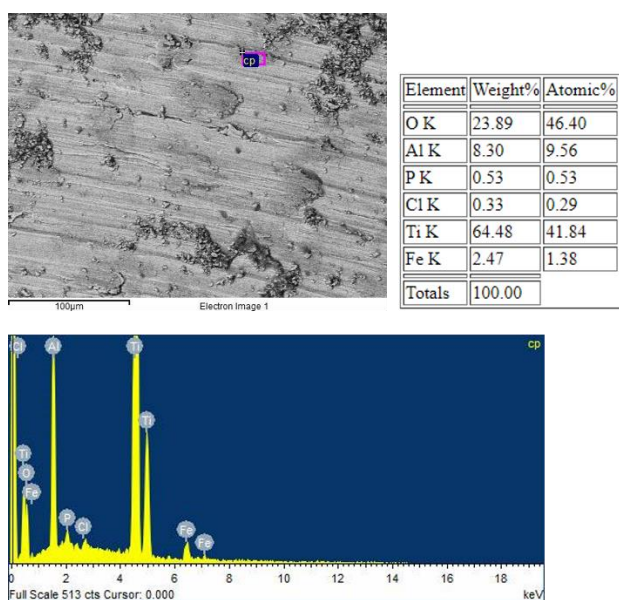


Figure C-1.2: Ti-6Al-1V-3Fe

C-2: EDX spectra for titanium alloys in normal HBSS tested under potentiostatic conditions

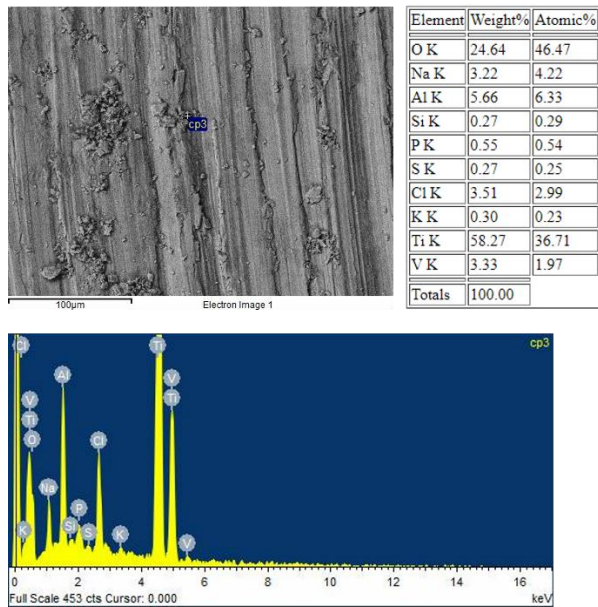


Figure C-2.1: Ti-6Al-4V

C-3: EDX spectra for titanium alloys in pre-diabetic HBSS tested under OCP conditions

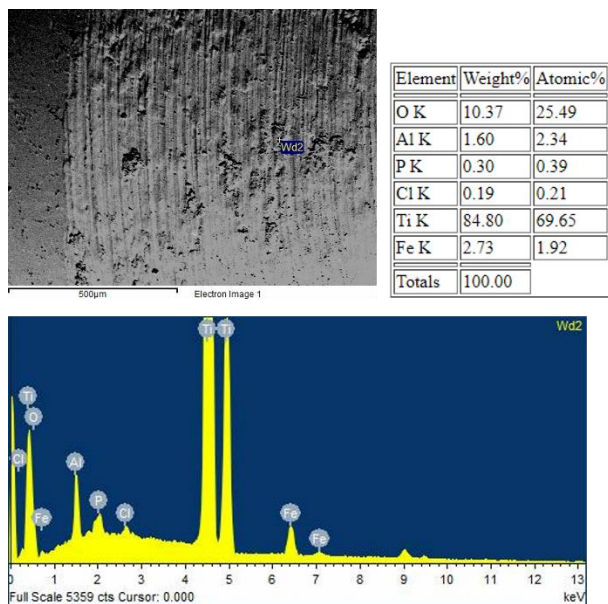


Figure C-3.1: Ti-6Al-4V

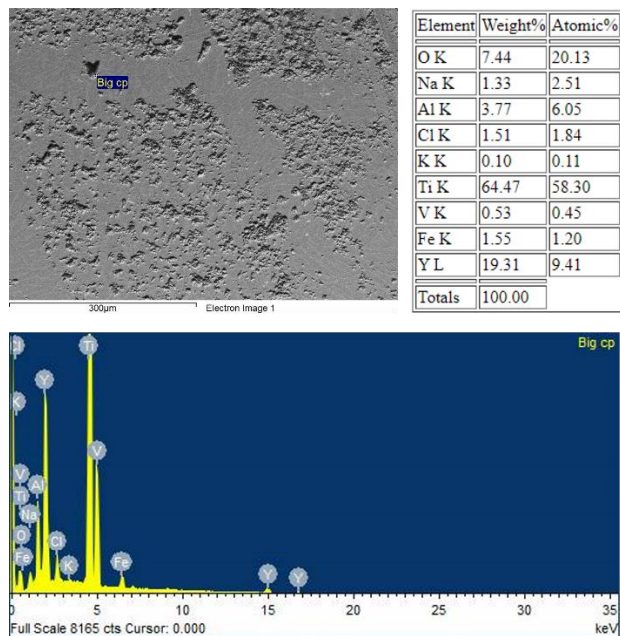


Figure C-3.2: Ti-4.5Al-1V-3Fe

C-4: EDX spectra for titanium alloys in pre-diabetic HBSS tested under potentiostatic conditions

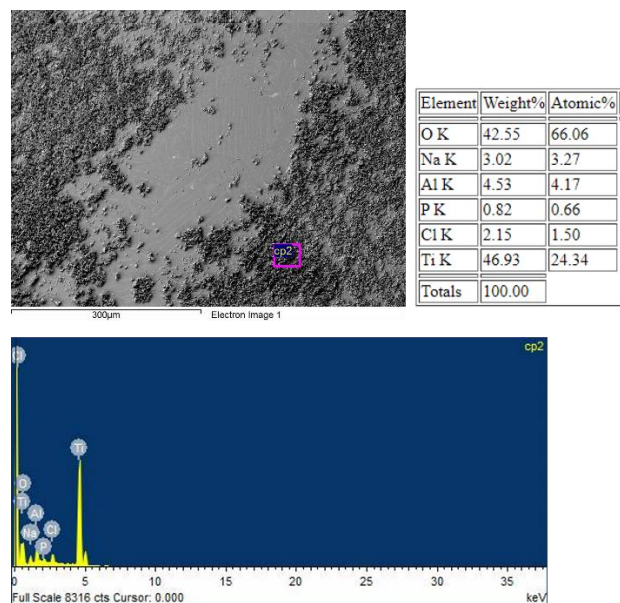


Figure C-4.1: Ti-4.5Al-1V-3Fe

C-5: EDX spectra for titanium alloys in diabetic HBSS tested under OCP conditions

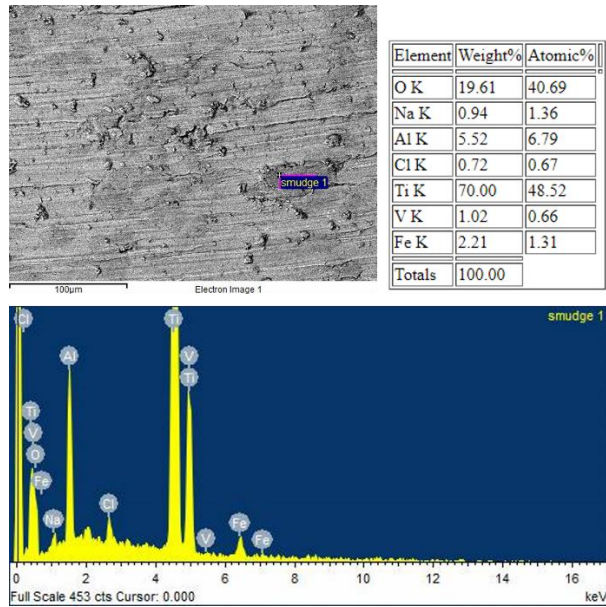


Figure C-5.1: Ti-4.5Al-1V-3Fe

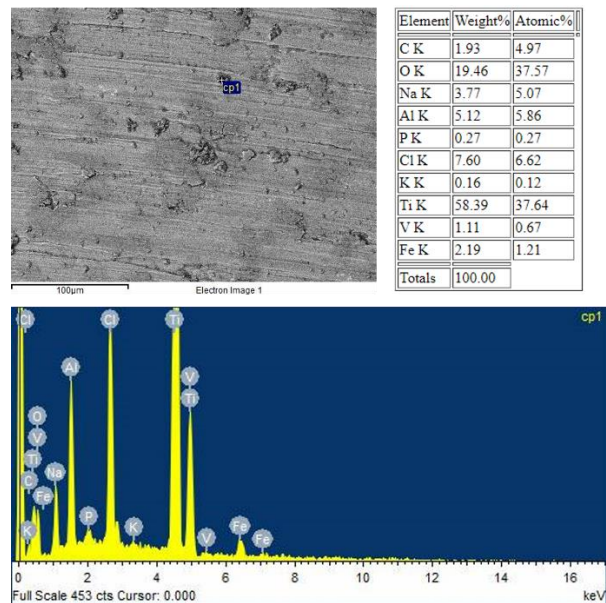


Figure C-5.2: Ti-6Al-1V-3Fe

C-6: EDX spectra for titanium alloys in diabetic HBSS tested under potentiostatic conditions

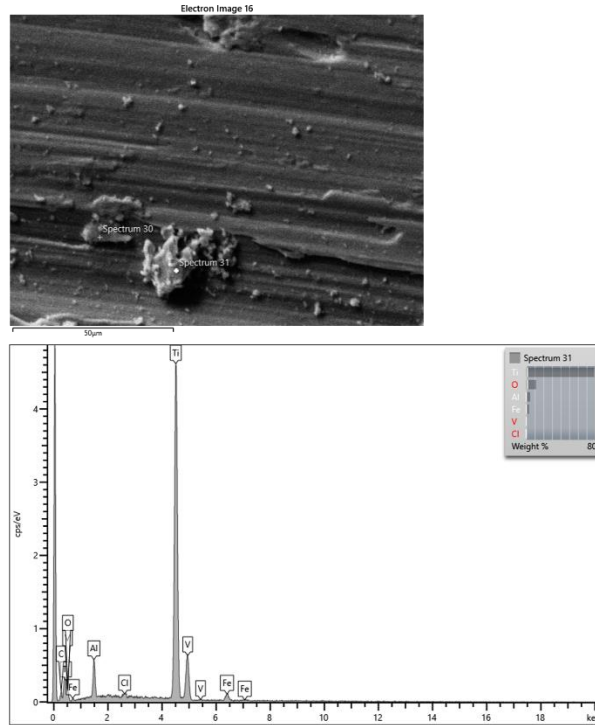


Figure C-6.1: Ti-6Al-1V-3Fe

Appendix D: Awards, presentations, and publications

D-1: Awards

- ❖ The Mary Veenstra Prize for Best Poster Presentation (Material Sciences) at the 57th Annual Meeting of the Microscopy Society of Southern Africa (2022)

D-2: Presentations

- ❖ 57th Annual Meeting of the Microscopy Society of Southern Africa, Johannesburg, South Africa, 2022 (Poster presentation)
- ❖ School of Chemical and Metallurgical Engineering Lunch Time Seminar, 2022 (Oral presentation)
- ❖ The Institute of Materials, Minerals & Mining (IOM3) Young Persons' Lecture Competition, Southern Africa, 2023 (Oral Presentation)
- ❖ Faculty of Engineering and the Built Environment, University of the Witwatersrand, Inaugural Research Seminar, 2023 (Oral presentation)

D-3: Journal article publication

Enhanced corrosion performance of low-cost titanium alloys in a simulated diabetic environment

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Abstract

Due to their excellent biocompatibility, titanium alloys are the preferred materials for manufacturing bioimplants. Low-cost titanium alloys have been developed as cheaper and less toxic alternatives for Ti-6Al-4V in the biomedical industry, but their suitability for diabetes patients is yet to be evaluated. With the growing number of diabetes patients globally, this research investigated the corrosion performance of low-cost Ti-3Fe, Ti-4.5Al-1V-3Fe, and Ti-6Al-1V-3Fe alloys in 0.9 wt.% sodium chloride solution and glucose-containing Hanks balanced salt solution (HBSS) compared with Ti-6Al-4V. Glucose was added to simulate the body fluids of patients with prediabetic and diabetic conditions. Open circuit potential and potentiodynamic polarization tests were performed. The results reveal that Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe alloys show superior corrosion resistance compared with the other alloys in the glucose-containing solutions, as they had the lowest corrosion rate and higher corrosion potential. Consequently, these alloys hold promise as effective implants, particularly for people living with diabetes.

KEYWORDS

corrosion, diabetes, glucose, low-cost, potentiodynamic, titanium

1 | INTRODUCTION

Since 1910, titanium and its alloys have been widely regarded as the benchmark material for use in various industries.^[1] The primary reason for this is the array of appealing properties that these materials exhibit, including high specific strength, outstanding high-temperature properties, remarkable toughness, good resistance to

corrosion in diverse corrosive environments, and high biocompatibility.^[2–4] Industries such as aerospace, sports, marine, electrical, desalination, oil and gas, automotive, chemical, and jewelry use these alloys due to their attractive properties.^[1,5,6] Titanium and its alloys are widely utilized in reconstructive surgery, particularly in orthopedics and dentistry, and are favored over stainless steel and cobalt-based alloys because of their

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exceptional biocompatibility, resistance to corrosion, and mechanical properties.^[7] Demand for titanium alloys in this field is growing rapidly, partly due to the increasing aging population, which is known to be at higher risk of hard tissue failure for various reasons,^[8] including bone weakening, commonly referred to as osteoporosis, trauma, and osteoarthritis, which is simply inflammation in bone joints.^[3]

One of the key factors driving the demand for bioimplants is the rapidly increasing prevalence of diabetes, considered one of the most significant health emergencies of the 21st century.^[9] Diabetes has become a critical health concern, with an estimated 537 million individuals affected by the disease worldwide as of the year 2021.^[9] Projections indicate that this number will likely climb to 643 million by 2030 and could rapidly increase to 783 million by 2045.^[9] Due to the growing occurrence of obesity, there has been a yearly rise in the incidence of type 2 diabetes among children and adolescents (up to 19 years old). This is a worrisome trend.^[9] Both type 1 and type 2 diabetes can lead to detrimental effects on multiple organs in the body, giving rise to severe, disabling, and potentially life-threatening health complications.^[9,10] Some of these complications include neuropathy, kidney disease, peripheral artery disease, and cardiovascular diseases.^[9,10] Diabetics also risk developing bone and joint diseases, such as osteoporosis and osteoarthritis.^[9] In extreme cases, they face the risk of leg and foot amputation, ultimately leading to the need for bioimplants.^[9] There is, therefore, a huge need for good biomaterials that are also affordable as their affordability will come under more scrutiny as more and more people will need them in the future.

Although titanium and its alloys possess desirable characteristics, their high cost has significantly limited their use in many industries, including the biomedical industry, restricting their use to applications where they are the sole option to meet specified operational needs.^[11] The expensive nature of titanium is attributed to the complex extraction process required to obtain the element from its ores, as well as the intricate processing methods involved in converting it into finished goods.^[12,13] Additionally, the use of costly alloying elements contributes to the high cost of the alloys.^[14] Commercially pure α -type titanium and $\alpha + \beta$ type Ti-6Al-4V and Ti-6Al-4V ELI (extra low interstitials) are the common alloys being employed in the biomedical industry today.^[14] However, the high cost and toxicity of the $\alpha + \beta$ type alloys resulting from the aluminum and vanadium alloying elements have made the inexpensive 316 L stainless steel seemingly attractive. However, the

drawbacks associated with 316 L stainless steel, such as its heightened vulnerability to localized corrosion and its high density, almost twice that of titanium, are concerning. Additionally, the high elastic modulus of 316 L stainless steel results in bone resorption and implant loosening.^[15,16]

Several research efforts have been geared toward combating the toxicity and high cost associated with titanium alloys. Some researchers replaced aluminum with oxygen and nitrogen in Ti-Fe-O-N $\alpha + \beta$ alloy.^[17,18] Fujii and Takahashi^[19] substituted iron for the costly beta stabilizer, vanadium, in Ti-Al-Fe $\alpha + \beta$ alloys. These were all modifications of the commercial alloy. Instead of fully replacing vanadium with other beta stabilizers like iron, chromium, and manganese, Bodunrin et al.^[4] developed a group of low-cost alloys by partially replacing vanadium with iron, a less expensive eutectoid β -stabilizing element. The retention of 1% vanadium inhibited the formation of brittle and degrading inter-metallic phases (titanium-iron). Bodunrin et al.^[4] found that this improved the alloy's mechanical properties, as well as its resistance to corrosion when compared with the commercial alloy. Our study aimed to further investigate the biocompatibility of these alloys by studying their corrosion behavior in simulated body fluids with various concentrations of glucose.

The blood glucose concentration is a significant measure for describing the bodily fluid environment. Glucose, like other organic molecules in the body, plays a vital role in the corrosion behavior of various metal alloys, including titanium alloys, cast iron, and mild steel.^[20] Investigating the properties of biomaterials in simple body fluids fails to accurately represent the human body environment because they lack the additions of essential proteins, bacteria, and other biomolecules, such as glucose, that are naturally found in the human body.^[21] The human body environment is quite intricate, and knowing exactly how bioimplants will behave in such an environment is important. Glucose inhibits the corrosion of mild steel and cast iron in acidic environments through a combination of physical and chemical interactions.^[22] Understanding the corrosion characteristics of implant materials in the body environment of typical diabetes patients is crucial, given the prevalence of diabetes. The experimental titanium alloys underwent corrosion testing in glucose-containing solutions representing diabetic and prediabetic patients to see how the alloys would hold when used in such environments. Prediabetic conditions were considered as these are conditions of elevated blood glucose concentrations above normal levels, which may also ultimately alter the corrosion properties of the metal implants. Although patients are treated to lower blood glucose

concentrations, it is important to perform these investigations as almost one in two adults living with diabetes are undiagnosed and thus unaware of their status.^[9]

2 | MATERIALS AND METHODS

2.1 | Materials

Four titanium alloys—one commercial alloy and three low-cost alloys—with compositions shown in Table 1 were previously produced using vacuum induction melting.^[4] The cast alloys were processed using hot isostatic pressing to eliminate any residual pores.^[4] For this study, small samples were cut from these alloys utilizing a Gold San computer numerical controls wire-cutting electrical discharge machine in preparation for the corrosion testing.

2.2 | Microstructural characterization

A high-resolution Zeiss Sigma field emission gun scanning electron microscope (FEG-SEM), equipped with back-scattered electron, secondary electron, and Oxford energy dispersive X-ray detectors, was used to examine the surface of the samples before and after the corrosion testing. The FEG-SEM was operated in back-scattered electron imaging and secondary electron imaging modes at 20 kV to reveal the microstructural features.

2.3 | Corrosion testing

The cut samples were hot-mounted in resin, ground, and polished until they had a mirror-like finish. Once the polishing was completed, the samples were rinsed in water and air-dried. The samples with a surface area of 0.283 cm² were subjected to corrosive solutions. To carry out the corrosion testing, a standard electrochemical cell with three electrodes connected to a Gamry®

potentiostat/galvanostat was used. The counter electrode was platinum, and the reference electrode was silver/silver chloride, saturated in a 3 M potassium chloride solution. The samples were tested in four different solutions: 0.9 wt.% sodium chloride solution, Hanks balanced salt solution (HBSS), 100 mg dL⁻¹ glucose-containing HBSS (simulating a prediabetic environment), and 200 mg dL⁻¹ glucose-containing HBSS (simulating a diabetic environment). The testing commenced by measuring the open circuit potential (OCP) for 3600 s. Then, potentiodynamic polarization tests were conducted, with measurements from −0.5 to 2.5 V at the standard scan rate of 0.1667 mV s⁻¹. The ASTM standard G59-97 was followed to determine the corrosion current density (I_{corr}), associated corrosion potential (E_{corr}), and corrosion rate.^[23]

3 | RESULTS

3.1 | Sodium chloride and Hanks balanced salt solution

The tested alloys are typically composed of two phases: the dark lamellae α -phase and the light β -phase, which form at the interfaces of the α - α lamellae. The SEM images captured after exposure to the various electrolytes show this. To evaluate the stability of the passive film on the surface of the experimental alloys compared with the commercial alloy in commonly used simulated body fluids (0.9 wt.% sodium chloride and HBSS), the OCP was analyzed for 3600 s. Figure 1 illustrates the OCP–time plots for the commercial and experimental alloys when submerged in 0.9 wt.% sodium chloride solution and HBSS. The OCP behavior of the alloys was similar in both solutions, ranging between −0.6 V and 0 V. All the alloys showed a gradual rise in OCP, shifting toward more positive values with increasing exposure time. This is the typical behavior of passive alloys as OCP indicates that a protective passive titanium dioxide film is forming, and thickening on the surface of the alloys is observed.^[24] The experimental alloys displayed a slightly

TABLE 1 Electrochemical parameters obtained after potentiodynamic tests in 0.9 wt.% sodium chloride.

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm year^{-1})	Rp (Ω)
Ti-3Fe	12.17	−0.14	0.08	0.0007	341 364
Ti-4.5Al-1V-3Fe	11.93	−0.10	0.14	0.0012	191 904
Ti-6Al-1V-3Fe	11.83	−0.25	0.28	0.0024	94 500
Ti-6Al-4V	11.82	−0.41	0.15	0.0014	168 793

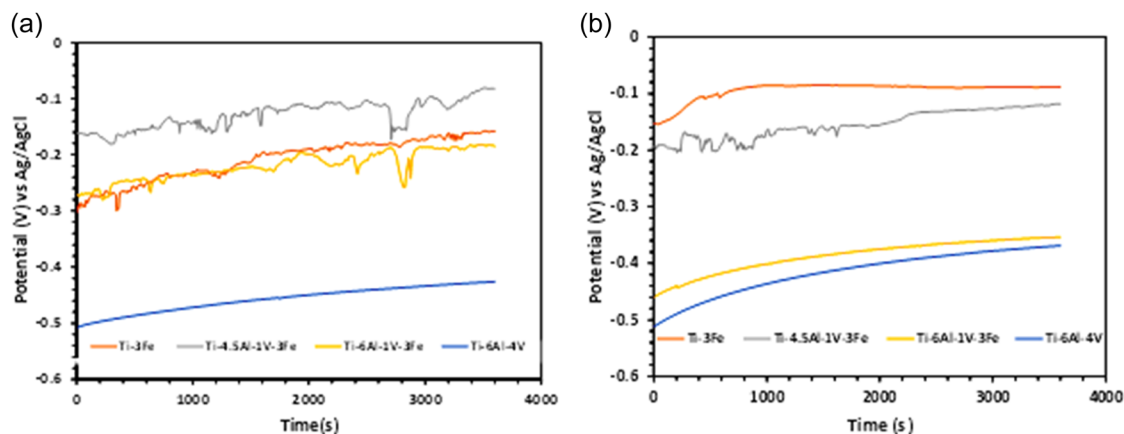


FIGURE 1 Open circuit potential (OCP)–time curve of titanium alloys in (a) 0.9 wt.% sodium chloride; (b) Hanks balanced salt solution (reference electrode is silver/silver chloride). [Color figure can be viewed at wileyonlinelibrary.com]

higher fluctuation in OCP when exposed to 0.9 wt.% sodium chloride solution compared with HBSS. This fluctuation can be explained by the dissolution and repassivation of the titanium dioxide film formed on the alloys, which can be attributed to the instability caused by anions like chloride ions in the corrosion media.^[25] The high diffusivity of chloride ions makes them easily penetrate the passive film.^[26]

Ti-4.5Al-1V-3Fe and Ti-3Fe alloys had the highest OCP values in both solutions. This indicates that these alloys have the least tendencies to corrode, with the Ti-3Fe alloy exhibiting the greatest OCP when immersed in HBSS. However, the OCP curve of Ti-4.5Al-1V-3Fe showed many fluctuations indicative of localized depassivation and repassivation of the passive film on its surface.^[27] Ti-6Al-4V had the lowest OCP in both solutions meaning that it has the highest tendency to corrode; however, its oxide film is more stable as it had a relatively smooth curve. These findings align with previous studies by Leshetla et al.^[28] and Bodunrin et al.^[4] The composition of titanium alloys influences the stability and integrity of the titanium dioxide film that forms on their surface.^[29] According to previous reports, oxide compounds of alloying elements such as aluminum and vanadium have been identified on titanium alloy surfaces.^[29] It has also been reported that because of the relatively simple composition and microstructure of commercially pure titanium and α titanium alloys, as well as the limited impurities found in these alloys, they are more resistant to corrosion than the $\alpha + \beta$ and β titanium alloys.^[24] This is because elements and impurities modify the oxide film, which can either improve or destroy the protective characteristics of the passive oxide film. The latter is observed in most commercial titanium alloys. Studies have shown that manganese, vanadium, and aluminum decrease the

protective nature of the oxide film.^[24] The protectiveness of this film is enhanced when noble alloying elements, such as palladium and ruthenium, are utilized.^[24]

Figure 2 exhibits the linear polarization curves of the experimental and commercial titanium alloys obtained after the OCP tests. The corrosion performance of the commercial and experimental alloys in both corrosive environments is comparable, as seen by the similarities in the alloys' passivation current densities. None of the alloys exhibited a distinct transition region from an active state to a passive state up to a stop potential of 2.5 V, indicating that they all underwent spontaneous passivation.

Transient currents were observed in the passive region of all the alloys in the sodium chloride environment. This is again due to the instability of the oxide film caused by the chloride ions in the solution. No transient currents were observed in the more complex HBSS, suggesting that these alloys can build up relatively stable anodic passive films in this environment. The corrosion parameters obtained during the linear polarization tests in the sodium chloride solution are displayed in Table 1. The corrosion potentials of the low-cost experimental alloys were similar while being significantly different from that of the commercial alloy. The corrosion current densities and corrosion rates of the alloys were generally similar, except for the low-cost Ti-6Al-1V-3Fe alloy, which exhibited some differences in its corrosion behavior. The Ti-6Al-1V-3Fe alloy, in particular, demonstrated the highest I_{corr} , indicating lower resistance to corrosion than the other alloys. This is further supported by its higher corrosion rate, indicating the alloy's faster degradation in the given solution.

The electrochemical parameters obtained when the samples were immersed in the HBSS (Table 2) are comparable to those obtained in the 0.9 wt.% sodium

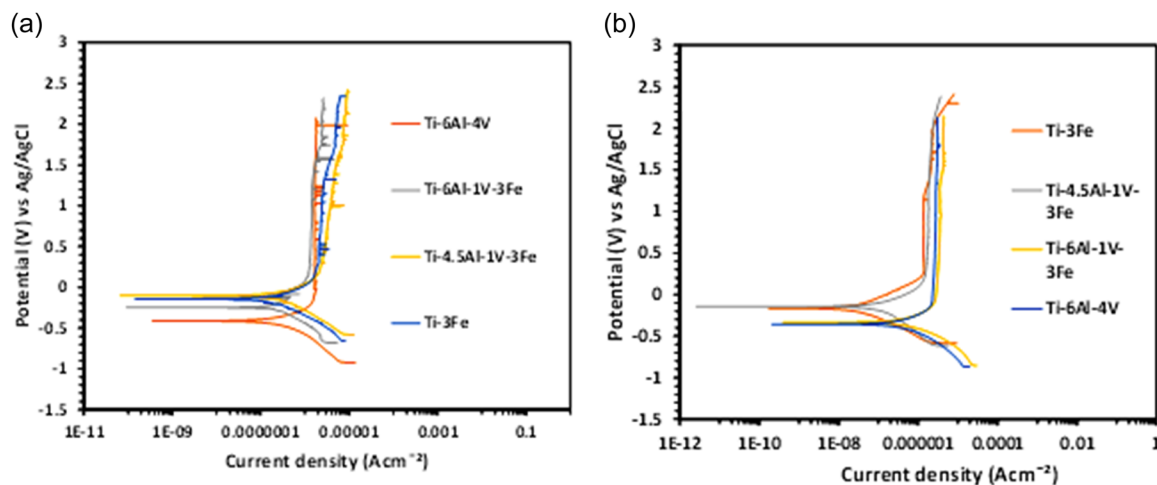


FIGURE 2 Polarization curves for titanium alloys in (a) 0.9 wt.% sodium chloride; (b) Hanks balanced salt solution (reference electrode is silver/silver chloride). [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Electrochemical parameters obtained after potentiodynamic tests in Hanks balanced salt solution.

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm year^{-1})	R_p (Ω)
Ti-3Fe	12.17	−0.17	0.07	0.0006	369 438
Ti-4.5Al-1V-3Fe	11.93	−0.14	0.09	0.0008	278 180
Ti-6Al-1V-3Fe	11.83	−0.33	0.29	0.0025	90 472
Ti-6Al-4V	11.82	−0.36	0.20	0.0017	132 990

chloride solution. It is important to highlight that apart from the commercial alloy, the titanium alloys under investigation are more susceptible to corrosion in HBSS than in 0.9 wt.% sodium chloride solution. This is seen through the higher corrosion potential values obtained in the HBSS. This observation is attributed to the difference in the complexity of the two solutions. The 0.9 wt.% sodium chloride solution has mainly one active anion, the chloride anion, while the HBSS consists of more than one active anion (chloride, carbonate, sulfate, and phosphate).^[30] This renders the HBSS environment more hostile than the sodium chloride solution environment, so it ultimately dissolves the passive layer on the alloys more readily.^[4,19,25] Once again, despite the commercial alloy being more prone to corrosion, the low-cost Ti-6Al-1V-3Fe alloy showed the highest corrosion rate. Therefore, this alloy can be characterized as having the poorest corrosion characteristics in both simulated body fluids. This finding was documented by Leshetla et al.^[28] The low-cost Ti-3Fe alloy once again shows the lowest corrosion rate, comparable to Ti-4.5Al-1V-3Fe.

The alloys' secondary electron images after the potentiodynamic tests are shown in Figures 3 and 4. From these images, it is evident that no significant

amount of corrosion took place. Most importantly, there was no sign of localized corrosion, such as pitting corrosion, indicating that uniform corrosion is the dominant form of corrosion in these alloys. This finding aligns with the observations reported by Leshetla et al.^[28] Some of the tested alloys in the HBSS exhibited a few notable chunks of corrosion product on their surfaces. However, overall, the amount of corrosion product observed on the alloy surfaces in 0.9 wt.% sodium chloride and HBSS was minimal, indicating that these alloys have favorable corrosion resistance in these environments.

3.2 | Prediabetic and diabetic Hanks balanced salt solution environment

Figure 5 displays the OCP curves of the alloys when submerged in HBSS containing varying concentrations of glucose. In the 100 and 200 mg dL^{-1} glucose solutions, the experimental Ti-4.5Al-1V-3Fe alloy exhibited a consistent and stable OCP from the initial period. In the 100 mg dL^{-1} solution, the OCP of the Ti-6Al-1V, Ti-3Fe, and Ti-6Al-1V-3Fe alloys stabilized after about

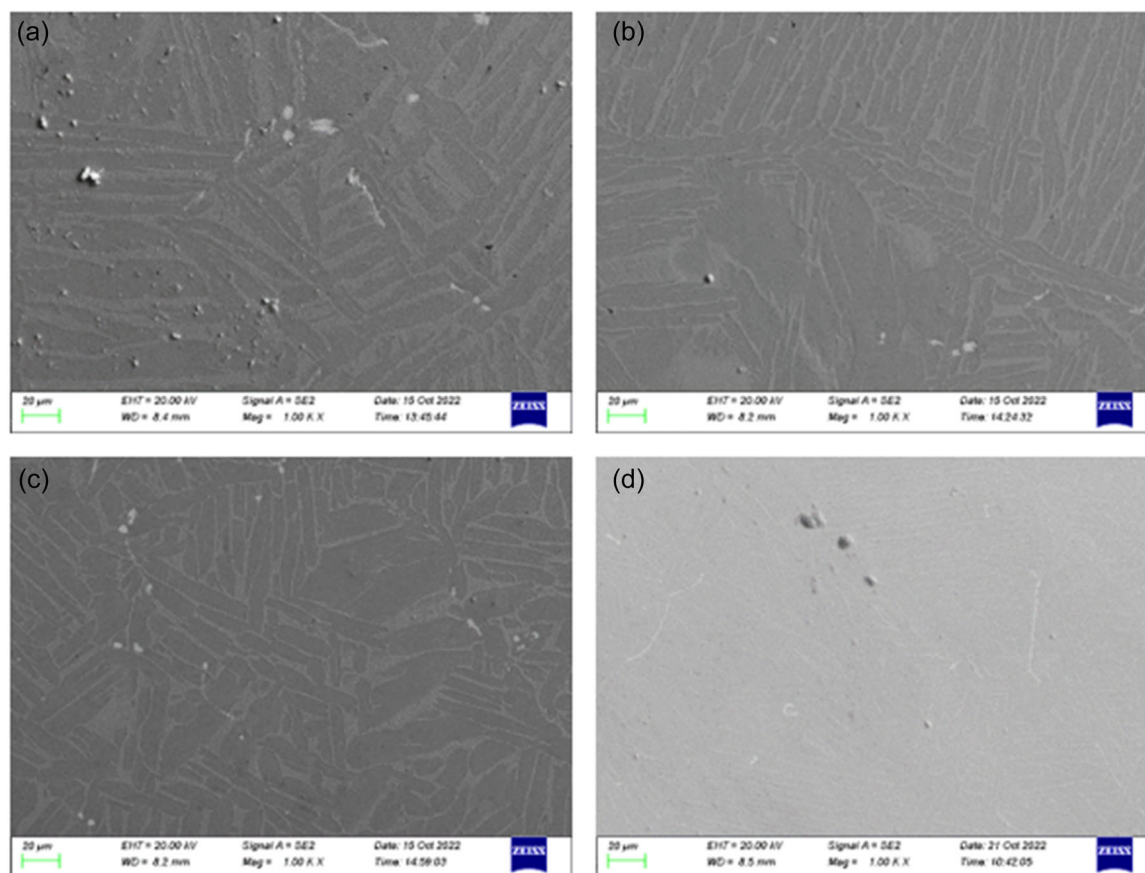


FIGURE 3 Scanning electron images of corroded titanium samples exposed to 0.9 wt.% sodium chloride solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202313927)]

2800 s. This similarity in OCP stability suggests that these alloys achieve a favorable balance between material dissolution and ion adsorption on their surfaces.^[31] In the 200 mg dL⁻¹ solution, the OCP of Ti-3Fe became stable shortly after the initial period, displaying a similar behavior to the Ti-4.5Al-1V-3Fe alloy in this solution, while the commercial alloy stabilized at around 3300 s. Although the Ti-6Al-1V-3Fe alloy had the highest OCP in the diabetic (200 mg dL⁻¹ glucose) environment, the passive film developed on its surface was very unstable. As observed from the breakdowns in the OCP, the downward trend suggests that this alloy struggles to build up its protective barrier in this solution.^[31] Similar to the observation in the sodium chloride and normal HBSS environments, Ti-6Al-4V had the lowest OCP in both glucose environments, suggesting its high tendency to corrode compared with the experimental alloys. According to the corrosion potential values in Tables 3 and 4, the E_{corr} of all the alloys except for Ti-3Fe was slightly higher at the diabetic glucose concentration of 200 mg dL⁻¹ than at the prediabetic glucose concentration of 100 mg dL⁻¹. This indicates that the corrosion resistance of the alloys seems to be higher at higher glucose

concentrations. Figure 6 illustrates the potentiodynamic polarization curves of the titanium alloys when immersed in HBSS with varying glucose concentrations.

The corrosion behaviors of these alloys exhibit a similar trend, as the curves show close resemblance in both media. In the prediabetic medium, transient currents were observed only in the commercial alloy. All the alloys displayed comparable passivation current values. In the diabetic environment, transient currents were observed in the commercial alloy, as well as in the Ti-4.5Al-1V-3Fe alloy. The measured corrosion potentials of the alloys in both solutions, as seen in Tables 3 and 4, were very similar. Apart from Ti-3Fe, the corrosion potentials in the diabetic solution are slightly higher than those in the prediabetic solution. The corrosion current densities were quite different from each other in both solutions. In the prediabetic environment, it is quite clear that the alloys have similar corrosion resistance as their corrosion rates lie within a similar range. Among these alloys, the Ti-4.5Al-1V-3Fe alloy has a reduced susceptibility to corrosion due to its higher corrosion potential, and it demonstrated the lowest corrosion rate in this particular solution. In the diabetic solution (200 mg/dL⁻¹ glucose),

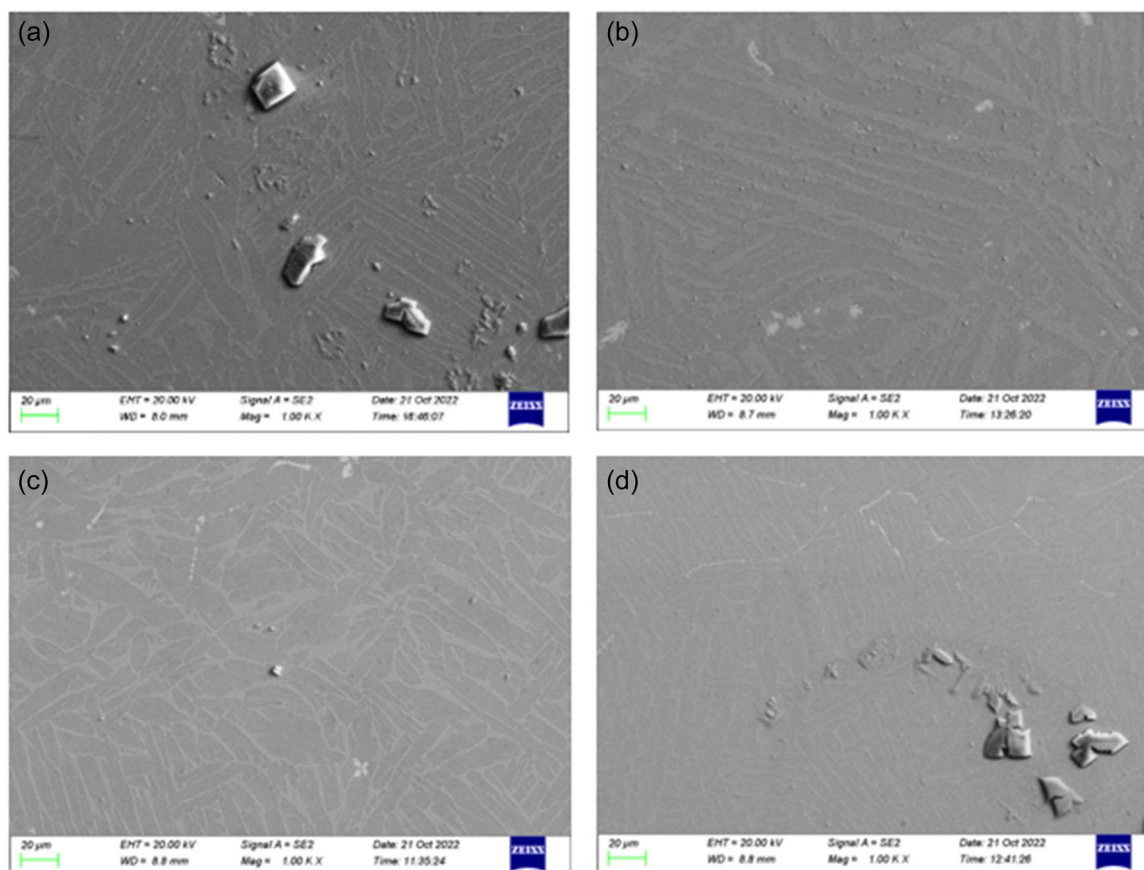


FIGURE 4 Scanning electron images of corroded titanium samples exposed to Hanks balanced salt solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; (d) Ti-6Al-4V. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202313927)]

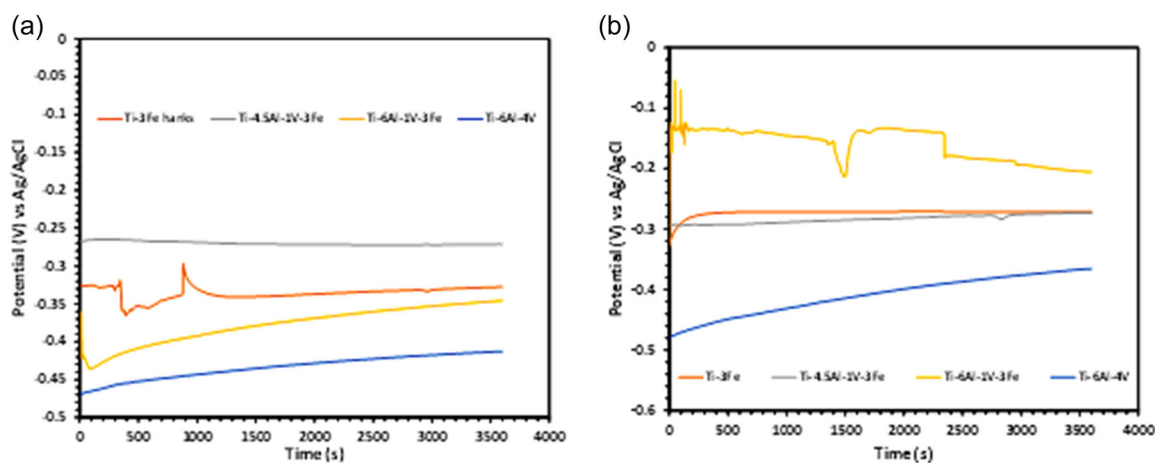


FIGURE 5 Open circuit potential (OCP) of the titanium alloys in (a) Hanks balanced salt solution (HBSS) + 100 mg dL⁻¹ glucose; (b) HBSS + 200 mg dL⁻¹ glucose. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202313927)]

the commercial alloy, with the highest tendency to corrode, had the poorest resistance to corrosion as it also had the highest corrosion rate. The Ti-6Al-1V-3Fe and Ti-4.5Al-1V-3Fe alloys exhibit the lowest corrosion rates, the least susceptible to corrosion in this solution.

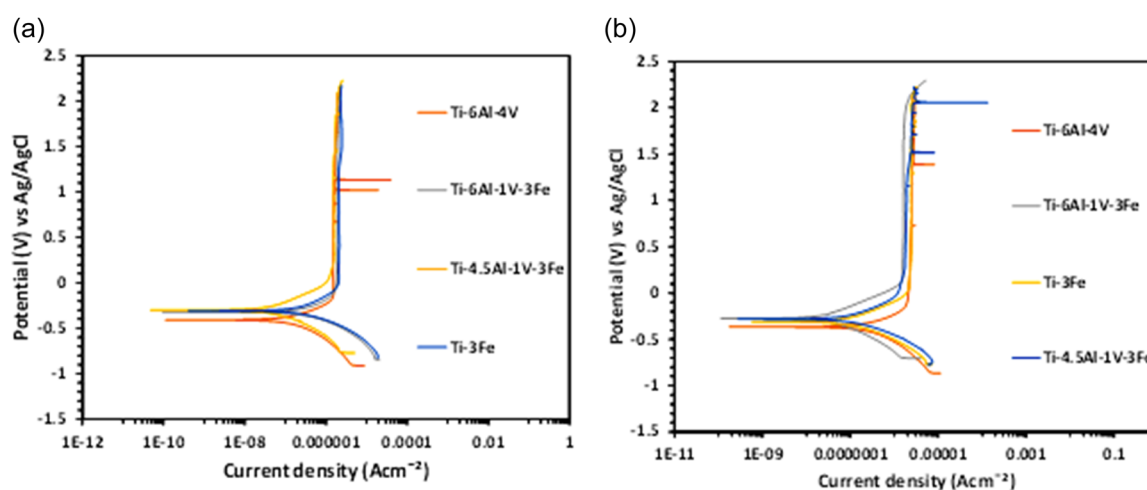
The SEM images after the potentiodynamic tests in the glucose solutions are displayed in Figures 7 and 8. It is evident from the images that no form of localized corrosion, such as pitting corrosion, was observed. The dominant corrosion mode for these alloys at both glucose

TABLE 3 Electrochemical parameters obtained after potentiodynamic tests in Hanks balanced salt solution + 100 mg dL⁻¹ glucose.

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm year^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.31	0.15	0.0013	169 971
Ti-4.5Al-1V-3Fe	11.93	-0.30	0.04	0.0003	706 713
Ti-6Al-1V-3Fe	11.83	-0.32	0.17	0.0015	152 595
Ti-6Al-4V	11.82	-0.41	0.09	0.0008	281 152

TABLE 4 Electrochemical parameters obtained after potentiodynamic tests in Hanks balanced salt solution + 200 mg dL⁻¹ glucose.

Alloy	Equivalent weight	Associated corrosion potential (V)	Corrosion current density ($\mu\text{A cm}^{-2}$)	Corrosion rate (mm year^{-1})	Rp (Ω)
Ti-3Fe	12.17	-0.31	0.08	0.0007	344 045
Ti-4.5Al-1V-3Fe	11.93	-0.28	0.06	0.0005	457 269
Ti-6Al-1V-3Fe	11.83	-0.27	0.04	0.0003	696 238
Ti-6Al-4V	11.82	-0.37	0.12	0.001	219 179

**FIGURE 6** Potentiodynamic curves of the titanium alloys in (a) Hanks balanced salt solution (HBSS) + 100 mg/dL⁻¹ glucose; (b) HBSS + 200 mg dL⁻¹ glucose. [Color figure can be viewed at wileyonlinelibrary.com]

concentrations was uniform corrosion. This can be seen as the alloys have relatively no defects on their surfaces, apart from the deposits of corrosion products on their surfaces. The quantity of corrosion product on the surface of the alloys does not directly impact their corrosion resistance, as all the alloys exhibited low corrosion rates within a similar range.

4 | DISCUSSION

The outstanding resistance to corrosion of titanium alloys can be primarily attributed to the development of a stable and adherent passive film on their surface upon

exposure to corrosive environments. This passive film typically consists of two layers composed of stable oxide compounds. These oxides are anatase, which serves as the inner layer, and rutile, which serves as the outer layer of the passive film.^[3,29] The formation of the hard titanium dioxide layers is a result of the diffusion of oxygen through the following reaction: $\text{Ti} + 2\text{H}_2\text{O} \rightarrow \text{TiO}_2 + 4\text{H}^+ + 4\text{e}^-$.^[3] The presence or addition of other elements to titanium can potentially modify the double-layered passive film. These modifications can either be beneficial or detrimental to the alloy's resistance to corrosion. Leshetla et al.^[28] reported that the vanadium and aluminum oxides formed in the passive film of the commercial alloy were detrimental to the corrosion

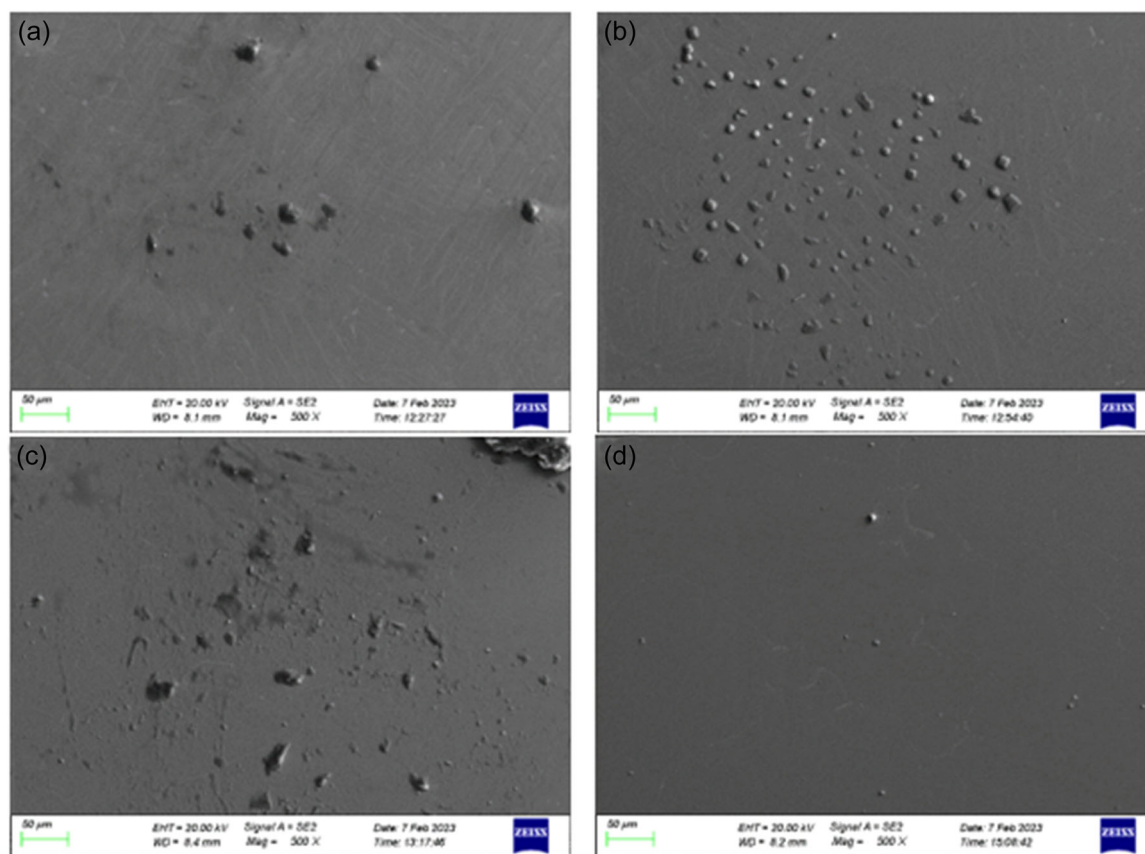


FIGURE 7 Scanning electron images of corroded titanium samples in 100 mg dL⁻¹ Hanks balanced salt solution: (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202313927)]

behavior of titanium alloys. This is because they render the oxide film unstable, while elements like ruthenium and palladium, which are predominantly found in β titanium alloys, promote excellent corrosion resistance. Also, they improve the protectiveness of the titanium oxide layer.^[28] In addition to this, the constituents, severity of the electrolyte, its temperature, the complexity of the ions in solution, and the immersion time have all been reported to influence the corrosion behavior of metallic alloys.^[4]

The corrosion performance of the inexpensive experimental titanium alloys was therefore evaluated in simulated body fluids to understand the effect of their compositions and the electrolyte's ion complexity on their resistance to corrosion. Similar corrosion behavior trends were observed for these alloys in 0.9 wt.% sodium chloride solution and HBSS. The transient currents observed in some of the alloys were due to the chloride ions in the 0.9 wt.% sodium chloride solution. These currents indicate a disruption in the development and stability of the passive films on the alloys' surfaces.^[32] Although there was no significant variation in the corrosion rates of the alloys in both solutions, the corrosion potentials of the experimental alloys are

slightly higher in the 0.9 wt.% sodium chloride solution than in HBSS. This suggests that the surface of the alloys is more activated in HBSS.^[28] In the 0.9 wt.% sodium chloride solution, the chloride ion is the main attacking anion on the surface of the alloys, while in HBSS, the anions responsible for corrosion include phosphate, chloride, sulfate, and carbonate.^[4] It has been reported that corrosive media with multiple anions can more easily dissolve the passive layer than electrolytes with a single anion.^[4]

The OCP and polarization results (Figures 1 and 2) and the electrochemical parameters in Tables 1 and 2 show that the experimental alloys have better resistance to corrosion due to their higher corrosion potentials. Ti-3Fe exhibits superior corrosion resistance compared with the other alloys in the sodium chloride solution and HBSS. This superior corrosion resistance can be attributed to its low corrosion rate, as evidenced by its high corrosion potential and low corrosion current density. Alloying titanium with iron as the sole beta stabilizer, however, has been found to degrade the mechanical properties of the alloy. This is due to the formation of some intermetallic compounds, such as titanium-iron phases, which make the alloys brittle, thus reducing their toughness.^[33,34]

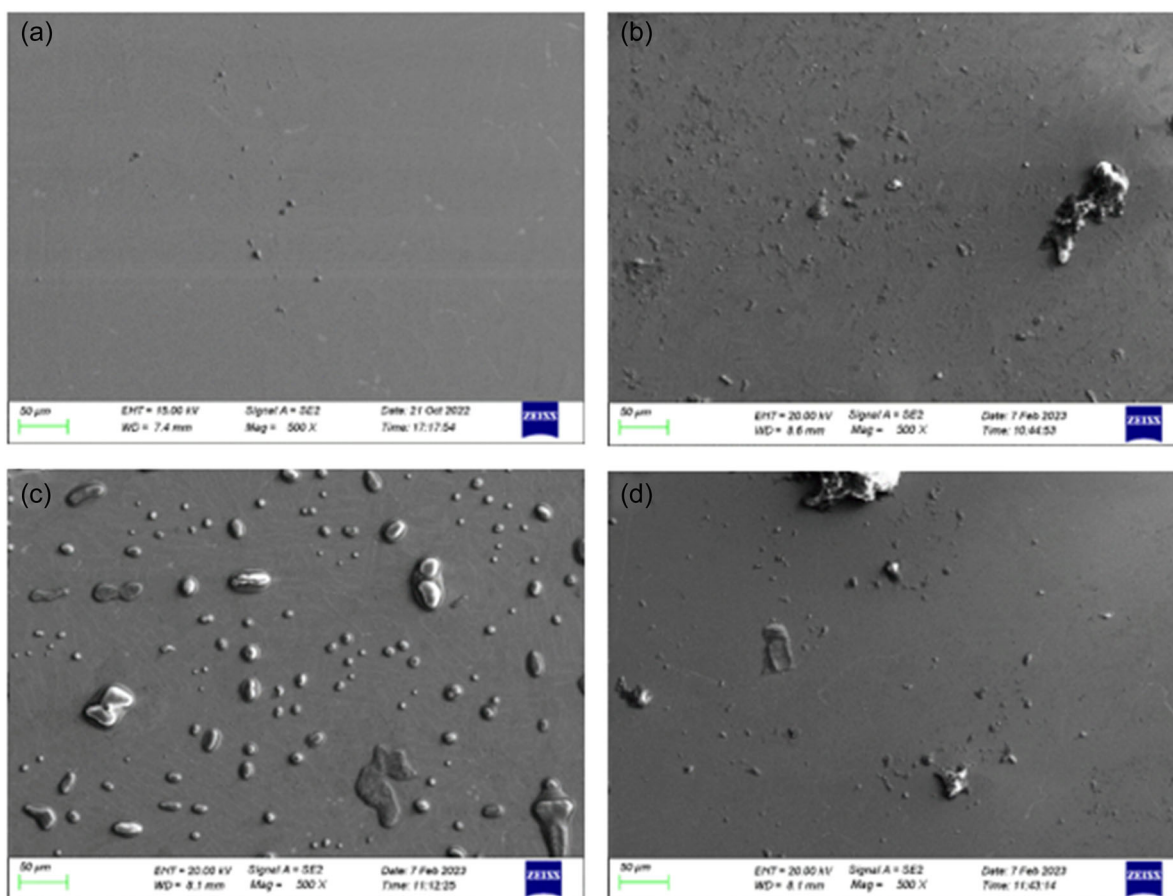


FIGURE 8 Scanning electron micrographs of corroded titanium samples in 200 mg dL^{-1} Hanks balanced salt solution (HBSS): (a) Ti-3Fe; (b) Ti-4.5Al-1V-3Fe; (c) Ti-6Al-1V-3Fe; and (d) Ti-6Al-4V. [Color figure can be viewed at [wileyonlinelibrary.com](https://onlinelibrary.wiley.com/doi/10.1002/maco.202313927)]

Some studies, however, found that it enhances the alloy's resistance to corrosion.^[26,27] This is evident in the results obtained from the current study, as Ti-3Fe has the lowest corrosion rate when exposed to both solutions. The precise mechanism by which iron enhances the stability and protectiveness of the titanium oxide passive film is still not completely understood. To acquire a more profound comprehension of the role of iron in the corrosion behavior of these alloys and the mechanisms underlying their superior performance, further tests and investigations are required. Despite the experimental Ti-6Al-1V-3Fe alloy having the highest corrosion rate among the examined alloys in both solutions, it displays a lower inclination to undergo corrosion than the commercial alloy. The corrosion rate is, however, well below the maximum acceptable corrosion rate for bioimplant materials (0.13 mm per year), just like the rest of the alloys.^[35] Additionally, while the corrosion rate may be higher for Ti-6Al-1V-3Fe, its overall corrosion resistance may still be superior to that of the commercial alloy, indicating that other factors, such as composition and microstructure, play a role in determining the alloy's

overall resistance to corrosion. These results are consistent with the observations made by Leshetla et al.,^[28] who tested these alloys in the same simulated body fluids. The current study's SEM images of the alloys confirm that the corrosion behavior is predominantly uniform corrosion, without any indication of localized corrosion such as pitting or crevice corrosion. The absence of localized corrosion further supports the low corrosion rates observed for these alloys in both solutions, indicating their good overall corrosion resistance.

Biomolecules in the human body environment play a role in an implant material's resistance to corrosion. Biomolecules such as proteins have been found to either enhance or degrade the corrosion resistance of implant materials.^[35–38] Because of the bone and joint disorders developed by diabetic people, it was important to understand the effects of glucose on the corrosion behavior of these titanium alloys. The corrosion rates of the alloys at both glucose concentrations are quite like each other, and they are well below the accepted rate of 0.13 mm per year . In the prediabetic environment, the Ti-4.5Al-1V-3Fe alloy exhibits superior corrosion

resistance compared with the other alloys. It demonstrated the lowest corrosion rate and corrosion current density, indicating its ability to withstand corrosion and maintain its integrity in this environment. Similarly, in the diabetic HBSS, the experimental Ti-6Al-1V-3Fe alloy outperforms the other alloys, showing the lowest corrosion rate and the least susceptibility to corrosion. The alloys tested in the prediabetic solution exhibit a higher tendency to corrode than those in the diabetic solution, indicated by their lower corrosion potential, suggesting a greater susceptibility to corrosion in the prediabetic environment. From this, we deduce that a high glucose concentration is more effective in inhibiting the corrosion of the alloys. The corrosion rates are, however, quite similar to each other. The glucose concentration in HBSS primarily affects the viscosity of the solution and the diffusion of ions within it.^[31] Higher glucose concentrations in HBSS increase its viscosity, leading to stronger ion adsorption on the surface of the titanium alloys but a slower rate of ion diffusion.^[31] This ion diffusion rate becomes lower in HBSS with higher glucose concentrations, thereby reducing the corrosion rate of the material surface.^[31] Consequently, higher glucose concentrations contribute to an increase in corrosion potential and a decrease in corrosion current density, ultimately resulting in a lower corrosion rate.

Apart from Ti-3Fe, the titanium alloys' corrosion rates are lower than those of the alloys tested in 0.9 wt.% sodium chloride solution and normal HBSS. In addition, the corrosion rates are well below the maximum acceptable corrosion rate for bioimplants. From these results, we conclude that the experimental alloys, as well as the commercial alloy, would perform well in the body environment of a normal person, as well as the body environment of prediabetic and diabetic patients. Liu et al.^[39] investigated the influence of different glucose concentrations in HBSS on the corrosion behavior of a pure titanium alloy (TA2). The glucose concentrations under investigation included concentrations that mimicked a healthy person before and after eating, as well as a diabetic person before and after eating. The results showed that the alloy was suitable for use by a diabetic patient as the glucose concentration before eating (180 mg dL⁻¹) provided an environment in which the alloy could perform well. They concluded that the alloy could perform well at normal (90 mg dL⁻¹ to 126 mg dL⁻¹) and slightly high glucose concentrations (180 mg dL⁻¹ to 216 mg dL⁻¹). However, the alloy would not be suitable for diabetic patients with a blood glucose concentration exceeding 216 mg dL⁻¹. These results correlate with our findings, as a glucose concentration of 200 mg dL⁻¹, which lies within the range reported by Liu et al.,^[39] was found to lower the titanium alloys'

corrosion rate. However, our study did not consider glucose concentrations above 200 mg dL⁻¹, so there is no evidence of how the alloys would perform at higher glucose concentrations, such as 216 mg dL⁻¹. Faverani et al.^[40] investigated the influence of glucose and lipopolysaccharide on the corrosion behavior of the commercial Ti-6Al-4V alloy. They concluded that glucose alone did not substantially impact the corrosion behavior of the alloy. Although the alloy's corrosion potential decreased, the overall corrosion properties were not altered. This does not fully correlate with our results and that of Liu et al.^[39] In this study, a glucose concentration of up to 200 mg dL⁻¹ improved the corrosion resistance of the titanium alloys, while in the study by Liu et al.,^[39] a glucose concentration of up to 216 mg dL⁻¹ improved the corrosion properties of TA2 and a glucose concentration beyond 216 mg dL⁻¹ was detrimental to the properties of TA2.

It is worth noting that the results in these studies, including ours, will not be entirely the same mainly because the alloys under investigation are different, which plays a crucial role in the results obtained. The alloying elements and types of the protective film formed would alter the corrosion properties of the different alloys. In addition, some inconsistencies in the results are also due to the differences in the electrolytes used and the conditions under which they were used. Faverani et al.^[40] used a simulated body fluid at 37°C and a pH of 7.4. Liu et al.^[39] used HBSS but conducted their potentiodynamic tests with different testing parameters (scanning range $\pm$ 200 mV and scanning speed = 10 mV s⁻¹) to ours. The scanning rate of 10 mV s⁻¹ is significantly higher than the recommended standard scanning rate (0.1667 mV s⁻¹) used in our study, which may render the testing system unstable, thus altering the results obtained.

5 | CONCLUSION

From this study, it can be inferred that the experimental alloys exhibited favorable corrosion resistance when exposed to simulated body fluid conditions. The corrosion resistance of these alloys was comparable, and even superior in certain instances, to that of the commercial alloy. In 0.9 wt.% sodium chloride solution and HBSS, the Ti-4.5Al-1V-3Fe and Ti-3Fe alloys display superior resistance to corrosion compared with the commercial alloy. The experimental alloys, which incorporated iron as a β -stabilizing element, exhibit reduced susceptibility to corrosion compared with the commercial alloy. This was evident from their higher corrosion potential values compared with the commercial alloy. Therefore, these alloys could serve as a suitable alternative to the toxic and

expensive Ti-6Al-4V alloy in making biomedical implants. The experimental alloys perform better in glucose environments. Ti-4.5Al-1V-3Fe and Ti-6Al-1V-3Fe show superior resistance to corrosion compared with the other alloys in the 100 and 200 mg dL⁻¹ glucose HBSS, respectively. Overall, the experimental alloys, including the commercial alloy, perform better at a slightly elevated glucose concentration of 200 mg dL⁻¹. Therefore, these alloys could be utilized by a person with a normal blood glucose concentration, as well as those living with diabetes. Notably, diabetic conditions are not the only cause of high blood glucose. Other disorders, such as pancreatitis, pancreatic cancer, Cushing's syndrome, Addison's disease, and other alterations of the adrenal glands, also cause elevated blood glucose levels.^[40] It is, therefore, important to conduct more investigations on the effect of glucose concentrations on the properties of titanium alloy biomaterials.

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CONFLICT OF INTEREST STATEMENT

The authors declare no conflict of interest.

DATA AVAILABILITY STATEMENT

The data that support the findings of this study are available from the corresponding author upon reasonable request.

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