PERFORMANCE IMPROVEMENT OF Ti-6Al-4V DENTAL BIOMATERIAL USING ISOTHERMAL HEAT TREATMENT AND BITTER LEAF EXTRACT AS INHIBITOR

BY

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M.sc/Eng/132/2011-2012

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AHMADU BELLO UNIVERSITY, ZARIA.

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Mercy Obianuju ENECHUKWU, (B.Eng) Met & Mat, N.A.U. (AWKA) 2009

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A THESIS SUBMITTED TO THE SCHOOL OF POSTGRADUATE STUDIES, AHMADU BELLO UNIVERSITY, ZARIA.

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DEPARTMENT OF METALLURGICAL AND MATERIALS ENGINEERING, FACULTY OF ENGINEERING

AHMADU BELLO UNIVERSITY, ZARIA.

NIGERIA.

SEPTEMBER, 2015.

DECLARATION

I declare that the work in this thesis entitled, “Performance improvement of Ti-6Al-4V dental biomaterial using isothermal heat treatment and bitter leaf extract as inhibitor” has been carried out by me in the department of Metallurgical and Materials Engineering. The information derived from the literature has been duly acknowledged in the text and a list of references provided. No part of this thesis was previously presented for another degree or diploma at this or any other institution.

Name of student

Signature

Date

CERTIFICATION

This thesis entitled “PERFORMANCE IMPROVEMENT OF Ti-6Al-4V DENTAL BIOMATERIAL USING ISOTHERMAL HEAT TREATMENT AND BITTER LEAF EXTRACT AS INHIBITOR” by Mercy Obianuju ENECHUKWU meets the regulation governing the award of the degree of the masters of science of Ahmadu Bello University, and is approved for its contribution to knowledge and literary presentation.

Dr. M. Abdulwahab ______________ ______________
Chairman, supervisory committee Signature Date

Prof. S. A. Yaro ______________ ______________
Member, Supervisory Committee Signature Date

Prof. S. A. Yaro ______________ ______________
Head of Department Signature Date

Prof. Kabir Bala ______________ ______________
Dean, School of Post Graduate studies Signature Date

DEDICATION

This work is dedicated to God Almighty for his wisdom strength and grace that was available all through the programme. To him alone be all the glory.

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ABSTRACT

This research evaluates the performance of Ti-6Al-4V alloy as a dental implant in simulated saliva +fluoride with varying concentration of bitter leaf (*Vernomia amygdalina*) extract as inhibitor. Electrochemical corrosion analysis and abrasive wear test were used as criteria to assess the performance of the thermally treated Ti-6Al-4V alloy for dental implant application. The bitter leave extract (inhibitor) was characterized using the Fourier Transform Infrared Spectroscopy. The as-received Ti-6Al-4V alloy was cut and machined into samples of 15mm×15mm×3mm as corrosion coupons and 30mm×25mm×3mm as abrasive wear samples. The samples were solution heat treated at 960^{o}C followed by an aging process at 480^{o}C for varying time of 2, 4, 6 and 8 hours soaking time. The samples for wear analysis were subjected to abrasive wear using a three body abrasive wear test machine with varying loads of 5N and 15N and silica sand as the abrasive medium. The corrosion coupons were subjected to degradation test using a potentiostat in simulated saliva fluid without and with varying concentrations of the inhibitor. From the results the wear loss of the heat treated titanium alloy decreased with applied load and the ageing time indicating a 99.05% and 98.21% wear resistance at 5N and 15N respectively. Equally the degradation resistance of the titanium alloy increased with ageing time and addition of inhibitor, with the lowest degradation rate at 2 hour and 1.5 ml inhibitor addition with a degradation reduction of 98.02%.

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LIST OF ABBREVIATIONS

Milimeter	mm
Hours	hrs
Gram	g
Percentage	%
Milliliter	ml
Vol	v
Milimeter per year	mm/yr
Ohms	Ω
Corrosion current density	A/cm^2
Rear earth metal	RE
Scanning Electron Microscope	SEM
Fourier Transform Infrared Spectroscopy	FTIR

CHAPTER ONE

1.0 INTRODUCTION

The sophistication in the knowledge of nature and accumulation of scientific facts and procedures has caused a remarkable change in the line of thoughts of man which have set landmarks on the tides of time. Science has proven not to be limited to any field of study and has chosen to cross across various fields of knowledge, also science has virtually interwoven all fields of study that none can actually stand solely on its own. Some centuries back, who would have thought it possible that metals and alloys would be used to replace some of the body functions that are deficient? The capacity of a man’s abstract thinking and a complementary growth in the technology has graced this opportunity to mankind. Man is no longer incapacitated, or would have to suffer dejection and societal rejection or even death, when he loses some certain parts of his body because of the science of biomaterial. These materials which are called biomaterials are non viable (non-living) synthesized materials that are intended to interact with the biological system in a safe, reliable, economic and physiological manner with minimal vivo reaction (Buddy *et al*., 2004).

Titanium is one of the strongest available metals, comparable to steel, while being 45% lighter (Seminole, 2009). Titanium and its alloys have proved effective over the years in marine, aerospace, medicine, automobile, missiles, and energy industries. Their unique properties; high strength to low weight ratio, excellent corrosion resistant, high young modulus, high temperature stability, have made them to be desired for commercial use in various industries (Popoola *et al*., 2013, Greg *et al*., 2007). Titanium being the fourth most abundant structural metal and the ninth most abundant mineral in the earth crust has made it available in good quantities for use in different industries (Greg *et al.*, 2007, Seminole, 2009). It is also used in some paints, rubbers and plastics industries. It is used in jewellery fabrication because it is physiologically inert, therefore hypoallergenic, and can be coloured easily. It is becoming one of the most popular metals in jewellery production. Titanium metal will burn in air, which makes it useful in fireworks, and it is also the only element that will burn in nitrogen (Seminole, 2009).

Biomaterials could be implants or prostheses which are used to assist or replace a body function (Hendra *et al*., 2012). Biomaterials are made from ceramics, metals, alloys, polymer and composite materials because of the individual properties they pocess, such as tensile modulus, yield strength, compression strength, ultimate tensile strength, corrosion resistance, toughness and density, even though they all posses these properties at different levels. They are adapted for medical applications and thus comprises of a whole or part of a living structure (Hendra *et al*., 2012). Biomaterials find daily applications in surgery, dental care, and drug delivery. A construct with impregnated pharmaceutical can be placed into the body, which permits the prolonged release of drug over an extended period of time. A good biomaterial must be compatible with the human body, and because of this high requirement, the issue of biocompatibility must be completely resolved before the product is sent into the market for use and because of these high requirements, biomaterials are subjected to the same procedures and requirements, a newly developed drug needs to meet before it is sent into the market (Hendra *et al*., 2012). This research would focus on using titanium alloy Ti-6Al-4V as a dental implant. The performance of the alloy would be investigated in simulated human saliva and fluoride environment/plant extract, using degradation and wear test as criteria.

1.1 Aims and Objective

The aim of this research is to evaluate the performance of TI-6Al-4V as a dental implant in saliva +fluoride and varying concentration of bitter leaf extract.

The following objectives were pursued in order to achieve this aim.

- Determination of the functional groups present in the bitter leaf extracts using the Fourier Transforms Infrared Spectroscopy (FTIR) and using the extract as inhibitor.
- Investigation of the role of isothermal heat treatment (solution heat treatment and aging) on the wear resistance and degradation behavior of Ti-6Al-4V in artificial saliva and fluoride with and without inhibitor.
- Determination of the wear property before and after the isothermal heat treatment.
- Study of the degradation resistance of the titanium alloy in simulated human saliva + fluoride environment + with and without varying concentration of inhibitor, using electrochemical technique.
- Investigation of the surface morphology of the treated Ti alloy before and after subjecting it to the environments.

1.2 Scope of study

The scope of this research included the followings;

1. The substrate was subjected to solution heat treatment at 960^oC for 1hr and aging of 480^oC and varying time to 2, 4, 6, 8 hours.
2. Characterization of the bitter leaf extract by Fourier Transform Infrared Spectroscopy (FTIR analysis).
3. A wear resistance test was conducted.

4. A degradation study of the alloy in artificial saliva and fluoride with and without varying concentration of inhibitor environment was carried out using electrochemical technique.
5. Surface characterization of the alloy using scanning electron microscope (SEM) was carried out.

1.3 Justification of research

Titanium is known for forming an adherent, stable, and continuous titanium oxide film (TiO) when heated to a temperature range of 450-800^{o}C. This oxide film wears out easily because of the poor wear resistance of titanium and its alloys when placed in an aggressive environment (acid, fluoride and saliva) and a corrosion process is initiated (Barao *et al*., 2012, Nikoloupu, 2006). These three parameters are present on daily basis in the oral cavity. The food we consume contains acids, the tooth paste we use contains fluoride, and the oral cavity (saliva) has a low oxygen level. The human saliva is partially aggressive; because of the constant alterations in the conditions of the mouth, which are as a result of the type of food we eat, the health condition of the individual, the type of medication an individual is placed on, use of mouth wash, smoking, pH and temperature fluctuations (steaming or iced) (Barao *et al*., 2012). These factors are also responsible for the difficulty in obtaining identical saliva composition.

However, Titanium has been used over the years as implants, but there is a need to improve its performance. Titanium and its alloys have also been used as dental implant but because of the poor stability of its oxide film due to its low wear resistance and the variations in the human saliva from one individual to the other. It has become very necessary to improve its properties. This research is aimed at using isothermal treatments and inhibitor to develop a titanium alloy/environment, whose behaviour would have a synergy of higher mechanical performance and elevated resistance to degradation in the studied environment.

1.4 Contribution to knowledge

To the best of my knowledge, no previous work has been done on the degradation inhibition of isothermally treated (solution heat treatment/ ageing) Ti-6Al-4V alloy using bitter leave extract. This research has been able to:

1. Achieved an improved wear and degradation resistance of Ti-6Al-4V in the environment through thermal treatment.
2. Identified an inorganic inhibitor that was able to reduce the corrosion rate.

CHAPTER TWO

2.0 LITERATURE REVIEW

2.1 Titanium and its alloy

The titanium mineral is defined as a strong, low density, highly corrosive resistant metal that when pure is lustrous white (Greg *et al*., 2009). Titanium was first identified as a new and unknown metallic element by Gregor in England in 1791, and was named Titanium several years later (1795) by Klapproth in Germany after the Titans of the Greek mythology (Greg *et al*., 2009, Reza *et al*., 2011). Titanium is present in the earth crust of about 0.6% and therefore it is the fourth most abundant structural metal after Aluminum, Iron and Magnesium (Greg et al., 2009). The mineral bearing ore is ileminite ($FeTiO_3$) and rutile (TiO_2). Titanium has a number feature that distinguishes it from other light materials, which makes its physical metallurgy interesting (Reza *et al*., 2011). It is a transition metal with an incomplete shell in its electronic structure and this enables it to form solid solutions with most substitution elements (Greg *et al*., 2009). The production of high-purity titanium proved to be difficult, because of the strong tendency of this metal to react with oxygen and nitrogen. Therefore, it was not until the middle of the 20th century (1938-1940) that a commercially attractive process was developed by W.J. Kroll in Luxemburg. This process involves the reduction of titanium tetrachloride with magnesium in an inert-gas atmosphere. The resulting titanium is called "titanium sponge" because of the porous, spongy appearance (Greg *et al*., 2007).

The commercial interest in titanium and its alloys was prompted by the relatively low density of the metal (between those of aluminum and iron) in combination with a high yield strength (especially in the 200-450°C range), and its excellent corrosion resistance (Greg *et al*., 2007). However, titanium and its alloys have poor abrasive wear resistance, low hardness values and high co-efficient of friction and these have caused them to find little use in the mechanical engineering industry (Bloyce *et al*., 1998, Popoola *et al*., 2012, Reza *et al*., 2011).

Therefore, titanium and its alloys are used primarily in three areas of applications: corrosion resistant areas, such as the chemical industry; areas where weight-savings and high strength are predominant, such as in aircraft and aerospace applications; then lastly in areas where corrosion resistance, biocompactability, low weights and high strength are predominant such as in biomaterials. The properties of titanium and its alloys depend to a great extent on the inevitable gas entrapped as gas impurities. Titanium contains an appreciable amount of oxygen in it and also it react even at low temperature with the gasses of hydrogen, oxygen and nitrogen, but its highest affinity is for oxygen (Reza *et al*., 2011). These impurities when occurring in traces add strength to the titanium and also the oxide film helps in resisting corrosion. Nevertheless, Titanium has a low wear resistance and this can lead to corrosion when the protective film is been worn out. The corrosion rate is increased when the alloy is subjected to an aggressive environment which could be an acid, a fluoride or saliva environment. This aggressiveness can lead to the loss of the protective oxide film and a corrosion process can be initiated (Nikolopoulou, 2006, Correa *et al*., 2009, Barao *et al*., 2011). The human saliva can be regarded as a partially aggressive environment in that so many alterations takes place in the saliva in a day. These alterations could be as a result of one or a combination of these factors; The type of food we eat, the temperature of the food which could be very hot or iced, the health condition of the individual, the medication an individual is placed on, the pH of the saliva which could be acidic or basic, depending on the above factors. These factors may affect the biocompatibility and function of dental implants and possibly lead to failure of the implant in the oral cavity (Barao *et al*., 2011, Nikolopoulou, 2006).

The oxide produced during air exposure observed on Ti and its conventional alloys is essentially $Ti0_2$ with a tetragonal rutile crystal structure, which is called scale (Greg *et al*., 2006). This layer is an n-type anion-defective oxide through which the oxygen ions can diffuse. The scale therefore grows into the base metal, which for example prevents the self-healing of cracks in Ti. The high chemical affinity and maximum solubility of oxygen in titanium is what leads to the formation of scale and an adjacent inner layer of the base metal, which is highly enriched in oxygen, called a-case. The deformation behavior of alpha-Ti changes from a wavy to a planar mode with increasing oxygen levels. Therefore, the hard, less ductile alpha-case induces surface cracks under tension loading which results in low overall ductility or causes early crack nucleation under fatigue loading because of large slip offsets at the surface. The application of conventional Ti alloys at higher temperatures is therefore limited to the regime below about 550°C where the diffusion rates through the oxide layer (scale) are low enough to prevent excess oxygen contents being dissolved in the bulk material (Greg *et al*., 2009).

In order to decrease the diffusion rate of oxygen through the scale, various additions of alloy elements were investigated. Slight improvements were found by adding elements with a valence number greater than 4, such as Nb^{5+}, which can substitute the Ti^{4+} ions in the $Ti0_2$ structure, thus reducing the number of anion vacancies. However, much more effective in lowering the diffusion rates are increasing amounts of Al, which forms the very dense and thermally stable alpha-Al_20_3 oxide. The resulting scale consists then of a heterogeneous mixture of $Ti0_2$ and Al_20_3 underneath a $Ti0_2$ surface oxide. The improved oxidation resistance of titanium aluminides, such as Ti_3Al based alloys or Y-TiAl, results from increasing volume fractions of Al_20_3 oxide in the scale. Due to the higher Al content Y-TiAl exhibits a better oxidation resistance as compared to alloys based on Ti_3Al. However, for surface protection by a continuous layer Al_20_3 even higher concentrations of about 57% Al would be required (Greg *et al*., 2007).

The crystal structure of titanium undergoes an allotropic phase transformation at 882.5°C, changing from a closed-packed hexagonal crystal structure (α phase), to a body-centered cubic crystal structure (β phase) above this temperature. The exact transformation temperature is strongly influenced by interstitial and substitutional elements, therefore depending on the purity of the metal (Reza *et al*., 2011, Greg *et al*., 2007, Moiseyev, 2006).

The intrinsic anisotropic behavior of the hexagonal crystal structure of the alpha phase has important consequences for the elastic and plastic deformation behavior of titanium and its alloys, besides numerous other physical properties (Reza *et al*., 2011).

2.2 Bio-medical materials

Bio-medical materials/ biomaterials are biocompatible materials that are used to construct artificial organs, rehabilitation devices, or prostheses to assist or replace a natural body tissue or organ (Houghton, 2004). For a biomaterial to be effective it must not be toxic, there must not be any foreign reactions i.e. in-vivo reaction and it must be biocompatible (it must be accepted by the surrounding tissues and body as a whole). Materials used as biomaterials include metals and alloys, ceramics, polymers and composites (Mallik *et al*., 2012).

The immune system is bound to attack any foreign body that gets into the body system that is why it is very necessary for the biomaterial to be very compatible with the surrounding tissues and the body as a whole. There is also a probability that there would be unwanted effect of the biomaterial on the body system, all these parameters are to be taken care of before a material is sent into the market to be used as a biomaterial (Diomidis *et al*., 2012).

Ceramics are used for biomaterials because they are very biocompatible, inert, and very strong but they are very brittle, lacks resilience and are difficult to fabricate. Polymers are very resilient easy to fabricate but they lack strength and degrades with time. The Composite's property depends on the matrix, reinforcing material, reinforcing ratio (ratio of mixing) and method of reinforcement. Metals and alloys are very strong, tough, ductile, excellent electrical and thermal conductivities but their shortcoming is their quick reaction in the vivo environment because of their tendency to release free electrons (Park *et al*., 2003).

Metals and alloy have been used over time for replacement of the total hip and knee joints, bone plates, screw and dental implants. The three most common groups of metal used as biomaterial are cobalt-chromium based alloys, stainless steels and titanium based alloys (Galk, 1983, Park *et al*., 2003). The first metal to be used as biomaterial in human was vanadium steel (Carlos *et al*., Anupam, 2011, Park *et al*., 2003), which was used to manufacture bone plates and screws but due to its quick reaction in the vivo-environment led to the manufacture of Cr-Ni stainless steel. It was the first stainless steel used for implants and it contained ~18wt% Cr and ~8wt% Ni which made it stronger than steel and more resistant to corrosion but its disadvantage is that it cannot still resist corrosion in chloride solutions and this lead to further developments. Further addition of molybdenum (Mo) to Cr-Ni stainless steel had improved its corrosion resistance, and it is known as type 316 stainless steel. Afterwards, the carbon (C) content had been reduced from 0.08 to 0.03 wt% which improved its corrosion resistance to chloride solution, and was named 316L. The reduction was done because chromium (Cr) reacting with carbon (C) will lead to the formation of chromium carbide (CrC) which will lead to intergranular corrosion. Although it was found that the 316L stainless steel could still corrode under some circumstances such as a highly stressed and oxygen depleted environment (Anupam, 2011, Park *et al*., 2003). All these limitations lead to the development of titanium and its alloys.

Titanium is featured by its light weight. Its density is only 4.4g/cm^3 compared to 7.9g/cm^3 for 316 stainless steel and 8.3g/cm3 for cast CoCrMo alloys (Flake, 2012, Brandes et al., 1992). Ti and its alloys, i.e. Ti-6Al-4V are known for their excellent tensile strength and pitting corrosion resistance. Titanium alloyed with Ni, i.e. Nitinol, forms alloys having shape memory effect which makes them suitable in various applications such as dental restoration wiring (Hendra *et al*., 2012).

In dentistry, precious metals and alloys often used are Au, Ag, Pt and their alloys. They possess good castability, ductility and resistance to corrosion. Included into dental alloys are AuAgCu system, AuAgCu with the addition of Zn and Sn known as dental solder, and AuPtPd system used for porcelain-fused-to-metal for teeth repairs (Hendra *et al*., 2012). CoCr alloys have been utilized for many decades in making artificial joints. They are generally known for their excellent wear resistance. We have both the cast and the wrought Co-Cr alloys. The wrought alloy (CoNiCrMo) has a higher wear resistance compared to the cast alloy (CoCrMo) and it has been used for making heavily loaded joints such as ankle implants. The molybdenum in the cast alloy added to provide fine grains which results in higher strength after forging or casting. The chromium enhances corrosion resistance and also strengthens the alloy (Park *et al*., 2003).

Other metals used for implants include tantalum (Ta), amorphous alloys and biodegradable metals. Tantalum which has excellent X-ray visibility and low magnetic susceptibility is often used for X-ray markers for stents. Amorphous alloys featured interesting properties compared to its crystalline counterparts whereas they exhibit higher corrosion resistance, wear resistance, tensile strength and fatigue strength. With low Young's modulus, amorphous alloys like that of Zr-based (Wang *et al*., 2011), may miniaturized metal implants. Up to now, metals proposed for biodegradable implants, named as biodegradable metals, are either iron-based or magnesium-based alloys. The Mg-based alloys include MgAl-, MgRE (RE=rare earth metal) (witte *et al*., 2005), and MgCa based alloys (Li *et al*., 2007). Meanwhile, the Fe-based alloys include pure iron and Fe-Mn alloys (Hermawan *et al*., 2008, Peuster, 2001).

Surface treatment or surface modification is considered as one major concern on recent developments in metallic biomaterials (Kohn, 1998). The treatment includes surface morphological modification and chemical modification. Surface morphology such as roughness, texture and porosity are important characteristics of implant since it influences the ability of cells to adhere to solid substrate (Peckner *et al*., 1977). For the case of chemical modification, the objective of the modification is to provide specific biological response on the metallic surface and increase the stability of bio-molecules (Hendra *et al*., 2012).

An appropriate surface roughness can be achieved by applying electro-polishing where an improvement in the corrosion resistance of stainless steels can be achieved. Surface grain refinement improves fatigue life of stainless steel alloys since ultra fine grain boundary of surface can impede the dislocation movement, whereas the compressive residual stress on the surface can delay the crack initiation ((Hendra *et al*., 2012). In addition, improvement on the corrosion resistance is also observed since more grain boundaries results in the more active site for diffusion of chromium (Mordyuk *et al*., 2007). The surface of material can also be modified by using laser where an improvement in the corrosion resistance of stainless steel was reported (Kwok *et al*., 2003 popoola *et al.*,2013).

This improvement is believed due to the dissolution or refinement of carbide particles and the presence of retained austenite after the process. Chemical modification on the stainless steel alloys by hybrid plasma surface alloying process using nitrogen and methane gas mixtures below 450°C was reported (Sun *et al*., 2008).

The formed dual layer of hard nitrogen-enriched on the hard carbon enrich-layer improves the corrosion resistance of the alloy. Another chemical modification was also reported by nitrogen ion beam processing on stainless steel alloy. A relatively low energy beam of nitrogen ions was used with the substrate temperature was held at 400°C during a 15 minutes treatment to introduce nitrogen onto the surface of the alloy and form N-rich layer that improve the surface hardness of the alloy (Hendra *et al*., 2012).

By applying cyclic potentiodynamic polarization to a 316L stainless steel between the potential of hydrogen and oxygen evolution, it was found that the passive surface film formed will possess very good resistance to general corrosion and pitting (Bou-Salah, 2007).

Cyclic potentiodynamic polarization in sodium nitrate or phosphate also significantly beefs up the pitting corrosion resistance of the same steel, because the density of oxygen vacancies, which may act as initiation sites for pits, in the passive film formed in this way is lowered (Shahryari, 2008).

2.3 Ti-6Al-4V Alloy

Commercial titanium alloys are classified conventionally in three different categories as alpha, alpha+beta, and beta alloys according to their equilibrium constituents, which varies with the types and concentrations of the alloying elements. Ti-6Al-4V is a well known alloy for its desirable mechanical properties, corrosion resistance and biocompatibility. The application of this alloy is particularly attractive to aerospace and biomedical industries. The mechanical and micro structural characteristics of Ti-6Al-4V depends on heat treatment or/and hot deformation. From available literature the alpha+beta transformation temperature is 995-1000^{o}C (Greg *et al*., 2007, Matthew, 2000). Ti-6Al-4V alloy have an elastic modulus of 106 and a density of (4.4g/cm^{3}) which is close to density of the human bone (2.0g/cm^{3}) compared to the other metal and alloys used as implants (Anupam, 2011, Nikolopoulou, 2006)

Ti-6Al-4V is an alpha+beta alloy. Alloys in this category contain, in addition to the alpha Al stabilizer, beta stabilizing elements such as V, Mo, Nb or Cr. These elements (i.e. beta stabilizers) decrease the alpha/beta transformation temperature and increase the width of the $\alpha+\beta$

phase field with increasing beta-solute content. Furthermore they lower the temperature, where the beta phase starts to transform by the martensitic process (Ms-temperature). With a further increase in beta stabilizing elements, beyond the content which lowers the Ms-temperature to room temperature, those alloys are then called metastable beta alloys. For these alloys the beta phase can be retained at room temperature even in large sections during air cooling. However, these metastable beta alloys can usually be transformed to α+β mixture by isothermal aging. At even higher beta stabilizer contents the alloys are stable beta alloys, which cannot be transformed to an alpha+beta mixture by further heat treatments (Greg *et al*., 2007).

The very high yield stresses which can be obtained in commercial Ti-alloys are mainly resulting from the precipitation of finely dispersed particles in the alpha and beta phases by suitable age-hardening treatments after cooling the alloys from their respective annealing temperatures to RT (Reza *et al*., 2011). All these alloys are of course additionally solid solution strengthened by interstitial or substitutional atoms (Greg *et al*., 2007).

The alpha+beta alloy (Ti-6Al-4V) exhibits higher strength due to the presence of both the alpha and beta phases. The final property of this alloy depends on the composition, the relative proportion of the alpha and beta alloying elements, thermal treatment and thermo mechanical processing conditions. The beneficial properties of Ti-6Al-4V alloy, such as low density, low modulus of elasticity and excellent biocompatibility have made the alloy to become a very interesting alloy.

Ti-alloys which are subjected simultaneously to mechanical stresses and aggressive environments can be severely influenced by hydrogen embrittlement or stress corrosion cracking. It is known that alpha and alpha+beta alloys are more prone to such brittle fracture, while beta alloys are more tolerable, that means the bcc phase can tolerate higher concentrations of hydrogen before brittle fracture occurs, while in the hcp phase, low concentrations of hydrogen can result in brittle fracture mainly along the basal planes (Greg *et al*., 2007).

2.4 Heat treatment of titanium alloys

Titanium and its alloy are heat treated for several reasons which include the elimination of residual stress, to increase strength, to produce an acceptable combination of ductility and machinability, to optimize special properties. Stress relieving heat treatments are probably the most common heat treatment given to titanium and its alloys, because this process can relieve the stress without adversely affecting strength and ductility. The stress relief treatment decreases the undesirable residual stress, while maximum strength levels are achieved in titanium alloys by solution annealing also known as solution heat treatment followed by aging. A wide range of strength levels can be obtained by solution annealing and aging of alpha-beta and beta alloys. If higher fracture toughness and improved resistance to stress corrosion is required, beta annealing or beta solution treating may be desirable but will lead to a considerable loss in ductility (Mathew, 2000).

Solution heat treatment and aging does not mean the same thing in titanium as it does in traditional age hardening systems. Solution heat treatment and aging (stabilization) usually but not always follow working operations to generate optimum mechanical properties. Solution heat treatment of titanium alloys normally involves heating to temperature either slightly above or below the beta transus line of the alloy. For Ti-6Al-4V the solution heat treatment temperature range is 955-970^{o}C for 1 hour and quenching followed by ageing at 480-595^{o}C for about 4-8 hours or 705-760^{o}C for 2-4 hours (Matthew, 2000 Greg *et al.*, 2009). If the beta transus line is exceeded, when an alpha-beta titanium alloy is heat treated, ductility is reduced and cannot be fully recovered by subsequent thermal treatment (Matthew, 2000). Selection of a solution heat treatment is made after consideration of the mechanical properties desired from the aging treatment. Selection is usually based on practical considerations, such as the desired level of tensile properties and the amount of ductility to be obtained after aging. To obtain high strength and adequate ductility, it is generally necessary to solution treat at a temperature high in the alpha-beta field, which is 25-85^{o}C below the beta transus line of the alloy. If higher fracture toughness and improved resistance to stress corrosion is required, beta annealing or beta solution treating may be desirable. However heat treating alpha-beta alloys in the beta ranges causes a considerable loss in ductility as noted. These alloys are treated below the beta transus line to obtain a balance of ductility, fracture toughness, creep and stress rupture resistance (Flake, 2008, Matthew, 2000).

The cooling rate from the solution treating temperature has an important effect on the strength of the alpha-beta titanium alloy. Appreciable diffusion can occur during cooling if the rate is too low. This diffusion changes the phase chemistry and/or ratios, and subsequently decomposition of the altered beta phase during aging may not provide effective strengthening. Quenching is required for most alpha-beta alloys after the solution heat treatment. Water, 5% brine, caustic soda solutions are preferred for quenching these alloys (Matthew, 2000). Maximum response to subsequent aging is achieved when decomposition of the beta phase present at the end of the solution heat treatment is minimized. The need for rapid quenching is emphasized by the requirement of short quench delay time; some alpha beta alloy can only tolerate a maximum delay of 7 seconds depending on the mass of the section being heat treated. The more highly beta stabilized alpha-beta alloy can tolerate delay of about 20 seconds (Matthew, 2000). For alloys that have high beta stabilizer content and products that have small section size air or fan cooling may be adequate. Beta alloys are generally air cooled from the solution treating temperature. The effect of quench delays on Ti-6Al-4V alloy shows that when the thickness exceeds 75mm it is difficult to cool the core of the specimen fast enough to maintain an unstable beta phase for later transformation during aging for this reason the solution treated and aged properties of Ti-6Al-4V specimen with large sections are usually similar to a titanium alloy of beta phase (Matthew, 2000 Flake, 2008).

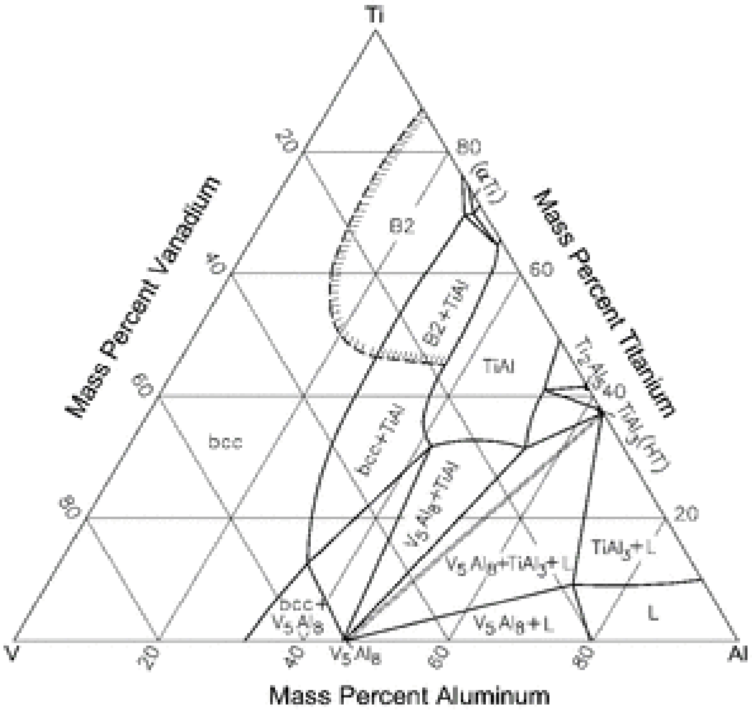

Figure 2.1 Ti Al V computed isothermal section at 1200^{o}C

The final step in heat treating of titanium alloy is aging which is reheating to an aging temperature between 425 ^{o}C and 650^{o}C (800 ^{o}F - 1200^{o}F). Aging of titanium is not the same as the aging process in aluminum and nickel alloys. In alpha-beta and beta titanium alloys, aging causes decomposition of the supersaturated beta phase retained in quenching and the transformation of any martensite in the alpha-beta alloy to alpha phase (Matthew, 2000).

Titanium reacts with oxygen, water and carbon dioxide normally found in the oxidizing heat treating atmospheres. It also reacts with hydrogen formed by the decomposition of water vapor.

Unless the heat treatment is carried out in a vacuum furnace or in an inert atmosphere and unless surface cleanliness is maintained there is a direct effect on the properties of the titanium (Flake, 2008, Mathew, 2000)

2.5 Sterilization and cleaning

In order to avoid bacterial contamination which could be transferred to patients, sterilization and cleaning are important requirements on metal implant. Descaling is a method to clean metal implant surface which can be done mechanically, chemically or by combination of both of the methods. Mechanically, it can be done with sand blasting process and chemical cleaning can be done by pickling using strong acid such as H_2SO_4.

On the other hand sterilization can be done by several processes such as autoclaving, glow discharge Argon plasma treatment and irradiation (Serro *et al*., 2003). Being a method to clean any contaminant from the surface, sterilization methods are also considered to play an important role in the bio-mineralization of Ti alloys (Serro *et al*., 2003).

2.6 Mechanism of degradation of metallic implants

Metal implants are prone to corrosion during its services due to corrosive medium of implantation site and in most cases subjected to cyclic loading. Types of corrosion that are frequently found in implant applications are fretting, pitting and fatigue. Fretting corrosion most frequently happens in hip joint prostheses due to small movement in corrosive aqueous medium (Geringera *et al*., 2005).

Fretting corrosion refers to corrosion damage at the small area of contact surface due to repeated load, the mechanism of which frequently refers to corrosion which is activated by friction (Tritscheler *et al*., 2009). Corrosive medium, chemical composition of alloy and level of stress at the contact surfaces are among important parameters that determine fretting corrosion behavior of metallic implant. It was reported that the presence of chlorides influences the degradation acceleration of the stainless steel surface (Tritscheler *et al*., 2009).

Prevention of corrosion will be greatly assisted by evaluation of corrosion behavior using methods which resemble the services condition of the metal implants. Since stress and corrosive medium play an important role, special devices that combine these two factors should be developed. Ultrasonic frequency was used in corrosive medium in order to evaluate the fatigue corrosion of metallic implant which enables the application of very-high stress cycle within reasonable testing period (Papakyriacou *et al*., 2000),. On the other hand the fretting corrosion behavior of metallic implant can be evaluated by a typical pin-on disc method in an artificial physiological medium. Parameters that are needed to be set include concentration of corrosive medium, load or friction forces, frequency and number of fretting cycles. In the case of pitting corrosion, it can be evaluated with the absences of applied forces. It was reported that a good example of pitting corrosion evaluation was obtained in a buffered saline solution using anodic polarisation and electrochemical impedance measurement (Mariano *et al*., 2009).

Titanium nitride coating on the metallic implant has been a popular method to improve corrosion resistance of metallic implant such as Ti alloy and Co based alloy by physical vapor deposition, plasma spray process, etc. Modification of metallic implant surface by electro-polishing, sand blasting or shot peening method were also reported to improve the corrosion resistance of the implant (Aparicioa *et al*., 2003). It is known that a significant improvement of corrosion resistance can be achieved for the electro-polished surfaces and sand blasted surfaces, where the former surfaces are corroded most slowly. The modification of corrosion resistance properties by the two methods are considered due to the increasing surface area and the introduction of compressive stress on the surface. In addition, surface modification is also possible by sand blasting process with the introduction of sand particle that form certain layer on the surface being blasted (Mariano *et al*., 2009).

2.7 Wear

Wear is a surface failure resulting from dynamic contact between two surfaces such as abrasion and erosion. Wear is specifically the removal and deformation of a material's surface as a result of mechanical action of the opposite surface. Wear can also be defined as a process where interaction between two surfaces or bounding faces of solids within the working environment results in dimensional loss of one or both solid. The need for relative motion between two surfaces and initial mechanical contact between asperities is an important distinction between mechanical wear compared to other processes with similar outcomes. Corrosive wear is defined as the damage caused by synergistic attack of wear and corrosion, i.e. when wear occurs in a corrosive environment. The term tribo-corrosion also refers to corrosive wear (Li, 2013). The damage to materials by wear can be enhanced significantly, depending on the corrosivity of the surrounding medium, which can be a fluid or gas. Corrosive wear can only occur when there is a combination of a wear situation (abrasive or adhesive) and a corrosive environment. The rate of material loss can be very high; as many times as that which would occur should the individual processes of wear or corrosion be acting alone. This is because loose corrosion products are easily removed by wear to continually reveal fresh metal beneath, which in turn can corrode quickly. Likewise, stable oxide films that would normally limit corrosion (in the absence of wear) are instantly worn away. Titanium and its alloys have had a reputation for poor tribological characteristics. Tribology is defined as the science and engineering of surface phenomena such as friction, wear, lubrication, adhesion, surface fatigue, erosion etc. Tribological design and materials selection play vital roles in the performance, operation and durability of all mechanical machines. Even our body faces tribological issues and problems especially at the joints. The study of the processes of wear is part of the discipline of tribology (Sujeet, 2013). Some commonly wear mechanisms (or processes) include: Adhesive wear, Abrasive wear, Surface fatigue, Fretting wear, Erosive wear. Wear in the form of Surface fatigue in a corrosive environment is our concern in this research work. Surface fatigue is a process by which the surface of a material is weakened by cyclic loading, which is one type of general material fatigue. Fatigue wear is produced when the wear particles are detached by cyclic crack growth of microcracks on the surface. These microcracks are either superficial cracks or subsurface cracks.

Aspects of the working environment which affect wear include loads and features such as unidirectional sliding, reciprocating, rolling, and impact loads, speed, temperature, but also different types of counter-bodies such as solid, liquid or gas and type of contact ranging between single phase or multiphase, in which the last multiphase may combine liquid with solid particles and gas bubbles.

2.8 Fatigue and fracture

During its service most of metallic implants are subjected to cyclic loading inside the human body which leads to the possibility for fatigue fracture. One of the factors that determine the fatigue behaviour of implant materials include the microstructure of the implant materials. It was reported that Ti6Al4V with equiaxed structure has a better fatigue strength property than the elongated structure (Akahor *et al*., 1998). Another important parameter is the frequency of the cyclic loading or the cycling rate (Lee *et al*., 2009, Karla *et al*., 2009) whereas a different fatigue behavior was found for the sample subjected to cyclic loading at 2Hz than 38Hz (Karla *et al*., 2009).

Design of the implants also plays an important role on the fatigue failure characteristics. It was reported that fatigue failure of femoral screw had initiated near a keyway, and suggestion on design improvement has been proposed by the lengthening the barrel around the lag screw. In addition, beside the type of fluid medium of the implant, the existence of other substances such as protein was also reported to have significant influence on the surface reaction and fatigue resistance of Ti implant (Fleck *et al*., 2010). Since fatigue failure is generally accompanied with corrosion process, in addition to cyclic loading, corrosive medium is needed to be introduced in order to evaluate the fatigue properties of implant materials.

2.9 Corrosion susceptibility of titanium alloys

It is generally accepted that the following four steps are involved in localized corrosion (i) adsorption of reactive anions on the oxide covered titanium surface, (ii) reaction of the adsorbed anions with the titanium cations in the titanium oxide lattice or with the precipitated titanium hydroxide, (iii) thinning of the oxide by dissolution; and (iv) direct attack of the exposed metal by the anions, perhaps assisted by anodic potential (Jerome, 2001). Ti-6Al-4V is susceptible to chloride, although being among the better of the titanium alloys in this regard. For marine environments silver plated bolts are not used, as silver bonds easily with chlorine in this environment. Ti-6Al-4V is also susceptible to SCC in environments such as methyl alcohol, red fuming HNO_3, and N_2O_4. In the case of red fuming nitric acid, the problem is limited to environments containing less than 1.5% water, or more than 6% NO_2. Failure in N_2O_4 has occurred when oxygen and chlorides were present as impurities (Rolled Alloys, 2011).

2.9.1 Corrosion inhibitor

A corrosion inhibitor is a chemical compound that, when added to an environment, decreases the rate of corrosion of a material, typically a metal or an alloy (Hubert et al., 2002). The effectiveness of a corrosion inhibitor depends on the composition of the environment, quantity of hydrogen atoms released, and flow regime. A common mechanism for inhibiting corrosion involves a passivation layer, which prevents access of the corrosive substance to the metal. Permanent treatments such as chrome plating are not generally considered inhibitors, however. Instead corrosion inhibitors are additives to the fluids that surround the metal or related object. The interaction between the inhibitor and the substrate depends to a large extent on the electrostatic force of attraction. The inhibition efficiency would be calculated to determine the degree of inhibition that was achieved.

2.10 Application of Ti-6Al-4V alloy

Ti6Al4V alloy**,** also known as grade 5 alloy, is the most commonly used titanium alloy. It has a chemical composition of 6% aluminum, 4% vanadium, 0.25% (maximum) iron, 0.2% (maximum) oxygen, and the remainder titanium (Mriano *et al*., 2009). It is significantly stronger than commercially pure titanium while having the same stiffness and thermal properties. Among its many advantages, it is heat treatable. This grade is an excellent combination of strength, corrosion resistance, weld and fabricability. This alpha-beta alloy is the workhorse alloy of the titanium industry. It is used in many aerospace airframe and engine component and also major non-aerospace applications in the marine industry, offshore and power generation industries in particular. Titanium has found successful application in field below (Mathew, 2000);

- Blades, Rings, and Discs
- Sporting Equipment
- Aircraft Structural Components
- Hand Tools
- Airframes
- Fasteners, Components
- Vessels, Cases, Hubs, Forgings
- Biomedical Implants

CHAPTER THREE

3.0 MATERIALS AND METHOD

3.1 Materials and Equipment

Some of the materials used in this research include: Titanium alloy (Ti-6Al-4V) sourced from South Africa, simulated saliva, sodium fluoride, bitter leaves sourced from Kaduna South, while some of the equipment include the Heat treatment oven, weighing balance, potentiostat equipment, three body abrasive wear test machine, Fourier Transform Infrared machine, Scanning Electron Microscope and Optical Microscope.

Table 3.1: The chemical composition of as-received Ti-6Al-4V alloy

Ti	Al	V	C	Fe	O	N	H
89.62	6.1	4	0.004	0.160	0.106	0.008	0.002

Table 3.2: The chemical composition of simulated human saliva (Mariano *et al*., 2009)

$Na.HPO_4$	$NaHCO_3$	$CaCl_2$	H_2O	HCl 1M
0.426g	1.68g	0.147g	800ml	2.5ml

3.2 Methods

3.2.1 Material Preparation

The Ti6Al4V alloy of chemical composition shown above was sectioned under flowing cooling solutions to 15mm×15mm×3mm and 30mm×25×3mm mm for electrochemical and wear analysis respectively using a mechanical cutting device. The samples were then degreased, cleaned and properly dried in preparation for solution heat treatment. After the heat treatment the surface of the samples was grinded and polished mechanically to remove the oxide film that was formed on the surface in order to obtain a smooth surface that reveals the adequate crystal structure of the titanium alloy and avoid alteration of the result obtained. This was done by sequentially using different coarse grades of silicon carbide abrasive paper ranging from 120 microns to 600 microns.

3.2.2 Heat Treatment of Titanium alloy

A total of 45 coupons were charge into the furnace for the heat treatment (solution heat treatment SHT) at 960^{o}C/1hr, careful monitoring of the temperature was done to ensure that the temperature did not exceed the beta transus line of 1000^{o}C which would cause a totally different phase transformation. Quenching in warm water (60^{o}C) followed by the ageing operation. Aging was carried out at a temperature of 480^{o}C and for varying time of 2, 4, 6, 8 hours respectively. After every 2 hours interval 11 samples were removed from the furnace (ten as corrosion coupons and one for wear resistance analysis) and allowed to cool in the open air, after which they were mechanically cleaned (grinding and polishing) and kept in a dry place. Figure 3.1 shows the heat treatment cycle used.

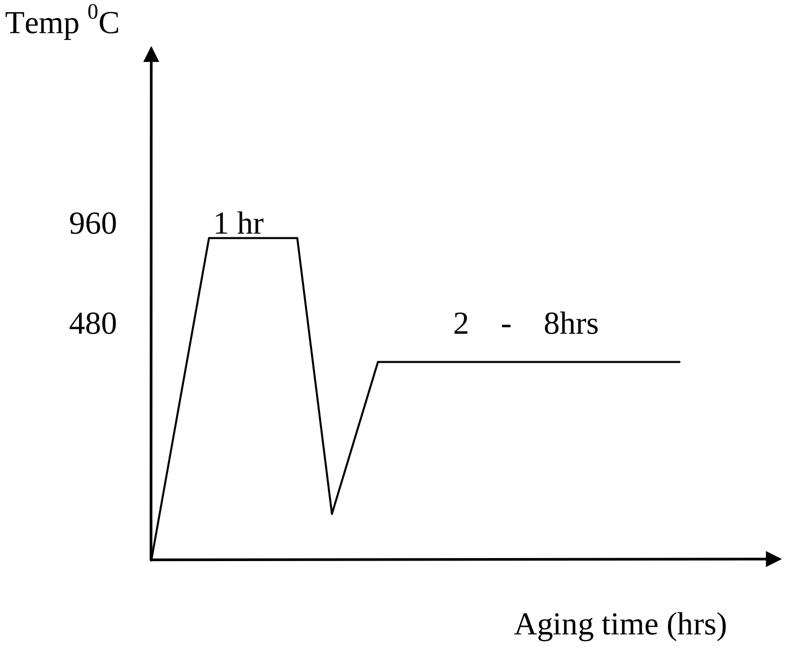

Fig 3.1 Schematic heat treatment cycle used

3.2.3 Characterization of the inhibitors

The bitter leave extract used as an inhibitor in this research was obtained by drying, grinding to powder, soaking in ethanol for 48 hours and then filtered. The filtrate was then subjected to evaporation in order to separate the ethanol from the desired extract. The extract was further subjected to fourier transform infrared (FTIR) analysis in order to reveal the functional group and constituents present. This will aid in predicting the ability/efficiency of the extract to inhibit degradation/corrosion.

3.2.4 Wear Analysis

After the thermal treatment of the alloy, a wear analysis was carried out on the surface of the coupons using 3 body abrasive wear machine. The machine used fine silica sand as the abrasive medium. Silica sand with particle size distribution ranging from 300-600 microns was used as the abrasive media. An applied load of 5N and 15N at 250rev/min wheel speed was used and a dwell time of 30 minutes. The mass loss was determined for each sample by finding the difference between the initial mass and final mass. The wear process which is a function of mass loss was used to extrapolate the wear rate. A greater mass loss signifies a greater wear loss and vice versa. For this research the applied load was varied but the flow rate of the silica sand was set constant.

3.2.5 Degradation test

Electrochemical corrosion test was carried out using the potentiodynamic polarization technique according to ASTM G 3-89 and ASTM 5-94 standards. The degradation of the thermally treated Ti6Al4V alloy was characterized by complete immersion measurement method, in simulated saliva solution with varying concentration of the bitter leaf extract as inhibitor. In addition to the simulated saliva solution; 1g sodium fluoride ((NaF) was added to 100 ml of simulated saliva. The conventional glass corrosion cell kit consisting of three electrode electrochemical system was used. The glass corrosion cell kit consisted of graphite rods as the counter electrode, a saturated Ag/AgCl 3M KCl electrode as the reference electrode and the Ti6Al4V alloy as the working electrode. The measurement started with testing for 2 hours aging time firstly in the simulated saliva solution without any inhibitor and this served as our control. Subsequently, four polished samples from 2 hours of aging time was taken and placed in four separate beakers containing 100 ml of fresh saliva solutions. The inhibitor of varying concentrations of 0.5 ml, 1.0 ml, 1.5 ml, 2.0 ml was then added respectively. The system was connected to a potentiostat and to a computer with the required electrochemical soft ware (NOVA 30) for reading the results. The polarization curves were determined at room temperature by operating with a scan rate of 0.003v/sec from a potential of -250 mV up to a potential of 250mV. The polarization curves were plotted using the Auto lab data acquisition system. The corrosion rate and potentials were estimated using the Tafel extrapolation method from the anodic and cathodic curves.

3.2.6 Micro-structural examination

The microstructure of the samples was examined using optical microscope (OPM) and scanning electron microscope (SEM). The samples were prepared by dehydration in series of percentage of ethanol. The samples were mounted on a stub of metal with adhesive, coated with palladium and observed under the microscope. The beam of very high energy primary electrons was scanned across the specimen thereby creating an image of the surface of the samples. The image was achieved by the detection of secondary electrons that were released from the surface of the samples and the image was processed by software called scandium. This was done to determine to what extent the surface integrity of the alloy was affected and the type of corrosion that had occurred.

CHAPTER FOUR

4.0 RESULTS

Figure 4.1 shows the infrared absorption (IR) spectra of bitter leaf extract with their corresponding functional groups deduced and recorded in Tables 4.1 (Appendix). Figures 4.2 – 4.5 showed the variation of wear rates against ageing time. In Figures 4.6 – 4.9, the potentiodynamic polarization curves used to extrapolate the degradation of Ti6Al4V alloy in simulated saliva with varying volumes of inhibitor were shown. Plates I – III showed the microstructural examination of the worn out samples. Tables 4.2 – 4.5 showed the variation of wear loss against soaking time while Tables 4.6 – 4.11 showed the electrochemical parameters obtained during the degradation of Ti6Al4V alloy in simulated saliva, saliva + sodium fluoride and saliva + fluoride + inhibitor (See Tables 4.1-4.11 in Appendix)

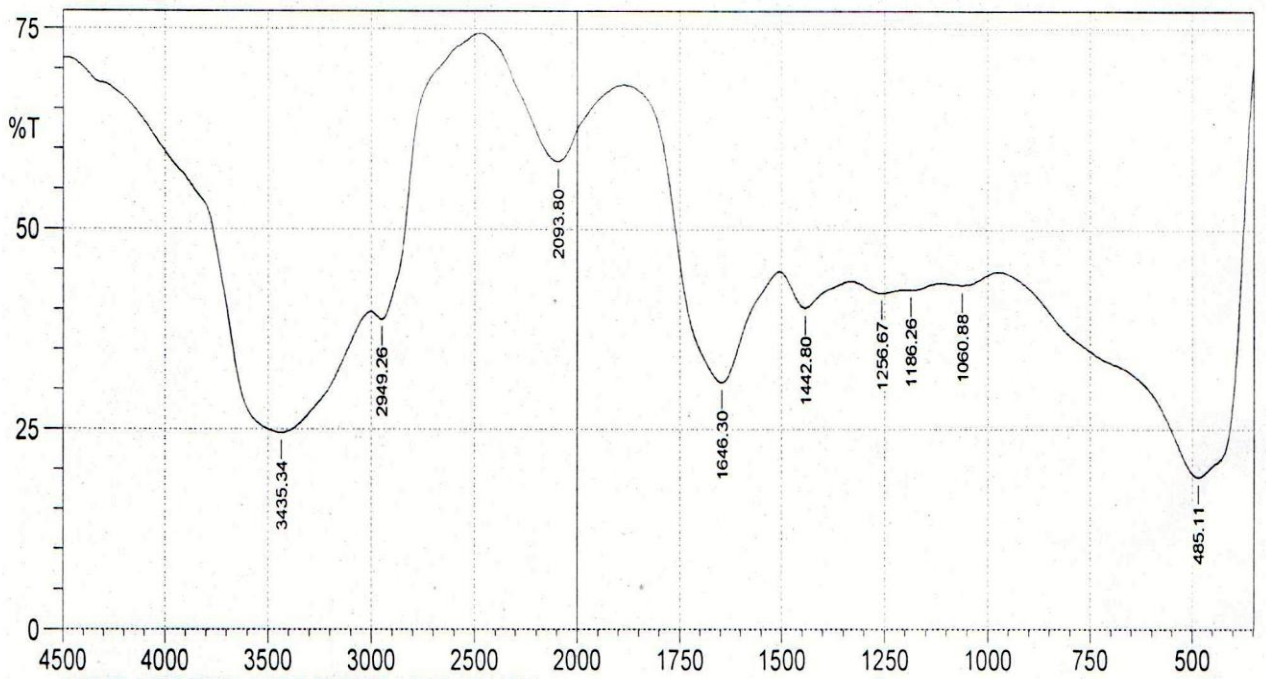

Figure 4.1: FTIR result showing the infrared spectrum of bitter leaf extract (*Vernonia amygdalina*).

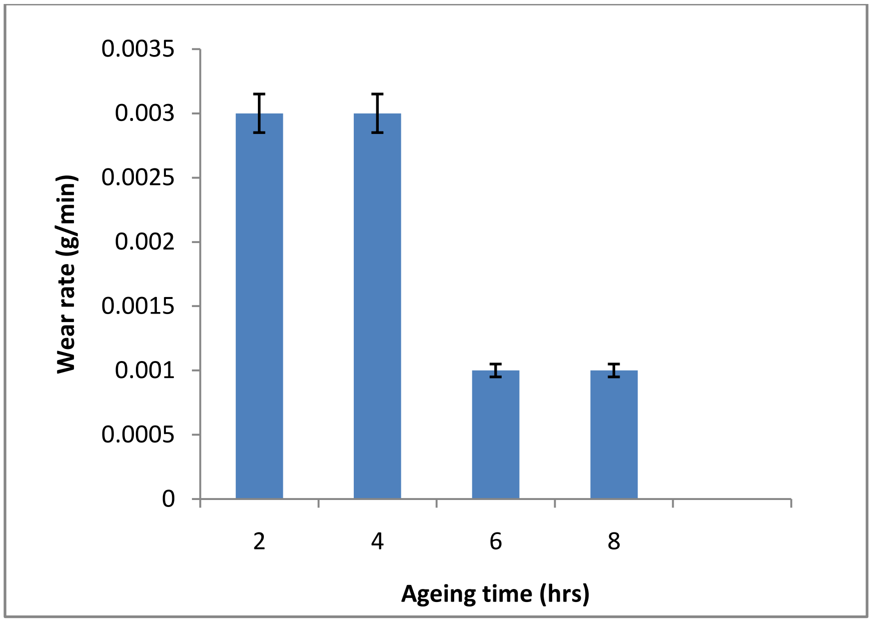

Figure 4.2: Variation of abrasive wear loss against soaking time for 5N load

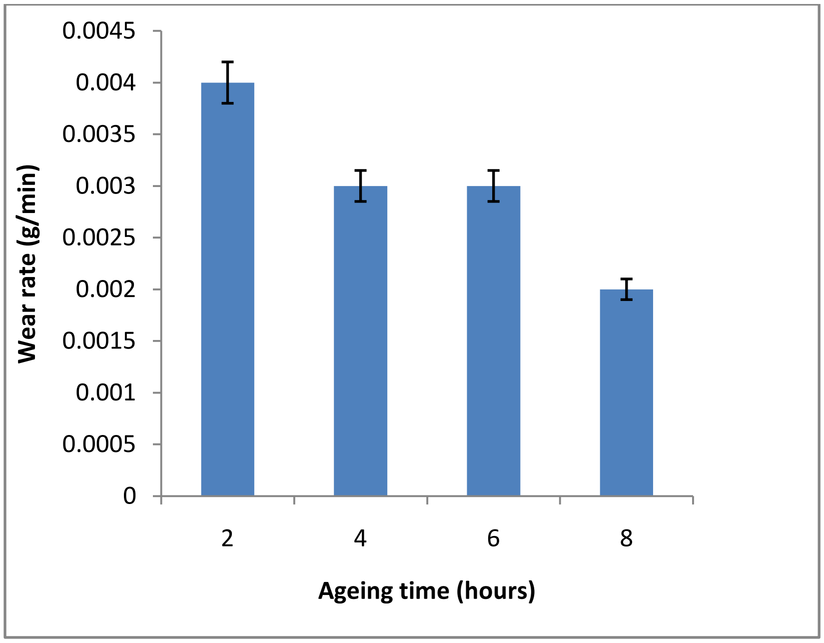

Figure 4.3: Variation of abrasive wear loss against soaking time for 15N load.

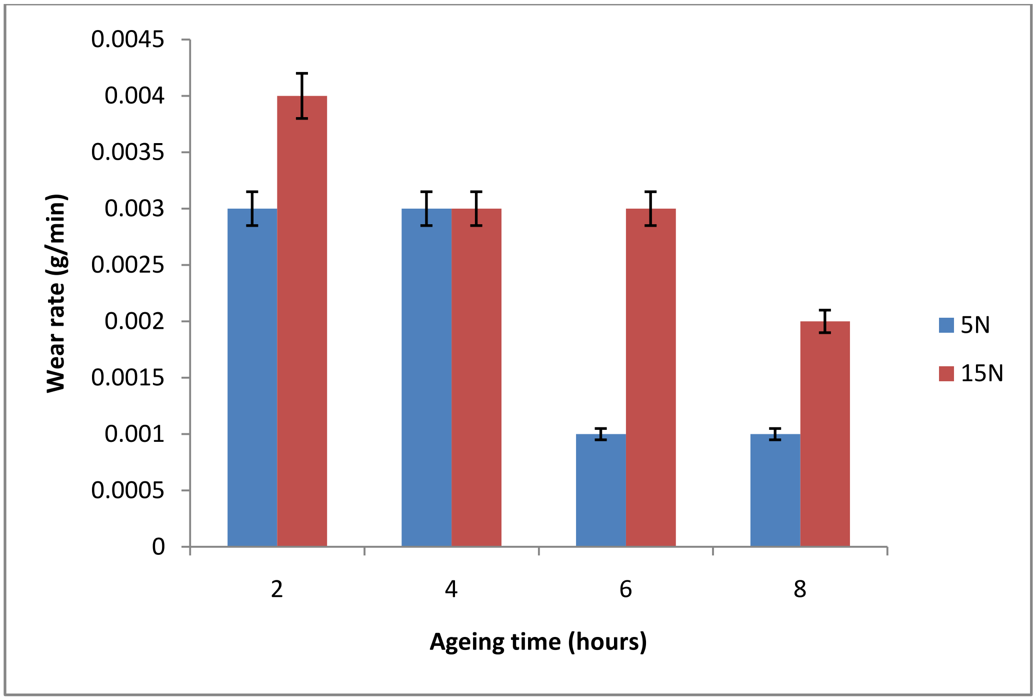

Figure 4.4: Variation of wear loss against soaking time for applied loads of 5N and 15N

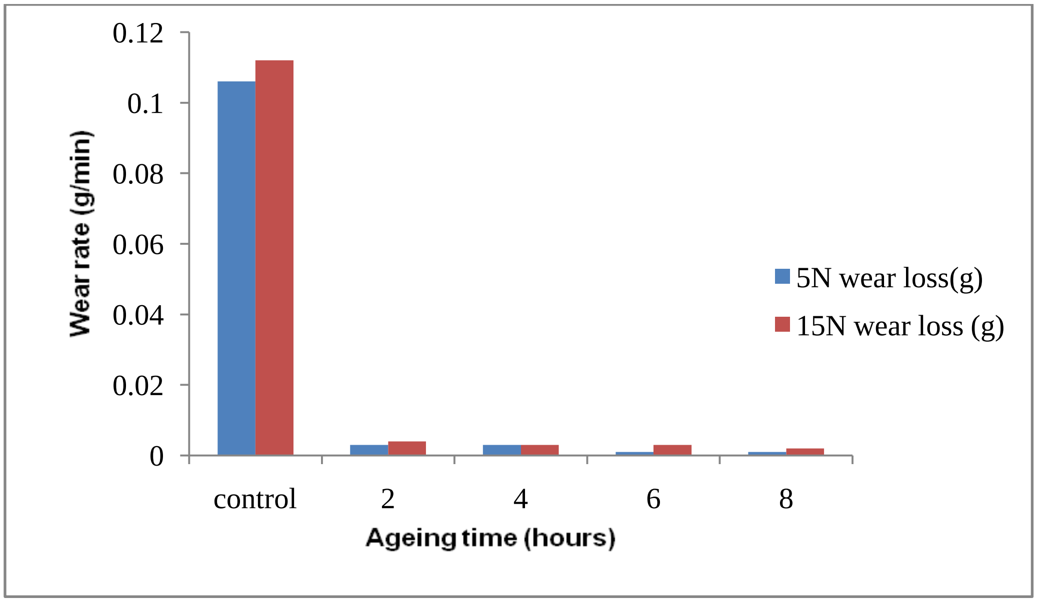

Figure 4.5: Variations in abrasive wear loss of both the unheat-treated and heat treated titanium alloy.

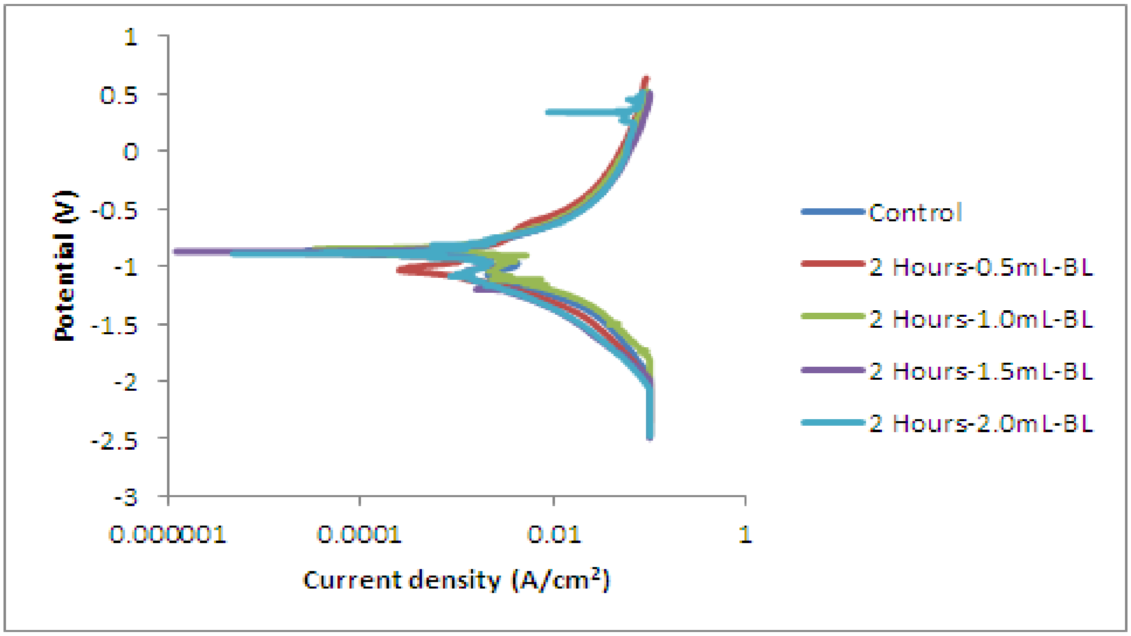

Figure 4.6: Potentiodynamic polarization curves of aged Ti6Al4V alloy soaked for 2hrs with varying concentration of inhibitor

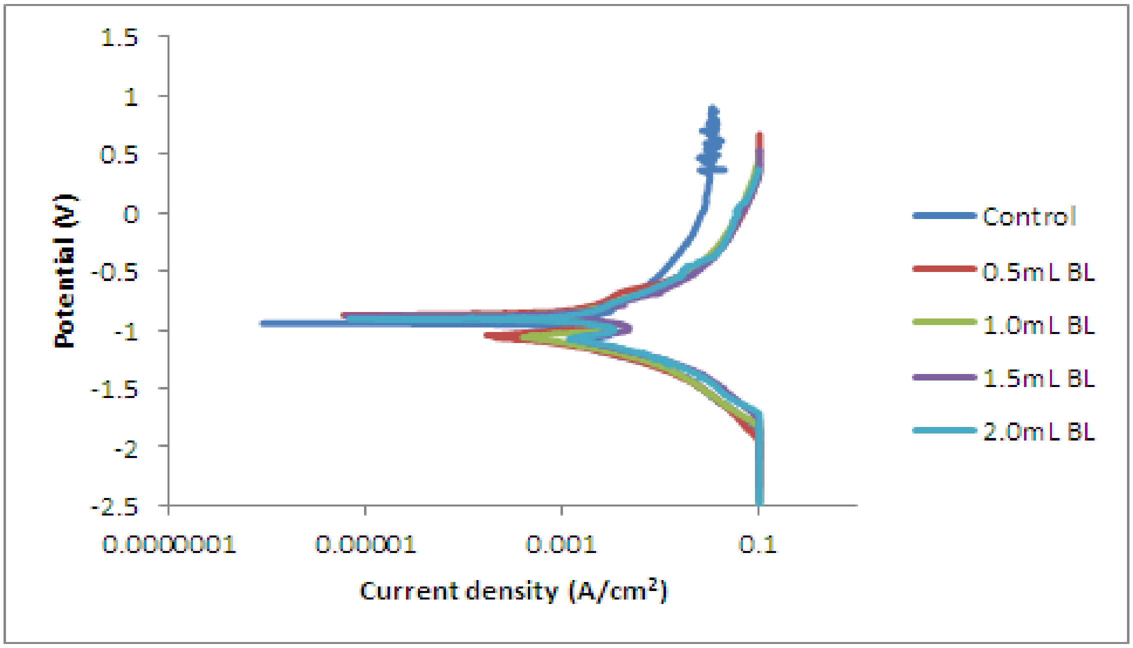

Figure 4.7: Potentiodynamic polarization curves of aged Ti6Al4V alloy soaked for 4hrs with varying concentration of inhibitor

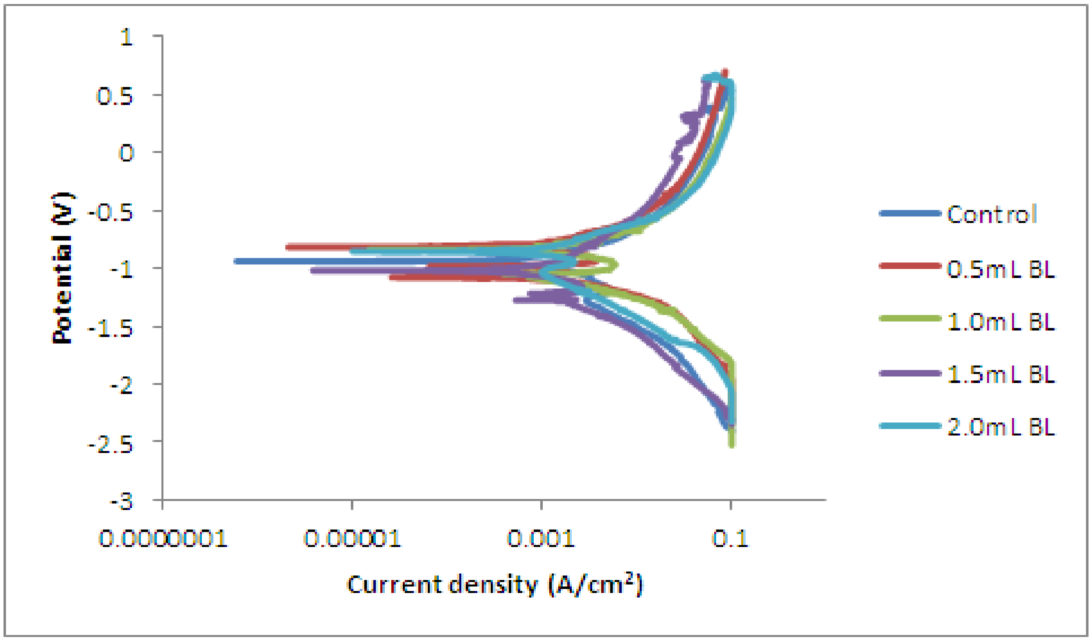

Figure 4.8: Potentiodynamic polarization curves of aged Ti6Al4V alloy soaked for 6hrs with varying concentration of inhibitor

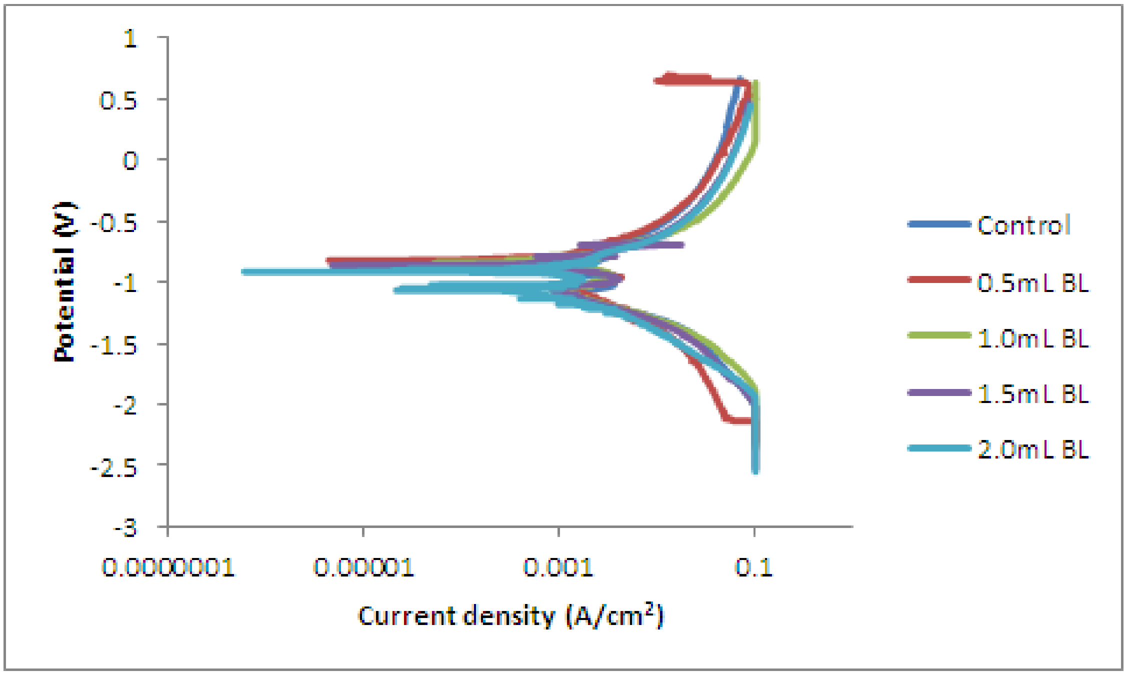

Figure 4.9: Potentiodynamic polarization curves of aged Ti6Al4V alloy soaked for 8 hrs varying with concentration of inhibitor

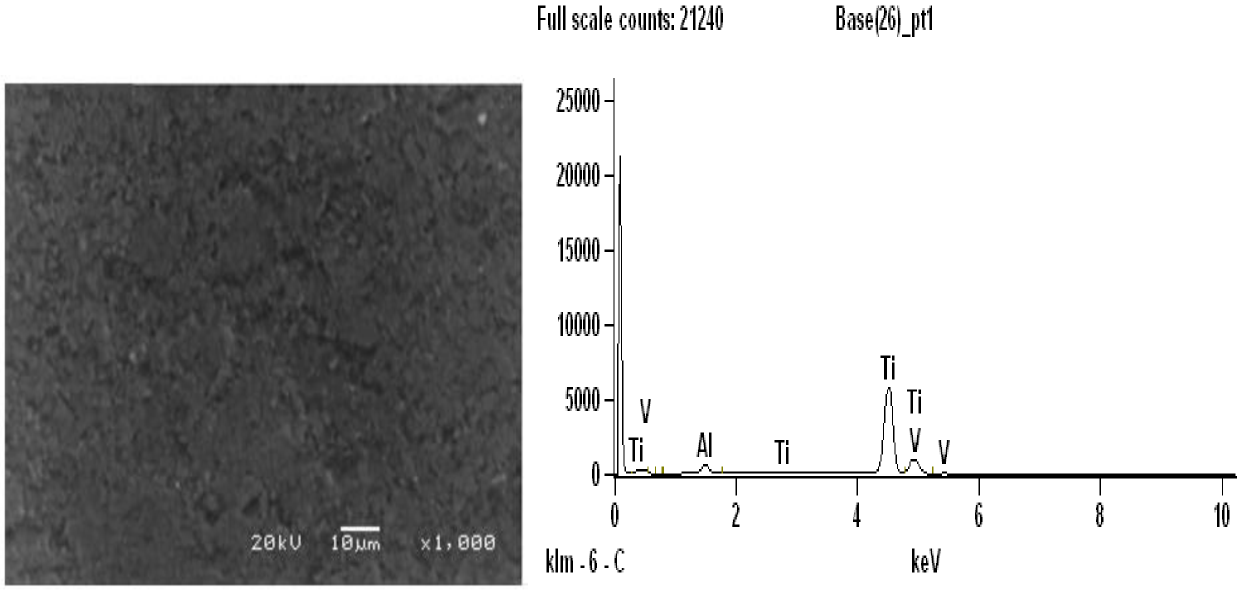

Plate I: SEM micrograph of wear scars for the least worn out sample (8 hours soaking time)

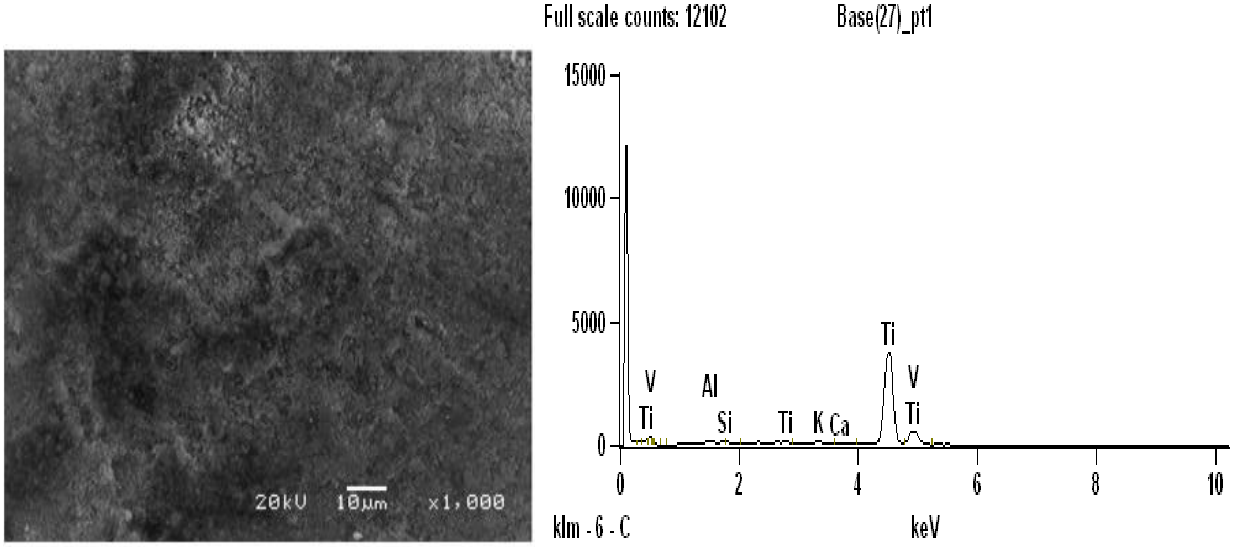

Plate II: SEM micrograph of wear scars for the most worn out sample (2 hours soaking time)

The optical microscopic structure of the worn out samples are as shown below:

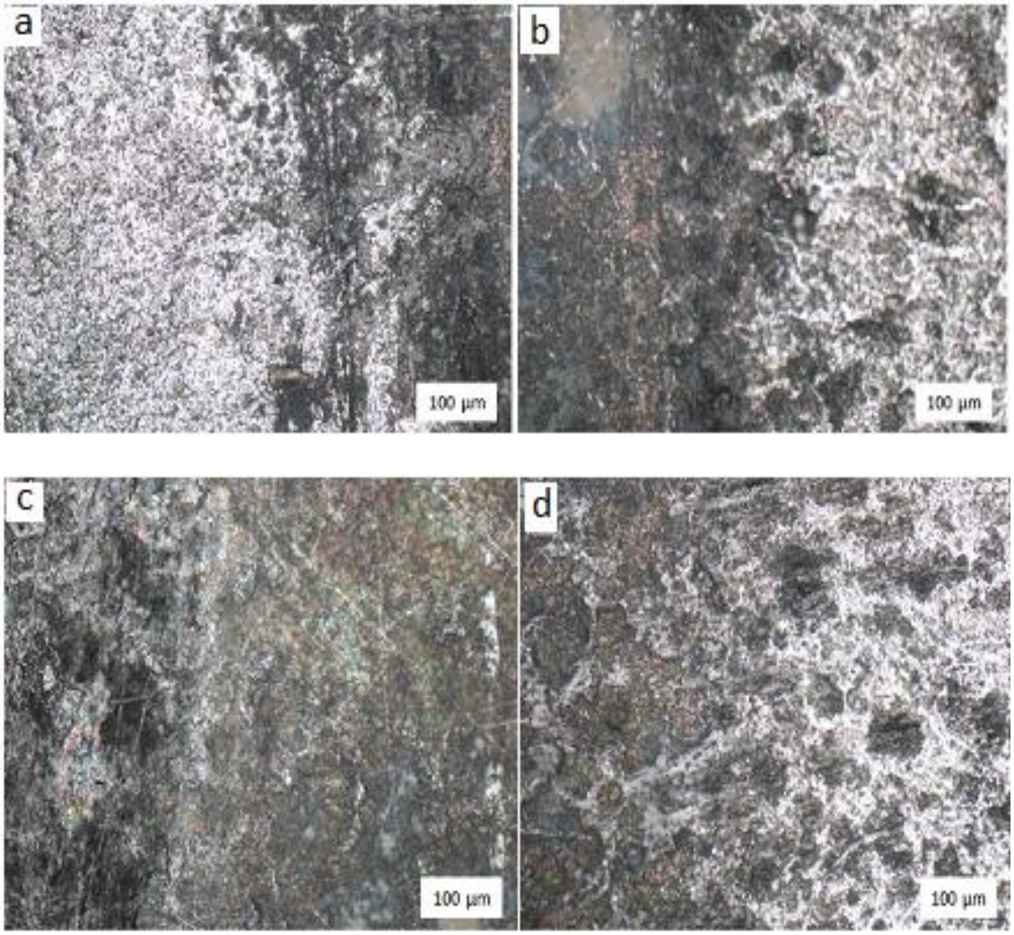

Plate III: Optical microstructure of the abrasive worn out samples of Ti-6Al-4V alloy SHT at 960^{o}C / aged at 480^{o}C and soaked for (a) 2 hours, (b) 4 hours, (c) 6 hours (d) 8 hours.

CHAPTER FIVE

5.0 DISCUSSIONS

5.1 FTIR result

The FTIR results of bitter leaf extract as shown in Figure 1, confirmed the presence of COOH(carboxylic acid), C-H (Alkanes and alkyls) C-X (Alkyls Halides), C≡C (Alkynes) and R-CH_2-OH(I^o) (C=O) (Alchohols), which are the functional groups readily available in organic tannins. The extract showed major peaks of 3435.33↔ strong COOH carboxylic acid, 2949.26↔ strong C-H alkanes, 2093.80↔ medium C≡C Alkyne, 1442.80 medium C-H (Alkanes and Alkynes), 1256.67, 1186.26 and 1060.88↔ Alchohols, 485.11↔ Alkyl halides.

There was no absorbance in between 2220-2800 which indicates the absence of cyanides which are generally toxic to the biological system. This result indicated that the bitter leaf extract is non toxic and contain a rich tannin and saponnin content.

The adsorption of inhibitor to the Ti-6Al-4V was accredited to the pairs of electron present in the functional groups. This brings the alloy to a more stable state and directly suppressing the continuous elimination of atoms from the alloy base which resulted to decrease in the degradation process.

5.2 Wear Analysis

The result from Figures 4.2 and 4.3 showed some degree of mass loss of the heat treated samples. The result showed that the abrasive mass loss decreased with increasing ageing time for the applied loads of 5N and 15N respectively (Figure 4.2- 4.3). It can be seen (Table 4.2 and

Table 4.3) that the highest mass loss was observed at the 2 hours ageing time and the lowest mass loss was observed at the 8 hours ageing time.

In Figure 4.4 the effect of increasing load on the abrasive wear for 5N and 15N applied loads; one can deduce that for the soaking time of 8hrs there was minimal loss to abbrasive wear even with the increase in load, and maximum loss was observe at 2hours. It is evident that higher mass loss was observed at 15N than 5N (Table 4.4). The information obtained from Figures 4.2- 4.4 indicates that as the aging temperature increases, the mass loss decreases and as the load increases the mass loss also increases. This was attributed to the longer hours required for absolute dissolution of the supersaturated solutes in the metal matrix.

From the results in Figure 4.5, the control sample (un– heat treated sample), showed a mass loss of 0.106g at 5N and 0.112g at 15N applied loads. This have been demonstrated that the worn out samples indicated that the thermally treated samples at 8 hours (Plate I) contained less debris and grooves as compared to the 2 hours (Plates II) that contained more. However plate III showed the degree of deformation upon wear with ageing time for all the ageing hours. The mass loss of the control was very high as compared to the heat treated samples. The result in Table 4.5 and Figure 4.5 showed 99.05% and 98.21% decrease in the mass loss between the controls (un-heat treated) and the heat treated alloy for 5N and 15N applied loads respectively as seen below.

$$\text{Inhibitor efficiency for 5N} = \frac{\text{mass loss without inhibitor – mass loss with inhibitor}}{\text{mass loss without inhibitor}} * \frac{100}{1}$$

$$\text{Inhibitor efficiency for 5N} = \frac{0.106g – 0.001g}{0.106g} * \frac{100}{1} = 99.05\%$$

$$\text{Inhibitor efficiency for 15N} = \frac{\text{mass loss without inhibitor} - \text{mass loss with inhibitor}}{\text{mass loss without inhibitor}} * \frac{100}{1}$$

$$\text{Inhibitor efficiency for 15N} = \frac{0.112\text{g} - 0.002\text{g}}{0.112\text{g}} * \frac{100}{1} = 98.21\%$$

5.3 Degradation Measurement

The addition of inhibitor into the saliva/fluoride/Ti6Al4V alloy generally decreased the rate of corrosion. From Table 4.6, it was observed that the coupon system aged for 2 hours without inhibitor addition, had the highest corrosion rate and the lowest polarization resistance than the systems with inhibitor additions. The lowest corrosion rate was observed in the system containing 1.5 ml bitter leaf extract indicating the system with the most favourable corrosion potential, that is to say that at 1.5ml, a decrease in current density and a higher polarization resistance was observed. The next most favourable system was that of 2.0 ml of inhibitor followed by 1.0 ml and 0.5 ml. This is evident from the potentiodynamic polarization curves in Figure 4.6.

From Table 4.7: it was observed that the polarization of coupons aged for 4 hours; that the addition of inhibitor decreased the rate of corrosion generally. The lowest rate of corrosion was observed in the system containing 0.5 ml inhibitor addition. Equally at 0.5 ml addition of the inhibitor we have the lowest corrosion potential accompanied with a decrease in current density and an increased polarization resistance as compared to that of 1.0, 1.5, and 2.0 ml inhibitor addition respectively. The next most favourable result is the system with 1.0 ml of inhibitor followed by 1.5 ml and 2.0 ml. This is evident from the potentiodynamic polarization curves in Figure 4.7. Also for 6 hours and 8 hours there was decrease in corrosion rate upon addition of inhibitor. The most favourable inhibitor addition was observed at 0.5 ml, then 2.0 ml, 1.5 ml, and 1.0 for 6 hours and 0.5 ml then 1.0 ml, 1.5 ml 2.0 ml for 8 hours this can be found in Figures 4.8 and 4.9/ Tables 4.7 and 4.8.

The electrochemical parameters of the Ti6Al4V in simulated saliva + fluoride without inhibitor is seen in Table 4.10 it was seen that without any inhibitor the best resistance to polarization 21.445 for the system aged for 4 hours, which was still very low and unfavourable. The summary of the most favourable concentration of inhibitor for each aging time can be found in Table 4.11. It was established that 2 hours ageing time with 1.5 ml inhibitor gave the lowest corrosion rate and current density. One can rightly say that the introduction of inhibitor in small quantities can reduce the ageing time from 8 hours to 2 with better corrosion inhibition.

Table 4.12 shows the best systems with and without inhibitor and this has proved that the introduction of bitter leaf extract in the system of saliva + fluoride reduced the corrosion rate drastically by 98.02% as shown below.

Inhibitor efficiency for 2hour +1.5ml inhibitor (most favourable system)

$$= \frac{\text{corrosion rate without inhibitor corrosion ratewith inhibitor}}{\text{corrosion rate without inhibitor}} * \frac{100}{1}$$

$$\text{Inhibitor efficiency} = \frac{0.86769 - 0.01716}{0.86769} * \frac{100}{1} = 98.02\%$$

5.4 Microstructural Examination

The SEM micrograph of the substrate upon wear test as seen in Plates I for 8 hours soaking time and Plates II for 2 hours soaking time shows an overview of the worn out surfaces. Plates I and II, showed that the mechanism of wear is by selective removal of the Ti-6Al-4V, this was observed through the presence of deep scratches on the material surface. Equally it was observed that there was evidence of worn out debris on the surface and also the evidence of deep grooves and scratches which indicates massive damaged regions caused by plastic deformation and fatigues as a result of the repeated actions of the abrasive sand. This is similar to the claim by popoola *et al*., 2012.

Comparatively the SEM results indicates that there was less damage on the surface of the sample aged for 8 hours (Plates I) than the massive damages and deep scratches that was observed on the surface of the sample aged for 2 hours (Plates II). Plate I showed a more even and general distribution of the scratches and grooves all through the surface while in Plates II there seem to be a more localized attack on the surface of the sample with deep scratches, grooves and pits. This could probably explain why there was more abrasive mass loss for the 2 hours (Plates II) than what was obtained 8 hours soaking time (Plates I).

The optical microscopic structures of the worn out plates as shown in Plates III shows the degree of wear by the presence of deep scratches, delamination of material from the surface. There was evidence of worn out debris on all the surfaces of the worn out samples.

CHAPTER SIX

6.0 SUMMARY, CONCLUSIONS AND RECOMMENDATIONS

6.1 Summary

Titanium and its alloys have been in use over the years as implants but have been found to degrade after a period of time. Ti-6Al-4V has been in use as dental implants till date because of its favourable mechanical properties, but still degrades over a period of time in the oral cavity. Researchers have proved that saliva which is usually acidic in nature favours the degradation of this dental implant (Mariano *et al.,* 2009) The fluoride content used in producing virtually all the tooth paste and mouth wash that are commercially available escalates the degradation of the Ti-6Al-4V based dental implant. It has become of great importance this unfavourable degradation process is hindered, while still maximizing the favourable mechanical properties of the alloy and making use of the pastes and mouth wash that are readily available. This research considered the prevailing situation and thought of heat treating and introducing an inhibitor into the system. The coupons were solution heat treated and accompanied by an aging process and addition of bitter leaf extract as an inhibitor. An electrochemical corrosion analysis and abrasive wear test were used as criteria to access the performance of the conditioned Ti-6Al-4V alloy for dental implant application. From the results, the wear rate of the heat treated titanium alloy decreased with applied load and the ageing time indicating a 99% and 98% wear resistance at 5N and 15N respectively. Equally the degradation resistance of the titanium alloy increased with ageing time and with addition of inhibitor; with the lowest degradation rate at 2 hour and 1.5ml inhibitor addition with a degradation reduction of 97.8%

6.2 Conclusions

1. The bitter leaf extract demonstrated to being a very good inhibitor for isothermally conditioned Ti-6Al-4V in simulated saliva + fluoride environment.

2. The increase in the soaking time decreased the effect of abrasive wear on the dental implant because the sample soaked for 8 hours showed the best resistance to abrasive wear.

3. Electrochemical studies revealed that introducing little concentrations of bitter leaf extract as inhibitor into the simulated oral environment showed a significant influence in elongating the life span of the titanium based dental implant. From the electrochemical studies, the sample that was aged for 2 hours and 1.5ml bitter leaf extract (inhibitor), was adopted as the best for its optimum properties.

4. From the results the behaviour of Ti-6Al-4V in the different solutions of simulated saliva + fluoride and simulated saliva + fluoride + inhibitor, it was deduced;

   i. The corrosion resistance of the isothermally conditioned Ti-6Al-4V in simulated saliva containing fluoride ions (a more acidic media) decreased further. This was attributed to the fluoride ion broke down the self-generated protective layer (TiO_2) of the alloy.
   ii. The corrosion resistance of the isothermally conditioned Ti-6Al-4V in simulated saliva containing fluoride ions with the introduction of bitter leaf extract as inhibitor increased remarkably, most probably by suppressing of the dissolution of the titanium ions via the formation of a thin film over the dental implant.

6.3 Recommendations

1. Investigate the use of non toxic surfactants as addition to the bitter leaf extract

2. The study of masciculatory force be investigated in the studied environment

3. The use of atomic force microscopy is recommended for thin film study

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Appendix

Tables 4.1: frequencies and peaks of infrared absorption bands of functional groups in bitter leaf (Vernonia amygdalina) extract.

S/N	Frequency (Cm^{-1})	Intensity (%)	Assignment	Class of compound
1	3435.34	24.495	O-H sstretch	Carboxylic acid/Phenols
2	2949.26	38.751	OH stretch	Phenols
3	2093.80	58.488	OH stretch	phenols
4	1646.30	30.866	C=C stretch	Alkynes
5	1442.80	40.252	C-H bend	Alkanes/ Alkynes
6	1256.67	42.130	C-O stretch	Alchohol
7	1186.26	42.493	C-O stretch	Alchohol
8	1060.88	42.131	C-O stretch	Alchohol
9	485.11	19.065	C-I stretch	Alkyl halides

Table 4.2: Experimental data for abrasive wear test with an applied load of 5N for heat treated Ti-6Al-4V

Ageing time (hrs)	**Initial mass (g)**	**Final Mass (g)**	**Mass Loss (g)**
2	13.613	13.61	0.003
4	12.612	12.609	0.003
6	13.593	13.592	0.001
8	13.157	13.156	0.001

Table 4. 3: Experimental data for abrasive wear test with an applied load of 15N for heat treated Ti-6Al-4V

Ageing time (hrs)	**Initial mass (g)**	**Final Mass (g)**	**Mass Loss (g)**
2	13.613	13.609	0.004
4	12.612	12.609	0.003
6	13.593	13.590	0.003
8	13.157	13.155	0.002

Table 4.4: Wear loss data comparism between the 5N and 15N applied loads.

sample Ageing time (hrs)	**5N Mass loss (g)**	**15N Mass loss (g)**
2	0.003	0.004
4	0.003	0.003
6	0.001	0.003
8	0.001	0.002

Table 4.5. Wear loss data of heat treated and unheat treated Ti6Al4V under different loads

	5N	**15N**
Ageing time (hrs)	**Mass Loss (g)**	**Mass Loss (g)**
Control (without heat treatment)	0.106	0.112
2	0.003	0.004
4	0.003	0.003
6	0.001	0.003
8	0.001	0.002

Table 4.6: Electrochemical parameters of Ti6Al4V heat treated at 960^{o}C and aged at 480^{o}C for 2 hours in saliva +fluoride with and without inhibitor

Bitter leaf extract Conc. (ml)	**Ecorr, Obs (V)**	**Icorr (A/cm^2)**	**Corrosion rate (mm/year)**	**Polarization resistance (Ω)**	**Inhibitor Efficiency %**
Control	-0.90305	0.002254	0.86769	24.196	-
0.5	-0.89221	0.001733	0.66719	28.435	23.11
1.0	-0.89104	0.001215	0.46762	37.591	46.11
1.5	-0.86547	4.46E-05	0.01716	800.16	98.02
2.0	-0.87399	0.000949	0.36523	43.601	57.91

Table 4.7: Electrochemical parameters of Ti6Al4V heat treated at 960°C and aged at 480°C for 4 hours in saliva +fluoride with and without inhibitor

Bitter leaf extract conc. (ml)	**Ecorr, Obs (V) (V)**	**Icorr (A)**	**Corrosion rate (mm/year)**	**Polarization resistance (Ω)**	**Inhibitor efficiency %**
Control	-0.94677	0.002018	0.776810	21.445	-
0.5	-0.87308	0.000259	0.099748	51.815	87.16
1.0	-0.88491	0.000762	0.293250	43.876	62.25
1.5	-0.88538	0.001664	0.640360	28.826	17.57
2.0	-0.90626	0.001856	0.714380	22.289	8.04

Table 4.8: Electrochemical parameters of Ti6Al4V heat treated at 960°C and aged at 480°C for 6 hours in saliva +fluoride with and without inhibitor

Bitter leaf extract conc.(ml)	**Ecorr, Obs (V)**	**Icorr (A)**	**Corrosion rate (mm/year)**	**Polarization resistance (Ω)**	**Inhibitor efficiency %**
Control	-1.0767	0.002095	0.80622	22.153	-
0.5	-0.8556	0.000337	0.12975	49.650	83.91
1.0	-1.0208	0.000680	0.14093	29.890	82.52
1.5	-1.0453	0.000949	0.26158	23.725	67.55
2.0	-0.9392	0.000366	0.36537	29.907	54.68

Table 4.9: Electrochemical parameters of Ti6Al4V heat treated at 960°C and aged at 480°C for 8 hours in saliva +fluoride with and without inhibitor

Bitter leaf extract conc. (ml)	**Ecorr, Obs (V)**	**icorr (A)**	**Corrosion rate (mm/year)**	**Polarization resistance (Ω)**	**Inhibitor efficiency%**
Control	-1.15120	0.005408	2.08160	36.779	-
0.5	-0.82187	5.83E-06	0.06777	1096.9	96.44
1.0	-0.84218	0.000307	0.11821	95.822	94.32
1.5	-0.86123	0.002044	0.78686	80.809	62.20
2.0	-0.89604	0.002982	1.14790	78.884	44.85

Table 4.10: Electrochemical parameters of the Ti6Al4V in simulated saliva + fluoride without inhibitor

Soaking time (hours)	**Ecorr(V)**	**Jcorr(A/cm^2)**	**Corrosion rate (mm/yr)**	**Polarization resistance(Ω)**
2	-0.90305	0.002254	0.86769	24.196
4	-0.94677	0.002018	0.776810	21.445
6	1.07671	0.002095	0.80622	22.153
8	-1.15120	0.005408	2.08160	36.779

Table 4.11 Summary of the electrochemical parameters of the most efficient inhibition process for each of the soaking time of Ti6Al4V in simulated saliva.

Ageing soaking time (hrs)	**Concentration of inhibition (ml)**	**Ecorr (V)**	**Jcorr (A/cm^2)**	**Corrosion rate (mm/yr)**	**Polarization resistance (Ω)**	**Inhibitor efficiency %**
2	1.5	0.86547	4.4 E-05	0.01716	800.16	98.02
4	0.5	0.87308	0.000259	0.09748	51.815	87.16
6	0.5	0.85560	0.000337	0.12975	49.650	83.91
8	0.5	0.82157	5.83 E-06	0.06777	1096.9	96.44

Table 4.12 Comparisms of electrochemical parameters of the best systems with and without inhibition.

Soaking time(hrs)	**Enviroment**	**Ecorr(V)**	**Jcorr(A/cm^2)**	**Corrosion rate (mm/yr)**	**Polarization resistance(Ω)**
4	Saliva + fluoride	-0.94677	0.002018	0.776810	21.445
2	Saliva +fluoride+ inhibitor (0.5ml)	0.86547	4.4 E-05	0.01716	24.196