ANALYSIS OF CORROSION FATIGUE FOR COMMERCIALY PURE TITANIUM USING NITROGEN ION IMPLANTATION

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ABSTRACT

The objective of this research is to determine the corrosion fatigue behaviours for commercially pure titanium (CpTi) using nitrogen ion implantation. A series of studies was conducted to obtain the mechanical properties, corrosion resistance and fatigue and corrosion fatigue behaviours and to develop model prediction of corrosion fatigue life of nitrogen ion implanted CpTi (Nii-Ti). Initially, nine specimens of CpTi were implanted nitrogen ion with the energy of 80, 100 and 115 keV and dose of $0.5 \times 10^{17}$, $1.0 \times 10^{17}$ and $2.0 \times 10^{17}$ ions/cm$^2$ to characterize its surface properties and to obtain corrosion resistance. The result shows that energy of 100 keV and dose of $2.0 \times 10^{17}$ ions/cm$^2$ was the optimal implanted parameter. In the second study, fatigue and corrosion fatigue test were performed to investigate the fatigue and corrosion fatigue behaviours. The fatigue specimens were implanted with the energy of 100 keV and dose of $2.0 \times 10^{17}$ ions/cm$^2$. The fatigue tests were carried out for Nii-Ti specimens in saline solution and for CpTi and Nii-Ti specimens in laboratory air by means of axial loading condition at stress level between 240 and 320 MPa. The results were nitrogen ion implantation improved slightly the fatigue life of CpTi and Nii-Ti with the fatigue strength of 250 MPa and 260 MPa, respectively. Finally, the prediction of corrosion fatigue life was developed based on corrosion pit growth law. The stress amplitudes of 250, 260 and 280 MPa were selected to measure penetration rate of specimens at various elapsed times using electrochemical method in saline solution, then established the empirical model. The result shows that the expression fits the experimental data well. In conclusion, the effects of nitrogen ion implantation on surface properties and adhesion strength of nitride layers improved the fatigue and corrosion fatigue life of Nii-Ti.
ABSTRAK

Objektif kajian ini ialah untuk menentukan tingkah laku lesu kakisah untuk titanium komersil murni (CpTi) menggunakan nitrogen ion implantasi. Satu siri kajian telah dijalankan untuk menentukan sifat-sifat mekanikal, rintangan kakisah, kelesuan dan tingkah laku lesu kakisah dan membangunkan pengiraan daripada model hayat lesu kakisah CpTi setelah ditanamkan ion nitrogen (Nii-Ti). Dalam kajian awal, sembilan spesimen CpTi yang telah ditanamkan ion nitrogen dengan tenaga 80, 100 dan 115 keV dan dose 0.5x10^{17}, 1.0x10^{17} dan 2.0x10^{17} ions/cm^{2} untuk ciri-ciri sifat permukaan dan rintangan kakisah. Hasil kajian menunjukkan bahawa tenaga 100 keV dan dose 2.0x10^{17} ions/cm^{2} adalah parameter optimum penanaman itu. Dalam kajian kedua, ujian lesu dan kakisah lesu telah dijalankan untuk melihat lesu dan hayat lesu kakisah. Spesimen lesu telah pun ditanam ion nitrogen dengan tenaga 100 keV dan dose 2.0x10^{17} ions/cm^{2}. Ujian lesu dengan dijalankan bagi spesimen CpTi dan Nii-Ti dalam persekitaran makmal dan ujian lesu kikisan untuk spesimen Nii-Ti dalam larutan masin dengan keadaan beban paksi dalam julat tegasan antara 240 MPa. 320 MPa. Berdasarkan kajian ini didapati bahawa penanaman ion nitrogen meningkat sedikit hayat lesu CpTi dan Nii-Ti dengan kekuatan lesu masing-masing iaitu pada 250 MPa dan 260 MPa. Dalam kajian akhir terhadap angaran hayat kakisah lesu telah dibangunkan berdasarkan hukum pertumbuhan kakisah lubang. Amplitud tegasan 250 MPa, 260 MPa dan 280 MPa telah dipilih untuk melihat kadar penuukan yang terjadi terhadap specimen Nii-Ti pada pelbagai masa berlaku menggunakan kaedah elektrikomia dalam larutan masin; kemudian menubuhkan model empirik bagi anggaran hayat kakisah lesu. Keputusan kajian menunjukkan, pengiraan dan ujikaji boleh dibandingkan dan bersesuian juga. Sebagai kesimpulan, kesan penanaman ion nitrogen pada sifat-sifat permukaan dan ketegasan lekatan lapisan nitrida boleh meningkatkan hayat lesu dan hayat lesu kakisah Nii-Ti.
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<tbody>
<tr>
<td>A</td>
<td>Area</td>
</tr>
<tr>
<td>ASTM</td>
<td>American Society for Testing and Materials</td>
</tr>
<tr>
<td>Al</td>
<td>Aluminium</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>Aluminium Oxide/ Alumina</td>
</tr>
<tr>
<td>At%</td>
<td>Atomic Percentage</td>
</tr>
<tr>
<td>a.u.</td>
<td>Auxiliary unit</td>
</tr>
<tr>
<td>BATAN</td>
<td>Badan Tenaga Nuklir Nasional (National Nuclear Energy Agency of Indonesia)</td>
</tr>
<tr>
<td>bcc</td>
<td>Body centred cubic</td>
</tr>
<tr>
<td>cm</td>
<td>Centimetre</td>
</tr>
<tr>
<td>C</td>
<td>Paris’s material constant</td>
</tr>
<tr>
<td>CE</td>
<td>Counter Electrode</td>
</tr>
<tr>
<td>CpTi</td>
<td>Commercially pure titanium</td>
</tr>
<tr>
<td>da/dN, da/dt</td>
<td>Fatigue crack growth rate</td>
</tr>
<tr>
<td>EW</td>
<td>Equivalent weight</td>
</tr>
<tr>
<td>E₉corr</td>
<td>Corrosion potential</td>
</tr>
<tr>
<td>f</td>
<td>Frequency</td>
</tr>
<tr>
<td>F</td>
<td>Corrosion degradation factor</td>
</tr>
<tr>
<td>fcc</td>
<td>Face-centred cubic</td>
</tr>
<tr>
<td>h</td>
<td>Hour</td>
</tr>
<tr>
<td>Hz</td>
<td>Hertz</td>
</tr>
<tr>
<td>HF</td>
<td>Hydrofluoric acid</td>
</tr>
<tr>
<td>HNO₃</td>
<td>Nitric acid</td>
</tr>
<tr>
<td>H₂O</td>
<td>Water</td>
</tr>
<tr>
<td>I₉corr</td>
<td>Total anodic current</td>
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$i_{corr}$ - Corrosion current density

$K$ - Stress Intensity Factor

$k$ - Strength coefficient

$Kc$ - Critical stress intensity factor

$K_{IC}$ - Fracture toughness

$K_{pc}$ - Stress intensity factor at instance of crack initiation

$K_t$ - Stress concentration factor

keV - Kilo electro Volt

$\Delta K$ - Stress intensity factor range

$\Delta K_{th}$ - Fatigue threshold stress intensity factor range

$l$ - Liter

$m$ - Paris’s material constant

$mV/s$ - Milivolt per second

$mg$ - Miligram

$mm$ - Milimetre

MPa - Mega Pascal

$m/s$ - Mil per year

$mV$ - Milivolt

$n$ - Number of element

$N$ - Number of cycle

$2N_f$ - Reversals to failure

$nA$ - nanoampere

NaCl - Sodium chloride

$N_2$ - Nitrogen

Nii-Ti - Nitrogen ion implanted Cp Ti

$O_2$ - Oxygen / Air

$R$ - Stress ratio, \((R = S_{a_{min}}/S_{a_{max}})\)

RE - Reference Electrode

$S_a$ - Stress amplitude

$S_{cf}$ - Fatigue strength in corrosive medium

$S_f$ - Fatigue strength in laboratory air

$S_m$ - Mean stress

$S'_f$ - Fatigue strength coefficient
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<th>Description</th>
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<tr>
<td>SBF</td>
<td>Simulated Body Fluid</td>
</tr>
<tr>
<td>SEM/EDS</td>
<td>Scanning Electron Microscopy/Energy Dispersive Spectroscopic</td>
</tr>
<tr>
<td>(\Delta S)</td>
<td>Stress range ((\Delta S = S_{\text{max}} - S_{\text{min}}))</td>
</tr>
<tr>
<td>Ti</td>
<td>Titanium</td>
</tr>
<tr>
<td>TiO(_2)</td>
<td>Titanium Dioxide</td>
</tr>
<tr>
<td>Ti(_x)N</td>
<td>Titanium Nitride</td>
</tr>
<tr>
<td>WE</td>
<td>Working Electrode</td>
</tr>
<tr>
<td>(\varepsilon_p)</td>
<td>Plastic strain</td>
</tr>
<tr>
<td>(\varepsilon_e)</td>
<td>Elastic strain</td>
</tr>
<tr>
<td>(\varepsilon)</td>
<td>Epsilon</td>
</tr>
<tr>
<td>(\sigma'_{f})</td>
<td>Fatigue strength</td>
</tr>
<tr>
<td>(\kappa)</td>
<td>Kappa</td>
</tr>
<tr>
<td>(\Theta)</td>
<td>Theta</td>
</tr>
<tr>
<td>(\alpha)</td>
<td>Alpha</td>
</tr>
<tr>
<td>(\rho)</td>
<td>Rho (density)</td>
</tr>
<tr>
<td>(\gamma)</td>
<td>Gamma</td>
</tr>
<tr>
<td>(x)</td>
<td>Chi</td>
</tr>
<tr>
<td>(\mu\text{A})</td>
<td>Microampere</td>
</tr>
<tr>
<td>(\mu\text{m})</td>
<td>Micrometer</td>
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<tr>
<td>(W)</td>
<td>Atomic weight of the element</td>
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<td>XRD</td>
<td>X Ray Diffraction</td>
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CHAPTER 1

INTRODUCTION

This chapter begins with the background of the research and important elaboration, followed by problem statements, objective, scope, contributions of the research and organization of the thesis.

1.1 Background of research

Metallic biomaterials are the most appropriate implant materials to replace failed hard tissue at present. Stainless steels, cobalt based alloys, titanium and its alloys are the three most used metals for biomaterials in fabrication of medical devices.

Recently, titanium and titanium alloys are getting much more attention as biomaterials because they have high specific strength, low density, good resistance to corrosion, moderate elastic module of 100-110 GPa (Leyens & Peters, 2003; Majumda et al., 2008), no allergic problems and good biocompatibility (non-toxic and not rejected by the human body) among other metallic biomaterials. They exhibit a high corrosion resistance due to the formation of a stable passive layer (TiO$_2$) on its surface.

Therefore, they have been extensively used in the last several decades as materials for dental implants, and medical devices. Nowadays, they are also considered by medical engineering as the material of choice for medical application (Elias et al., 2008; Niinomi, 1998; Van Noort, 1987), i.e. the prosthetics, internal fixation, inner body devices and instrumentation.

Since significant benefit of titanium for patients, surgeons and engineers, the use of the titanium would steadily increase in the near future. Besides the increasing
of titanium used as implant materials are due to the increase in the older generation or aging population worldwide, the trend toward more active lifestyles, and the ability to control health care cost.

The population ratio of the aged people has grown rapidly, so the number of the elder demanding and replacing failed tissue with artificial devices from biomaterials is also increasing, particularly, the amount of usage of instruments for replacing failed hard tissues such as artificial hip joints, and dental implants.

Pure titanium and Ti–6Al–4V are still the most widely used among the titanium alloys where they meet a demand almost the market of titanium biomaterials. Basically, they are developed as structural materials particularly for aerospace structures (Niinomi, 2003; Luetjering & Williams, 2003).

Therefore, the development of titanium targeted for biomedical applications are highly required. Accordingly, the research and development on titanium composed of non-toxic elements were started (Silvaa et al., 2004), and are under development which increase continuously. Although commercially pure titanium (CpTi) exhibit several advantages as biomaterial, but its resistance to wear is lower than Ti alloy. It is therefore necessary of surface treatment of commercially pure Titanium (CpTi) to enhance the resistance to wear by ensuring no decline in corrosion resistance.

Some surface processing, such as sandblasting, induces rough and contaminated surfaces and it might be an increasing in risk to failure due to this surface condition results in higher corrosion susceptibility. Electrochemical investigations of the corrosion behaviour of CpTi and Ti alloys have always demonstrated very good passivity condition of the surface. However, the study about ensuring reliability of medical implant is still insufficient. Therefore, the prediction of the corrosion fatigue life of pure titanium with nitrogen ion implanted surface as the implant material would be a valuable contribution on ensuring the sustainability of the implant devices.

1.2 Problem statements

Nitrogen ion implantation was introduced onto CpTi to modify the surface condition for more reliable performance and to increase its surface resistance to wear and corrosion. However, the problem with ion implantation is crystallographic damage,
produces implantation damage on the surface (Rautray et al., 2011) and point defect in target crystal on impact resulting imperfection in lattice crystal such as vacancies and interstitials known as point defects. Ion implantation introduces both a chemical change in the target surface and a structure change in the crystal structure that could be surface defect in the form of a void or micro crack those can cause premature failure of the implanted device.

Several research works studied on corrosion behaviour of CpTi and Titanium alloys (Fukumoto et al., 1999; Sundararajan, & Prunseis, 2004; Raman et al., 2005), however more work are necessary in the area of fatigue as well as corrosion fatigue for the nitrogen ion implanted CpTi (Vardiman & Kant, 1982).

This study focuses more comprehensive on the analysis of corrosion fatigue for commercially pure titanium using nitrogen ion implantation. The nitrogen ion implantation might create surface damage and lattice disorder in the near surface of the material. Therefore, the nitrogen ion implanted CpTi, with surface damage, when it is applied a cyclic stress in body fluid or saline solution environment could be the potential factors caused the corrosion fatigue failure for the proposed biomedical material. Intensive research is needed to prove the fatigue behaviour of CpTi after implantation with nitrogen ion.

1.3 Objective

The objective of this research is to analyze corrosion fatigue behaviours for commercially pure Titanium using nitrogen ion implantation. A series of studies was conducted to achieve specific objectives as follows:

1. To obtain the optimum parameter of CpTi after nitrogen ion implantation.
2. To investigate the influence of the nitrogen ions implantation on fatigue and corrosion fatigue properties.
3. To develop an empirical model based on experimental data for corrosion fatigue life prediction.

1.4 Scope of research

The scopes of this research are as follow:
1. Introducing the nitrogen ion onto surface of CpTi by ion implantation method to modify the surface hardness that can improve the wear and corrosion resistance. Beam energy of 80, 100 and 115 keV and dose of $0.5 \times 10^{17}$, $1.0 \times 10^{17}$ and $2.0 \times 10^{17}$ ions/cm$^2$ are used as the variables proposed for nitrogen ion implantation process.

2. Specimens that had been implanted with nitrogen ion were analyzed for the formation of nitride phase. Surface hardness and corrosion rate of the Nii-Ti specimens were tested to verify the optimal parameter of implantation process. In addition, the tensile and wear resistance tests were also to be carried out on the nitrogen ion implantation specimens.

3. The nitrogen ion implanted specimens were tested the fatigue in laboratory air and in saline solution with the frequency of 10 or 20 Hertz and stress ratio, R, of -1.

4. Based on the experimental results, the empirical model was developed for estimation of corrosion fatigue life for CpTi using nitrogen ion implantation.

1.5 Contributions of research

Corresponding to the above objective, some important points could be expressed as contribution to the knowledge and professional usage as well as industrial application. There are three prominent contributions that can be provided from the result of this research.

1. Improvements in corrosion resistance and mechanical properties for Ti used biomedical applications have practical importance. Different energies at different doses for implanting nitrogen ion are a good approach.

2. The use of nitrogen ion implantation is a good technique for the improvement of fatigue strength of Ti base materials.

3. The penetration growth law for Nii-Ti was established for contribution to the service life estimation of Ti base materials in acidic environments.

1.6 Thesis organization

The present thesis comprised of five chapters that were organized in order to address the objectives referred to in section 1.3 which are:
• Chapter 1: The description of research overview was discussed and the investigations performed in this area was briefly reviewed. The knowledge gap for significant corrosion behaviour and mechanical properties of CpTi with surface modification is extracted from the state-of-art to define the research objectives. The problem statements, research objective, scope of the research and the research contributions are described. The overall contents of the thesis are also summarized in this chapter.

• Chapter 2: The basic theory to support the implementation of the whole research is discussed in this chapter.

• Chapter 3: The details of the experimental investigations are presented. The properties of the CpTi, the fabrication process and equipment used in the research activities are described. The loading set-up, experimental conditions and measuring systems employed to collect the experimental data are explained.

• Chapter 4: The achieved results of the research are presented and discussed following the objective of the research. The most important findings are also described.

• Chapter 5: The conclusions derived from experimental and theoretical investigations are presented. The future works as recommendations are also stated in this chapter.
CHAPTER 2

LITERATURE REVIEW

The current research on the effect associated with nitrogen ion implanted commercially pure titanium (Nii-Ti) in body fluid environment are important to understand and keep up to date as it changes with the latest technology and materials. Establishing a framework for the present study, the basic concept involved in surface modification, corrosion and corrosion-fatigue are reviewed. Later, specific examples are outlined to show basic trends found in the literature. Finally, empirical model of fatigue-life time prediction was briefly described.

2.1 Titanium in biomedical applications

Titanium is found in the earth’s crust at the level of about 0.63% by mass and it is the seventh-most abundant element metal (73.8%) (Barksdale, 1968; Barbalace, 2006). It is recovered from TiO$_2$ which is rich with deposits of rutile and ilmenite, FeTiO$_3$, that are found on every continent (Luetjering & Williams, 2003). Since its discovery in 1791, and up until Kroll’s innovative process development in 1932, there had been no practical methods to recover titanium metal from these ores because of its prominent affinity for oxygen. Since the modern ore extraction, beneficiation and chemical processes are discovered, then it is enabled the large-volume manufacturing of high-grade TiO$_2$. This compound became an important pigment for paints and commercial products, and of titanium metal for the production of the CpTi grades, titanium-based alloys and other alloys systems. The Dupont Company was the first to produce titanium commercially in 1948. Today, the primary consumer of titanium is
the aerospace field, whereas the other market such as medicine, automotive are gaining increased acceptance (Leyens & Peters, 2003).

Commercially pure titanium is unalloyed titanium. At service temperatures it consists of 100% -hcp phase. As a single-phase material, its properties are controlled by chemical elements (iron, oxygen and interstitial impurity elements) and grain size. It is classified into Grades 1 through 4 depending on strength and allowable levels of the chemical elements i.e. iron, carbon, nitrogen, and oxygen. CpTi ASTM Grade 2 has the yield strength of 275 MPa. (Luetjering & Williams, 2003 and Niinomi, 1998).

In the galvanic series of metals, titanium has a standard reduction potential of -1.63 Volts which is close to aluminum of -1.662 Volts. Therefore, titanium is very active in Electro-motif force (Emf) series about 1.2 V more active than iron with standard electro potential of -0.44 (Winston & Uhlig, 2008). The excellent resistance of titanium to general corrosion in most environments is well-known. This is the result of stable protective surface film, which basically consists of TiO$_2$. This thin oxide film makes the titanium passive as long as the integrity of film is continuously formed and maintained, generally caused by which most oxidizing environment. On the other hand, titanium is not corrosion resistant under reducing condition, where the protective nature of oxide film breaks down such as in sulfuric, hydrochloric and phosphoric acid is not good (Luetjering & Williams, 2003).

Titanium (Ti) and its alloy have been widely used for medical implants or fixtures, owing to their superior specific strength, corrosion resistance, and biocompatibility. The use of such materials can be proposed in response to a need for artificial hard tissue, because they have characteristics that are advantageous to biomedical engineering purposes (Balazic et al., 2007; Jagielski et al., 2006; Liu et al., 2004; Fukumoto et al., 2000; Niinomi, 1998). Figure 2.1(a)-(c) show examples on usage of Titanium for artificial hip joint bone plate implant and hip replacement, respectively.
The material properties of Ti and its alloy have been proven to be well accepted by human tissues, compared to other metallic biomaterials (Liu et al., 2004; Jagielski et al., 2006). Table 2.1 shows the physical properties of unalloyed titanium (Liu et al., 2004). The unalloyed titanium presented in Table 2.1 is classified as high grade titanium. Its ultimate strength and yield strength are almost equal to the titanium alloys with ultimate strength of 860-965 MPa (Sun et al., 2001; Geetha et al., 2009).

The performance of biomedical implants relies on the biocompatibility, corrosion behaviour, mechanical properties, formability, and availability of the materials (Liu et al., 2004; Balazic et al., 2007). CpTi is now widely used for hard
tissue replacement due to the fact that its properties are suited for the needs of medical applications, except wear resistance when used for artificial hip joints.

Table 2.1 Physical properties of unalloyed titanium
(Liu et al., 2004)

<table>
<thead>
<tr>
<th>Properties</th>
<th>Values</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>22</td>
</tr>
<tr>
<td>Number of electrons</td>
<td>2</td>
</tr>
<tr>
<td>Atomic weight (g/mol)</td>
<td>47.90</td>
</tr>
<tr>
<td>Equivalent Weight (EW)</td>
<td>23.95</td>
</tr>
<tr>
<td>Crystal structure</td>
<td></td>
</tr>
<tr>
<td>Alpha, hexagonal closely packed (hcp)</td>
<td></td>
</tr>
<tr>
<td>c(Å)</td>
<td>4.6832±0.0004</td>
</tr>
<tr>
<td>a(Å)</td>
<td>2.9504±0.0004</td>
</tr>
<tr>
<td>Beta, body centered cubic (bcc) a(Å)</td>
<td>3.28±0.003</td>
</tr>
<tr>
<td>Density (g/cm³)</td>
<td>4.54</td>
</tr>
<tr>
<td>Coefficient of thermal expansion, α, at 20°C (K⁻¹)</td>
<td>8.4×10⁻⁶</td>
</tr>
<tr>
<td>Thermal conductivity (W/(mK))</td>
<td>19.2</td>
</tr>
<tr>
<td>Melting temperature (°C)</td>
<td>1668</td>
</tr>
<tr>
<td>Boiling temperature (estimated) (°C)</td>
<td>3260</td>
</tr>
<tr>
<td>Transformation temperature (°C)</td>
<td>882.5</td>
</tr>
<tr>
<td>Electrical resistivity</td>
<td></td>
</tr>
<tr>
<td>High purity (μΩCm)</td>
<td>42</td>
</tr>
<tr>
<td>Commercial purity (μΩCm)</td>
<td>55</td>
</tr>
</tbody>
</table>

The nature of CpTi is its inherent corrosion resistance, which is attributed to the spontaneous formation of a strong passivation oxide layer. The extent of this corrosion resistance dictates its biocompatibility and is suitable to be used in a physiological saline solution (Pompe et al., 2004). The nature of CpTi is also sufficient elasticity, which has become necessary for apt design of hip joint replacements; elasticity is a decisive factor for hard tissue replacement. The characteristics of Ti and its alloy are characterized by the inert nature within the human body: immune from the attack of bodily fluids, compatible with bone growth, strong, and flexible.

2.2 Mechanical loading imposed on an implant device in human body

An implant is often subjected to cyclic loading during daily activity of the human body. It can also be chemically attacked by the body fluid medium, under certain conditions. Among the mechanical and chemical parameters that can influence the
corrosion-fatigue behaviour of such material, cyclic stress's parameter in body fluid (saline solution) is need to be highlighted and verified its effect on stress cycles before the final failure of implant devices. Another factor that also assists the fatigue failure is crack length of material implant. Therefore, fatigue and other mechanical properties such as toughness and wear resistant of biomaterial structure in a living environment need to be evaluated and improved in order to confidently use the implants for a long period of time.

The complexity of the service conditions and loads encountered on devices implanted in the human body is generally quite high. Depending on the activities of the patient, implanted device experiences of both static loading in the form of body weight and also dynamic in the form of cyclic stress during walking or running. These stresses are actually far under fatigue limit of the material implanted, however, the implanted device can fail before its life time due to the mechanical and chemical loading of implanted device. Figure 2.2 shows a schematic picture of the cross-section of a deformed metallic biomaterial surface, surrounded in a physiological environment (Teoh, 2000). The Figure 2.2 illustrates three distinguishable layers, namely (1) the molecular absorbed layer, (2) the passive oxide film, and (3) the deformed layer. The molecular absorbed layer is an aqueous sandwich layer of biological components to establish a good bond between the host tissue and the biomaterial. The passive oxide film is protective passive film consist of either metal oxides or hydroxides and act as a burrier protecting the metal surface from the corrosive environment (Kim, J. J. & Young, Y. M., 2013), and deformed layer is surface and subsurface damage arising from a spherical indentor.

The implant device is introduced into a patient must have sufficient strength to sustain and transmit the load actions resulting from joint and muscular forces. The actual stress working on the material implant in human body depends on the body weight where a value of 2.5 BW (Body Weight) seems to be reasonable in hip implants design. Peak forces are considered to be equal to 2.5 BW. While for loading frequency is taken 0.5 Hz with an assumption that we could walk 2 h per day with a pace of one step per second. (Cicero et al., 2007).
Figure 2.2 Schematic illustration of a cross-section of a deformed metallic biomaterial surface showing the complex interactions between the material’s surface and the physiologic environment (Teoh, 2000)

Another researcher (Mudali et al. 2003) argued that mechanical forces imposed on the implant as follows: (1) the load varies with the position in the walking cycle and reaches a peak of about four times of body weight at hip and three times the body weight at the knee. The frequency of loading and load cycles encountered over a specific time period are also important. A past rate of walking corresponds to one to two million steps per year. For an active person, the number of steps taken may be two or three times more taken by a normal person (2) the human body is a harsh environment for metals and alloys having to be in an oxygenated saline solution with salt content of about 0.9%, at pH 7.4 and temperature of 37±1 (Mudali et al., 2003)

2.3 Ion implantation technique for surface modification

Surface modification is a technique used to change the physical, chemical, electrical or mechanical properties of metallic material surface such as wear resistant, corrosion behaviour, fatigue properties and of enhancement of biocompatibility particularly subjected to medical application. Several established methods of surface modification are employed: shot peening, plasma nitriding, plasma immersion ion implantation (PIII), magnetoelectropolishing, chemical etching, anodizing, ion implantation etc. Ion implantation technique will be discussed in detail in this section.
2.3.1 **Review of ion implantation technique**

Ion Implantation is a potential enhancement method for modifying the surface properties of materials by insertion of accelerated atoms, within the first atomic layers of the component using a high technology approach. It is similar to a coating process, but it does not involve the addition of a layer on the surface. Originally, this technique was developed to produce controlled doping of semiconductors, and still used extensively in that capacity today and now it had being used to modify or change the material’s near-surface chemical composition or defect state. Consequently, there can be a distinct modifications to the near-surface microstructure and chemical, physical and mechanical properties which for example can appear as changes in corrosion behaviour, electronic properties, stiffness, hardness, wear resistance, friction response (Al Jabbari *et al*., 2012), or other surface-region-sensitive mechanical properties such as fatigue and contact fracture toughness (Tanaka *et al*., 1996; Nastasi & Mayer, 2006).

Using highly energetic beams of ions (positively charged atoms), this technique is used to modify surface structure and chemistry of materials at low temperature. The moderate heating associated with the process virtually eliminates any risks of distortion or oxidation effects and mostly the operating process is between 150°C and 200°C which depend on the level of the ion beam flux (Woolley, 1997). The process does not adversely affect component dimensions or bulk material properties. It has been used extensively and successfully for studying the mechanism under-laying the so called reactive element effect. In general it is found that influence of the implanted element is applied as a coating or present as an alloy or oxide dispersed addition.

Ion Implantation is also a powerful method for modifying the near surface properties of material. To cater for diverse research and application, the implanting facilities must be flexible. For example, ion beams of elements are desirable, dose can cover the range from $10^9$ ions cm$^{-2}$ to $10^{18}$ ions cm$^{-2}$, In ion implantation, high energy ions are generated in an ion accelerator and implanted into the alloy surface. The penetration depths are typically in the order of 1-100 nm while the concentration distribution has a maximum value of up to several tens of percent (Stroosnijder, 1998; Nastasi & Mayer, 2006). In addition, more recent investigations have reported that ion implantation had improved fatigue and corrosion resistance in metallic
alloys, polymers and ceramics. Currently, the technique is most commonly employed to treat the surface of cutting and machining tools, moulds, casting dies, alloys for nuclear reactors containers, food packaging materials, medical implants, biocompatible materials, etc (Agarwal & Sahoo, 2000). Figure 2.3 and Figure 2.4 show schematic of an ion implantation system and ion implantation process, respectively.

![Figure 2.3 Schematic of an ion implantation system (Nastasi & Mayer, 2006)](image1)

![Figure 2.4 Schematic of the ion implantation process (Denison et al., 2004)](image2)

Improvement of the surface hardness as well as corrosion resistance that yielded by ion implantation technique is influenced by the implantation parameters involve
energy, dose or time. The two key parameters defining the final-implantation profile are dose $D$ (in ions/cm$^2$) and energy, $E$, (in kilo electro Volt, keV). The dose is related to the beam current, $I$, expressed by the following formula (Equation 2.1): (Spitzlsperger, 2003; Nastasi & Mayer, 2006; Wen & Lo, 2007).

$$D(dose) = \frac{I(nA)\tau(s)}{1.6x10^{-19}qA(cm^2)}$$

(2.1)

where $D$ denotes implantation dose, $I$ represent the beam current (nA), $\tau$ is beam time (s), $q$ is charge state of the ion, and $A$ is defined as the striking area (cm$^2$).

A significant advantage of ion implantation is that the treated surface is an integral part of the work piece and does not suffer from possible adhesion problems associated with coatings. The moderate heating associated with the process virtually eliminates any risks of distortion or oxidation effects. The process does not adversely affect component dimensions or bulk material properties. Ion implantation produces no dimensional changes in the work piece (Woolley, 1997). Figure 2.5 illustrates the path of an individual ion in ion implantation process.

![Figure 2.5 Schematic view of the path of an individual ion in process of ion implantation (Hirvonen & Sartwell, 1994).](image)
2.3.2 Theoretical prediction of penetration depth

The penetration depth of the implanted ions depends on the ion weight or mass, energy and on material substrate (Hunsperger, 2009). As the ions penetrate into substrate of the specimen, they lose their energy due to the interaction with the electrons and the atoms of the specimen. Their energy continuously decreases when the ion is traveling deeper into the substrate.

The energies of ion implantation range from several hundred to several million kilo electrons volt (keV), yielding in ion distributions with average depths from < 10 nm to 10 µm. Doses range from $10^{11}$ ions/cm² for threshold adjustment to $10^{18}$ ions/cm² for buried dielectric formation. Theoretical calculation was made using the simulation program Transport of ions in matter (TRIM)-Stopping and Range of Ions in Matter (SRIM) simulation software providing an approach of the penetration depth penetration. SRIM is a computer program used to calculate interaction of ions with matter and the core of SRIM is a program Transport of ions in matter (TRIM). This open source computer programs were developed by Ziegler et al., 1985 and are being continuously upgraded with the major changes occurring approximately every five years. SRIM is based on a Monte Carlo simulation method, namely the binary collision approximation with a random selection of the impact parameter of the next colliding ion. It needs the ion type and energy (in the range 10 keV - 2 GeV) and the material of one or several target layers as the input parameters.

The predictions of the implantation depth in the near surface of specimens were provided from that software, and calculated the depth of implanted ions using following equation:

$$x_i = R_i + \delta R_i$$  \hspace{1cm} (2.2)

where, $x_i$ is penetration depth of implanted ions, $R_i$ is ion range and $\delta R_i$ is the longitudinal straggling (Nastasi & Mayer, 2006; Saryanto et al., 2009; Suzuki, 2010).

2.3.3 Surface modification of CpTi by nitrogen ion implantation

Surface modification methods such as anodic oxidation treatment, (Song et al., 2007) sandblasting, (Jiang et al., 2006) carbide coating, (Velten et al., 2002) plasma
nitriding, (Kapczinski et al., 2003) electrochemical treatment (Guilherme, 2005) and nitrogen ion implantation (Jagielski et al., 2006; Fukumoto et al., 2000; Shikha et al., 2008; Arenas et al., 2000) have been proposed to increase corrosion-resistant and wear-resistant of material. CpTi with modified surface has good mechanical and chemical properties as well as biocompatibility in human body environment.

The most common ion used for application in metallurgical surface treatment is nitrogen. When the nitrogen ions penetrate and diffuse the surface of the specimen, some of them wedge micro cracks, some occupy lattice spaces in crystalline structures, and some form compounds through the chemical reaction (i.e.; titanium nitride: TiN; Ti$_2$N), resulting a new lattice properties as inherent of face center cubic (fcc) and tretragonal space lattice. It has been established that nitrogen implantation into metals can alter their surface properties such as hardness, friction, wear and corrosion resistant, etc.

Among the treatment options, as mentioned previously, the nitrogen ion implantation technique is a good method to enhance passivity and to reduce the corrosion rate. This is due to the fact that the formation of TiN and Ti$_2$N phases elude the migration of ions and stabilize the TiO$_2$ film growth on the surface of titanium (Arenas et al., 2000; Mudali et al., 2003). Nitrogen ion implantation can modify the Ti surface to produce wear-resistant species such as nitrides (TiN; Ti$_2$N) other than TiO$_2$ from the surface. The surface of nitrogen ions implanted Cp Ti appeared to consist of a mixture of TiO$_2$ and TiN/Ti$_2$N or a Ti oxynitride as shown in Figure 2.6 (Liu et al., 2004). Figure 2.6 illustrates the cross-sectional view of thin film and surface-modified layer formation for surface modification of titanium by ion implantation technique. Surface modification had been performed at specific energies to assess the formation of the nitride phase, surface hardness, wear resistance, and corrosion behaviour in various doses (Sundararajan, & Praunseis, 2004; Arenas et al., 2000; Fukumoto et al., 1999). Still, the mechanical properties, chemical composition, and corrosion resistance for CpTi surface implanted nitrogen ions in various doses and energy need to be verified for achieving good result from combining parameter between energy and dose as optimal parameter of the ion implantation process.
2.4 Corrosion effects associated with biological environment

A multidisciplinary approach is necessary in studying corrosion-fatigue that involves chemistry, electrochemistry, mechanics and metallurgy. In this section, the chemistry, electrochemistry and mechanics that cause corrosion related failures are described. First, it reviewed the various forms of corrosion that lead to failure in pure titanium related with chemistry or electrochemistry that caused them. Then, the mechanisms responsible for the effects of corrosion fatigue are discussed.

2.4.1 Corrosion forms of pure titanium

Pourbaix (1966; 1974) demonstrated that a metal could react in one of four ways when exposed to a corrosive solution. He proposed the diagrams which are called Pourbaix Diagram by varying the electrode potential and pH of the solution. The diagrams demonstrate the corrosion activity that is thermodynamically favored in a given system. A Pourbaix diagram for titanium in water at 25°C is shown in Figure 2.7. The diagram shows conditions of corrosion, immunity and passivation of titanium in dependency of oxidizing potential and pH.

The diagram consists of four areas that represent the ways that a metal can react to a corrosive solution. He demonstrated that a metal could be immune (passive TiH$_2$ region) from chemical reaction (passive TiH$_2$ region), shown active corrosion (Ti$^{+2}$region) displayed passivity due to formation of a protective oxide film (TiO$_2$
region), or suffered from pitting corrosion due to localize breakdown of a passive film. If the protective oxide film breaks down locally, then the surface metal is exposed to the solution and released its ion forming the pit.

Figure 2.7 Theoretical conditions of corrosion, immunity and passivation of titanium (Pourbaix (1966; 1974))

The above diagram shows the significant differences in corrosion behaviour resulting from different properties of TiO$_2$ film. This film is very chemically resistant and is attacked by very few substances. The following reactions are the basic corrosion of Titanium in aqueous environment (Equation 2.3 – 2.4):

\[ T_i \rightarrow T_i^{2+} + 2e^- \quad E^o = -1.63V \tag{2.3} \]

\[ 2H^+ + 2e^- \rightarrow H_2 \quad \text{and} \]

\[ H_2O + O_2 + 4e^- \rightarrow 4OH^- \tag{2.4} \]
The basic reaction of Titanium in water is (Equation 2.5 – 2.6):

\[
T_i + 2H \rightarrow T_i^{2+} + H_2 \tag{2.5}
\]

\[
T_i + 4H_2O \leftrightarrow T_i(OH)_4 + 2H_2 \tag{2.6}
\]

\(T_i(OH)_4\) is a passive film of Titanium by a direct electrochemical reaction. Balakrishnan et al., (2008) observed the formation of passive film on titanium surface in SBF solution with the presence of Ca, P, Ti and O elements. The surface passive TiO\(_2\) layer reacts with SBF solution which can be illustrated in Equations 2.7 – 2.11 as follows (Liu et al., 2004):

\[
TiO_2 + OH^- \rightarrow HTiO_3^- \tag{2.7}
\]

\[
Ti + 3OH^- \rightarrow Ti(OH)^+ + 4e^- \tag{2.8}
\]

\[
Ti(OH)^+ + e^- \rightarrow TiO_2.H_2O + 1/2H_2 \uparrow \tag{2.9}
\]

\[
Ti(OH)_4^+ + OH^- \rightarrow Ti(OH)_4 \tag{2.10}
\]

\[
TiO_2.nH_2O + OH^- \rightarrow HTiO_3^-nH_2O \tag{2.11}
\]

The Ti–OH groups formed on the surface from the above reaction are negatively charged and have a chemical affinity for Ca\(^{2+}\) and Na\(^+\) ions in the Simulated Body Fluid (SBF) solution.

2.4.2 Effect of nitrogen ion implantation on corrosion resistance of titanium

Besides the design of the joint replacement, material selection plays an important role. Materials for human body implants must be biocompatible, corrosion resistant, and strong and have sufficient elasticity (Pompe et al., 2004).

Because it is absolutely inert in the human body, immune to attack from bodily fluids, compatible with bone growth and strong, and flexible, titanium is most biocompatible of all metallic implant, i.e. Stainless Steel 316L, cobalt alloys (Nasab & Hassan, 2010; Niinomi, 2008). Biocompatibility and corrosion resistance of the Ti metal are the result of passive TiO\(_2\) film of 2 to 6 nm thickness formed on the surface of Ti (Balakrisnan et al., 2008; Tamilselvi & Rajendra, 2006; Raman et al., 2005; Dearnley et al., 2004; Arenas et al., 2000). The corrosion behaviour of Ti and its
alloys has been studied using certain types of biological media (Tamilselvi & Rajendra, 2006; Raman et al., 2005; Dearnley et al., 2004).

The implantation of nitrogen ion can enhance the passivability and reduce the corrosion kinetics of the alloy surface with increasing tendency for repassivation and with a significant decrease in ion release rates (Gordin et al., 2013), and thus can enhance corrosion resistance. This improvement arises from the formation of precipitates of TiN and Ti2N, which screen underlying titanium atoms, avoiding their migration and stabilizing the growth of the oxide film (Arenas et al., 2000).

Introducing to commercially pure titanium, Nitrogen-ion implantation showed an improvement in the electrochemical behaviour of the passive film. Doses between 4x10^{16} and 7x10^{16} ion/cm^2 is recommended for orthopedic applications. A detrimental effect is shown by implantation with higher doses due to the formation of nitride phases (Sundararajan & Praunseis, 2004; Kapczinski et al., 2003) that can accumulate surface damage, thus leading to increasing the corrosion resistance and nanohardness (Shikha et al., 2008).

2.5 Fatigue and corrosion fatigue of metals

Fatigue is a process of progressive localized permanent structure change occurring in a material subjected to condition that produce fluctuating stress and strain at point that may culminate in crack or complete fracture after a sufficient number of fluctuations.

The load histories for a real components, structures and vehicle are quite diverse, at one extreme, they may be rather simple and repetitive, at the other extreme, may be completely random. The constant amplitude loading is used to obtain material fatigue behaviours/properties for used in fatigue design. Figure 2.8 illustrates schematically the basic fatigue loading for constant amplitude loading pattern. The load ration (R-ratio) is defined as the ratio of minimum to maximum stress amplitude as shown in Equation 2.12.

\[
R = \frac{S_{a_{\text{min}}}}{S_{a_{\text{max}}}}
\]

(2.12)

Where: \(S_a\), \(S_m\) and \(\Delta S\) (\(S_{\text{max}} - S_{\text{min}}\)) denote stress amplitude, mean load and stress range respectively and \(f\) denote the frequency of the cycle stress. The R-ratio value of fully reversals is -1 (R=-1) which means that the mean stress, \(S_m = 0\) and \(S_a = -S_a\).
Most mechanical components and structures made of metal and alloy are subjected to cyclic loading. Some of those mechanical components such as super-heaters, propeller shafts, turbines and pump elements, drilling equipment in the petroleum industry severely suffer from corrosion fatigue problem. Once cyclic loading occurs in an inert environment, the structures or components suffer from fatigue failure. However, when the components and structures are subjected to cyclic loading and corrosive environment even fresh water or atmospheric air, the Corrosion Fatigue “C-F” can occur (Ebara, 2007; Genel et al., 2000; Murtaza & Akid, 1996).

The first study of metal fatigue is believed to occur around 1829 by German mining engineer Albert. The detailed research effort into metal fatigue was initiated in 1842 following the railway accident in France. The cause of this accident was traced to fatigue failure. A systematic investigation of fatigue failure was conducted by Wöhler, during the period 1852-1869 in Berlin. His work led to characterization of fatigue in terms of Stress-life (S-N) curves and to the concept of fatigue ‘endurance limit’. Another well-known fatigue researcher of this era was Fairbairn, (1864), Geber, (1872), Goodman (1899), Ewing & Rosenhain (1900), Ewing and Humfrey (1903). The development of metal fatigue research came in a new era was begun by Griffith (1921) and Paris et al., (1961). They applied the fracture mechanic concept to solve fatigue problem of notch specimen. Later it will be described some detail concepts of development in fatigue as well in corrosion fatigue.

In order to understand the fatigue mechanism, it is important to consider various technical conditions that influence fatigue life and fatigue crack growth. There are three technical conditions involved (a) material surface quality, (b) residual
stress and (c) environment effect. This understanding is necessary to analyze fatigue properties of engineering structure in term of fatigue as a crack initiation process (crack initiation period) followed by a crack growth period as shown in Figure 2.9.

Corrosion fatigue is the metal cracking caused by combined action of a cyclic loading and a corrosive environment. The severity of the action depends on the range and frequency of the stress, the nature of the corroding condition and the time under stress (Murtaza & Akid, 1996; Sivaprasad et al., 2006). So, corrosion fatigue is influenced by various mechanical, chemical and structural parameters that interact locally.

Corrosion fatigue is similar to stress corrosion cracking in many aspects. The principal difference between these two types of environment enhanced cracking is in the character of loading, which is static in stress corrosion cracking and repeated loading in corrosion fatigue. Both fatigue life and fatigue limit are reduced in the presence of corrosive environment as compared to the fatigue in neutral environment. These are caused by interaction of electrochemical, metallurgical and mechanical processes at the crack tip (Ramsamoj & Shugar, 2001a).

The aim of the above review is to describe some phenomenological observation of corrosion fatigue failure of mechanical components and structures and method of evaluation. In addition, some results proposed by previous researcher in term of stress-life, strain-life and crack initiation and crack growth rate-stress intensity range will be presented.
2.5.1 Mechanism of corrosion-fatigue

Under cyclic loading conditions, the embrittling environment can accelerate the initiation of a surface flaw in an initially crack-free material and propagate the flaw to certain critical size. Corrosion fatigue is a term which is commonly used to denote the damage and failure of material under the combination action of cyclic stress and any embrittling medium, although most wide spread adaptation is in the context of aqueous environments. The corrosive environment produces corrosion products. Corrosion fatigue is associated with two different mechanisms: Anodic dissolution mechanism of corrosion fatigue and hydrogen assisted corrosion fatigue (Ramsamooj & Shugar, 2001a; Marcus, 2002).

The mechanism of anodic dissolution cracks initiate at the surface sites of localized concentration of tensile strength. A crack progresses along a specific path which is composed of specific crystal planes within the grains. The mechanism of anodic dissolution is mainly referred to as corrosion fatigue of carbon steels and Stainless steels (Makhlof et al., 2003) in water and also corrosion fatigue of Aluminum alloys (Chlistovsky et al., 2007) and Titanium alloys in aqueous chloride solutions. Genel et al., (2000) reported that cathodic polarization suppressed the metal dissolution and pit formation, resulting in a noticeable increase in corrosion fatigue strength up to 2.6 times that of free corrosion fatigue. In contrast to anodic dissolution mechanism, hydrogen assisted corrosion fatigue is enhanced by cathodic reaction: \(2H^+ + 2e^- = H_2\) occurring on the crack tip surface. The atomic hydrogen dissolves in the metal where its ions interact with the dislocations of the crystal lattice causing decrease of the metal ductility (Suresh, 1998).

2.5.2 Stress-life approach in corrosion fatigue

Corrosion fatigue in aqueous media is an electrochemical behaviour. Cracks are initiated either by pitting or at persistent slip bands “PSB” (Xie et al., 2002). Corrosion fatigue can hence be reduced by alloy additions, inhibition, and cathodic protection all of which reduce pitting (Congleton & Craig, 1982). Since corrosion fatigue cracks initiate at the metal surface, surface treatments like plating, cladding, nitriding (Genel et al., 2000) and shot-peening or sandblasting (Jiang et al., 2006) were found to improve the materials' resistance to this phenomenon.
The important concept of stress-life was proposed by Wöhler. The method characterizes the total fatigue life in terms of nominal stress amplitude and cyclic number (S-N) curve (Stephens et al., 2001). The total fatigue is defined as accumulation crack initiation, short crack, long crack and critical fracture or final failure (Kaynak et al., 1996; De-Guang et al., 1998). The fatigue life equation is written as follows (Equation 2.13):

\[ S_a = \alpha - \beta \log N_f \]  

(2.13)

where \( S_a \) is stress amplitude, \( \alpha \) and \( \beta \) are constants and \( N_f \) is number of cycle. Basquin modified Wöhler’s formula in term of correlation log-log scale, a linear and power law relationship are commonly observed, as shown in Equation 2.14 and Equation 2.15. The stress-life curve characterizes the contribution of crack initiation and crack propagation processes to total fatigue life in nominally smooth specimen.

\[ \ln S_a = \alpha - \beta \ln N_f \]  

(2.14)

or

\[ \frac{\Delta S_a}{2} = S_a = S'_f (2N_f)^b \]  

(2.15)

where \( S_a \) is stress amplitude, \( N_f \) is number of cycle and \( \alpha \) and \( \beta \) are constants, \( S'_f \) is fatigue strength coefficient and \( 2N_f \) is reversals to failure and \( b \) is fatigue strength exponent (Basquin’s exponent).

A new approach on the study of early stages of corrosion fatigue cracking was proposed by Acun’a-Gonza’lez et al., (2008). A visual recurrence analysis applied to the electrochemical current oscillations registered during corrosion fatigue tests allowed us to characterize the electrochemical dynamics on stainless steel samples surface showing clearly the dynamics of localized corrosion, as well as the formation and initial growth of short corrosion fatigue cracks.

Experimental study of corrosion fatigue behaviour welded steel structures has found that the fatigue crack propagation in the corrosive medium is influenced strongly by important weld-geometry parameter and accordingly, Paris’s material constant need to be determine experimentally to evaluate the corrosion fatigue life (Wahab & Sakano, 2001). Ramsamooj & Shugar (2001b) proposed a new model for
REFERENCES


