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BORANG PENGESAHAN STATUS TESIS♦

JUDUL: **EFFECT OF HEAT TREATMENT ON CORROSION BEHAVIOR OF SS316 STAINLESS STEEL IN SIMULATED BODY ENVIRONMENT**

SESI PENGAJIAN: 2010/2011

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2010

EFFECT OF HEAT TREATMENT ON CORROSION BEHAVIOR OF SS316 STAINLESS STEEL IN SIMULATED BODY ENVIRONMENT

MOHD ASYRAF BIN CHE AZMI

Thesis submitted in fulfilment of the requirement
for the award of the degree of
Bachelor of Mechanical Engineering

Faculty of Mechanical Engineering
UNIVERSITI MALAYSIA PAHANG

DECEMBER 2010

UNIVERSITI MALAYSIA PAHANG

FACULTY OF MECHANICAL ENGINEERING

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Younger Brother: Mohd Asyrul Afiz & Zulhamizan

Younger Sister: Nor Amy Atikah

and all my friend

ACKNOWLEDGEMENTS

I am grateful and would like to express my sincere gratitude to my supervisor Pn Juliawati Binti Alias for her germinal ideas, invaluable guidance, continuous encouragement and constant support in making this research possible. She has always impressed me with her outstanding professional conduct, her strong conviction for science, and her belief that a Degree program is only a start of a life-long learning experience. I appreciate her consistent support from the first day I applied to graduate program to these concluding moments.

My sincere thanks go to all my lab mates and members of the staff of the Mechanical Engineering Department, UMP, who helped me in many ways and made my stay at UMP pleasant and unforgettable. Many special thanks go to instructor engineer and assistance instructor for their excellent co-operation, inspirations and supports during this study.

I acknowledge my sincere indebtedness and gratitude to my parents for their love, dream and sacrifice throughout my life. I cannot find the appropriate words that could properly describe my appreciation for their devotion, support and faith in my ability to attain my goals. Special thanks should be given to my committee members. I would like to acknowledge their comments and suggestions, which was crucial for the successful completion of this study.

ABSTRACT

This thesis is entitled about the effect of heat treatment on corrosion behavior on SS316 stainless steel in simulated body environment. Biomedical materials are very important in the modern world to manufacture the variety of prosthetic devices which are the artificial replacements for human body. These artificial replacements are use in a biological system such as the human body in an effort to provide the function of the original parts. When a metal device is implanted into human body, it is continually exposed to extracellular tissue fluid. This interaction can lead to either failure of the implant or have an adverse effect on the patient resulting in the rejection of the implant by the surrounding tissue or both. The objective of this project is to investigate the effect of stress relief on corrosion behavior of SS316 stainless steel in simulated body fluid. Stress relief had been performed to the sample with two different time and temperature. Stress relief is used to relieve stresses that remain locked in a structure as a consequence of a manufacturing sequence such as machining. The sample was prepared for electrochemical test. Electrochemical tests using a potentiostat WPG1000 have also been conducted and reported in this thesis. The corrosion rates of the alloys were then compared.

ABSTRAK

Tesis ini mengkaji tentang pengaruh proses pemanasan terhadap kelakuan pengaratan terhadap keluli tahan karat SS316 dalam simulasi larutan badan. Bahan bioperubatan amat penting pada zaman yang moden ini untuk menghasilkan pelbagai jenis peranti buatan sebagai tulang gantian. Peranti buatan ini digunakan dalam sistem biologi seperti tubuh manusia dalam usaha untuk menyediakan fungsi dari bahagian-bahagian yang asli.Apabila peranti ini ditanam di dalam tubuh manusia pendedahan terhadap cecair rangkaian ekstraseluler berlaku secara berterusan. Interaksi ini boleh menyebabkan kegagalan implan atau mempunyai kesan buruk pada pesakit yang mengakibatkan penolakan implan dengan rangkaian sekitarnya atau kedua-duanya.. Tujuan projek ini adalah untuk mengetahui pengaruh legaan tekanan bagi keluli tahan karat SS316 dalam larutan simulasi badan. Legaan tekanan telah dilakukan pada sampel pada dua waktu dan suhu yang berbeza. Legaan tekanan digunakan untuk melegakan tekanan tetap yang tersimpan di dalam struktur sebagai kesan daripada proses pembuatan seperti pemesinan. Sampel disediakan untuk ujian elektrokimia. Ujian elektrokimia dengan mnggunakan WPG 100 potentiostat telah dijalankan dan dilaporkan di dalam tesis ini. Kadar karatan keluli ini seterusnya dibandingkan.

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E_p	Primary passivation potential
I_c	Critical current density
I_p	Passive current density
β_c	Cathodic slopes
β_a	Anodic slopes
e_{corr}	Corrosion potential
i_{corr}	Current density
Log I	Log Current
Fe	Ferum
Cr	Chromium
KH_2PO_4	Potassium dihydrogen
KCl	Kalium chloride
HCl	Hydrochloric acid
HNO_3	Nitric acid
HPO_4^{2-}	Mono hydrogen phosphate
Ca^{2+}	Calcium ion
Mg^{2+}	Magnesium ion
Cl^-	Chlorine ion
Na^+	Sodium ion
CO_2	Carbon dioxide
Na_2HPO_4	Disodium phosphate
NaCl	Kalium chloride

LIST OF ABBREVIATIONS

PBS	Phosphate buffered saline
HBSS	Hank’s balanced salt solution
ASTM	American Standard for Testing and Material
SCC	Stress corrosion cracking
CoCrMo	Cobalt-chromium-molybdenum
WE	Working electrode
RE	Reference electrode
SCE	Saturated calomel electrode
SBF	Simulated body fluid
MEM	Minimum essential medium

CHAPTER 1

INTRODUCTION

1.1 BACKGROUND OF STUDY

Biomedical materials are very important in a modern world to manufacturing the variety of prosthetic device which is the artificial replacement. These artificial replacements as shown in Figure 1 are use in a biological system such as the human body in an effort to provide the function of the original parts. Stainless steels, cobalt-chromium based alloys and titanium alloys are three major biomedical materials that we use as implant (Douglas C. Hansen, 2008).

As the global population increases in age, there is a parallel increase in the number of implantation procedures. On the other hand, as new devices and technologies are developed, there will be a continuing research for the understanding and characterization of how metal surfaces of implants interact with their surrounding physiological environment.

The first requirement for any material to be placed in the human body is that it should be biocompatible and not cause any adverse reaction in the body Biocompatibility is the capability of a prosthesis implanted in the body to exist in harmony with tissue without causing deleterious changes and the ability of a material to perform with an appropriate host response in a specific application (Buddy D. Ratner, 2000). The material must withstand the body environment and not degrade to a point that it cannot function in the body as intended.

Figure 1.0: Implant components

Source: Douglas C. Hansen (2008)

Artificial implants are generally made of polymeric, metallic, ceramic material or combinations of this material and depending on the intended use. Metals or alloys used in the human body must have a high corrosion resistance and must not be treated or used in a configuration that would degrade the corrosion behavior. Therefore, various in vitro and in vivo tests have to be carried out in order to identify the suitable material for use as artificial implants (Gurappa, 2002).

Nowadays, corrosion is one of the major issues resulting in the failure of biomedical implant. The types of corrosion that occur to the currently used alloys as an implant are pitting, crevice, galvanic, stress-corrosion cracking, corrosion fatigue, and fretting corrosion. Any time a foreign material is placed inside the human body, the manner in which that material will affect the body must be considered. There are many causes that contribute to the corrosion of metals when placed inside the human body. After surgery the pH surrounding the implant is reduced to a pH between 5.3-5.6 typically due to the trauma of surgery. Infectious microorganisms and crevices formed between components can reduce oxygen concentration, both of which contribute to the corrosion of the implant. Besides, corrosion and surface oxide film dissolution are the two mechanisms for introducing additional ions into the body. Extensive release of ions from prosthesis can result in adverse biological reactions and can lead to mechanical failure of the device.

Austenite stainless steel in particular type 316 is the common biomedical material use in medical implant such as stents and orthopedic replacements. This is because SS316 are relatively low cost, ease of fabrication and reasonable chemical stability (Yee-Chin Tang et al. 2006). Type 316 is an austenitic chromium nickel stainless steel containing molybdenum. This addition increases general corrosion resistance, improves resistance to pitting from chloride ion solutions, and provides increased strength at elevated temperature. Surface modification of SS316 stainless steel is one alternative that is already in practice such as the coating of the alloy with hydroxyapatite to minimizing the release of metal ions by making it more corrosion resistant. Besides there are many surface modification such as hard coating, stress relieving, laser nitriding, ion-implantation and bioceramics to improve the performance characteristic of the biomedical implants and improving the lives of their recipients.

1.2 PROBLEM STATEMENT

To investigate the effect of stress relief to the stainless steel SS316 either it can reduce or contribute to corrosion to the SS316 stainless steel. Stress relief is used to relieve stresses that remain locked in a structure as a consequence of a manufacturing sequence such as machining. Artificial implant such as hip prostheses must be formed to exacting size and shape specification to fit the internal dimensions of the human bones. The stress is directly proportional to the bigger and more complex part. These stresses can cause distortions in the part long term. If the parts are clamped in service, then cracking could occur. As a conclusion, for these reasons, stress relieving process is often necessary.

1.3 PROJECT OBJECTIVES

The main purpose of this project is to study the effect of heat treatment on corrosion behavior of SS316 in phosphate buffered saline (PBS) and Hank’s balanced salt solution (Hank’s solution) as simulated body environment. Besides, this study is mean to investigate experimentally, the behavior by performing the electrochemical test to the SS316 stainless steel.

1.4 PROJECT SCOPES

In order to obtain the objectives, it should have proper arrangement of project scopes. The lists of scopes are as followed.

(i) Sample preparation for electrochemical study of SS316 in simulated body environment
(ii) Stress relieving sample at temperature 415°C and 900°C for 1 hour and 1 ½ hours. Then, followed by slow cooling at room temperature.
(iii) Metallographic process consists of grinding, polishing and etching to get the microstructure of the sample.
(iv) Microstructure analysis of specimen by using Inverted Microscope.
(v) Electrochemical study of SS316 stainless steel by using potentiodynamic polarization.
(vi) Corrosion rate analysis by using IV man software.

CHAPTER 2

LITERATURE REVIEW

2.1 INTRODUCTION

Corrosion is the gradual degradation of materials by electrochemical attack. It is a concern particularly when a metallic implant is placed in the hostile electrolytic environment provided by the human body. Even though the freely corroding implant materials used in the past have been replaced with modern corrosion resistant super alloys, deleterious corrosion processes have been observed in certain clinical settings (D.Sharan, 1999). Corrosion is one of the major processes affecting the life and service of orthopedic devices made of metals and alloys used as implants in the body. Chemical stability, mechanical behavior and biocompatibility in body fluids and tissues are the basic requirements for successful application of implant materials in bone fractures and replacements. In order for a material to be biocompatible, it must not adversely affect the physiological environment and the environment should not have detrimental effects on the material.

Implantable materials or biomaterials are utilized to repair, assist or replace living tissue or organs that are functioning below an acceptable level. A wide range of metals and their alloys, polymers, ceramics and composites are used in surgically implanted medical devices and prostheses and dental materials. Most implanted devices are constructed of more than one kind of materials. Since the early 1900s, metal alloys have been developed for these applications to provide improved physical and chemical properties, such as strength, durability and corrosion resistance.

2.2 STAINLESS STEEL

There are three main types of stainless steels austenitic, ferritic, and martensitic. These three types of steels are identified by their microstructure or predominant crystal phase.

Austenitic steels have austenite as their primary phase (face centered cubic crystal). These are alloys containing chromium and nickel (sometimes manganese and nitrogen), structured around the Type 302 composition of iron, 18% chromium, and 8% nickel. Austenitic steels are not hardenable by heat treatment. The most familiar stainless steel is probably Type 304, sometimes called T304 or simply 304. Type 304 surgical stainless steel is austenitic steel containing 18-20% chromium and 8-10% nickel.

Ferritic steels have ferrite (body centered cubic crystal) as their main phase. These steels contain iron and chromium, based on the Type 430 composition of 17% chromium. Ferritic steel is less ductile than austenitic steel and is not hardenable by heat treatment.

The characteristic orthorhombic martensite microstructure was first observed by German microscopist Adolf Martens around 1890. Martensitic steels are low carbon steels built around the Type 410 composition of iron, 12% chromium, and 0.12% carbon. They may be tempered and hardened. Martensite gives steel great hardness, but it also reduces its toughness and makes it brittle, so few steels are fully hardened (H.S Khatak and Baldev Raj, 2006).

Type 316 is an austenitic chromium nickel stainless steel containing molybdenum. This addition increases general corrosion resistance, improves resistance to pitting from chloride ion solutions, and provides increased strength at elevated temperatures.

In medical implants, stainless steel in particular Type 316 is commonly used such as to make stents and orthopedic replacement. This is because stainless steel 316 are relatively low cost, ease of fabrication and reasonable chemical stability. The compositions of this metal are 17-20% Cr, 13-15 % nickel and 2-3 %molybdenum, and small amounts of other elements (Table 1). The "L" means "low carbon", the (<0.03%) carbon is a maximum value, in % by weight and is therefore not susceptible to intergranular corrosion due to precipitation of Cr-carbides at the grain boundaries. Chromium is the element mainly responsible for the high passivation ability of these alloys. The minimum amount of chromium is necessary to form a stable passive chromium oxide film because this film that is the basis for the corrosion resistance of all stainless, and most nickel base, corrosion-resistance alloys.

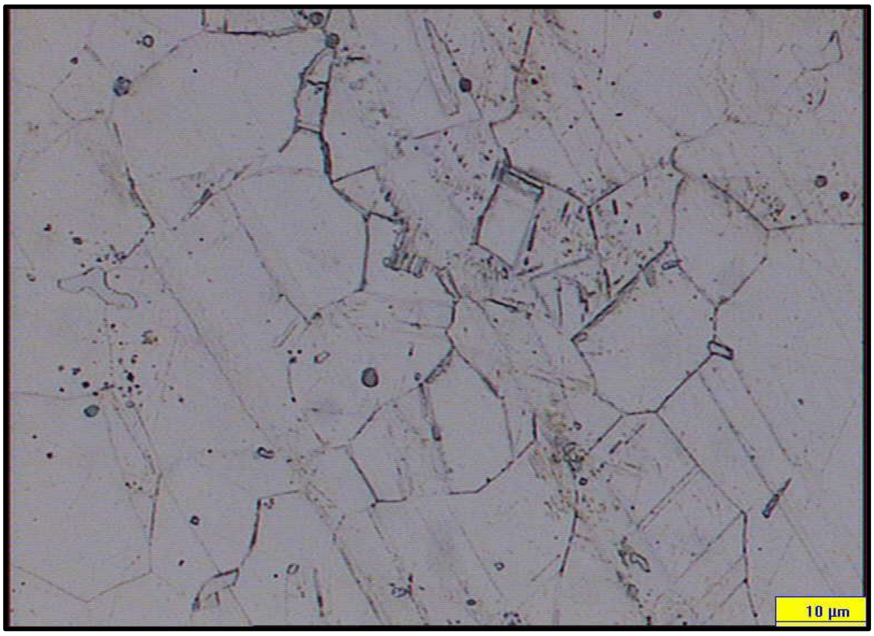

Figure 2.1: Microstructure of SS316 Stainless Steel at magnification 10x

Source: Biomedical Engineering Handbook (2000)

Table 2.1: Mechanical properties of SS316 stainless steel

Grade	Tensile Strength (MPa) min	Yield Strength 0.2% Proof (MPa) min	Elongation (% in 50mm) min	Hardness Rockwell B (**HR B**) max	Hardness Brinell (**HB**) max
SS316	515	205	40	95	217

Source: AK Steel Sheet Product (2007)

Table 2.2: Stainless Steel SS316 Composition

Element	**Composition %**
Carbon	0.08
Manganese	2.00
Phosphorus	0.045
Sulfur	0.030
Silicon	1
Chromium	17
Nickel	13
Molybdenum	2.5
Iron	Balance

Source: Heat Treating Volume 4, ASM International Handbook (1991)

2.3 METALLURGY

2.3.1 Heat Treatment

Heat treatment is the process of controlled heating and cooling of metals. The purpose of heat treatment is to cause desired changes in the metallurgical structure and thus in the properties of metal parts (George E. Totten et al. 2002). Heat treatment is sometimes done due to manufacturing processes that either heat or cool the metal such as welding or forming. In addition, heat treatment also to increasing the strength of material, but it can also be used to alter certain manufacturability objectives such as improve machining, improve formability and restore ductility after a cold working operation.

Thus it is a very enabling manufacturing process that can not only help other manufacturing process, but can also improve product performance by increasing strength or other desirable characteristics. Steels are particularly suitable for heat treatment, since they respond well to heat treatment and the commercial use of steels exceeds that of any other material.

2.3.2 Stress Relieving

Stress relieving is the process to relieve the internal stresses and there is no microstructure change happen during the process. Internal stresses are those stresses which can exist within a body in the absence of external forces. There are also known as residual stresses or locked in stresses. The internal stresses are happen during the different operation such as solidification of castings, welding, machining, shot peening, case hardening and precipitation. Besides, the internal stresses under certain conditions can have adverse effects. It can prove by steel with residual stresses under corrosive environment fail by stress-corrosion cracking but in general failure by stress-corrosion cracking occurs under the combined action of corrosion and externally applied stresses (Janez Urevc et al. 2009).

Austenitic stainless steels are typically heated between 425°C and 925°C to achieve an adequate stress relief. One (1) hour at 870°C typically relieves about 85% of the residual stresses. However, the process under this temperature can precipitate grain boundary carbides and resulting in sensitization that severely impairs corrosion resistance. So, to avoid this thing to happen for extra-low-carbon type such as 316L and 304L the time required of the stress relief need to extend. For the low temperature stress relieving when austenitic stainless steels have been cold worked to develop high strength, low-temperature stress relieving will increase the proportional limit and yield strength (particularly compressive yield strength). Low temperature stress relief in the 160°C to 415°C range will reduce residual stress with little or no effect on the corrosion resistance and/or mechanical properties (Ashok Karma et al. 2002).

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2.4 PASSIVITY

Passivity is a condition of corrosion resistance due to the formation of thin surface film under oxidizing conditions (highly positive cathodic reaction) at high anodic polarization. Some metals and alloys, having simple barrier fills with reduced corrosion at active potentials and little anodic polarization, and these were not to be considered to be passive by this definition.

The conditions of solution oxidizing power (potential) and acidity or alkalinity (pH) for various possible phases can be shown by using pourbaix diagram. The Pourbaix diagram is a plot of regions of corrosion, passivity and immunity as shown in Figure 2.2. Boundary lines on the diagram dividing areas of stability for different phases can be derived by Nernst equation. Pourbaix diagrams for most metals show stability of one or more oxides at noble potentials in oxidizing solutions. For iron, can be shown in figure 2.2, horizontal lines of the Poubaix diagrams correspond to the redox reactions, which are independent of pH ($Fe(s) = Fe^{2+}(aq) + 2e^-$), vertical lines of the Poubaix diagrams correspond to the non-redox reactions (electrons are not involved), which are dependent on pH ($Fe^{2+}(aq) + 2OH^-(aq) = Fe(OH)_2(s)$)and for diagonal lines of the Poubaix diagrams correspond to the redox reactions, which are dependent on pH($2Fe^{2+}(aq) + 3H_2O = Fe_2O_3(s) + 6H^+(aq) +2e^-$).

The state of immunity exists if the thermodynamically stable form of ion is the metal, which is the metal cannot corrode. A corroding metal can be brought into the state of immunity by polarising it cathodically to make its potential more negative such that it falls within the immunity zone. If the thermodynamically most stable state of iron is an oxide then it is possible for a protective oxide film to form on the metal surface so that the iron is a passive state. However, the passivating film may not be protective and the corrosion may occur in passive state. In Pourbaix diagram, the only condition which can be predicted with some certainty is the zone of immunity. For the zone of corrosion and passivity, the kinetic factors controlling the rate of formation and dissolution of surface films are generally more important than the thermodynamic stability of the ions or oxide of the metal in order to determine the significant corrosion occurs or not.

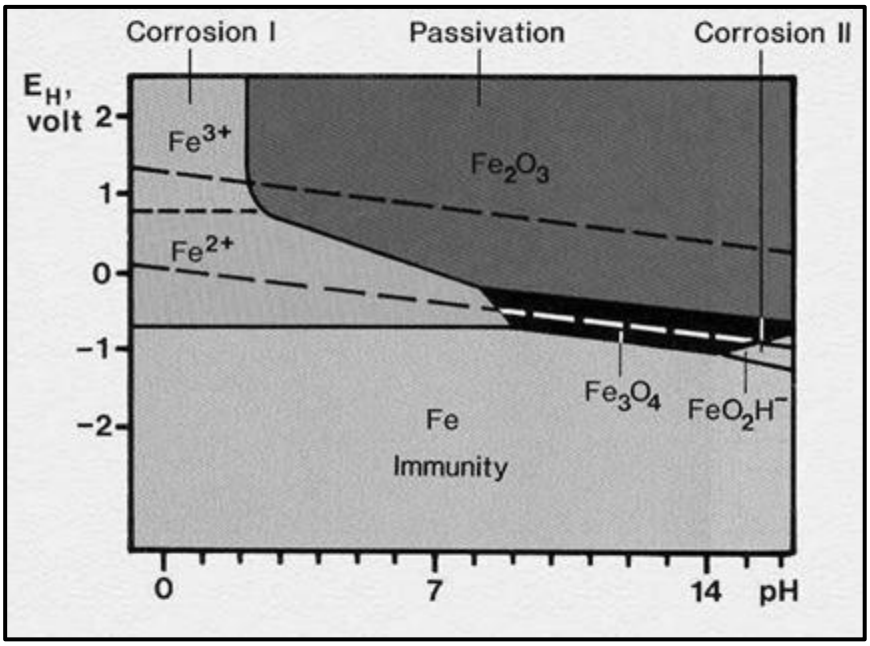


Figure 2.2: Pourbaix Diagram of Immunity, Corrosion and Passivation region

Source: Revie R.W (2008)

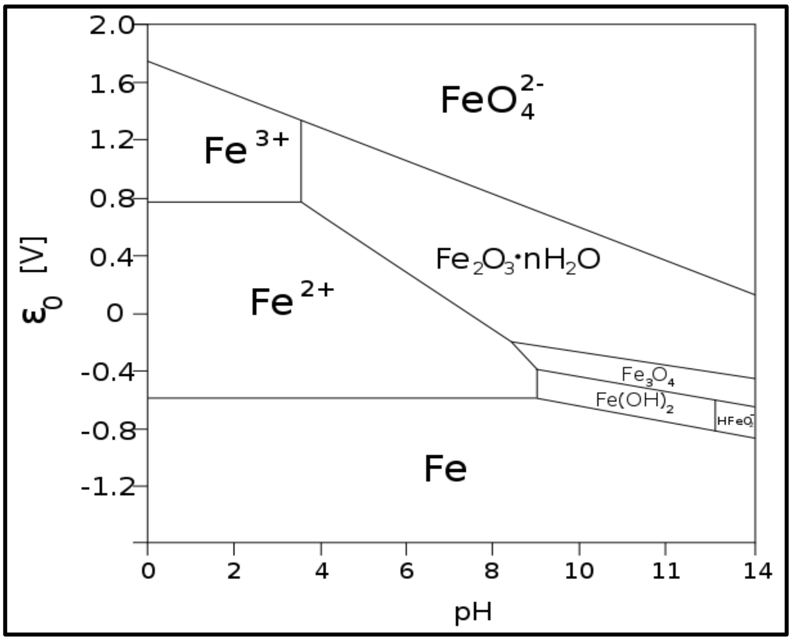


Figure 2.3: Pourbaix Diagram of Iron

Source: ASM Handbook of Alloy Phase Diagrams (2003)

2.5 CORROSION IN BIO IMPLANTS

Corrosion is the gradual degradation of materials by electrochemical attack. It is a concern particularly when a metallic implant is placed in the hostile electrolytic environment provided by the human body. Even though the freely corroding implant materials used in the past have been replaced with modern corrosion resistant super alloys, deleterious corrosion processes have been observed in certain clinical settings (M. Navarro et al. 2008). Corrosion is one of the major processes affecting the life and service of orthopedic devices made of metals and alloys used as implants in the body. Chemical stability, mechanical behavior and biocompatibility in body fluids and tissues are the basic requirements for successful application of the implant materials in bone fractures and replacements. In order for a material to be biocompatible, it must not adversely affect the physiological environment (D. Sharan, 1999).

2.5.1 Biocompatibility

Biocompatibility is the capability of a prosthesis implanted in the body to exist in harmony with tissue without causing deleterious changes and the ability of a material to perform with an appropriate host response in a specific application (Williams .D.F, 1999). There are many factors which influence implant biocompatibility such as implant size, shape and material composition. For a material to be biocompatible, any adverse reactions which may ensure at the blood with material or tissue with material interface must be minimal, while resistance to biodegeneration must be high.

The scope of the first definition is so wide that D Williams tried to find suitable subgroups of applications in order to be able to make more narrow definitions:

(i) Biocompatibility of long-term implantable devices

The biocompatibility of a long-term implantable medical device refers to the ability of the device to perform its intended function, with the desired degree of incorporation in the host, without eliciting any undesirable local or systemic effects in that host.

(ii) Biocompatibility of short-term implantable devices

The biocompatibility of a medical device that is intentionally placed within the cardiovascular system for transient diagnostic or therapeutic purposes refers to the ability of the device to carry out its intended function within flowing blood, with minimal interaction between device and blood that adversely affects device performance, and without inducing uncontrolled activation of cellular or plasma protein cascades.

(iii) Biocompatibility of tissue-engineering products

The biocompatibility of a scaffold or matrix for a tissue-engineering products refers to the ability to perform as a substrate that will support the appropriate cellular activity, including the facilitation of molecular and mechanical signaling systems, in order to optimize tissue regeneration, without eliciting any undesirable effects in those cells, or inducing any undesirable local or systemic responses in the eventual host.

In these definitions the notion of biocompatibility is related to devices rather than to materials as compared to top three definitions.

2.5.2 Corrosion Process

Corrosion is defined as the deterioration of a substance or its properties because of a reaction with its environment. In bio implant it is a concern particularly when a metallic implant is placed in the hostile electrolytic environment provided by the human body. Even though the freely corroding implant materials used in the past have been replaced with modern corrosion resistant super alloys, deleterious corrosion processes have been observed in certain clinical settings It can be driven by two primary factors, thermodynamic driving forces (oxidation/reduction) and kinetic barriers (N. Adya, et al. 2005).

During electrochemical corrosion, the process of metal dissolution in the electrolytes, which proceeds in accordance with the electrochemical mechanism, two conjugated reactions take place which are anodic reaction of metal ionization. The anodic and cathodic reactions always take place concurrently whenever there is corrosion. The anodic reaction involves oxidation of the metallic implant and yields metallic ions. The cathodic reaction is dependent on the nature of the electrolyte (the body aqueous). It involves reduction process and reacts with the electrons generated from the anodic reactions. The rate of anodic reaction must equal the rate of cathodic reaction for electrochemically-based metallic corrosion to occur.

The oxidation or anodic reaction that produced electron for example

$$Fe \rightarrow Fe^{+2} + 2e^- \qquad (1)$$

And a reduction or cathodic reaction that consumes the electrons produced by the anodic reaction, such as

$O_2 + 2H_2O + 4e^- \rightarrow 4OH^-$ (2.1)

$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O$ (2.2)

$2H^+ + 2e \rightarrow H_2$ (2.3)

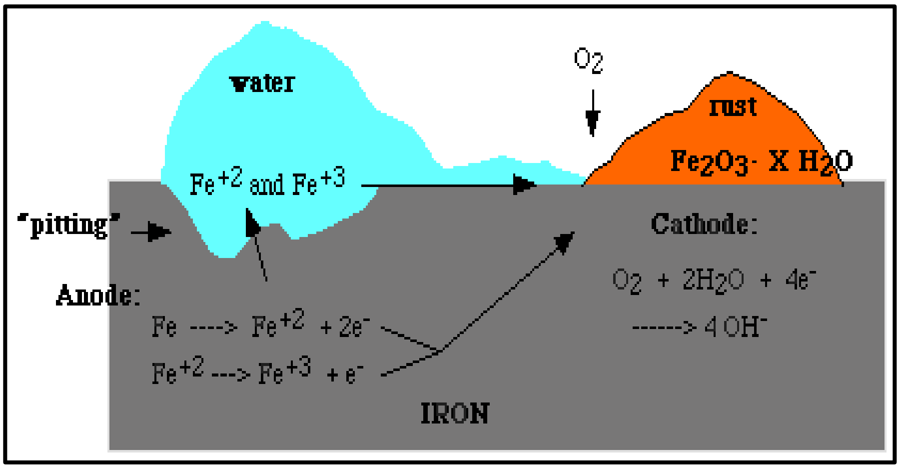


Figure 2.4: Corrosion Process

Source: Corrosion Engineering Handbook (2004)

The cathodic reaction represented by equation 2 is usually the one of the most relevance to implant corrosion since such as corrosion occurs at nearly neutral pH values. Equation 2.2 and 2.3 sometimes is considered in confined areas (pits or crevices) where the pH can reach acidic because of hydrolysis reactions.

2.5.3 Type of Corrosion

2.5.3.1 Stress Corrosion Cracking (SCC)

SCC is the conjoint action of stress and a corrosive environment which leads to the formation of a crack which would not have developed by the action of the stress or environment alone. It can happen 'unexpectedly' and rapidly after a period of satisfactory service leading to catastrophic failure of structures. The stresses that cause

SCC are either produced as a result of the use of the component in service or residual stresses introduced during manufacturing (Karen Ng, 2003).

The environment is either the permanent service environment i.e. sea water or a temporary one caused by operations such as cleaning of the system which can leave a residue, or if the stress is applied during the operation initiate cracking. SCC is a corrosion mechanism that requires the pairing of a material with a very particular environment and the application of a tensile stress above a critical value.

2.5.3.2 Pitting Corrosion

Pitting corrosion is a localized form of corrosion by which cavities or "holes" are produced in the material as shown in Figure 2.5. Pitting is considered to be more dangerous than uniform corrosion damage because it is more difficult to detect, predict and design against. Corrosion products often cover the pits (Huajuan et al. 2006).The pits are the anodes in the corrosion reaction and the remainder of the surface is the cathode. Pits initiate at defects in the protective oxide layer, or passive layer, on the surface. Commonly, these defects are inclusions that form from impurities, such as sulphur, in the steel. These impurities can result in very local depletion of the alloying elements, thereby preventing the protective oxide from being totally uniform.

The conditions that lead to pitting are moderately high temperatures, high concentrations of chloride ions (from salt), and other halides such as fluorides, bromides and iodides. Acidic conditions (low pH) also aid the growth of the pits. In biomedical the pitting corrosion was frequently observed in older stainless steel fracture fixation hardware, e.g., on the underside of screw heads. It also occurs infrequently on the neck or the underside of the flange of proximal femoral endoprostheses.

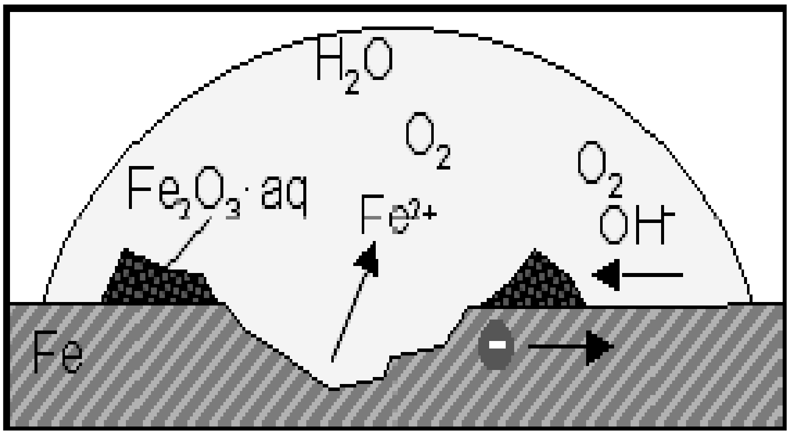


Figure 2.5: Pitting Corrosion Mechanism

Source: Bingchun Zhang (2006)

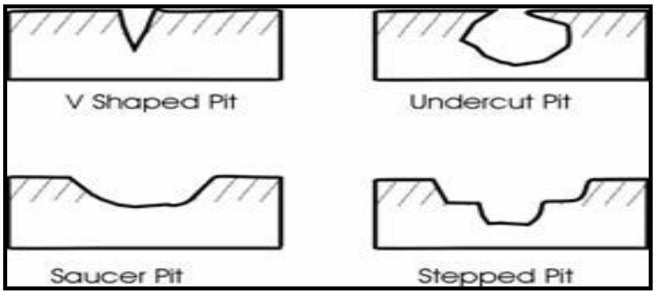


Figure 2.6: Different pits shapes.

Source: Bingchun Zhang (2006)

2.5.3.3 Crevice Corrosion

This is a form of local corrosion due to differences in oxygen tension or concentration of electrolytes or changes in pH in a confined space, such as in the crevices between a screw and a plate as shown in Figure 2.7. The narrower and deeper the crack is, the more likely crevice corrosion is to start (Seifedine Kadry, 2008).

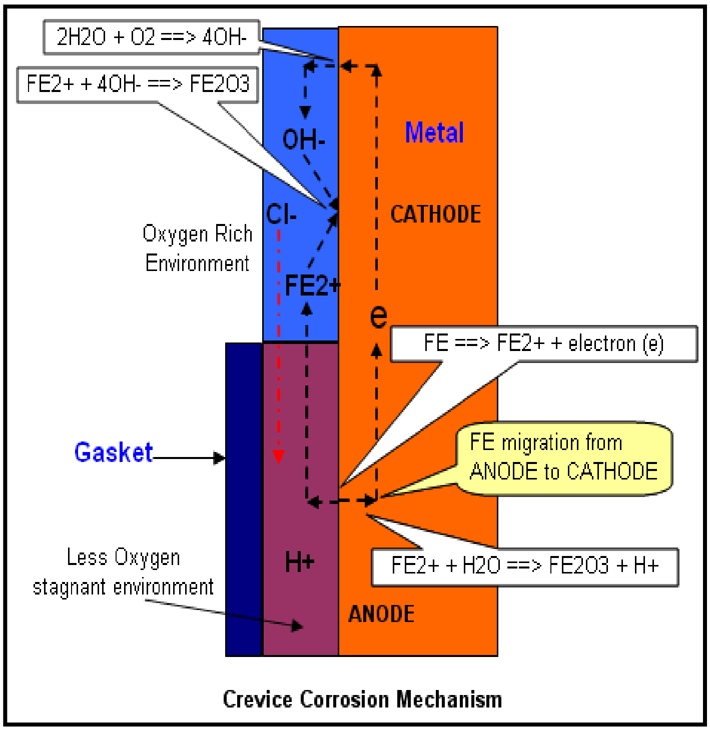


Figure 2.7: Crevice Corrosion Mechanism

Source: Crevice Corrosion Mechanism & Prevention Handbook (2009)

2.5.3.4 Fretting Corrosion

Fretting is the interaction of two surfaces in contact and subject to relative tangential slips in an oscillatory manner. In the case where this interaction leads to surface damage and wear products determined by chemical reactions with the environment, the phenomenon is usually termed fretting corrosion. The majority of previously reported work has considered fretting between metal surfaces in gaseous environments, but the incidence of fretting in an aqueous environment is being increasingly reported. For example, the occurrence of fretting has been noted between adjoining embossed stainless steel plates in heat exchangers for cooling liquids, where vibration arises from the pumping of the liquids which causes fretting of the points of contact of the plates (Pierre R. Roberge, 2003).

A further example has been observed in surgical implants used for joining or replacing fractured bone as shown in Figure 2.8. The implant is attached to the bone with screws and local movement may occur between the bevel under the head of the screw and tile countersink of the hole in the implant. Repetitive flexing and tensioning is known to cause fretting between the strands and wires of steel ropes and since they are often used in industrially polluted atmospheres and marine environments the fretting is occurring in an aqueous medium.

The processes which may occur during fretting are as follows:

(i) Disruption of otherwise protective oxide films due to the mechanical action.

(ii) Formation of local welds between contacting high spots as a result of the shearing action.

(iii) High strain fatigue of these welds involving plastic deformation and resulting in loose particles of metal as fatigue cracks run together.

All these processes will be influenced by electrochemical reactions occurring at the metal surface, and conversely the electrochemical reactions will be profoundly influenced by these mechanical processes.

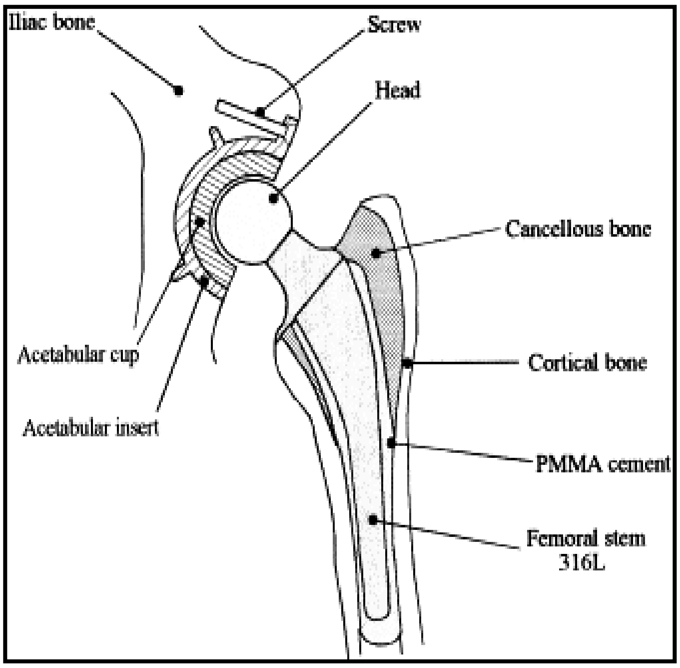


Figure 2.8: Diagram showing cemented implantation of total hip joint prosthesis.

Source: Corrosion Engineering Handbook (2003)

2.5.3.5 Intergranular Corrosion

Intergranular corrosion is a form of relatively rapid and localised corrosion associated with a defective microstructure known as carbide precipitation. When austenitic steels have been exposed for a period of time in the range of approximately 425 to 850°C, or when the steel has been heated to higher temperatures and allowed to cool through that temperature range at a relatively slow rate (such as occurs after welding or air cooling after annealing), the chromium and carbon in the steel combine to form chromium carbide particles along the grain boundaries throughout the steel. Formation of these carbide particles in the grain boundaries depletes the surrounding metal of chromium and reduces its corrosion resistance, allowing the steel to corrode preferentially along the grain boundaries. Steel in this condition is said to be "sensitised".

2.5.3.6 Galvanic Corrosion

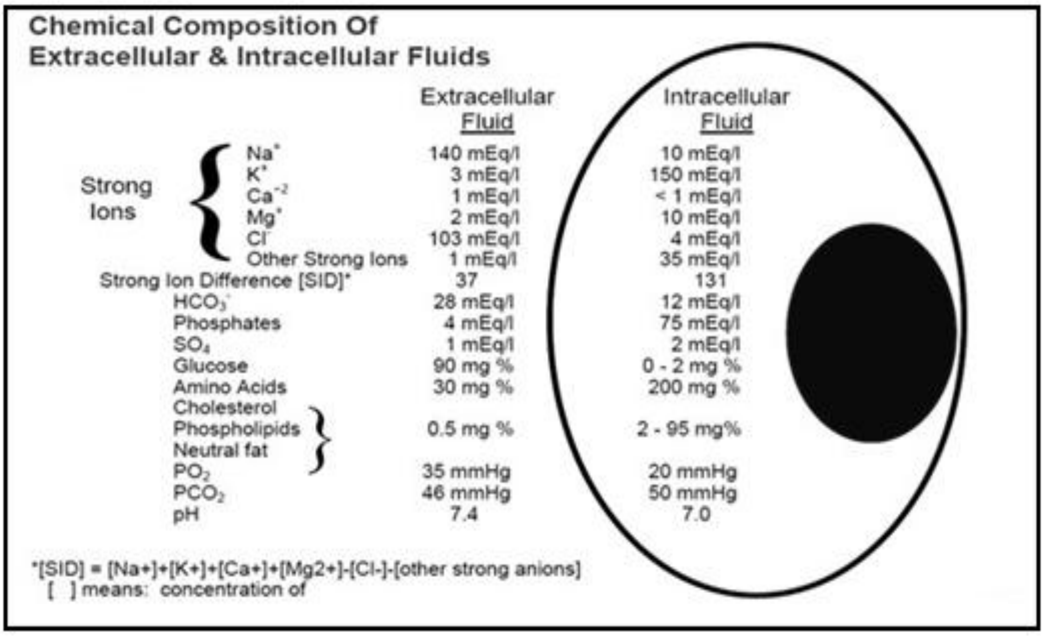
Galvanic corrosion may occur when dissimilar metals are in contact in an electrolyte solution and there is an electrical potential difference between them. The different of electrical potential make a current flow between the two metals from the more active to the more noble metal. As a result the corrosive attack on the active metal (anode) and in relative protection of the more noble metal (cathode). Contact between dissimilar metals immersed in an electrolyte may occur commonly in orthopedic clinical practice. Examples include a stainless-steel cerclage wire in contact with a cobalt or titanium-alloy femoral stem, a cobalt-alloy femoral head in contact with a titanium-alloy femoral stem, and a titanium-alloy screw in contact with a stainless-steel plate. Although it is generally good practice to avoid contact between dissimilar metals, the presence of a passivating oxide film alters the kinetics of the corrosion reaction so that certain combinations of dissimilar metals are not accompanied by accelerated galvanic corrosive attack.

2.6 HUMAN BODIES AS CORROSIVE ENVIRONMENT.

The human body is a very demanding environment because it is so salty. When metal ions are dissolved from the points where the oxide layer is not fully developed, they form metal hydroxide. This is immediately surrounded by water molecules and then attaches to the passive layer. When there are chloride ions present, as in human plasma, these replace the water molecules from the passive layer. If the passive layer is not fully developed, the dissolved metal ions form a metal-chloride complex which dissolves into body fluids. This impairs local passivity, and may lead to pitting corrosion (Williams et al. 1996). When the passive layer breaks locally, this anodic area is very small and the surrounding catodic area is very large. This may lead to very rapid local corrosion and unexpectedly fast destruction of the material (Kruger, 1983).

In addition, from thermodynamic point the position of the metal in the electrochemical series indicates the order with which the metal will be displaced from the compounds. The higher the position of the metal in the series, the more stable and unreactive, hence the lower the corrosion rate will be. The overall reaction of the human body on an implant is a system property that includes many different aspects, such as surface chemistry, implant movement, biodegradation and surgical aspects. The highly corrosive environment of the human body restricts the materials to be used for implants.

The mechanism that can cause implants to fail is aqueous corrosion. Corrosion is unavoidable because the body is an aqueous medium containing various ions and organic substances, forming an electrolyte solution. It's depending on the amount, type of ions present and the body temperature, the pH of the body aqueous is typically around 7.4 at normal body temperature of 38°C. The ions present can be grouped into anions (negative ions) and cations (positive ions). Main anions present are chloride, phosphate, bicarbonate and dissolved oxygen. Cations on the other hand, consists mainly of principle ions Na^+, K^+, Ca^{2+} and Mg^{2+} and many other cations in smaller amounts as shown in Figure 2.9. These ions react electrochemically with the surface of metallic biomaterials to cause corrosion.



Chemical Composition Of Extracellular & Intracellular Fluids

		Extracellular Fluid	Intracellular Fluid
Strong Ions	Na^+	140 mEq/l	10 mEq/l
	K^+	3 mEq/l	150 mEq/l
	Ca^{+2}	1 mEq/l	< 1 mEq/l
	Mg^+	2 mEq/l	10 mEq/l
	Cl^-	103 mEq/l	4 mEq/l
	Other Strong Ions	1 mEq/l	35 mEq/l
Strong Ion Difference [SID]*		37	131
	HCO_3^-	28 mEq/l	12 mEq/l
	Phosphates	4 mEq/l	75 mEq/l
	SO_4	1 mEq/l	2 mEq/l
	Glucose	90 mg %	0 - 2 mg %
	Amino Acids	30 mg %	200 mg %
	Cholesterol Phospholipids Neutral fat	0.5 mg %	2 - 95 mg%
	PO_2	35 mmHg	20 mmHg
	PCO_2	46 mmHg	50 mmHg
	pH	7.4	7.0

*[SID] = [Na+]+[K+]+[Ca+]+[Mg2+]-[Cl-]-[other strong anions]
[ ] means: concentration of

Figure 2.9: Chemical Composition of Extracellular and Intercellular Fluids.

Source: ASM International Handbook (1997)

2.7 SIMULATED BODY FLUID

As we all known the human body environment is very aggressive. So, each biomaterial that placed in human body should be tested to evaluate the influence of the human body environment on its properties. The biomaterial can lose their stability and corrosion happen or degrade in the presence of the physical and chemical conditions prevalent in the human body. From that point, a simulated body fluid (SBF) has been used widely for in vitro studies of the bioactivity of artificial implant. The fluid contains ion concentration nearly equal to those of human blood plasma and a pH of 7.4 but higher concentration of ion Cl^- and lower concentration of HCO^{3-} as shown in Table 2.3 below.

Table 2.3: Ion concentrations (mmol/L) of SBF, Hank's solution, PBS and human blood plasma

Ion	Hank's solution	PBS	Simulate Body Fluid	Blood plasma
Na^+	142.77	157.17	127.76	142.0
K^+	5.85	4.17	5.0	5.0
Mg^{2+}	0.81	-	1.5	1.5
Ca^{2+}	1.27	-	2.5	2.5
Cl^-	145.87	140.70	148.8	103.0
HCO^{3-}	4.17	27.01	4.2	27.0
HPO_4^{2-}	0.34	9.58	1.0	1.0
SO_4^{2-}	0.81	-	0.5	0.5

Source: M.Diener and R. Spolenak (1999)

2.7.1 Phosphate Buffered Saline (PBS).

PBS is a buffer solution commonly used in cell biology experiments to maintain the osmolarity of the cells. It contains salt ions, which balances the amount of salt ions inside the cell. If the cells are immersed into a solution that has too many salt ions, water will leak out from the cell, causing the cell to shrink as shown in Table 2.4. Conversely, if the cells are immersed into a solution that has too few salt ions, water will enter the cell, causing the cell to burst.

PBS is also often used as a buffer in biochemistry experiments to maintain the pH of proteins. Proteins require a certain pH range to maintain neutrality or charges on certain amino acids, which allow the structure of the protein to be maintained in its native state.

Table 2.4: Phosphate buffered saline (PBS) and its components.

Solution	Cations	Anions	Amino acids
PBS	Na^+ , K^+	Cl^- , PO_4^{2-}	-

Source: Data for Biochemical Research, Third Edition, Oxford Science Publication (2006)

2.7.2 Hank's Solution

Hank's solution is a salt solution usually used in combination with naturally occurring body substances (blood serum, tissue extracts) or more complex chemically defined nutritive solutions for culturing animal cells as shown in Table 2.5.

Table 2.5: Hanks Solution and its components

Solution	**Composition**
Hank's solution	0.185 $CaCl_2 .2H_2O$, 0.06 KH_2PO_4 (Anhyd.) , 0.04788 Na_2HPO_4 (Anhyd.), KCl 0.40, 8.00 NaCl, 1.00 D-Glucose, 0.09767 $MgSO_4$(Anhyd.), 0.35 $NaHCO_3$

Source: Data for Biochemical Research, Third Edition, Oxford Science Publication (2006)

CHAPTER 3

METHODOLOGY

3.1 INTRODUCTION

A successful experiment comes from systematic planning that we followed during running the experiment. The structure of the research is an important thing that should be considered in order to make sure the experiments that we conduct are running smoothly and give the best result as we expected. Besides, the experiment with proper planning can be conducted with the guideline based on the objective that had been stated earlier.

In this chapter, the methodology of this study will be clearly elaborated and discussed. The methodologies included in this study are sample preparation for surface analysis, stress relieving process, metallographic process, electrochemical study of SS316 by using potentiodynamic polarization and corrosion rate analysis by IV man software. The steps in this research were referred from the American Standard for Testing and Material (ASTM), depending on the suitability.

3.1.1 General Experiment Procedure

The general experiment procedure for this project had been shown in Figure 3.1.

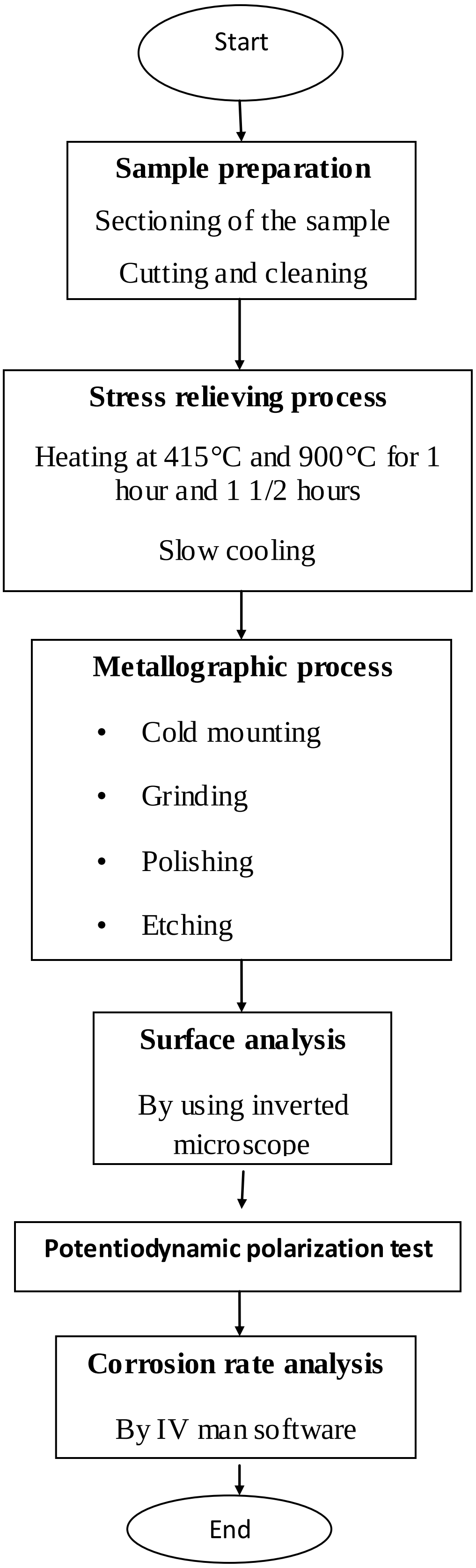


Figure 3.1: Experimental procedure

3.2 SAMPLE PREPARATION

In this project, SS316 stainless steel was used as a sample. The SS316 were cut into ten pieces in the form of cylinder which is 2.5 cm width and 10 mm height by using linear precision saw machine as shown in Figure 3.2. Then the sample were divide into two groups as shown in Table 3.1 which are too immersed into PBS and Hank's solution as a simulated body environment. The surfaces of the stainless steel SS316 had been cleaned from dirt by degreasing with a solvent cleaner and scrubbing.

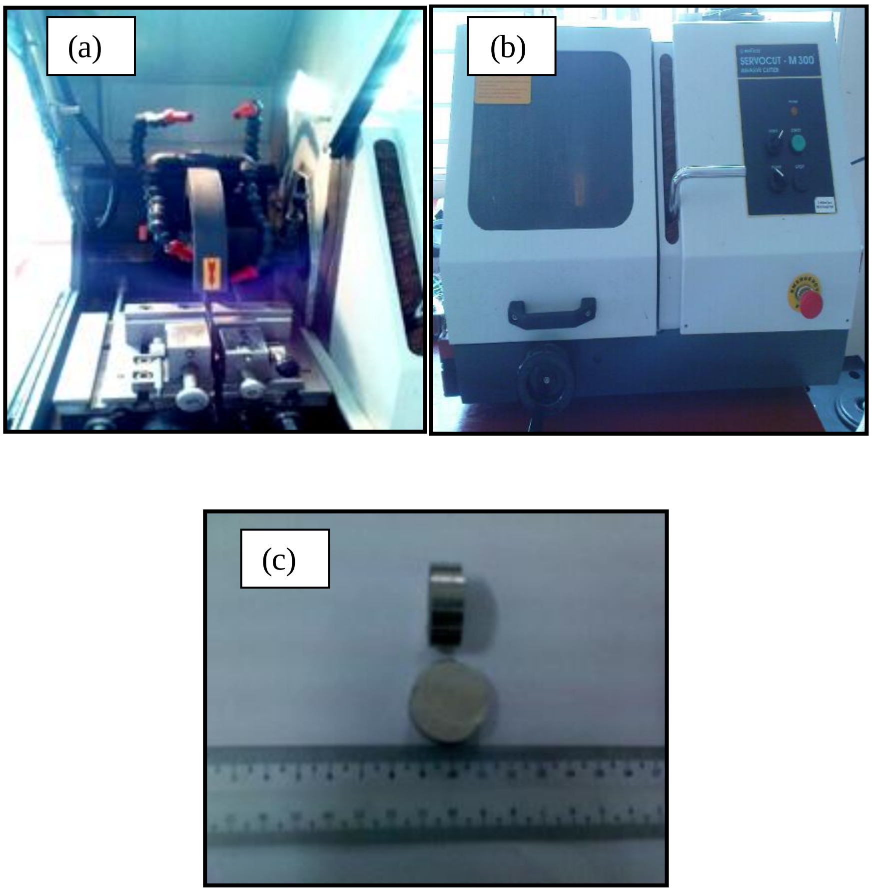


Figure 3.2: (a) and (b) linear precision saw machine (c) sample after cutting process (2.5 cm width x 10 mm height)

Table 3.1: (a) Table of Sample Testing for Hank's solution (b) Table of Sample Testing for PBS

(a)

Sample	**Process**
S1	No stress relieving
S2A	Stress relieving at 415°C for 1 hour
S2B	Stress relieving at 415°C for 1 ½ hours
S3A	Stress relieving at 900°C for 1 hour
S3B	Stress relieving at 900°C for 1 ½ hours

(b)

Sample	**Process**
S1	No stress relieving
S2A	Stress relieving at 415°C for 1 hour
S2B	Stress relieving at 415°C for 1 ½ hours
S3A	Stress relieving at 900°C for 1 hour
S3B	Stress relieving at 900°C for 1 ½ hours

3.3 STRESS RELIEVING PROCESS

Stress relieving is the process to relieve the internal stresses and there is no microstructural change happened during the process. Internal stresses are those stresses which can exist within a body in the absence of external forces. There are also known as residual stresses or locked in stresses.

For this process, the SS316 stainless steel sample was heated to the temperature 415°C for 1 hour which is sample S2A. For other samples the heat treatment configuration is as shown in Table 3.1.

Figure 3.3: Furnace for stress relieving process

Firstly, the furnace as shown in Figure 3.3 had been heated up to 415°C. For this temperature, two specimens had been prepared and put into the furnace for the stress relieving process by using tongs and heat resisting gloves. Then, after 1 hour two specimen of SS316 had been take out and cooled outside of the furnace at room temperature. This step had been repeated to the other two specimens when it reaches 1 ½ hours time for heating in the furnace.

Secondly, for four other specimens need to be heated at temperature 900°C for 1 hour and 1 ½ hours, repeating the same steps as the first process.

3.4 METALLOGRAPHIC PROCESS

After the stress relieving process, the next step was metallurgy process. For the metallurgy process the sample had underwent mounted, grinded, polished and etched to reveal the microstructure of the heat treated SS316 stainless steel.

3.4.1 Mounting

Mounting of specimens are usually necessary to allow them to be handled easily. It also minimizes the amount of damage on the specimen itself. The mounting material used should not influence the specimen as a result of chemical reaction or mechanical stresses (Polmear I.J, 1995).

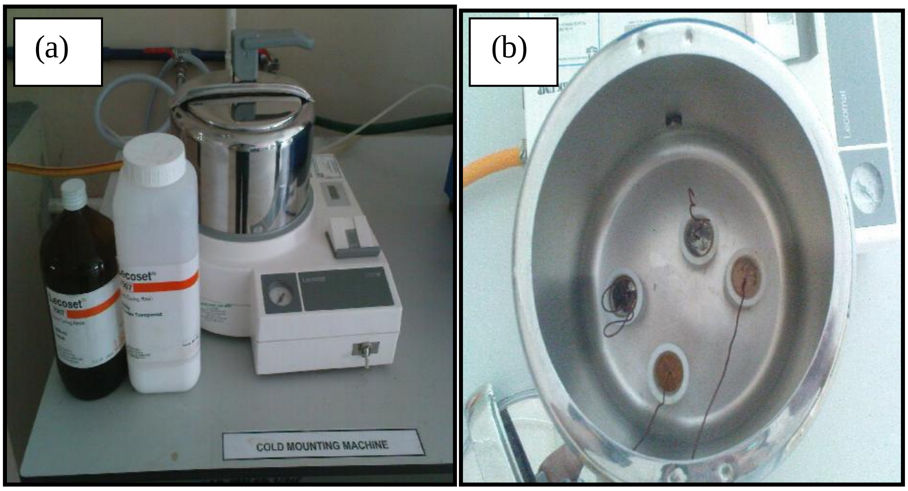


Figure 3.4: (a) Powder transparent with liquid of cold-curing resin and cold mounting machine (b) Sample that had been put in the cold mounting machine

Firstly, the powder transparent and liquid of cold-curing resin as shown in Figure 3.4 had been weighted with the same weight and mixed together. After that, the mixing solution had been put into boxes that contain the samples and had been put into the cold mounting machine. After 20 minutes the samples had been put out and the boxes were removed from the sample.

3.4.2 Grinding

Surface layers damaged by cutting were removed by grinding. Mounted specimens are grounded with rotating discs of abrasive paper, for example wet silicon carbide paper. The grinding procedure involves several stages, using a finer paper (higher number). Each grinding stage removes the scratches from the previous coarser paper. This can be easily achieved by orienting the specimen perpendicular to the previous scratches. Between each grade the specimen is washed thoroughly with soapy water to prevent contamination from coarser grit present on the specimen surface.

Figure 3.5: Grinding machine

For this step, the sample had been grinded to get smooth surface and remove the damaged surface that was caused by cutting as shown in Figure 3.5. The surface of the papers was flushed by a current of water, which serves not only as a lubricant in grinding, but also carries away coarse emery particles, which might otherwise scratch the surface of the specimen. The silicon carbide papers used in achieving the proper grinding of the specimen were in the following grades of 120, 240, 320 and 400 grits, grinding respectively in that order of grades.

3.4.3 Polishing

Polishing discs are covered with soft cloth impregnated with abrasive diamond particles and an oily lubricant or water lubricant. Particles of two different grades had been used to polish the material. A coarser polish typically with diamond particles 6 microns (polycrystalline diamond) in diameter which should remove the scratches produced from the finest grinding stage and a finer polish typically with diamond particles 1 micron (nanopolish alumina) in diameter, to produce a smooth surface as shown in Figure 3.6. After the polishing, the sample had been cleaned by using distilled water and then dried by using cold air dryer.

Figure 3.6: Polishing machine

3.4.4 Etching

Etching is used to reveal the microstructure of the metal through selective chemical attack on the surface of material. In alloys with more than one phase etching creates contrast between different regions through differences in topography or the reflectivity of the different phases. The rate of etching is affected by crystallographic orientation, so contrast is formed between grains, for example in pure metals. The reagent will also preferentially etch high energy sites such as grain boundaries (J. Will et al. 1998). This results in a surface relief that enables different crystal orientations, grain boundaries, phases and precipitates to be easily distinguished.

The microstructure of the sample of stainless steel had been revealed by etching with mixing solution. From Figure 3.7 stainless steel had been etched by mixing of 20 ml hydrochloric acid (HCl), 20 ml glycerol and 10 ml nitric acid (HNO_3) for 5 minutes (Todd A. Christman et al. 2003). To etch these specimens, they were washed free of any adhering polishing compound and plunged into the etching solution, agitated vigorously for 3 minutes. The specimens were then very quickly transferred to running water, in order to wash away the etchant as rapidly as possible.

Figure 3.7: Etching solution 20 ml hydrochloric acid (HCl), 20 ml glycerol and 10 ml nitric acid (HNO_3)

3.5 MATERIAL CHARACTERIZATION

Surface visualization had been carried out after the etching process. Observations on the material microstructure of the samples to determine the type of corrosion had been observed by using inverted microscope (IM7000 series) as shown in Figure 3.8 in the UMP mechanical laboratory at Pekan campus.

Figure 3.8: Inverted microscope (IM7000 Series)

3.6 ELECTROCHEMICAL TEST AND MEASUREMENT

In this project, the electrochemical studies were conducted using a potentiostat / galvanostat WPG100. The software that was used to interprete data and show result in this project is WPciPG Software that was connect to WPG100 potentiostat as shown in Figure 3.9. Referring from ASTM G 5 - 94, Standard Reference Test Method for Making Potentiostatic and Potentiodynamic Anodic Polarization Measurements, the potential of the working electrode was measured against saturated calomel electrode (SCE) which is used as the reference electrode.

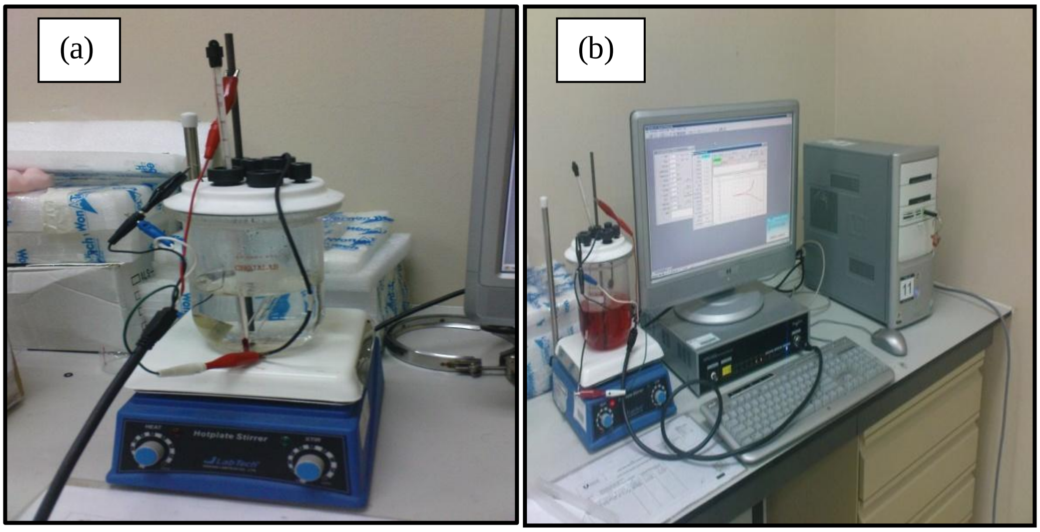


Figure 3.9: (a) Electrochemical set up (b).WPG100 Potentiostat interfaced with computer

3.6.1 Electrochemical Cell Set-up

Firstly, before the electrochemical test had been performed the entire component must be assembled and appropriately prepared. According to the schematic view in Figure 3.10 and Figure 3.11 the working electrode, WE (black cable) are connected to the sample which is SS316, a graphite wire as the counter electrode, CE (red cable) and saturated calomel electrode as the reference electrode, RE (blue cable).

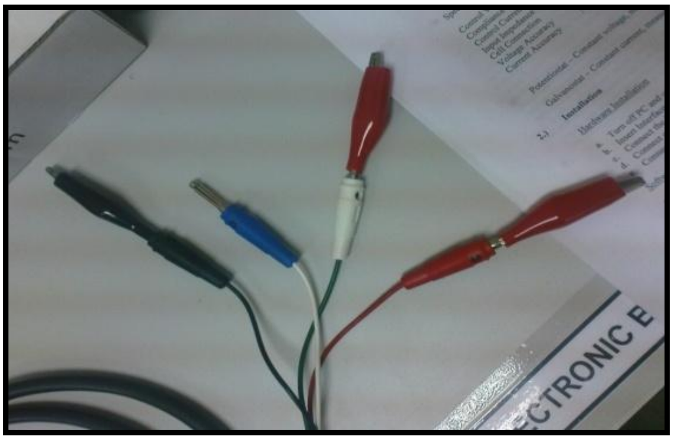


Figure 3.10: Type of Electrodes

A saturated calomel electrode will be used as reference electrode as it is provides a stable 'reference' against which the applied potential may be accurately measured. The counter electrode is used to provide the applied current and as such should be composed of highly corrosion resistance material. Counter electrode that have been used in this cell is a graphite rod. This cell is then connected to a computer with software program and plotter to record and analysis polarization data. A constant electrolyte temperature of 37±2°C was maintained using hot plate.

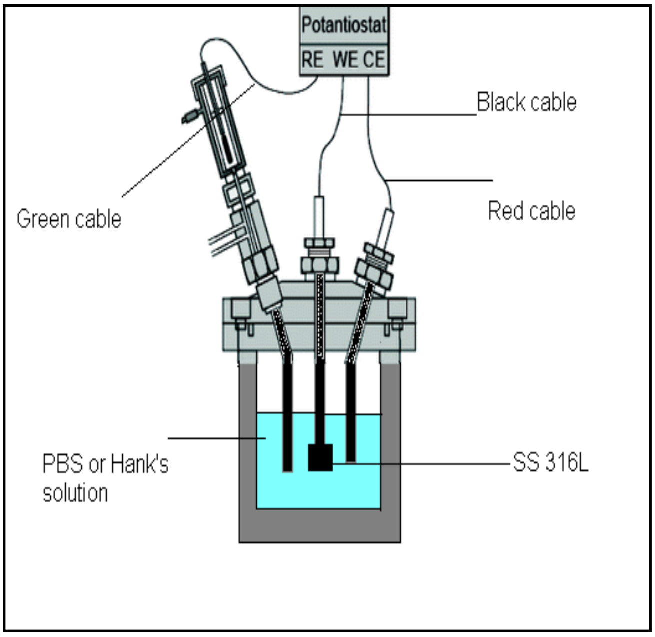


Figure 3.11: Schematic View of SS316 Experimental Set-Up including A Potentiostatic Set-Up.

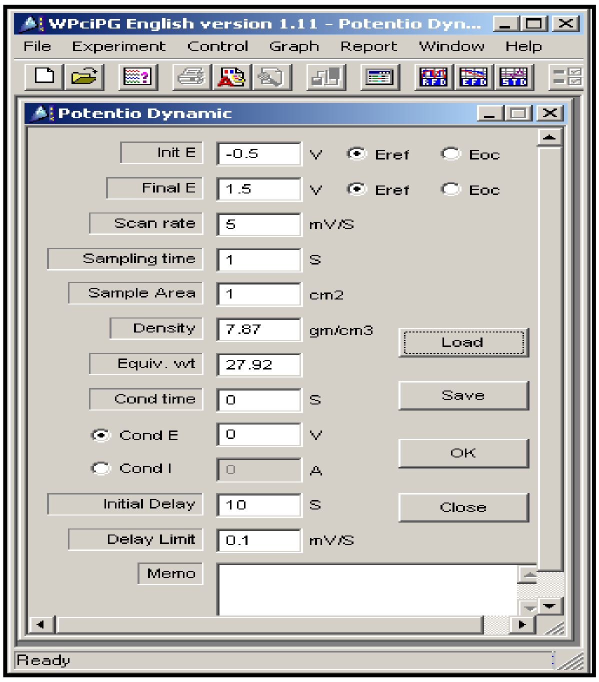
Source: J. Alan (2005)

3.6.2 General Parameters

There are a number of parameters which must be specified and can be controlled by this IVMan software. The first is the initial and final potentials which define the 'path' which the scan will take. In this software, the default value for initial and final potential is -250 mV to 250 mV. For this project, the parameter that had been used as below:

i. Sample area =4.909 cm^2
ii. Density =7.98 gm/cm^3
iii. Equivalent weight =25.5
iv. Initial E and Final E =-0.25 V and 0.25 V

The scan rate that has been used is 2 mV/s to get more accurate data when plotted the Tafel plot. The value for initial E and final E are -0.25 V and 0.25 V were used to get the smooth plot when run the IV man software. The sample area that was used is 4.909 cm^2 for the sample that had been sectioning by 2.5 cm width and 10 mm height. The density and the equivalent weight that were used are the constant value for the SS316 stainless steel.



Init E -0.5 V ● Eref ○ Eoc
Final E 1.5 V ● Eref ○ Eoc
Scan rate 5 mV/S
Sampling time 1 S
Sample Area 1 cm2
Density 7.87 gm/cm3
Equiv. wt 27.92
Cond time 0 S
● Cond E 0 V
○ Cond I 0 A
Initial Delay 10 S
Delay Limit 0.1 mV/S

Figure 3.12: Sample parameters of Potentiodynamic Polarization

3.6.3 Potentiodynamic Polarization

Potentiodynamic plots are potentiostatic tests that allow qualitative observations on the corrosion behavior of the sample. A wide voltage range is scanned (1-2 V). The passivation characteristics of the sample can be determined.

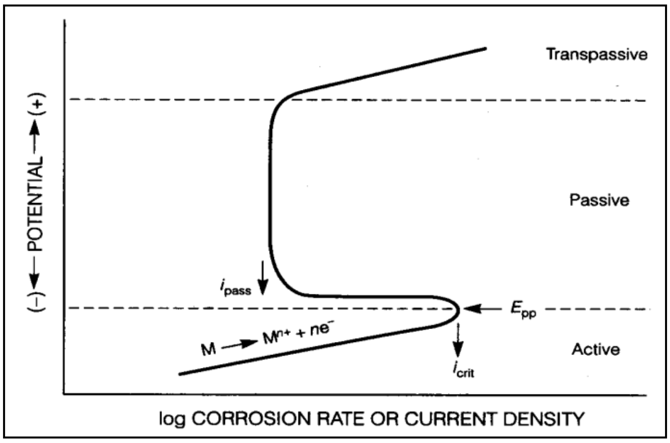


Figure 3.13: Graph Current Density versus Potential

Source: Fundamentals, Testing, and Protection, Volume 13A of the ASM Handbook (2003)

From the Figure 3.13, E_{pp}=Primary Passivation Potential, I_{cri}= Critical Current Density, I_{pass}= Passive Current Density.The Shape of the Polarization Curve Depends on the Relative Positions of the Anodic and Cathodic Half Reactions

3.6.4 Phosphate buffered saline and Hank’s solution

The electrochemical test were conducted in an aqueous solution (electrolyte) used for simulating human body fluid conditions namely phosphate buffered saline (PBS) and Hank’s solution as shown in Figure 3.14. All of the solution had been stored at the required temperature to prevent from any condition that might affect the solution. PBS and Hanks solution had been stored at temperature 4°C. The pH of the solution was precisely maintained at 7.4 based on the nature of the human body solution by the addition of NaOH or HCl. All the potential measurement had been analyzed by using IVman software.

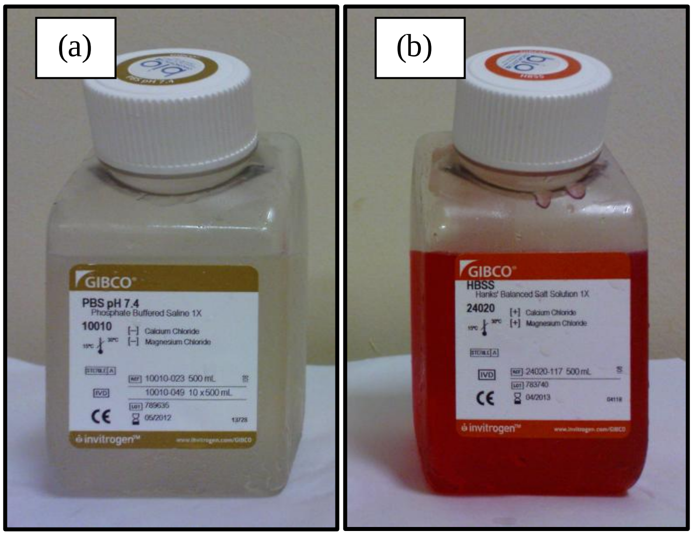


Figure 3.14: (a) Phosphate Buffered Saline (PBS) (b) Hank's Balanced Salt Solution

Table 3.2: Types of Solution used and it's Component

Solution	**Composition (g/l)**
Phosphate Buffered Saline (PBS)	8.0 NaCl, 0.2 KCl, 1.44 NaH_2PO_4, 0.2 KH_2PO_4
Hank's Balanced Salt Solution (HBSS)	0.185 $CaCl_2 .2H_2O$, 0.06 KH_2PO_4 (Anhyd.) , 0.04788 Na_2HPO_4 (Anhyd.), KCl 0.40, 8.00 NaCl, 1.00 D-Glucose, 0.09767 $MgSO_4$(Anhyd.), 0.35 $NaHCO_3$

Source: Data for Biochemical Research, Third Edition (2006)

3.7 CORROSION RATE ANALYSIS

During this experiment, IVMan software will be connected to WPG100 potentiostat as a function to interpret data and result. Through this software, corrosion rate can be obtained by using potentiodynamic polarization and Tafel plot analysis.

3.7.1 Tafel Plot

Tafel plots allow the direct measurement of the corrosion current from which the corrosion rate can be quickly calculated. The vertical axis is potential and the horizontal axis is the logarithm of absolute current. The theoretical current for the anodic and cathodic reactions are shown as straight lines.

The curved line is the total current, which is the sum of the anodic and cathodic currents. This is the current that you measure when you sweep the potential of the metal with your potentiostat. The sharp point in the curve as shown in Figure 3.15 is actually the point where the current changes signs as the reaction changes from anodic to cathodic, or vice versa. The sharp point is due to the use of a logarithmic axis. The use of a log axis is necessary because of the wide range of current values that must be displayed during a corrosion experiment. This point determines the potential (e_{corr}) and current density (i_{corr}) for corrosion.

The cathodic (β_c) and anodic (β_a) Tafel slope, the estimated corrosion current density (i_{corr}) and estimated corrosion potential (e_{corr}) also determined from the Tafel plot. The value of the i_{corr} was used to calculate the corrosion rate of the sample using IVMAN Software as shown in Figure 3.16.

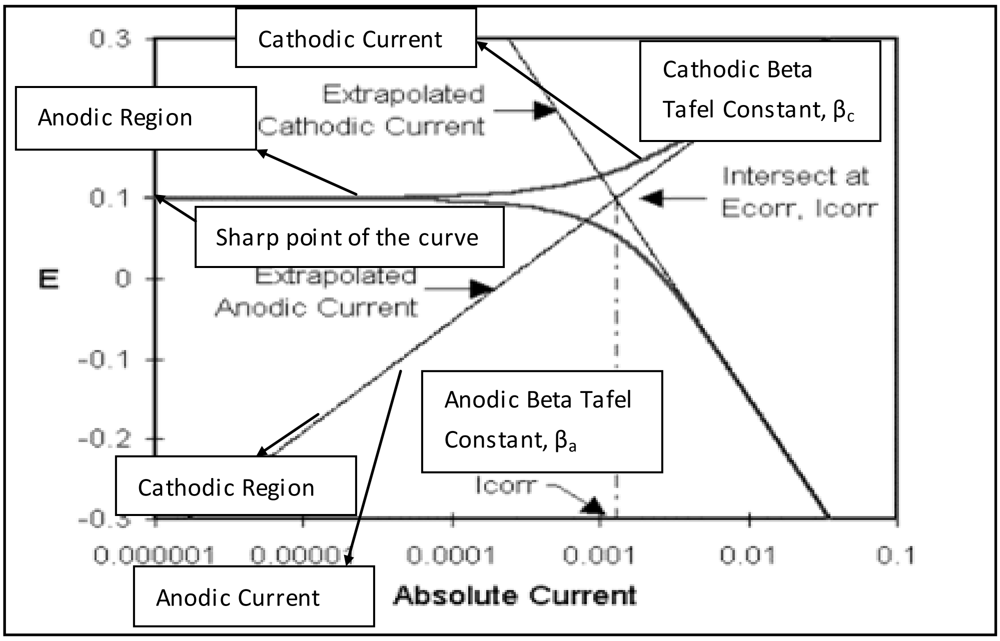
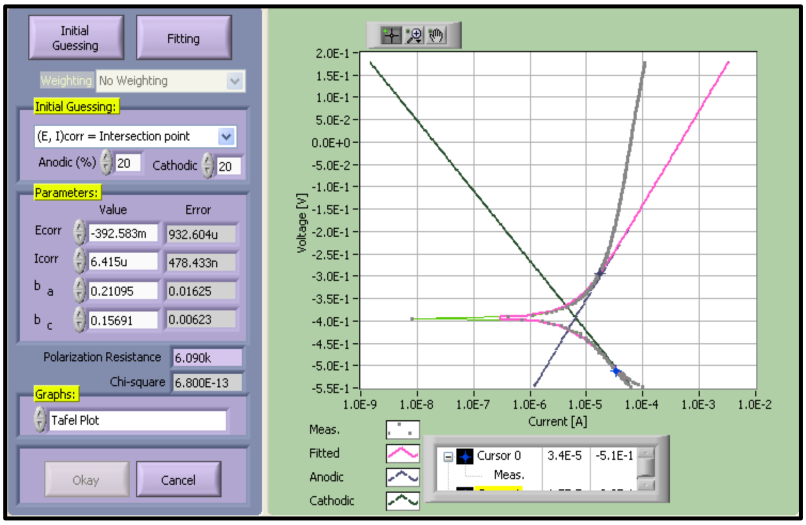


Figure 3.15: Graph E ref vs. Log I

Source: John Wiley and Sons, New York, (1985)



Weighting: No Weighting

Initial Guessing:

(E, I)corr = Intersection point

Anodic (%) 20 Cathodic 20

Parameters:

	Value	Error
Ecorr	-392.583m	932.604u
Icorr	6.415u	478.433n
b a	0.21095	0.01625
b c	0.15691	0.00623

Polarization Resistance 6.090k

Chi-square 6.800E-13

Graphs:

Tafel Plot

Cursor 0	3.4E-5	-5.1E-1
Meas.		

Figure 3.16: Tafel analysis using IVMAN software

CHAPTER 4

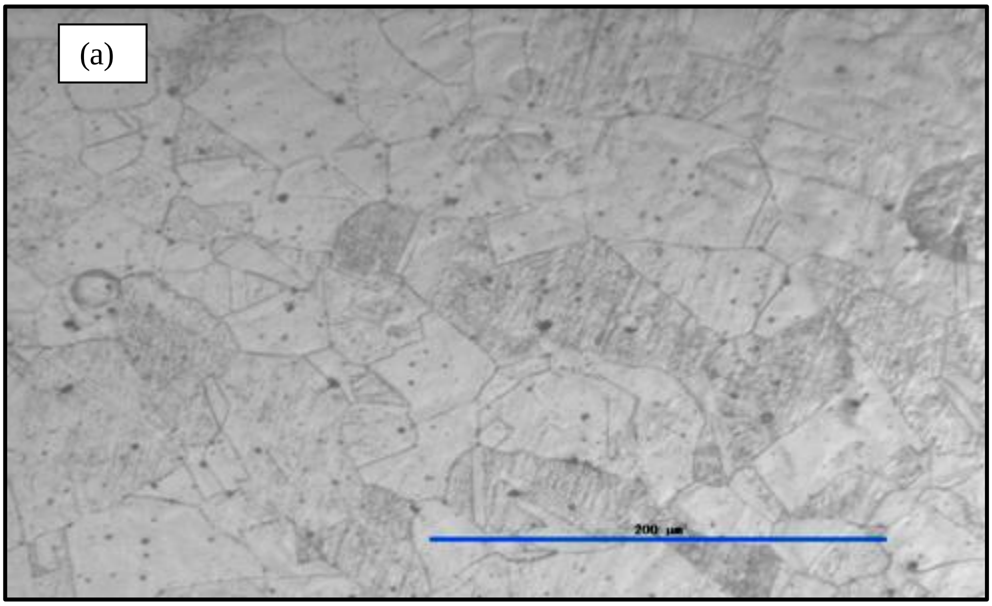
EXPERIMENTAL RESULT AND DISCUSION

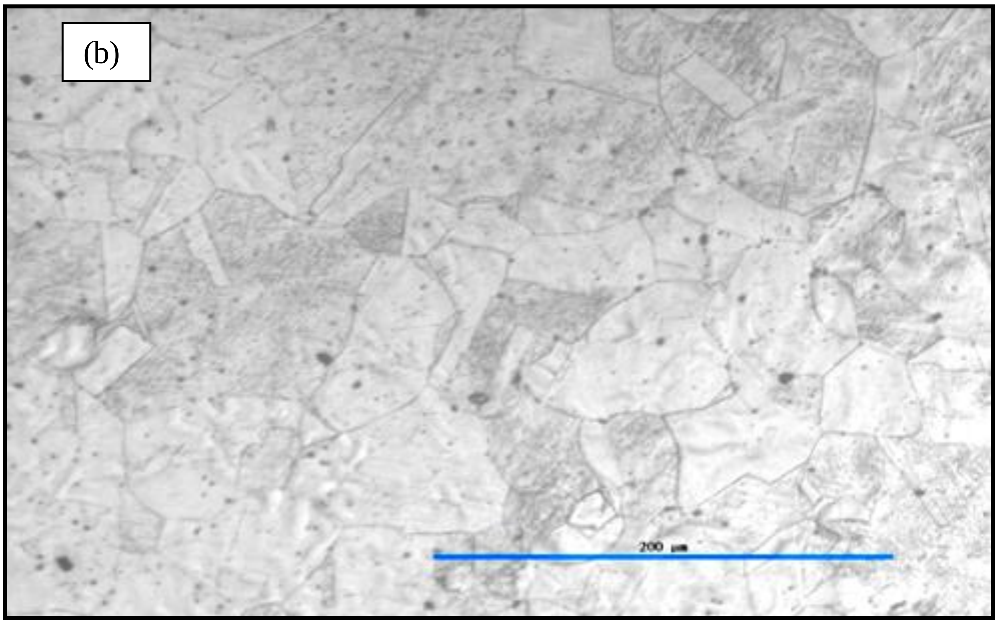
4.1 INTRODUCTION

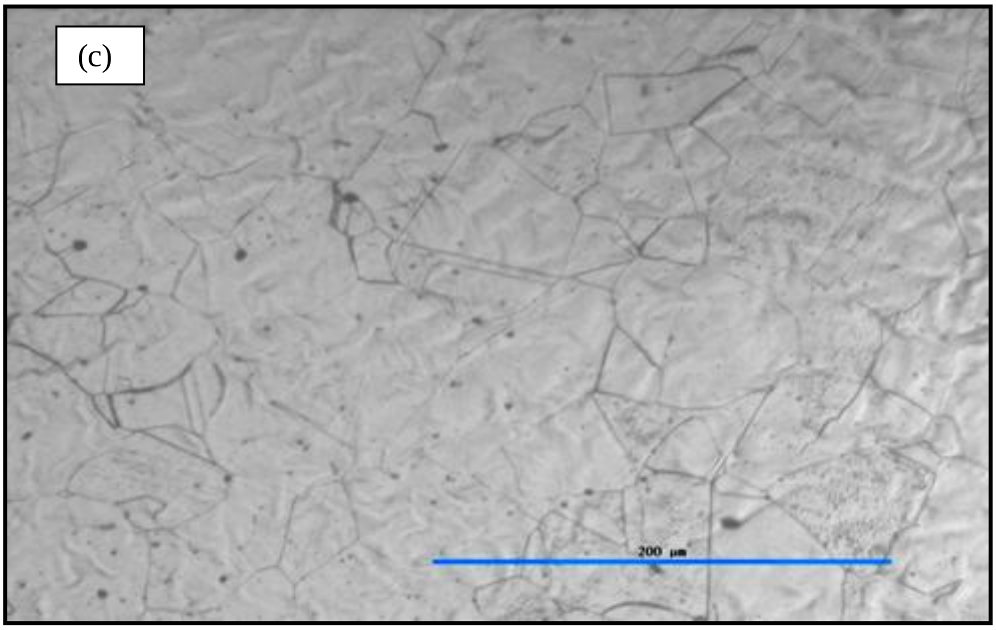
This chapter is to discuss the results that have been obtained from the previous experiment. The experiments that have been done were stress relieving with different temperature and time. The objective of this chapter is to determine the effects of heat treatment on corrosion behavior of SS316 stainless steel in simulated body environment. The outcome of the experiment had been discussed in detail by next topic.

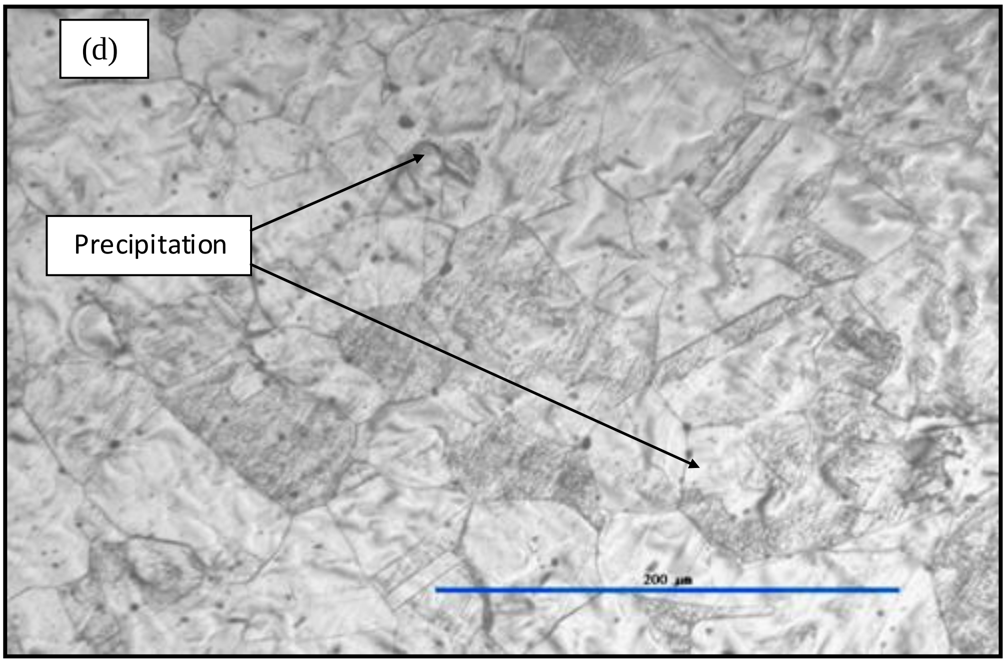
4.2 SAMPLE CHARACTERIZATION

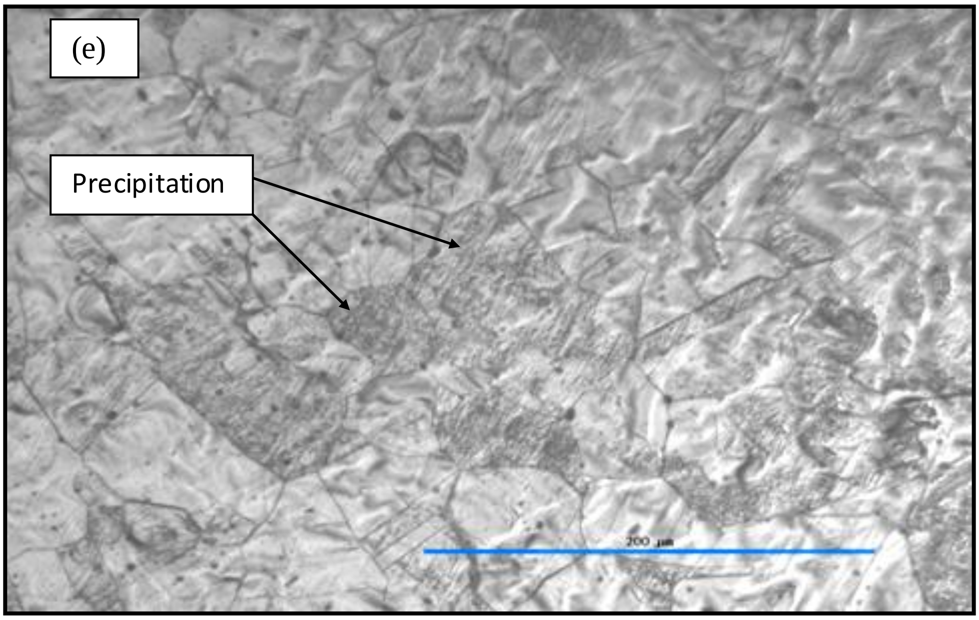
The microstructure of the sample had been revealed by using inverted microscope. Stainless steel SS316 had been etched by mixing of 20 ml hydrochloric acid (HCl), 20 ml glycerol and 10 ml nitric acid (HNO_3) for 5 minutes. After immersed in the mixing etching solution, the sample had been cleaned by water and drying by using cold air drier. The microstructure had been revealed at magnification at 200x.


(a)
200 µm


(b)
200 µm


(c)
200 µm


(d)
Precipitation
200 µm



(e)

Figure 4.0: Microstructure of SS316 stainless steel under magnification 200x (a) No stress relieving process (b) Stress relieving at temperature 415°C and 1 hour (c) stress relieving at temperature 415°C and 1 ½ hours (d) Stress relieving at temperature 900°C and 1 hour (e) Stress relieving at temperature 900°C and 1 ½ hours

Stress relieving is the process to relieve the internal stresses and there is no microstructure change happen during the process. Internal stresses are those stresses which can exist within a body in the absence of external forces. The internal stresses are happen during the different operation such as solidification of castings, welding, machining, shot peening, case hardening and precipitation. Besides, the internal stresses under certain conditions can have adverse effects. It can prove by steel with residual stresses under corrosive environment fail by stress-corrosion cracking but in general failure by stress-corrosion cracking occurs under the combined action of corrosion and externally applied stresses (Janez Urevc et al. 2009)

From the Figure 4.0b and 4.0c which had been through low temperature stress relieving process at temperature 415°C for 1 hour and 1 ½ hours . At this temperature heat treatment for samples S2A and S2B there were no sensitization happened and the corrosion rate seen to be lower than samples S3A and S3B. Low temperature stress relieving can develop high strength, will increase the proportional limit and yield strength. Low temperature stress relieving will reduce residual stress with little or no effect on the corrosion resistance and/or mechanical properties (Daniel H. Herring, 2006).

For the Figure 4.0d and 4.0e which were heat at temperature 900°C for 1 hour and 1 ½ hours. At this temperature heat treatment procedure had significant effect on the chromium concentration profile. The process of short time heat treatment brought about sensitization. Sensitization is associated with the precipitation of the chromium-rich carbide such as $Cr_{23}C_6$ or Cr_7C_3 along the grain boundaries.

During the carbide precipitation, interstitial carbon diffuses rapidly to the grain boundary. However, chromium diffusion which is much slower resulted in the chromium depleted zones at the grain boundaries. In this state the steel is susceptible to intergranular corrosion (P. Atanda, A. Fatudimu and O. Oluwole, 2010).

4.2 POTENTIODYNAMIC TEST

There were at least two electrochemical reactions, an oxidation and a reduction reaction, occur during corrosion at a metal-electrolyte interface. It is because the corrosion is due to an electrochemical mechanism, it is clear that electrochemical techniques can be used to study corrosion reactions and mechanisms. This behavior was noted for all the samples in the two solutions, Hank's and PBS with pH7.4 at 37°C.

Figure (a), illustrate a potentiodynamic polarization curve for sample in PBS and Hank's solution with pH 7.4 and temperature 37°C which corresponds to human body temperature. Figure (b) illustrates a Tafel extrapolation for the potentiodynamic polarization curve of the sample. This graph can determine the corrosion rate of the sample during the test. The polarization curves indicated that all the steel passivated immediately on immersion in the solution and the behavior can be termed as stable passivity.

The experimental Tafel extrapolation plots were analyzed. From Figure 4.1b, the vertical axis is potential and the horizontal axis is the logarithm of absolute current. The theoretical current for the anodic and cathodic reactions are shown as straight lines. The curved line is the total current, which is the sum of the anodic and cathodic currents. This is the current that you measure when you sweep the potential of the metal with your potentiostat. The sharp point in the curve is actually the point where the current changes signs as the reaction changes from anodic to cathodic, or vice versa. The sharp point is due to the use of a logarithmic axis. The use of a log axis is necessary because of the wide range of current values that must be displayed during a corrosion experiment. This point determines the potential (e_{corr}) and current density (i_{corr}) for corrosion.The cathodic (β_c) and anodic (β_a) Tafel slope,the estimated corrosion current density (i_{corr}) and estimated corrosion potential (e_{corr}),corrosion resistance (R_p) and corrosion rate are tabulated in table for PBS and Table for Hank's solution. The corrosion rate was discussed and compared between each sample that had been stress relieving with difference temperature and time.

For the sample S3A and S3B in the Figure 4.4 and 4.5, the corrosion rate seen were higher than sample S2A and S2B. This result also happens in PBS as simulated body fluid. It is because when stress relieving at this temperature the sensitization happened that severely impairs corrosion resistance for the SS316 stainless steel. Although stress relieving reduce the internal stress but in this state the sensitization might be happened and affect the corrosion resistance of the SS316 stainless steel. During sensitization the chromium and carbon in the steel combine to form chromium carbide particles along the grain boundaries throughout the steel. Formation of these carbide particles in the grain boundaries depletes the surrounding metal of chromium and reduces its corrosion resistance, allowing the steel to corrode preferentially along the grain boundaries. In this condition, intergranular corrosion can happen when localised corrosion associated with a defective microstructure carbide precipitation.

As can be seen in Table 4.1 and 4.2, the corrosion rate for the SS316 in Hank's solution is higher than the corrosion rate in PBS solution as simulated body fluid. This is due to the higher concentration of chlorine ions (Cl^-) in Hank's solution (M.Diener and R. Spolenak, 2010). This ion is among the most aggressive and corrosive to metal.

Besides that, additional inorganic compounds such as magnesium (Mg^{2+}), and sulfate (SO_4^{2-}) present in the Hank's solution. These ions react electrochemically with the surface of the material that affected the corrosion behavior and increase the corrosion rate of the SS316 stainless steel.

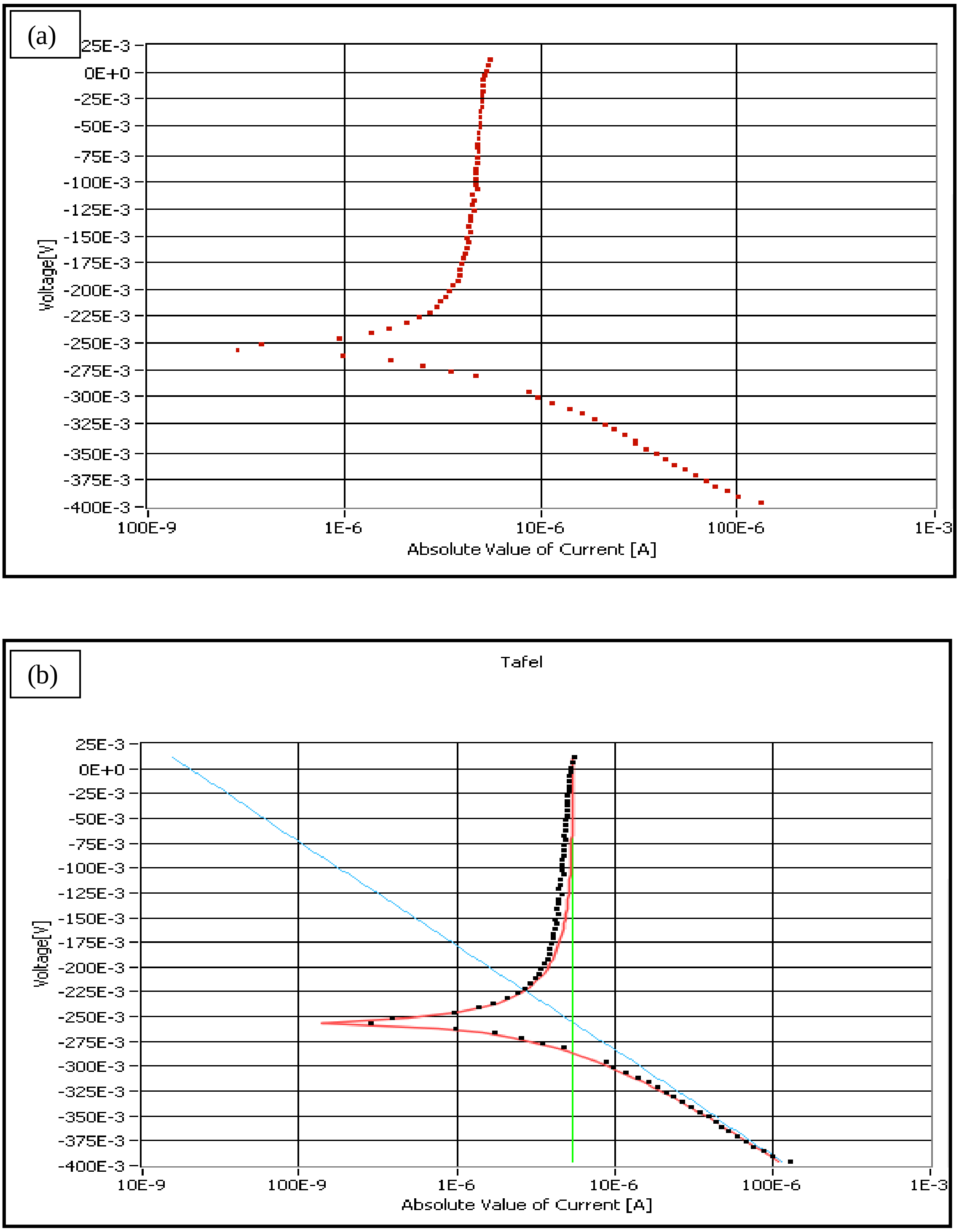


Figure 4.1: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in PBS solution at pH 7.4 and 37±2°C for SS316 stainless steel

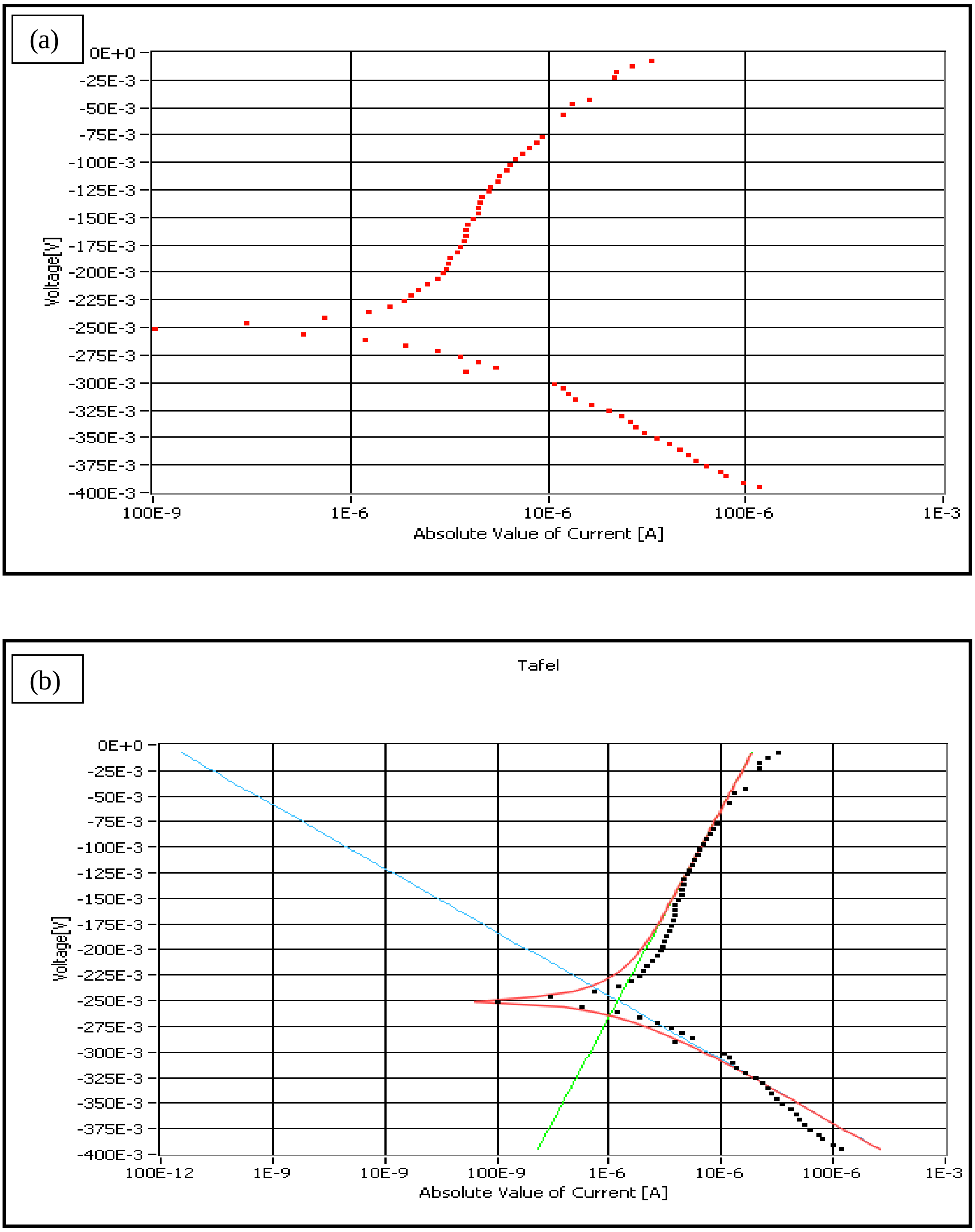


Figure 4.2: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in PBS solution at pH 7.4 and 37±2°C for stress relieving SS316 stainless steel at temperature 415°C and 1 hour.

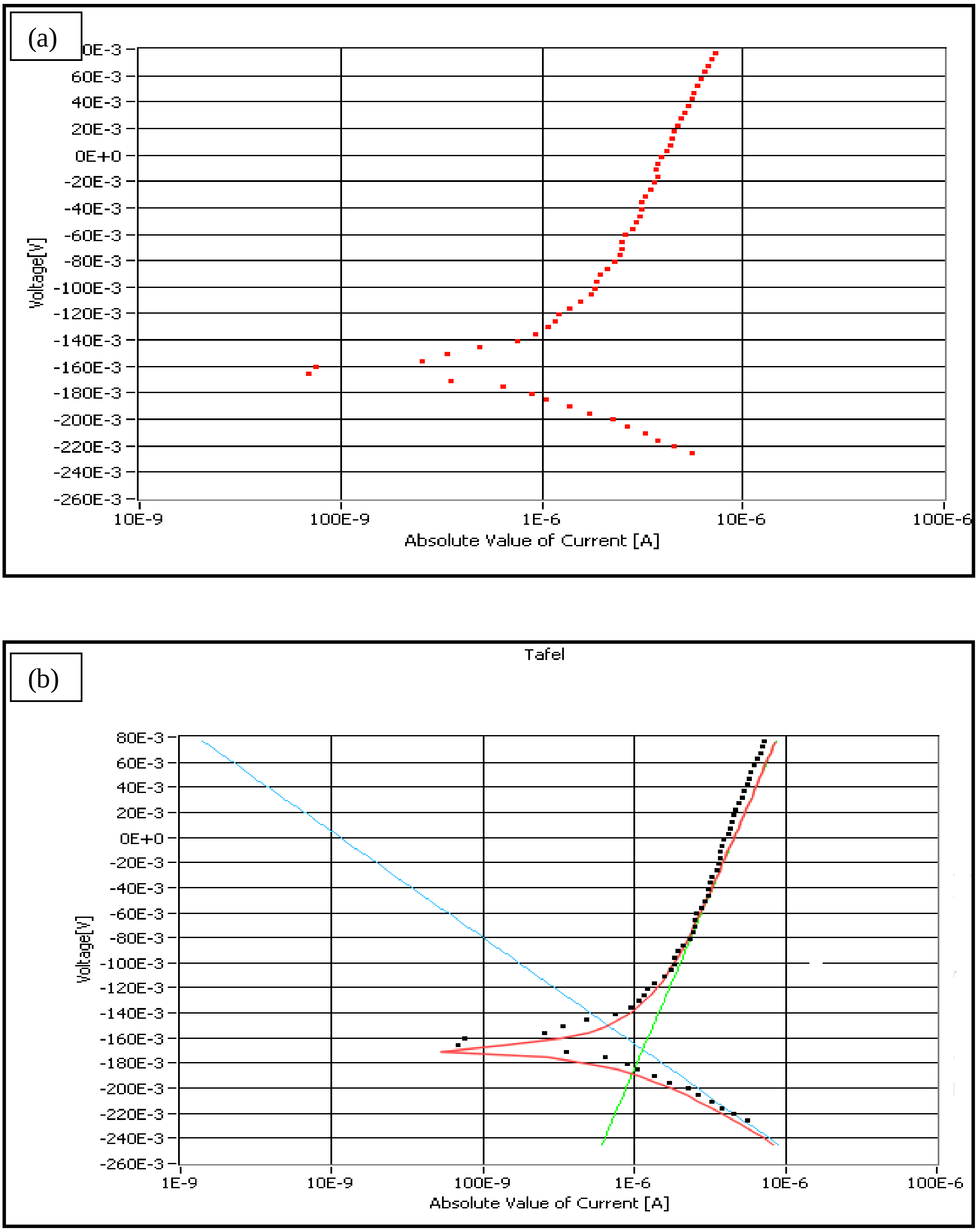


Figure 4.3: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in PBS solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 415°C and 1 ½ hours

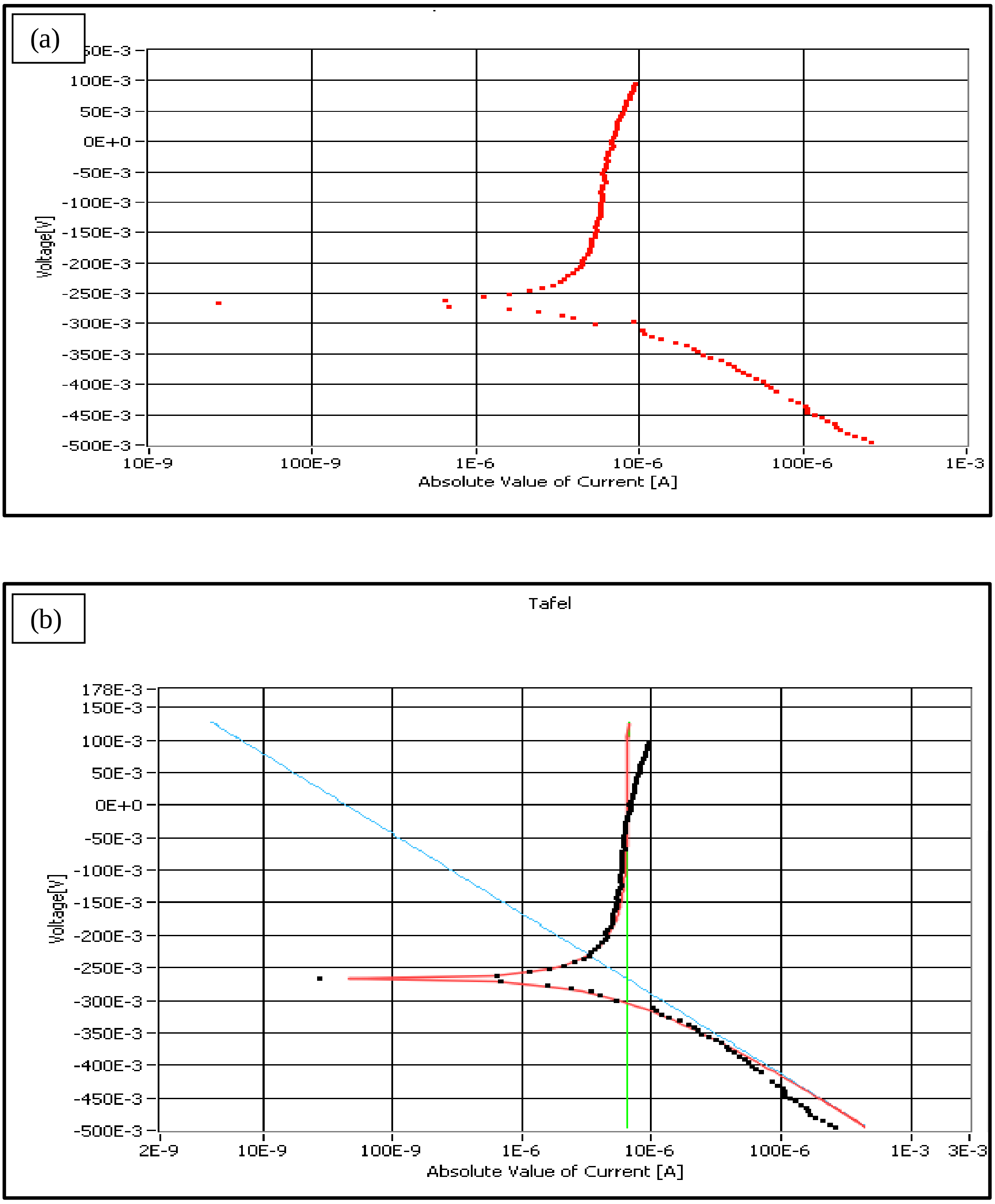


Figure 4.4: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in PBS solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 900°C and 1hour.

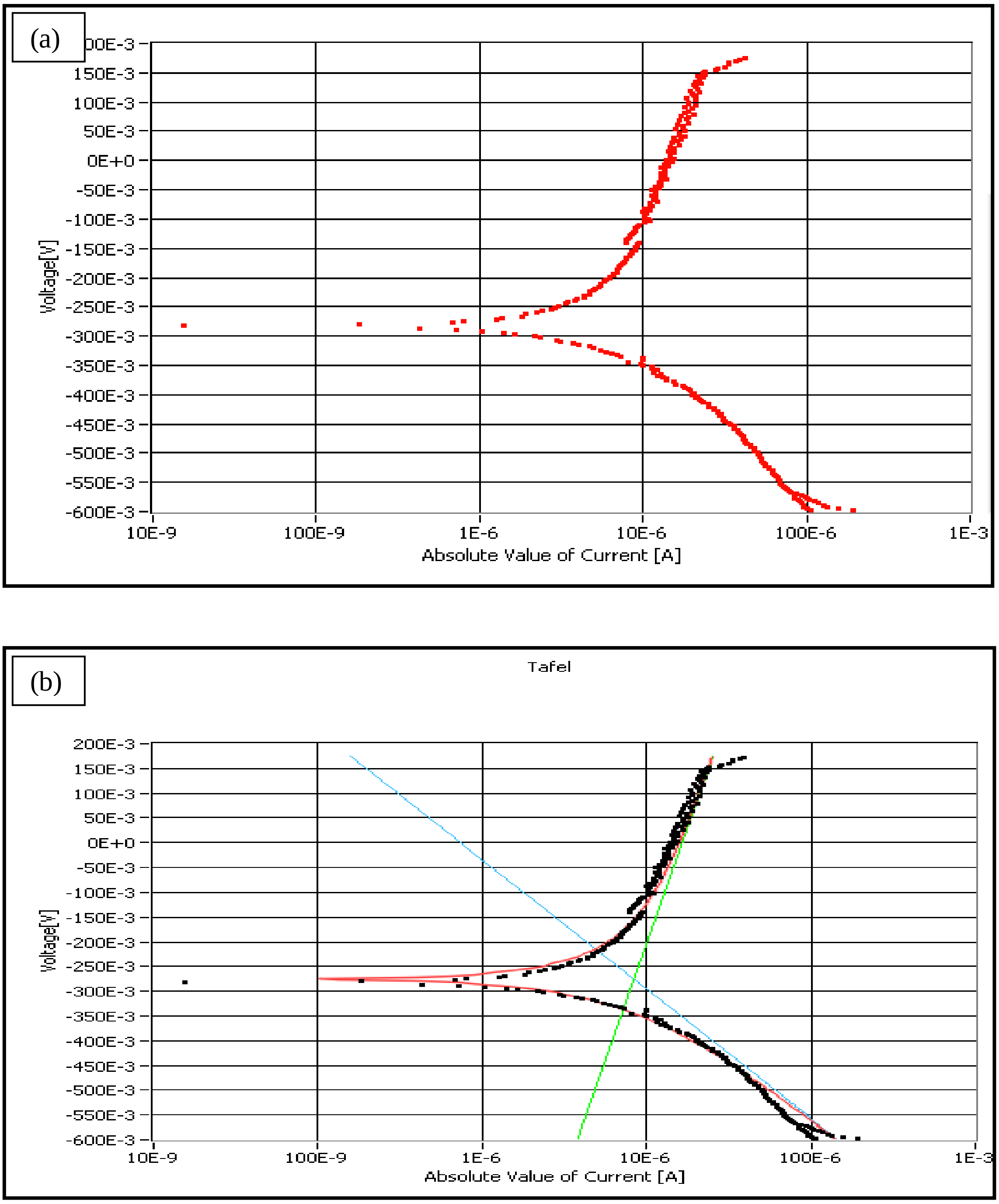


Figure 4.5: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in PBS solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 900°C and 1 ½ hours.

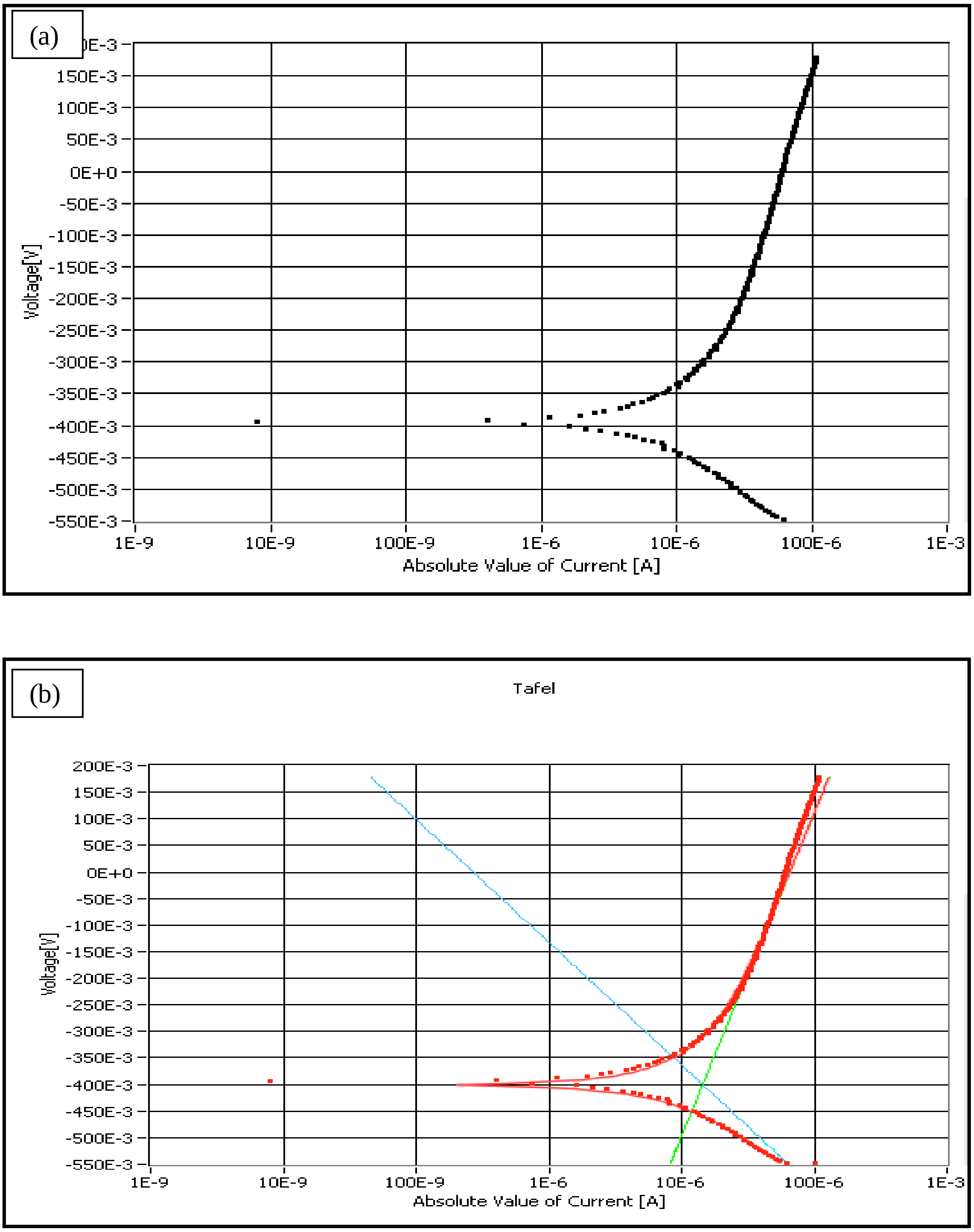


Figure 4.6: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in Hank’s solution at pH 7.4 and 37±2°C for SS316 stainless steel

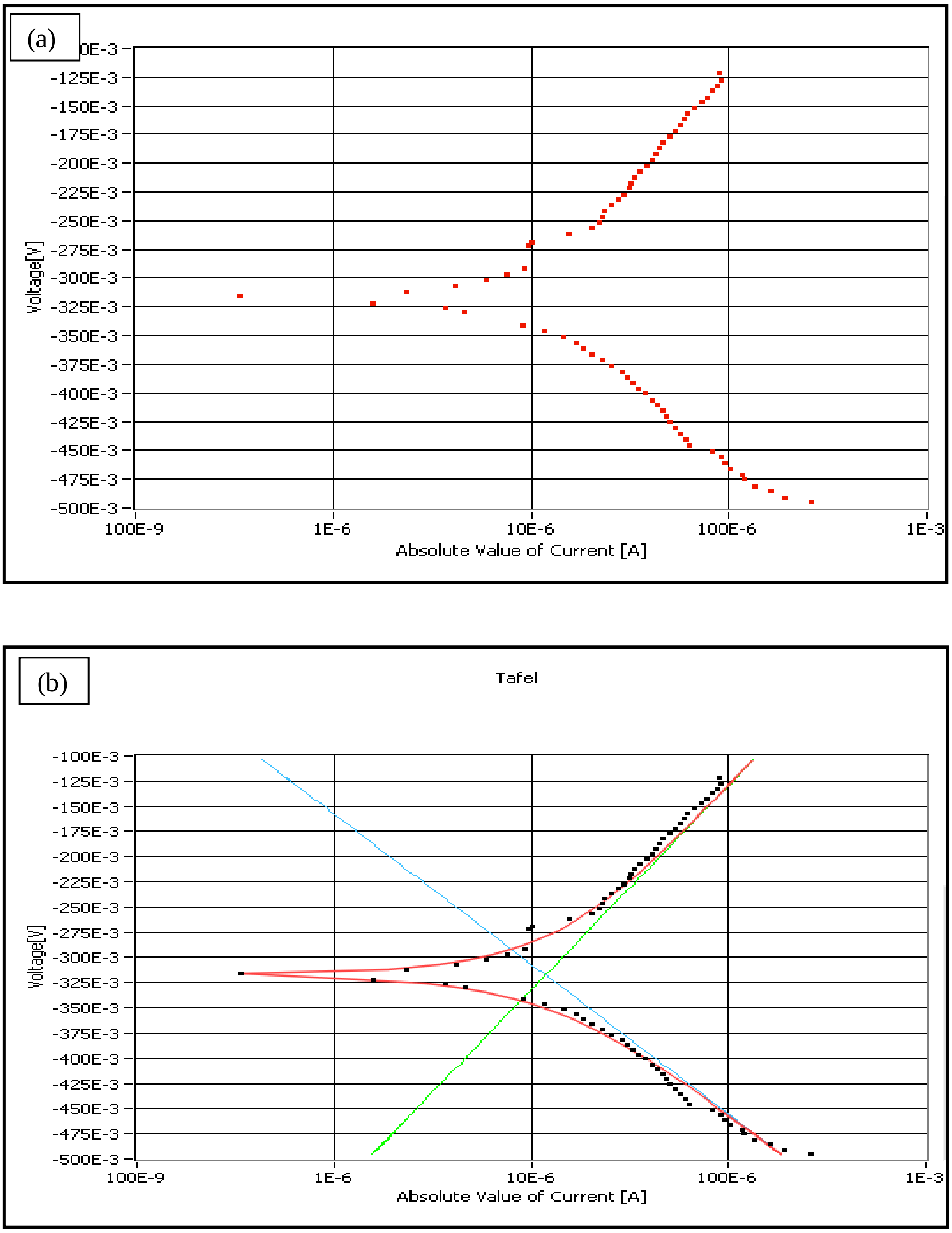


Figure 4.7: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in Hank's solution at pH 7.4 and 37±2°C for stress relieving SS316 stainless steel at temperature 415°C and 1 hour.

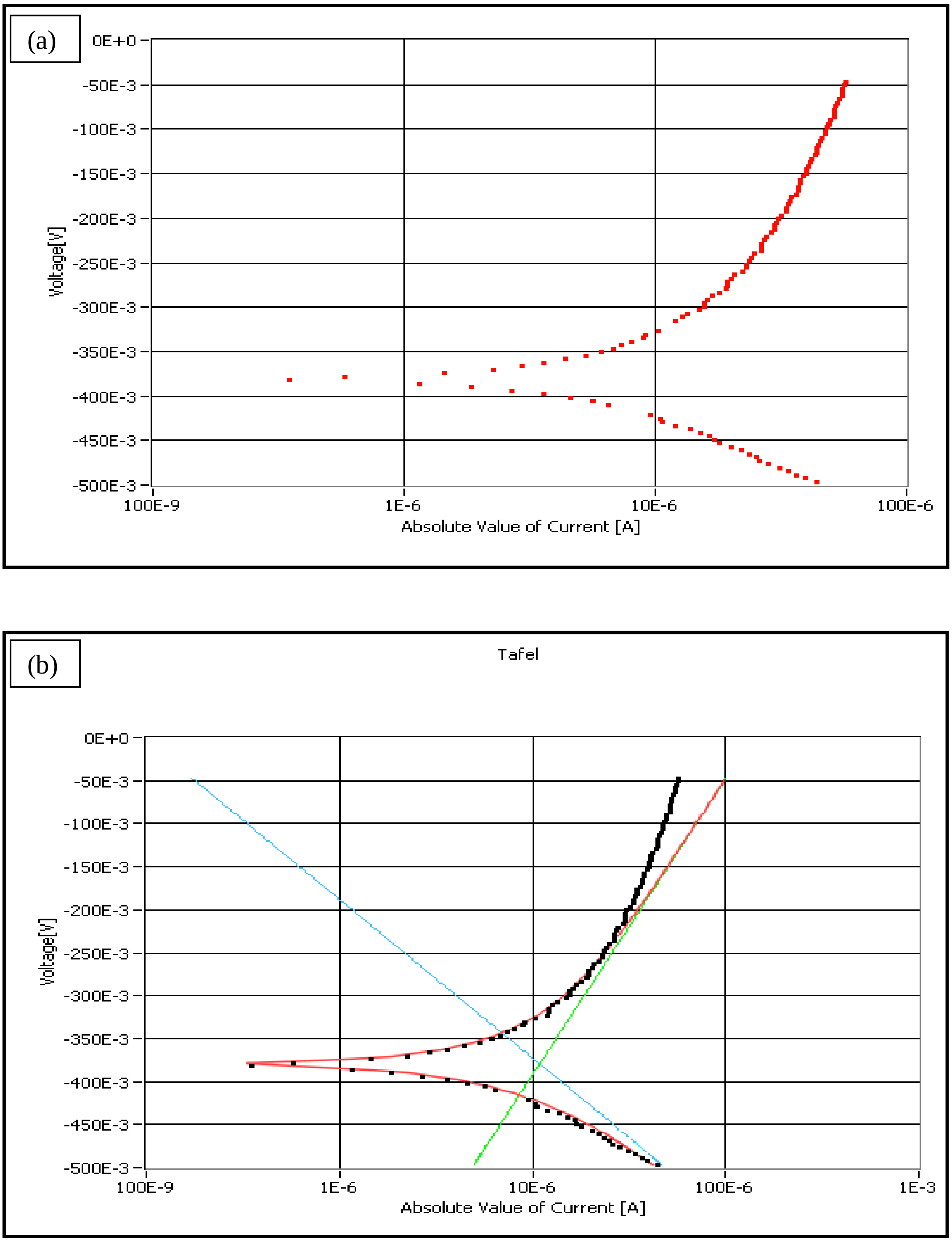


Figure 4.8: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in Hank's solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 415°C and 1 ½ hours.

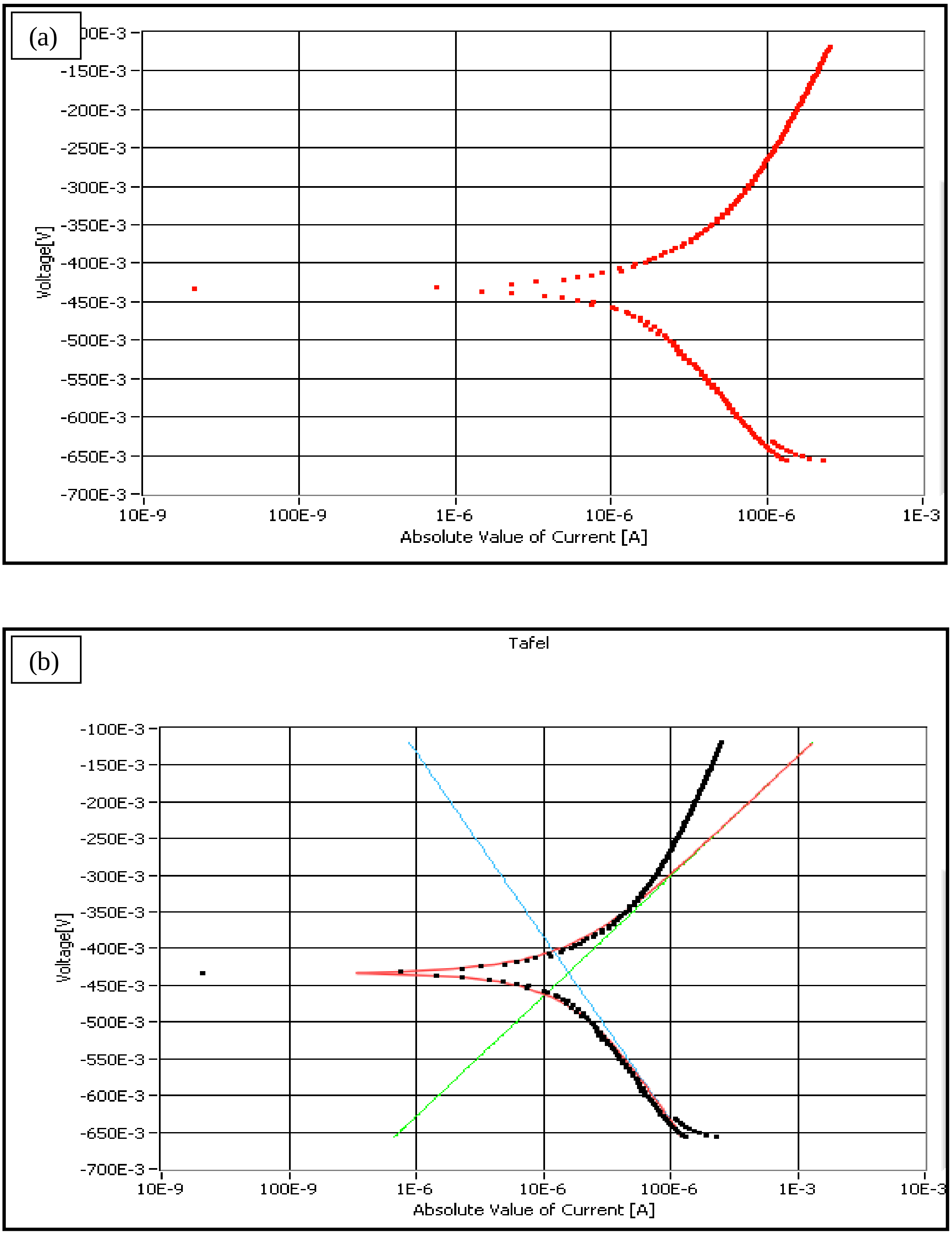


Figure 4.9: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in Hank's solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 900°C and 1 hour.

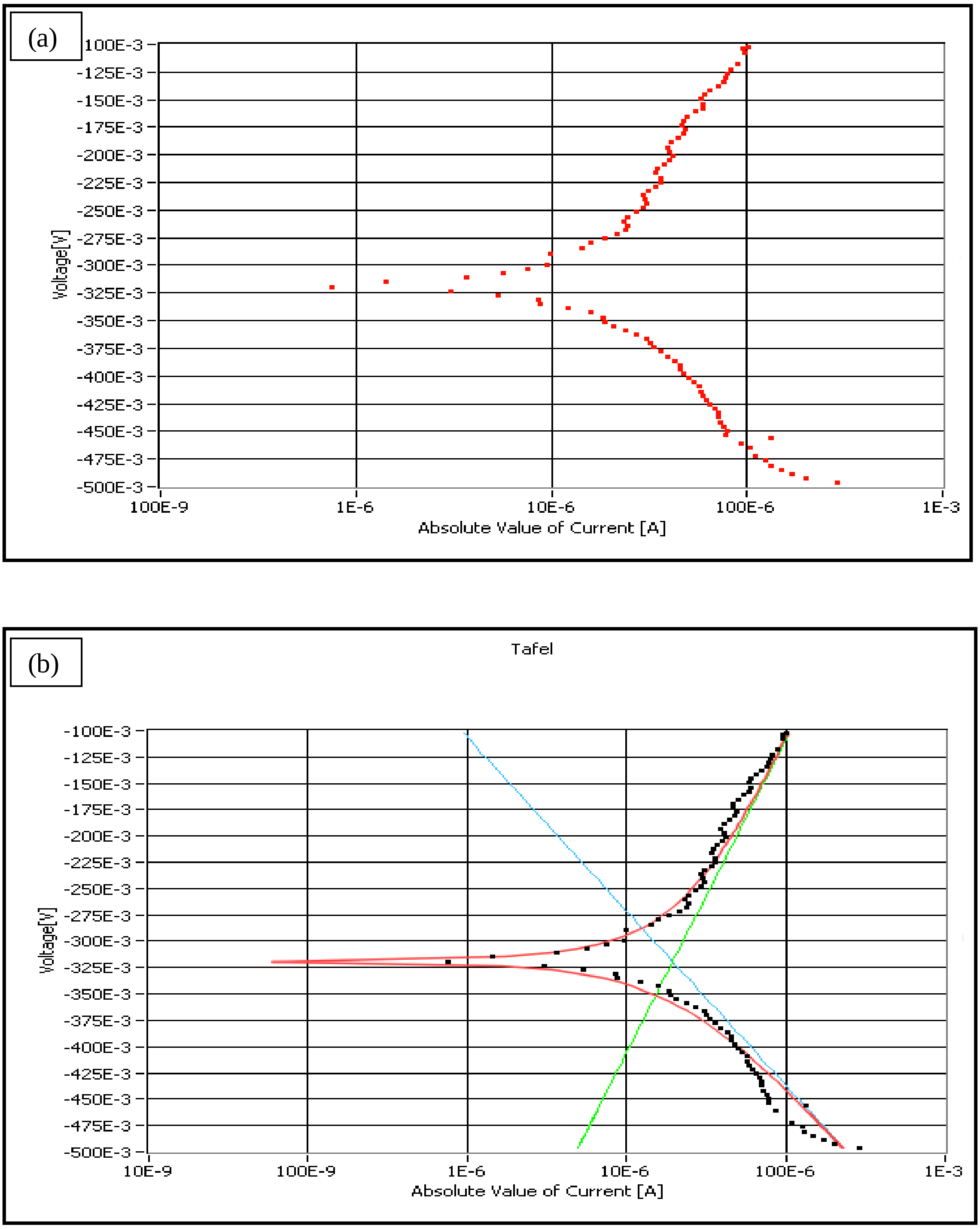


Figure 4.10: (a) Potentiodynamic polarization curve and (b) Tafel extrapolation plot obtained in Hank's solution at pH 7.4 and 37±2°C for SS316 stainless steel at temperature 900°C and 1 ½ hours.

Table 4.1: Corrosion rates determined by Tafel Extrapolation Method in PBS Solution.

Sample	E_{corr} (V)	I_{corr} (µA)	B_a (V/dv)	B_c (V/dv)	R_p (k ohm)	Cr (mm/year)
S1	-0.2715	3.758	0.879	0.087	9.185	0.008004
S2A	-0.2500	4.400	0.203	0.062	7.228	0.009556
S2B	-0.2593	4.894	0.280	0.085	7.797	0.010423
S3A	-0.2669	6.470	0.443	0.123	8.240	0.013780
S3B	-0.2756	8.377	0.939	0.261	10.599	0.017834

Table 4.2: Corrosion rates determined by Tafel Extrapolation Method in Hank's Solution.

Sample	E_{corr} (V)	I_{corr} (µA)	B_a (V/dv)	B_c (V/dv)	Rp (k ohm)	Cr (mm/year)
S1	-0.4001	14.446	0.609	0.231	5.040	0.030767
S2A	-0.3174	14.644	0.203	0.149	3.151	0.031191
S2B	-0.3794	15.111	0.345	0.185	4.797	0.032185
S3A	-0.4325	15.878	0.164	0.251	2.708	0.035818
S3B	-0.3192	19.547	0.297	0.165	2.357	0.041633

CHAPTER 5

CONCLUSION AND RECOMMENDATIONS

5.1 INTRODUCTION

For this project, the corrosion and microstructure analysis had been carried out in order to disclose the corrosion rate of the SS316 stainless steel sample in different solution namely PBS and Hank's solution when it had been through the stress relieving process.

5.2 CONCLUDING REMARKS

The following conclusions can be drawn from this study:

i. SS316 stainless steel shows increased in corrosion rate after the stress relieving process in simulated body fluid due to the formation of chromium carbides resulting in sensitization that severely impairs corrosion resistance.

ii. Lower temperature stress relieving will reduce residual stress with little or no effect on the corrosion resistance.

iii. The corrosion rate for the SS316 stainless steel in PBS solution is lower than the corrosion rate in Hank's solution as simulated body fluid. This is due to the higher concentration of chlorine ions (Cl^-) in Hank's solution that react electrochemically with the surface of metallic SS316 stainless steel to cause corrosion.

5.3 RECOMMENDATIONS

The investigation and study about the effect of heat treatment SS316 stainless steel to the corrosion behavior of steel in PBS and Hank's solution as a simulated body environment should been continued.

i. Using the other heat treatment process for introducing carbon into stainless steels without formation of carbides. It is possible to reclaim steel which suffers from carbide precipitation by heating it above 1000°C, followed by water quenching to retain the carbon and chromium in solution and so prevent the formation of carbides.

ii. Using variety solutions to see the expected effect of the SS316 performance during immersion in variety of simulated body fluid solution such as Ringer, Eagle's minimum essential medium (MEM) and Medium with cells and without cells.

iii. Using Scanning Electron Microscope (SEM) to know whether SS316 stainless steel can react in the Hank's solution and PBS as simulated body fluid.

The test and experiment should also be conducted in a good condition. In addition to that, the pH value of the solution need to be maintain at pH 7.4 according to the human body pH. Besides that, the temperature also should be maintained at 37°C as to stimulate as human body temperature. The electrochemical setup also should be connected and prepared well besides correct analysis on the polarization and Tafel plot analysis to get more accurate measurements for result analysis.

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APPENDIX A

PROJECT PLANNING (GANTT CHART): FINAL YEAR PROJECT 1

Work Progress	Week														
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Get the project title and arrange discussion time with supervisor.	■														
	▨														
Find the problem statement and project objectives.	■	■	■												
	▨	▨	▨												
Find scope of the project, hypothesis. Verify problem statement, project objectives, scope and hypothesis.			■	■											
			▨	▨											
Do research and collect the information		■	■	■	■	■	■	■	■	■	■	■	■		
		▨	▨	▨	▨			▨	▨			▨	▨		
Study and Learning the theory					■	■	■	■	■	■	■				
						▨	▨	▨	▨	▨	▨	▨	▨		
Do the design of the experiment and state the experimental procedure									■	■	■	■	■	■	■
									▨	▨	▨	▨	▨	▨	▨
Report Writing (Chapter 1, 2, 3) (Introduction, Literature review, Methodology)			■	■	■	■	■	■	■	■	■	■	■		
			▨	▨	▨	▨	▨	▨	▨	▨	▨	▨	▨		
Submit draft thesis and prepare slide presentation														■	
														▨	
Final year project 1 presentation															■
															▨

Remark:

■ Planning progress
▨ Actual progress

PROJECT PLANNING (GANTT CHART): FINAL YEAR PROJECT 2

Work Progress	**Week**															
	1	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15-18**	**19**	**20**
Material selection(SS316 stainless steel) and specimens preparation	■	■	■	■													
	▨	▨	▨	▨													
Experiment setup (stress relieving)				■	■	■											
				▨	▨	▨											
Metallographic process(grinding, polishing and mounting)							■	■									
							▨	▨									
Surface Analysis(by using inverted microscope)									■								
									▨								
Experiment setup (electrochemical method)										■	■						
										▨	▨						
Report writing (chapter 4 and 5)							■	■	■	■	■	■	■				
							▨	▨	▨	▨	▨	▨	▨				
Submit draft thesis and prepare slide presentation													■	■			
														▨			
Submission draft 2,3,4 and logbook															■		
															▨		
Final year project 2 presentation																■	
																▨	
Submit thesis report																	■
																	▨

Remark:

■ Planning progress
▨ Actual progress