FINAL YEAR PROJECT II

NITRIDING OF 2205 DUPLEX STAINLESS STEELS TO ENHANCE CORROSION RESISTANCE

By

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CERTIFICATION OF APPROVAL

Of Research Project

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A project dissertation submitted to the

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TRONOH, PERAK

JANUARY 2016

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

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ABSTRACT

Nitriding process had become favorable surface heat treatment in order to improve the corrosion resistance by case hardening process on the material. The case hardening is produced by diffusion of nitrogen and precipitation of the nitride layer on the surface of material. Due to high alloying element, duplex stainless steel shows complex precipitation behavior by forming different intermetallic phase which reduce corrosion resistance in harsh environment such as high temperature in seawater, carbon dioxide and hydrogen sulphide environment. Thus, high temperature gas nitriding process is introduced. In this project, the high temperature gas nitriding process was conducted on 2205 duplex stainless steel at 1200°C for 8 hours and subjected to re-heating at temperature of 700°C to prevent the effect of sensitization. The corrosion resistance is analyzed by immersion test using weight loss method. The samples are subjected to metallographic process to investigate the effect of microstructure after nitriding process using optical microscopy (OM) and scanning electron microscopy (SEM). The uniformity of nitrogen diffusion is identified by using energy dispersive spectroscopy (EDS) on SEM. Based on the results, the corrosion resistance is increased 43.85% after nitriding process due to formation of austenite phase on surface layer. From microstructure analysis, three zones were formed in nitrided samples which is fully austenitic layer zone, a transition zone composed of an austenitic matrix containing islands of remaining ferrite, and inner zone composed of austenite and ferrite phase. Based on EDS of SEM, the interstitial diffusion of nitrogen diffusion is uniformed from sample 1 to sample 5 with tolerance of $\pm 1.2\%$. Therefore, the nitriding process improves 43.85% corrosion resistance of 2205 duplex stainless steel compared to untreated sample.

Keywords: Gas Nitriding; Duplex Stainless Steels; Corrosion; Microstructure; Uniformity

ACKNOWLEDGEMENT

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

Duplex stainless steels (DSS) are used in variety of applications and have good corrosion resistance but poor wear resistance. This steel contains minimum chromium composition of 21% thus posses good corrosion resistance. One of the major problem is the corrosion and wear in the inner and outer surface of the piping especially in oil and gas industry where duplex stainless steel is still not good enough to withstand the very corrosive environment. The environment includes the tertiary recovery method such as corrosion and wear problem in gas injection well pipe and production well pipe. To overcome this problem, duplex stainless steels are subjected to nitriding process to improve mechanical properties, wear and corrosion resistance.

There are three types of nitriding process such as gas nitriding, salt bath nitriding and plasma nitriding. For this project, the work was concentrated on high temperature gas nitriding where it was conducted in the range of 1000 °C to 1200°C in order to avoid the formation of nitrides which cause the decreasing in corrosion resistance. Basically, DSS produce surface films which have chromium-rich oxide nature that is formed and heals itself in the presence of oxygen to avoid direct contact between metal and environment. Duplex stainless steels have been widely used in many industry application for example for pressure vessels, underwater pipeline and offshore facilities in oil and gas industry while for other industries such as marine environments, pollution control equipment, pulp and paper manufacturing and many more.

1.2 Problem Statement

Duplex stainless steels have been widely used especially in oil and gas industry such as offshore platforms, oil and gas refineries and many more. Due to high alloying element, duplex stainless steel shows complex precipitation behavior by forming different intermetallic phase which reduce corrosion resistance in harsh environment such as high temperature in seawater, carbon dioxide and hydrogen sulphide environment.

The exposure to carbon dioxide environment will lead to sweet corrosion and exposure to hydrogen sulphide environment will lead to sour corrosion. The sweet and sour corrosion problem can occur in tertiary recovery method such as gas injection method as shown in Figure 1.1
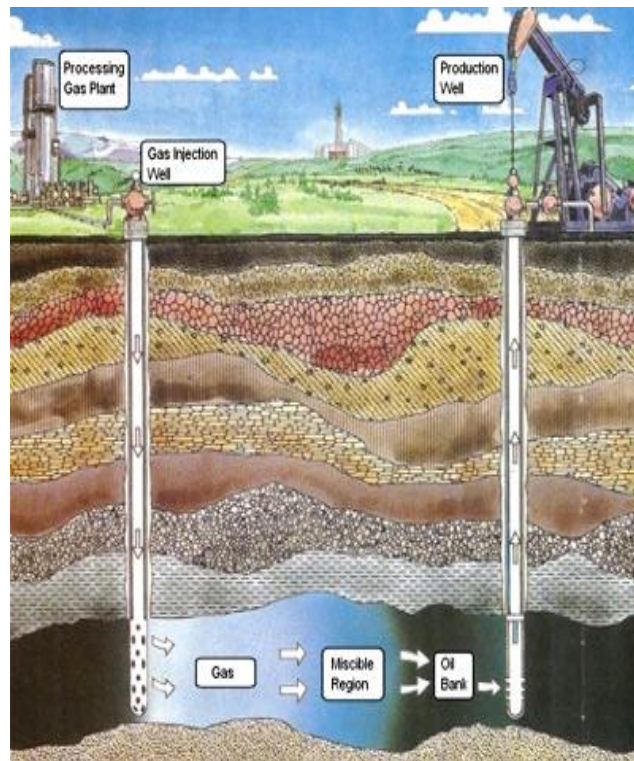
Figure 3.1: Gas Injection and Production Well

The corrosion is susceptible to gas injection well piping, production well piping and up to blow up preventer until downstream piping. The gas injection process introduces miscible gas into the reservoir. The gases can either expand and push gases through the reservoir or mix and dissolve in the oil. Thus it will decrease the viscosity of the flow and increasing the flow into the production well piping. Most common gas used for injection gas is carbon dioxide which becomes source of sweet corrosion. The composition of oil and natural gas in the reservoir contain hydrogen sulphide which becomes source to sour corrosion. Moreover, in the presence of hydrogen sulphide and chloride environment, the risk of stress corrosion racking at low temperature is increase. In addition, the deficiencies during fabrication such as heat treatment and welding, the volume ratio of ferrite and austenite is slightly varies than it supposed to be which is 1:1 due to precipitation of various compounds for example chromium carbides and nitrides will have an impact on mechanical and corrosion resistance properties.

1.3 Objectives

The objectives of this project are:

- To study the effect of nitriding of duplex stainless steels on corrosion resistance
- To investigate the effect of nitriding on microstructure of duplex stainless steels
- To identify the uniformity of nitride layer after nitriding process

1.4 Scope of Study

This project is mainly focus on effect of gas nitriding process on the 2205 duplex stainless steel piping especially on the corrosion resistance which uses immersion test method. This study also covers the investigation of microstructure changes using Optical Microscope and Scanning Electron Microscope (SEM). The uniformity of nitrogen diffusion is identified using Energy Dispersive Spectroscopy (EDS) on SEM

CHAPTER 2

LITERATURE REVIEW

2.1 Stainless Steels

Stainless steels have been widely used in industry application where corrosion resistances play a very important role. One of the compositions in stainless steel which is chromium as alloying element forms a very stable passive layer to protect the steel. However, stainless steel have disadvantage of extensive wear which cause problems in existing application and limit the applicability of material. There are several types of stainless steel which are ferritic, martensitic, austenitic and duplex [1]. The ferritic steels comprise of magnetic, low carbon content and chromium as the prime alloying element, typically at the 13% and 17% levels. The martensitic steels are magnetic, containing typically 12% chromium and moderate carbon content. They are hardenable by quenching and tempering like plain carbon steels and find their main application in cutlery manufacture, aerospace and general engineering. The austenitic steels are non-magnetic and, in addition to chromium typically at the 18% level, contain nickel, which increases their corrosion resistance. They are the most widely used group of stainless steels. Duplex steels are used where combinations of higher strength and corrosion resistance are needed. Super austenitic grades and precipitation hardened grades of steel are also available

2.2 Duplex Stainless Steel

Duplex stainless steels basically comprise of 2 phase which is the mixture of austenite and ferrite phases [2]. The mechanical properties of austenitic stainless steels are low which is low strength and low resistance to stress corrosion cracking while ferrite stainless steel mechanical properties also low in strength but higher a bit than austenitic,

poor toughness in low temperature and poor weldability in thick section [3]. The combination of austenite and ferrite phase produce duplex stainless steels which are higher mechanical properties in terms of strength and ductility and good corrosion resistance especially stress corrosion cracking. Table 1.1 shows the chemical composition of the duplex stainless steel grade S31803 [4].

Table 3.1: Chemical Composition of S31803

Composition	Weight (%)
Carbon	0.03 (max)
Manganese	2 (max)
Phosphorus	0.03 (max)
Sulfur	0.02 (max)
Silicon	1 (max)
Chromium	21-23
Nickel	4.5-6.5
Nitrogen	0.08-0.2
Molybdenum	2.5-3.5

Nilsson has divided the modern duplex stainless steel into four different types [5] according to their alloying element amount. First was low cost molybdenum free [6]duplex stainless steel of the type 23Cr-4Ni-0.1N or also called as lean duplex and these steels provide alternatives to AISI 304 and 306. The second category is DSS of the type 22Cr-5Ni-3Mo-0.17N or called as standard duplex. This type of DSS lies between AISI 316 and 6% Mo + N super austenitic grades. The third category is super DSS of the type 25Cr-7Ni-3.7Mo-0.27N having PRE values greater than 40. Lastly is hyper duplex which having PRE greater than 48.

2.3 High Temperature Gas Nitriding Process

Nitriding is nitrogen diffusion into the metal process in order to generate case-hardened surface. Generally, there are three types of nitriding which is gas nitriding where applied in this project, salt bath nitriding and plasma nitriding. All of these types of nitriding shared the same purpose which is to generate case-hardened surface but the only different is the process involved. Nitrogen diffusion in the steels will improve mechanical properties, corrosion and wear resistance. High temperature gas nitriding process allows nitrogen to infuse through diffusion process by addition of nitrogen. It is usually applied to chromium based materials such as austenitic, martensitic and duplex stainless steel where these materials contain high nitrogen solubility in austenite phase [7].

High temperature nitriding process is solid state nitrogen alloying technique which permeates nitrogen gas into stainless steels in the range of 1000°C-1200°. The nitrogen atom is extracted from nitrogen gas (N_2) or ($N_2 + Ar$) gas and permeate into the core direction which allow high nitrogen content around (0.5 to 1.0 wt%) to dissolve in austenitic range without nitride formation [8]. This treatment is slightly different from conventional nitriding where generally conducted between 475°C to 575°C which cause chromium nitride precipitation that will increase the hardness but impairing the corrosion resistance [8]. The nitrogen atom is small enough to diffuse into interstitial position inside the work piece [9]. The result of series of nucleated growth areas is generated on the surface of the steel or called as compound layer with the diffused and reacted nitrides formed along the surface called the diffusion zone is the beginning formation of case-hardened.

The nitriding process is expected to improve mechanical properties such as strength and hardness, wear and corrosion resistance and also improvement in term of arrangement, stability and bonding in microstructure. In the traditional gas nitriding, the growth of the

nitrided layer is limited. The sensitization often the problem in stainless steel usually occur on elevated temperature where the depletion of chromium happens by formation of the chromium nitride or chromium nitride which avoid the formation of Cr_2O_3 passive layer in stainless steels. Hence, it leads to reduction of corrosion resistance in stainless steels [10]. Besides, the expanded austenite or S phase was formed during nitriding process. The expanded austenite or S phase contain nitrided layer which was free from the chromium nitride precipitation and supersaturated with nitrogen in solid solution. In addition, it contributes to increase corrosion resistance owing to presence of chromium in solid solution which acts as corrosion protection [11]. Nitrogen concentration at the surface cannot be properly controlled and excessively porous and brittle superficial compound layer can formed due to oversaturation of the nitrogen. The corrosion and wear resistance only improved when the porosity of the work piece is low [9].

2.4 Corrosion Resistance

DSS is considered as good corrosion resistances especially pitting corrosion and stress corrosion cracking. These advantages cause DSS is preferable in such pressure vessels, pipe lines and offshore facilities [12]. However, in very harsh environment containing hydrogen sulphide and chloride at low temperature, the risk for pitting and stress corrosion is high. Generally, pitting corrosion is localized corrosion where dissolution of the metal happens owing to breakdown of protective passive film on metal surface. This occurs due to presence of aggressive anionic species mainly by chloride ion [13] . Ion from the anode is transferred to the cathode through electrolyte allow pitting corrosion to happen which result in only small amount of metal is corroded or called as localized attack [14]. Pitting corrosion leads to other corrosion because it initiates sites for fatigue cracks and stress corrosion crack. Basically the chemical composition mainly chromium, molybdenum and nitrogen is the main factor assisting to pitting corrosion resistance. The effects of these chemical compositions in pitting corrosion can be calculated using the empirical parameter termed as pitting resistance equivalent number (PREN) as defined as in equation (1) below:

$$PREN = \%\,Cr + 3.3(\%Mo) + 16(\%N) \qquad\qquad (1)$$

where Cr = Chromium

Mo = Molybdenum

N= Nitrogen

The PREN value higher than 32 is considered seawater (corrosion) resistance. Usually, the PREN for duplex stainless steel is equal or higher than 40. Even though this empirical parameter is only limited to three elements, it can be use to estimate the pitting corrosion resistance. The alloying additions of nitrogen during the manufacturing of duplex stainless steel also increase the pitting corrosion resistance especially in the chloride environment such as the seawater [6].

Stress corrosion cracking is the corrosion that happens by the process involving conjoint corrosion and straining of metal due of the stress applied and corrosion environment [15]. Both stress and corrosion environment must be present for this type of corrosion to happen. Stress corrosion cracking is very harmful because it can unexpectedly happen and rapidly which lead to failures of the structure. In addition the stress also may come during the manufacturing process which called as residual stress. There are three conditions for stress corrosion cracking to happen which are a susceptible material, the corrosion environment and sufficient tensile stress to induce stress corrosion cracking. The mechanism of stress corrosion cracking is the active path dissolution where the most common path is grain boundary. The passivation of the metal is disturbed and makes it harder to happen due to segregation of impurity element. Second mechanism is hydrogen diffuse and dissolve in metal atoms. Hydrogen tends to attracted to high tensile strength and at once it is diffused to the region of cracks under the stress. The hydrogen contributes to crack by making a cleavage easier and develop plastic deformation in the metal.

CHAPTER 3

METHODOLOGY

3.1 Project Flowchart

```
            ┌─────────────────┐
            │      START       │
            └─────────────────┘
                     │
            ┌─────────────────┐
            │ Identify problem and │
            │ gather information   │
            └─────────────────┘
                     │
         ┌──────────────────────┐
         │ Project Methodology Planning │
         │   and nitriding process      │
         └──────────────────────┘
                     │
         ┌──────────────────────┐
         │   Apparatus, equipment       │
         │   and sample preparation     │
         └──────────────────────┘
                     │
   ┌────────────┬────────────┬────────────┐
┌──────────┐ ┌──────────┐ ┌──────────┐
│ Microstructure │ Corrosion │ Chemical │
│   Analysis     │ Resistance Analysis │ Composition Analysis │
└──────────┘ └──────────┘ └──────────┘
   └────────────┬────────────┘
         ┌──────────────────┐
         │  Documentation    │
         └──────────────────┘
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         ┌──────────────────┐
         │       END         │
         └──────────────────┘
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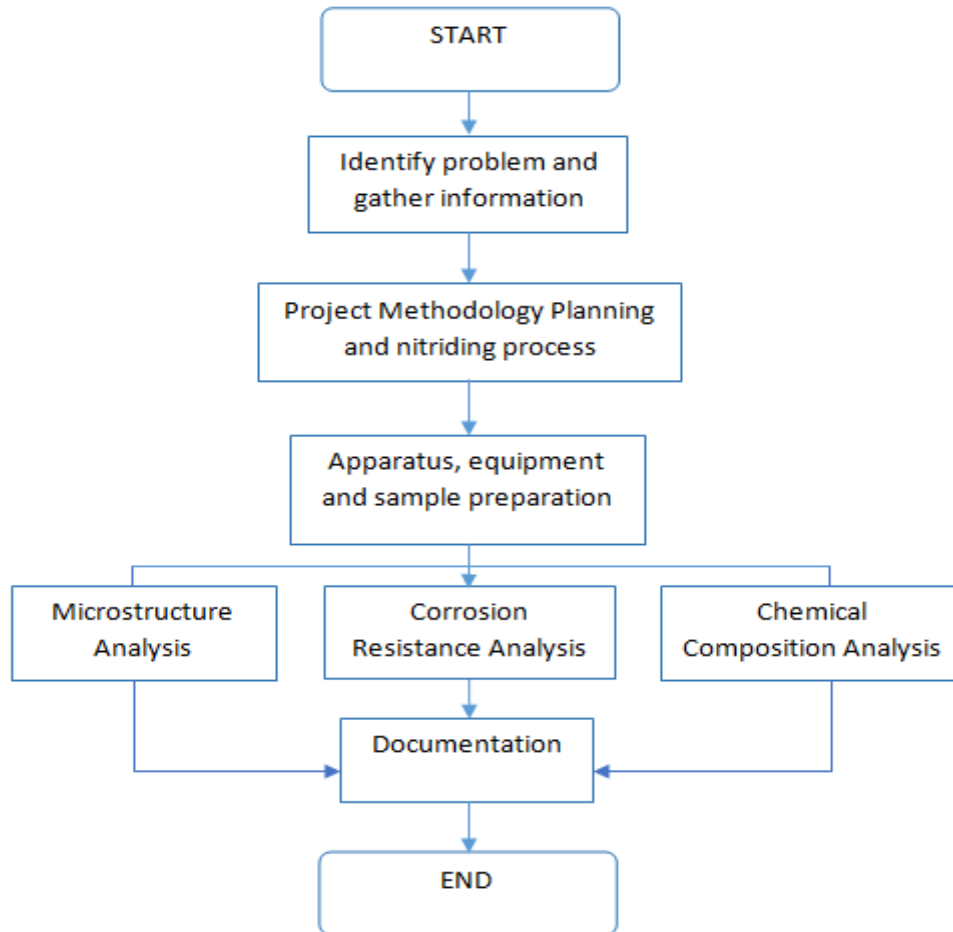
Figure 3.1: Project Flowchart

Figure 3.1 shows the project flowchart as a guide for overall process in this project. The project starts with identifying problem and information gathering. The planning of methodology method was identified and preparations of apparatus set up were done. Three analyses were done which include microstructure, corrosion resistance and chemical composition analysis. Lastly the documentation for report compilation was done.
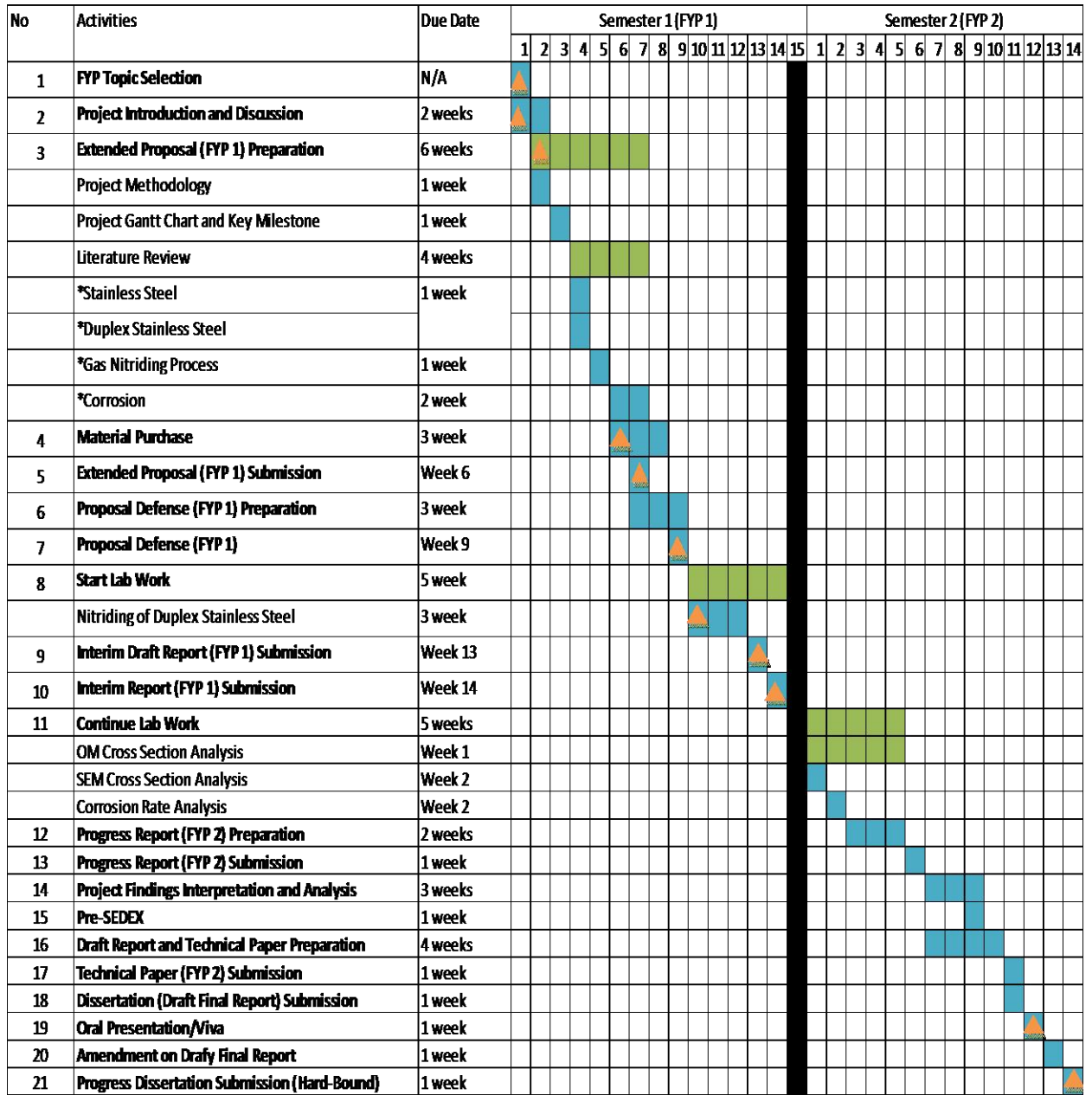
3.2 Gantt Chart

No	Activities	Due Date	S1-1	S1-2	S1-3	S1-4	S1-5	S1-6	S1-7	S1-8	S1-9	S1-10	S1-11	S1-12	S1-13	S1-14	S1-15	S2-1	S2-2	S2-3	S2-4	S2-5	S2-6	S2-7	S2-8	S2-9	S2-10	S2-11	S2-12	S2-13	S2-14
1	FYP Topic Selection	N/A	▲																												
2	Project Introduction and Discussion	2 weeks	▲	░																											
3	Extended Proposal (FYP 1) Preparation	6 weeks		▲	▓	▓	▓	▓																							
	Project Methodology	1 week		░																											
	Project Gantt Chart and Key Milestone	1 week			░																										
	Literature Review	4 weeks				▓	▓	▓																							
	*Stainless Steel	1 week				░																									
	*Duplex Stainless Steel					░																									
	*Gas Nitriding Process	1 week					░																								
	*Corrosion	2 week						░																							
4	Material Purchase	3 week					▲	░	░																						
5	Extended Proposal (FYP 1) Submission	Week 6						▲																							
6	Proposal Defense (FYP 1) Preparation	3 week							░	░	░																				
7	Proposal Defense (FYP 1)	Week 9									▲																				
8	Start Lab Work	5 week										▓	▓	▓	▓																
	Nitriding of Duplex Stainless Steel	3 week										▲	░	░																	
9	Interim Draft Report (FYP 1) Submission	Week 13													▲																
10	Interim Report (FYP 1) Submission	Week 14														▲															
11	Continue Lab Work	5 weeks																▓	▓	▓	▓										
	OM Cross Section Analysis	Week 1																▓	▓	▓	▓										
	SEM Cross Section Analysis	Week 2																░													
	Corrosion Rate Analysis	Week 2																	░												
12	Progress Report (FYP 2) Preparation	2 weeks																		░	░										
13	Progress Report (FYP 2) Submission	1 week																				░									
14	Project Findings Interpretation and Analysis	3 weeks																					░	░	░						
15	Pre-SEDEX	1 week																					░								
16	Draft Report and Technical Paper Preparation	4 weeks																						░	░	░					
17	Technical Paper (FYP 2) Submission	1 week																									░				
18	Dissertation (Draft Final Report) Submission	1 week																									░				
19	Oral Presentation/Viva	1 week																											▲		
20	Amendment on Drafy Final Report	1 week																												░	
21	Progress Dissertation Submission (Hard-Bound)	1 week																													▲

Figure 4.2: Gantt Chart for FYP 1 and FYP 2

▓ Major Process
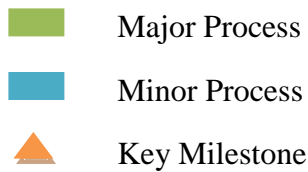
░ Minor Process

▲ Key Milestone

Figure 3.2 shows the gantt chart of project planning for Final Year Project 1 and Final Year project 2. The gantt chart is created based on the guideline and suitable timeline

3.3 Key Milestone

Table3.1: Key Milestone

Key Milestone	Description
FYP Topic Selection	FYP topic is selected based on interest and experience
Project Introduction and Discussion	Briefing on topic selected and discussion of further improvement
Extended Proposal Preparation	Prepare and submit to supervisor for checking purpose and fulfill criteria in form 04
Material Purchase	Start buying material needed and estimate arrival of material to start the project
Extended Proposal Submission	Finish and submit extended proposal to supervisor and FYP Coordinator for endorsement of supervisor
Proposal Defense	Oral presentation to supervisor and internal examiner
Nitriding of Duplex Stainless Steel	Place duplex stainless steel piping inside the furnace and ensure the flow of nitrogen gas
Study on microstructure changes after nitriding	Analysis the microstructure changes after nitriding using optical and scanning electron microscope
Interim Draft Report Submission	Prepare and submit the draft of interim report based on guideline given
Interim Report Submission	Submit interim report to supervisor, internal examiner and FYP Coordinator for endorsement from FYP Coordinator

Table 3.1 shows the key milestone for this project. This key milestone should be achieved based to ensure the project follow the timeline.

3.4 Procedure

3.4.1 Material

In this project, 2205 duplex stainless steel with grade S31803 piping undergo nitriding process and analysis of corrosion, microstructure, uniformity of diffusion and hardness is done. The quantity of pipe purchased is only one with specification in Table 3.2:

Table 4.2: Specification of Sample

Specification	Dimension (mm)
Length	1000
Diameter	33.4
Thickness	3.8

3.4. 2 Project Activities

Task 1: Sectioning

Figure 3.3: Abrasive Cutter

Procedure:

1) Abrasive cutter machine as shown in Figure 3.3 is used to cut the piping into 2 sections with dimension of 5cm length, 3.34cm diameter and 0.38cm thickness where 1 part undergo nitriding process and another part is untreated sample

2) The piping was clamped and locked to ensure no excessive vibration and fix the position

3) The machine cover was closed for safety purpose during cutting process

4) The machine cover was opened and samples are removed

Task 2: High Temperature Gas Nitriding Process

Figure 3.4: Alumina Tube Furnace

Procedure:

1) The native oxide layer was removed before nitriding process to ensure the nitrogen can diffuse efficiently into the piping outer and inner surface by grinding using grit paper

2) Figure 3.4 shows the alumina tube furnace. The sample was put into the furnace on the crucible to ensure the surface of the pipe not touching the alumina tube to avoid the scratch of alumina tube

3) The nitriding temperature is adjusted to 1200°C with heating rate of 20°C/min. The time set for temperature to rise 1200° C is 1 hour

4) The flow meter is calibrated to 2 atm and the bubble will start to produce in conical flask contained water to ensure presence of nitrogen flow into the furnace

5) After temperature stable reach to 1200°C, the valve of nitrogen tank will be opened as the source of nitrogen to flow into gas mixing system and through tube furnace

6) After 8 hour, the tank will be closed and the furnace will be leaved until reach the room temperature.

7) The sample is re-heated again at temperature of 700°C for 1 hour to minimize the effect of sensitization. The time set for temperature to rise to 700°C is 1 hour with heating rate of 11.7°C/min

8) The furnace will be opened and the sample will be removed

Task 3: Sectioning
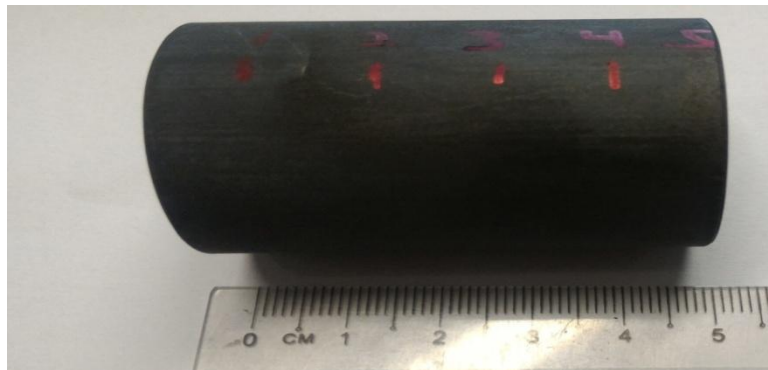
Figure 3.5: Sectioning of Nitrided Sample

Procedure:

1) Abrasive cutter machine is used to cut the nitride sample into 5 sections as shown in Figure 3.5

2) The sample is clamped and locked to ensure no excessive vibration and fix the position

3) The machine cover was closed for safety purpose during cutting process

4) The machine cover was opened and samples were removed

5) Step 2 until 4 is repeated to cut the cross-section of the all section into half

Task 4: Sample Preparation for Optical Microscopy (OM) and Scanning Electron Microscopy (SEM)

    I.   Hot Mounting
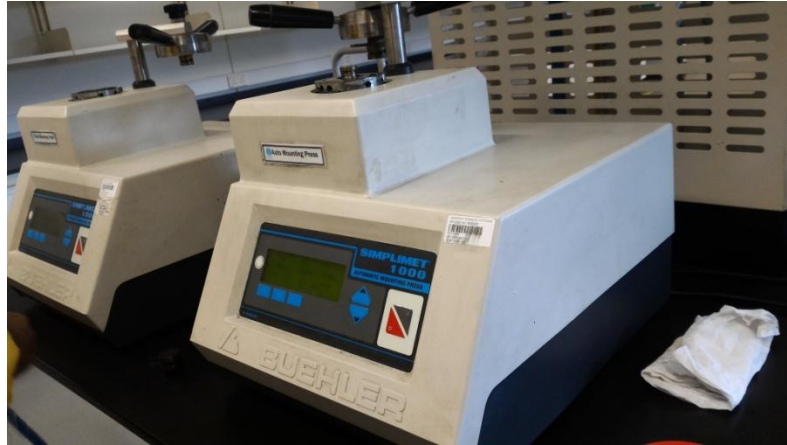
Figure 3.6: Auto Mounting Press Machine

Procedure:

1) Figure 3.6 shows auto mounting press machine. The samples mounted by using auto mounting press machine.

2) The surface of the sample is cleaned and release agent phenolic was used to ensure the surface was free from dust. The powder then added into mounting machine with the surface for microscopy analysis was faced down to the machine.

3) The water was opened and the cycle started based on the parameter required such as heating for 3 minute, cooling for 2 minute and pressure of 4000psi. The pre heat duration is 6 minutes.

II. Grinding and Polishing

Figure 3.7: Motor Driven Wheel

Procedure:

1) Figure 3.7 shows the motor driven wheel. The abrasive paper that mounted was used in grinding process.
2) The water is used which acted as lubricant throughout the process.
3) The grinding of the sample started with the grinding paper with grit size of 400
4) The sample is then grinded with the new grinding paper in increasing grade order (400,600,800 and 1200 grit).
5) The surface of the sample was grinded until the mirror surface was obtained from the sample.
6) The sample was polished using 3micron polisher
7) Step 1 until 6 is repeated for another 4 nitrided samples and 1 untreated sample

III. Etching

Procedure:

1) The etching of the sample was applied to carpenters stainless steel etchant where the compositions were $FeCl_3, CuCl_2$, hydrochloric acid, nitric acid and ethanol
2) The microstructure of the samples were ready to be observed

Task 5: Optical Microscope (OM) analysis

Figure 3.8: Optical Microscope (OM)

Procedure:

1) The magnifications of 100X and 500X was used using Optical Microscope (OM) as shown in Figure 3.8.

2) The surface of unitrided and nitrided duplex 2205 stainless steel piping was cleaned and dried first

3) The optical microscope and the computer was switched on

4) The image in the computer was saved after put the untreated sample under magnifying glass

5) step 2 to 4 was repeated using nitrided sample

6) The optical microscope is switch off

Task 6: SEM Cross-Section Analysis

Figure 3.9: Scanning Electron Microscope

Procedure:

1) The samples were placed in the scanning electron microscope as shown in figure 3.9.
2) The chemical composition, and microstructure was analyzed and observed using camera magnifications
3) The data was recorded and saved

Task 7: Corrosion (Immersion Test) Analysis

Figure 3.10: Immersion Test

Procedure:

i.   Preparation of samples (Based on ASTM G48)

1) Figure 3.10 shows the immersion test set up

2) The cross-section of untreated and nitride S31803 stainless steel was cut into half

3) The samples were rinsed with alcohol and acetone

4) The samples were put in the vacuum chamber to prevent corrosion

ii.   Preparation of Solution (Based on ASTM G48)

1) 600ml of distilled water was filled into a beaker

2) 68.72g of $FeCl_3$ is dissolved into the 600ml distilled water and 16ml of 1M HCl was added

3) The solution was put into a glass cell.

iii. Immersion Test (Based on ASTM G48)

1) The weight and total surface area of the samples were measured before immersion test

2) After immersion test for 48 hours, the samples were removed from solution

3) The cleaning process was done and the weight loss was measured

4) The corrosion rate is calculated using the formula:

$$Corrosion\ Rate\ (CR) = \frac{KW}{DAT}$$

Where K = constant (87.6mm/yr)

W = weight loss (mg)

D = density $(\frac{g}{cm^3})$

A = area (cm^2)

T = time (hr)

CHAPTER 4

RESULT AND DISCUSSION

4.1 Sample Preparation for Optical Microscopic (OM) and Scanning Electron Microscopy (SEM)

The 2205 duplex stainless steel were nitrided with N_2 gas at temperature of 1200°C for 8 hours. The nitrided samples are cut into 5 parts as shown in Figure 4.1 and named as sample 1, 2, 3, 4 and 5. Sample 1 is the beginning section where nitrogen first entered and sample 5 is the last section.
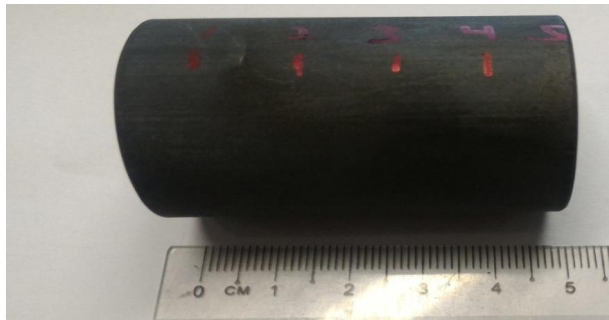
Figure 4.1: Sectioning of Nitrided Sample

The samples were then polished and etched with Carpenter Solution to reveal the microstructure of the specimen. Figure 4.2 shows the untreated and nitrided sample after etching.

(a) (b) (c)

(d) (e) (f)
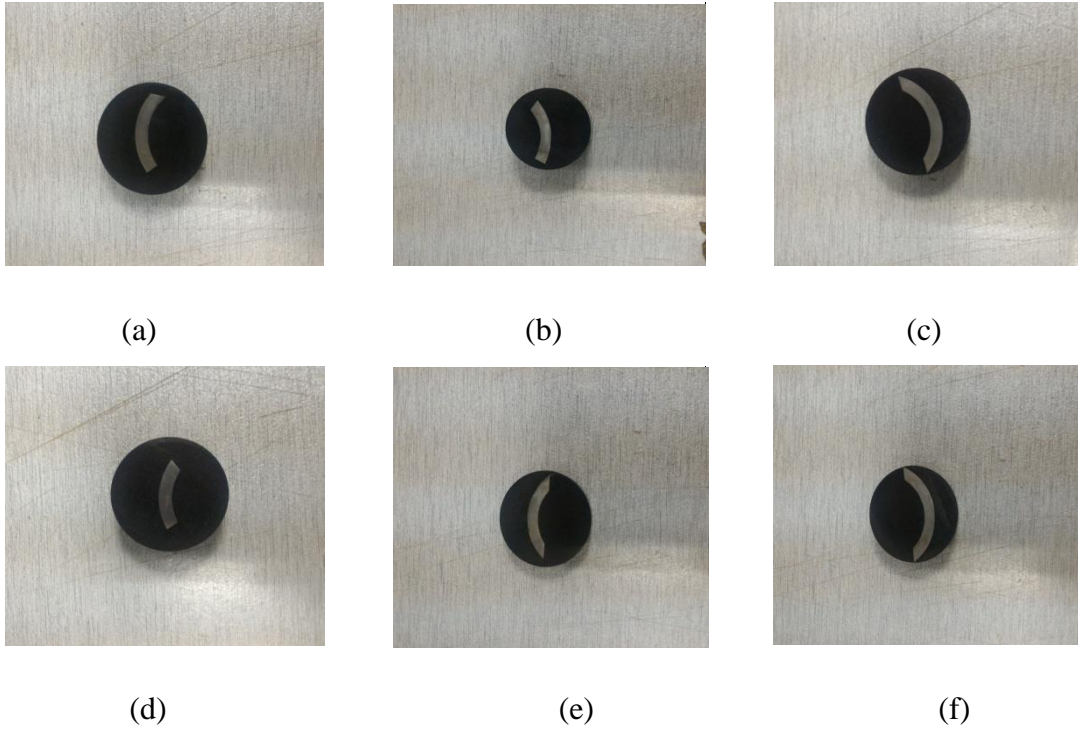
Figure 4.2: Surface of (a) untreated sample (b) sample 1 (c) sample 2 (d) sample 3 (e) sample 4 (f) sample 5 after etching

4.2 Metallographic Analysis

The etched surface samples were observed under Optical Microscope (OM) and Scanning Electron Microscope (SEM) study microstructure for unitrided and nitrided 2205 duplex stainless steels. The microstructure was observed on the surface area to ensure the nitrogen diffusion into sample. Figure 4.3 shows the result of image from Optical Microscopic of at the surface of untreated sample before nitriding process. The light orange color and island-shape illustrate as austenite phase which evenly dispersed in the dark orange color and band-shape illustrate as ferrite phase. Austenite phase is the majority phase that clearly appears while ferrite phase is minority phase. From this result it can be concluded this sample is proven as duplex stainless steel.
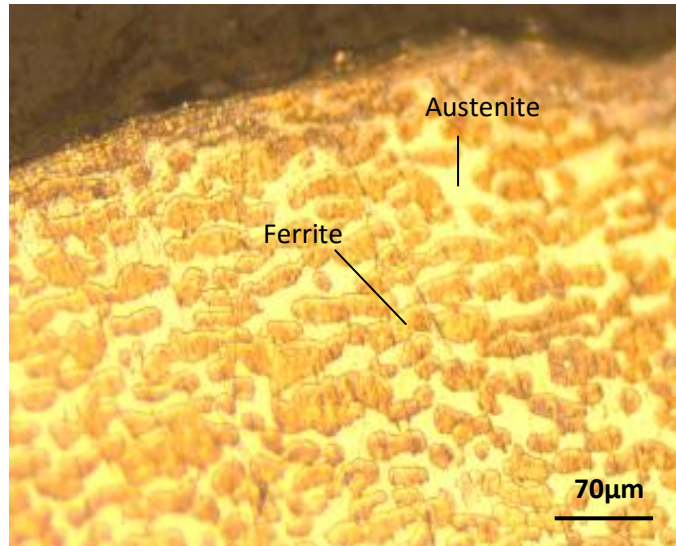
Figure 4.3: Optical Microscopic Image for Untreated Sample

Figure 4.4 shows optical microscopy image of sample 1, 2, 3, 4 and 5. Three zones with different microstructure were obtained from the surface to the centre of the sample. The formation of layer on the surface area is observed. The surface layer is identified as austenite phase using electron dispersive spectroscopy (EDS) scanning electron microscopy (SEM). Second zone is the inner zone consists of dual phase which is austenite and ferrite phase. Third zone is transition zone between austenite zone and dual phase zone. This zone consists of austenite matrix containing island of non-transformed ferrite. Nitrogen is very strong austenite stabilizer. The diffusion of nitrogen into the surface area of sample is high enough to cause enlargement of austenitic phase and prevent the stabilization of ferrite during nitriding process when temperature increase to 1200°C.
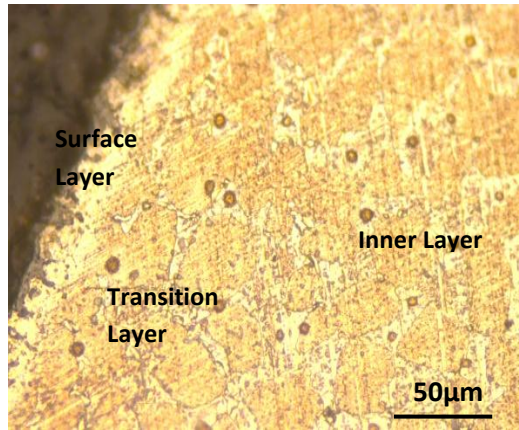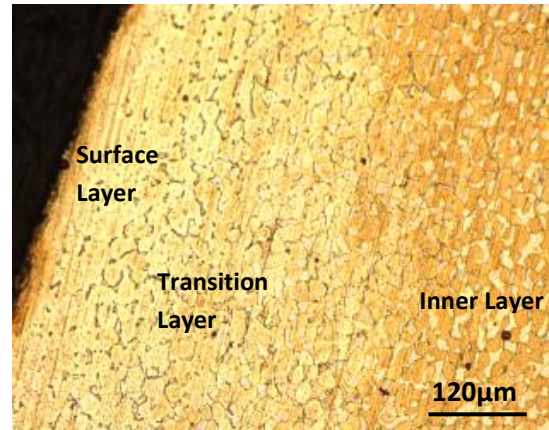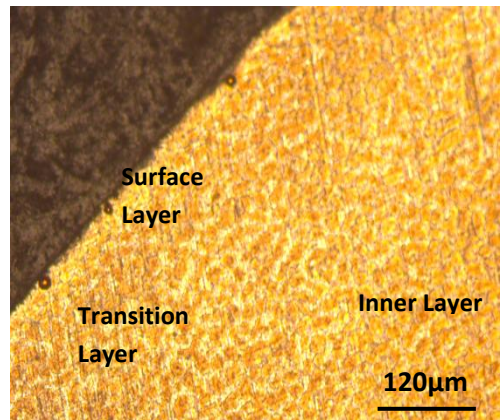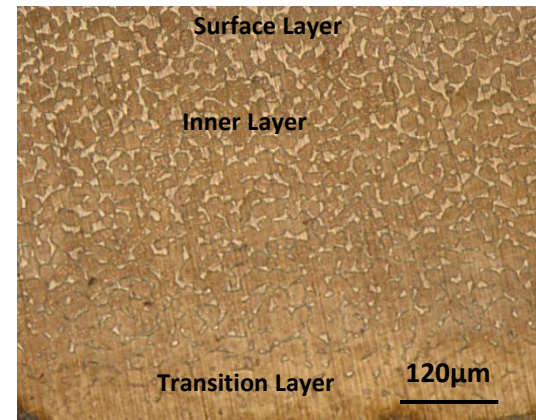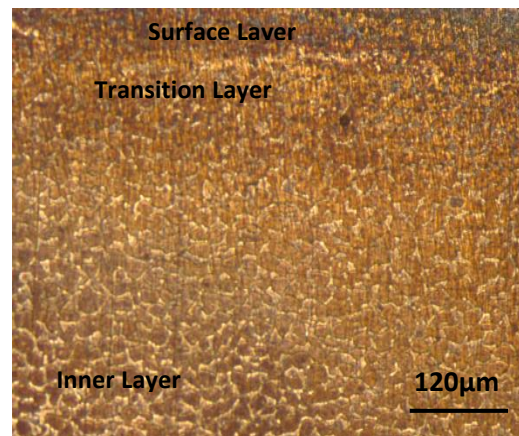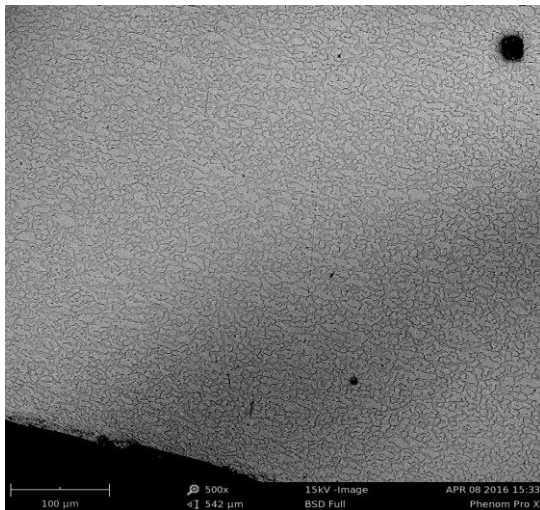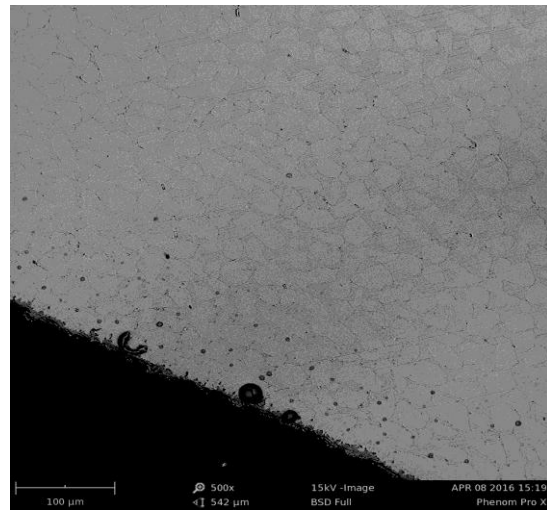
Figure 4.4: Optical Microscopic Image for (a) sample 1 (b) sample 2 (c) sample 3 (d) sample 4 (e) sample 5
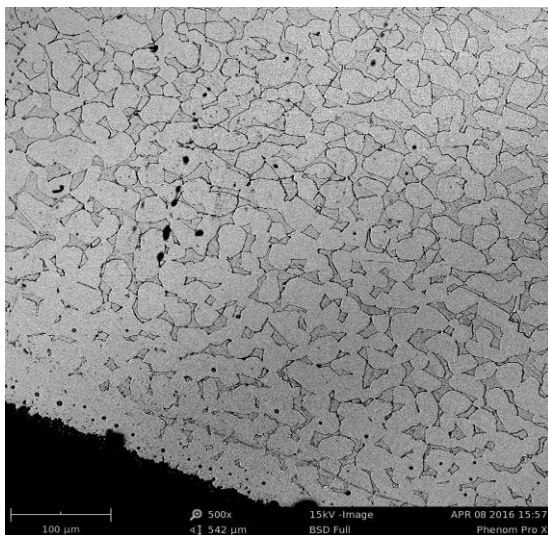
Figure 4.5 shows the microstructures of untreated and nitrided samples under Scanning Electron Microscopy (SEM). The austenite and ferrite phase can be observed for untreated sample while for nitrided samples, the austenite layer, ferrite and austenite phase is observed.
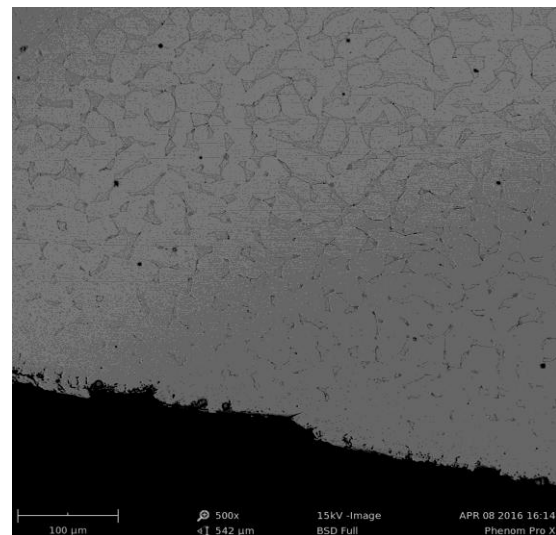

(a)
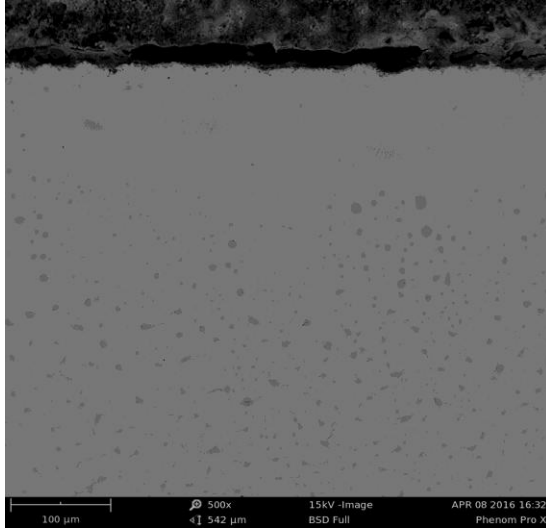

(b)
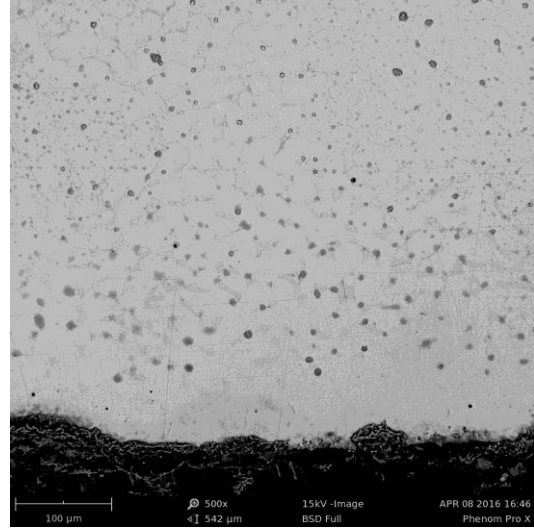

(c)

(d)

<div align="center">(e)</div> <div align="center">(f)</div>

Figure 4.5: Scanning Electron Microscopic Image for (a) untreated sample (b) sample 1 (c) sample 2 (d) sample 3 (e) sample 4 (f) sample 5

4.3 Element Analysis

The composition for each samples are taken by using Energy Dispersive Spectroscopy (EDS) Scanning Electron Microscopy (SEM) at 3 spot. The first spot is light spot, second spot is dark spot and the third spot is surface layer. The nickel composition can identify the phase existed in each spot. The uniformity of nitrogen diffusion is determined by nitrogen composition in each nitrided sample.

4.3.1 Identification of Phase Existed by Nickel Composition

Nickel composition for each sample at each spots is investigated to identify the phase existed for light colored-island, dark colored-island and surface layer that are produced after nitriding process. Based on Figure 4.6 the iron pseudobinary phase diagram can be used to identify the phase existed in the sample. Light colored and dark colored spot is in the inner zone which consists of austenite and ferrite phase while surface zone consist of austenite phase.
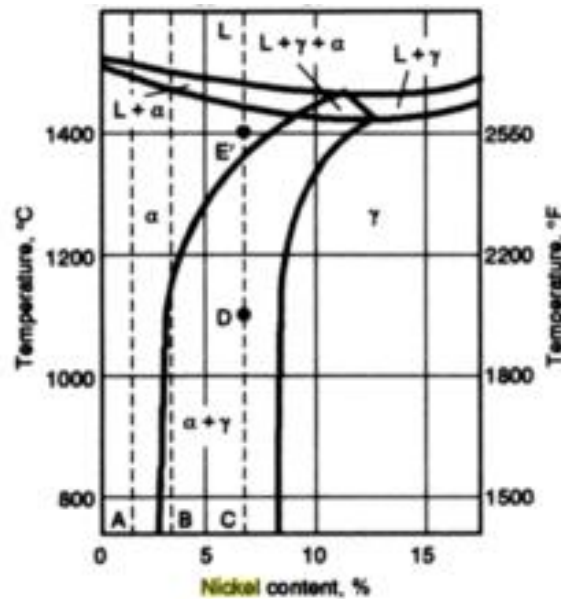

Figure 4.6: Iron Pseudobinary Phase Diagram

Based on Figure 4.7, the light colored region has high weight concentration of nickel which is around 4.5 to 7% of weight concentration. From iron pseudobinary phase diagram, the weight concentration between 3 to 8% of nickel consists of austenite and ferrite phase when subjected to 1200°C. Below 3% is ferrite phase and higher than 8% of nickel weight concentration is austenite phase. Thus, the higher weight concentration between light colored and dark colored spot is identified as austenite phase. Hence, the light colored region is austenite phase while dark colored region is ferrite phase since the nickel composition is lower in this region. The layer produced after nitriding process is identified as austenite phase because it contained high nickel composition which is higher than 8% nickel weight concentration.
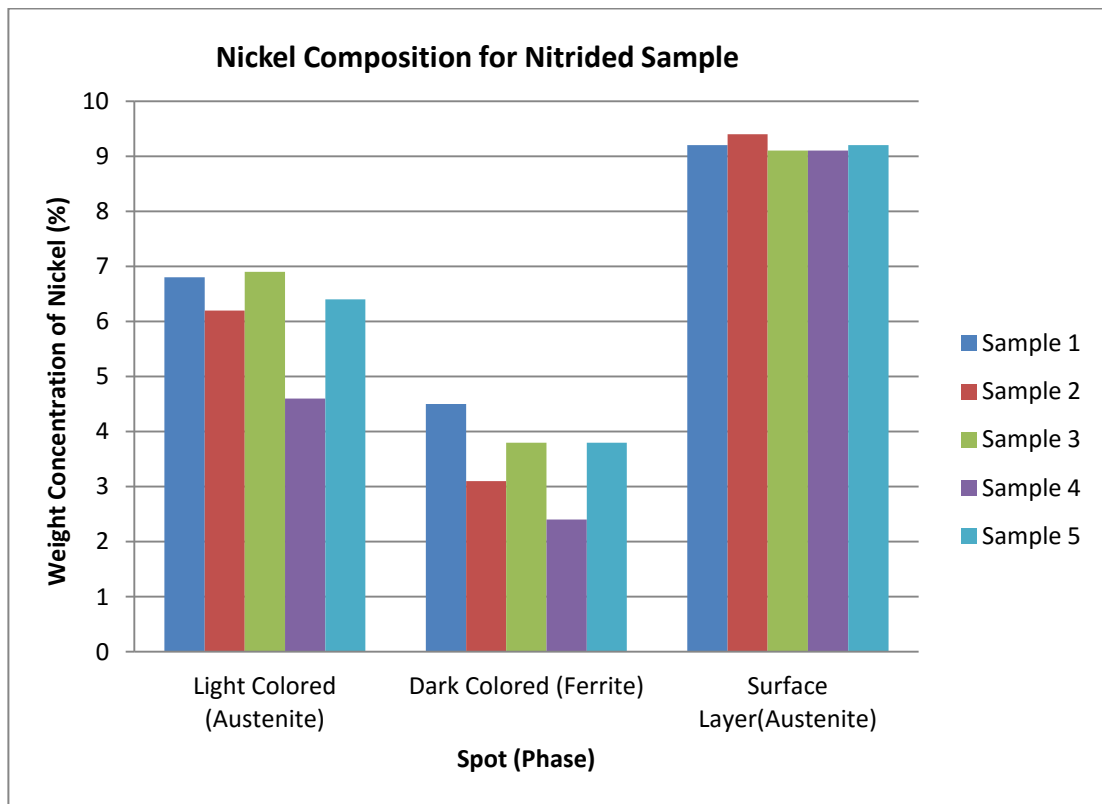

Figure 4.7: Nickel composition for nitrided samples

4.3.2 Uniformity of Nitrogen Diffusion by Nitrogen Composition

The average nitrogen concentration for each samples is obtained from EDS SEM are shown in Table 4.1 where the lowest concentration at sample 1 and highest at sample 4. This is due to velocity of the nitrogen which faster at sample 1 and cause the diffusion not evenly diffused into the sample. The uniformity is shown in Figure 4.8 where the nitrogen is almost equal for all samples with tolerance of $\pm 1.2\%$ only. The nitrogen diffusion can be concluded as uniformed.

Table 4.1: Composition of Nitrogen in All Nitrided Samples

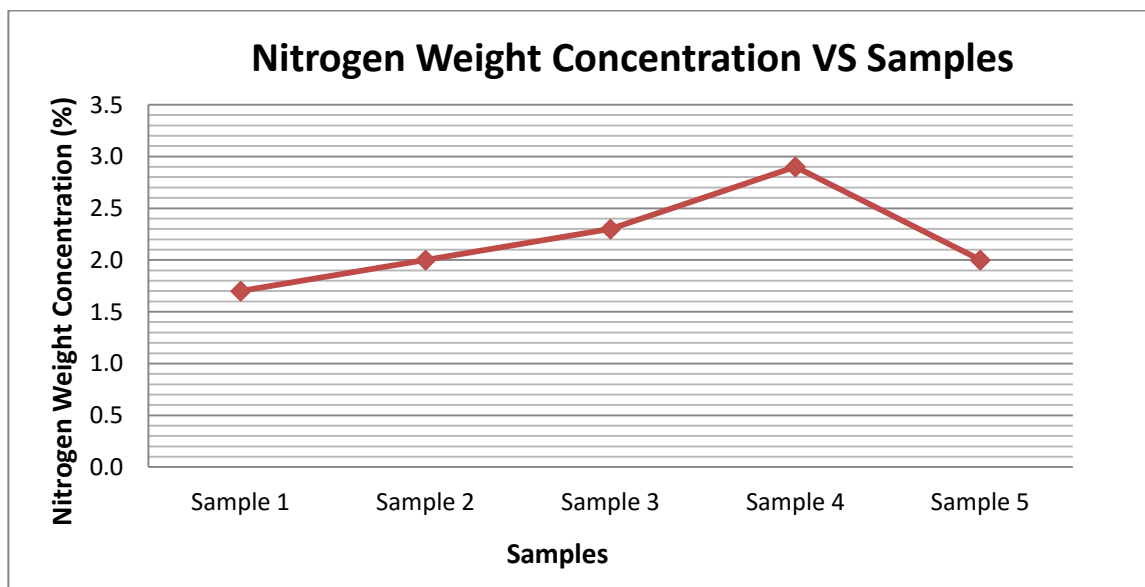| Sample	Nitrogen Weight Concentration (%)
1	1.7
2	2.0
3	2.3
4	2.9
5	2.0

Figure 4.8: Uniformity of Nitrogen Diffusion in Nitrided Samples

4.4 Corrosion Rate Analysis

4.4.1 Immersion tests in 6% $FeCl_3$ and 1% HCl solution

Table 4.2 shows the weight loss of untreated S31803 stainless steel during immersion test for 48 hours. The initial weight is 7.9533g and the dimension and total surface area of untreated S31803 stainless steel was shown in Table 4.3. The cleaning cycles were done 4 times after the weight almost stable as shown in Figure 4.9. The corrosion rate calculated is 35.7977 mm/yr.

Table 4.2: Weight Loss per Cleaning Cycle of Untreated Sample

Initial Weight (g)	7.9533	
Cleaning cycle	Instantaneous Weight(g)	Weight Loss (g)
0		0
1	5.6331	2.3202
2	5.5686	2.3847
3	5.5458	2.4075
4	5.5454	2.4079

Table 4.3: Dimension of Untreated Sample

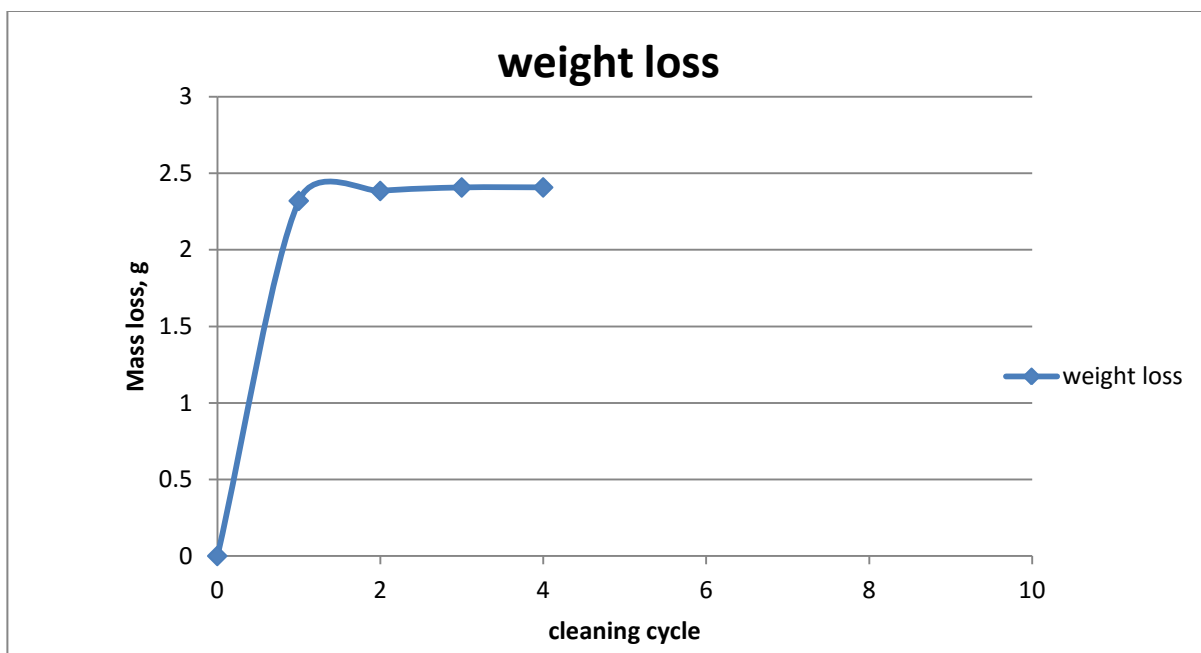| Dimension of sample	unit (cm)
2 Cross-section	7.52
Outer	4.4
Inner	3.2
2 Ends	0.684
Total surface area (cm2)	15.728
Total time (h)	48

Figure 4.9: Graph of Weight Loss per Cleaning Cycle of Untreated Sample

Table 4.4: Corrosion Rate of Untreated Sample

Formula	K x W	A x T x D	(K x W)/(A x T x D)
corrosion rate (mm/yr)	2.11E+05	5.89E+03	35.79768215
	Area ,A	15.728	cm2
	density ,D	7.81E+00	g/cm3
	K	8.76E+04	

Table 4.5 shows the weight loss of nitrided S31803 stainless steel during immersion test for 48 hours. The initial weight is 8.7091g and the dimension and total surface area of untreated S31803 stainless steel was shown in Table 4.6. The cleaning cycles were done 4 times and the weight loss per cleaning cycle was shown in figure 4.10. The corrosion rate calculated was 20.0991 mm/yr.

Table 4.5: Weight Loss per Cleaning Cycle of Nitrided Sample

Initial Weight (g)	8.7091	
Cleaning cycle	Instantaneous Weight (g)	Weight Loss (g)
0		0
1	7.6482	1.0609
2	7.5548	1.1543
3	7.4242	1.2849
4	7.3115	1.3975

Table 4.6: Dimension of Nitrided Sample

Dimension of specimen	unit (cm)
2 Cross-section	7.52
Outer	4.8
Inner	4
2 Ends	0.608
Total surface area (cm2)	16.982
Total time (h)	48

Figure 4.10: Graph of Weight Loss per Cleaning Cycle of Nitrided Sample

Table 4.7: Corrosion Rate of Nitrided Sample

Formula	K*W	A*T*D	(K*W)/(A*T*D)
corrosion rate (mm/yr)	1.27E+05	6.34E+03	20.09912503
	Area ,A	16.928	cm2
	density ,D	7.81E+00	g/cm3
	K	8.76E+04	

The corrosion rate of nitride 2205 stainless steel, in mm/year is lower which is 20.0991 mm/yr compared to untreated S31803 which is 35.7977mm/yr. The difference between both stainless steel corrosion rates are 15.6986mm/yr. By calculation as shown in (2) to (6), the corrosion rate of untreated sample is 43.85% higher than nitrided sample.

$$difference\ in\ corrosion\ rate = corrosion\ rate\ of\ untreated\ sample -$$
$$corrosion\ rate\ of\ nitrided\ sample$$

(2)

$$difference\ in\ corrosion\ rate = 35.7977mm/yr - 20.0991mm/yr$$

(3)

$$difference\ in\ corrosion\ rate = 15.6986mm/yr$$

(4)

$$corrosion\ rate\ improvement\ of\ nitrided\ sample = \frac{15.6986}{35.7977} \times 100$$

(5)

$$corrosion\ rate\ improvement\ of\ nitrided\ sample = 43.85\%$$

(6)

Hence, corrosion resistance of nitrided sample is improved 43.85% higher than untreated sample. The results indicated the corrosion resistance of nitrided stainless steel is higher than untreated samples and thus, it can be concluded high temperature gas nitriding process enhance the corrosion resistance of S31803 in the water solution containing 6% $FeCl_3$ and 1% HCl. The solution simulates the real environment such as natural seawater at ambient temperature and strongly oxidizing, low pH and chloride containing environment as recommended in ASTM G48.

The image shown during optical microscopy (OM) and scanning electron microscopy (SEM) shows the formation of austenite phase layer on the surface area. The formation of austenite layer on the surface increase corrosion resistance compared to untreated duplex stainless steel. Austenite phase consist of high chromium and nitrogen composition. In addition it has higher nickel composition. Chromium provide the protective layer of chromium oxide on the surface and this layer exhibit self-repairs as chromium in the stainless steel react rapidly with oxygen and moisture in the environment to reform oxide layer. Nitrogen will improve the mechanical properties of the sample and provide corrosion resistance to localized corrosion. Nickel increased the corrosion resistance in acidic media. These factors enhance the corrosion resistance of nitride sample.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

This project basically focuses on the effect after nitriding process on duplex stainless steel. Corrosion resistance, microstructure and uniformity of nitrided layer are investigated. The corrosion rate is calculated from immersion test by weight loss method. The microstructure of unitrided samples were analyzed by using OM and SEM analysis and the uniformity of nitride layer are obtained from EDS of SEM. Based on the results, the corrosion resistance is increased 43.85% after nitriding process due to formation of austenite phase on surface layer. Austenite phase consist high weight concentration of chromium for self-repair of protective layer and high weight concentration of of nitrogen and nickel to improve corrosion resistance to localized corrosion and acidic media. From microstructure analysis, three zones were formed in nitrided samples which is fully austenitic layer zone, a transition zone composed of an austenitic matrix containing islands of remaining ferrite, and inner zone composed of austenite and ferrite phase. Based on EDS of SEM, the interstitial diffusion of nitrogen diffusion is uniformed from sample 1 to sample 5 with tolerance of $\pm 1.2\%$. Therefore, the nitriding process improves 43.85% corrosion resistance of 2205 duplex stainless steel compared to untreated sample.

5.2 Recommendation

The recommendations for this project are as follow:

    I.   The hardness test should be done using Vickers machine to measure and compare the hardness of the samples

    II.   The grain size should be measure to know the exact value of the enlargement of the grain size after subjected to the gas nitriding process.

    III.   The nitrogen content in the surface of the samples should be analyzed by using the X-Ray Diffraction (XRD)

REFERENCES

[1] S. S. A. Service, "Stainless Steel," *Introduction to Stainless Steel,* no. 02, p. 3, 2001.

[2] T. Chen, K. Weng and J. Yang, "The effect of high-temperature exposure on the microstructural stability and toughness property in a 2205 duplex stainless steel," *Material Science and Engineering,* pp. 259-270, 2002.

[3] Y. Sato, T. Nelson, C. Sterling, R. Steel and C. Petterson, "Microstructure and mechanical properties of friction stir welded SAF super duplex stainless steel," *Materials Science and Engineering,* pp. 376-384, 2005.

[4] N. A. Stainless, "Flat Product Stainless Steel Grade Sheet," pp. 1-9.

[5] R. Silverstein, D.Eliexer, B.Glam, S.Eliezer and D.Moreno, "Journal of Alloys and Compounds," *Evaluation of hydrogen trapping mechanisms during performance of different hydrogen fugacity in lean duplex stainless steel,* pp. 601-608, 2015.

[6] J. Nilsson, "Super Duplex Stainless Steel," *Materials Science and Technology,* vol. 8, pp. 684-700, 1992.

[7] H.W.Lee, J. Kong, D. Lee, H.Y.On and J.H.Sung, "A study on high temperature gas nitriding and tempering heat treatment," *Material and Design,* pp. 1691-1696, 2009.

[8] C. Garzon and A. Tschiptschin, "EBSD texture analysis of a high temperature gas nitrided," *Material Science and Engineering ,* pp. 230-238, 2006.

[9] S. Akhtar, A. Arif and B. S. Yilbas, "Evolution of gas nitriding process with in-process variation of nitriding potential for AISI H13 tool steel," *Int J Adventure Manufacturing Technology,* pp. 687-698, 2010.

[10] P. Husain, A. Triwiyanto and M. Ismail, "Low Temperature Thermochemical Treatments of Austenitic Stainless Without Impairing Its Corrosion Resistance," *Corrosion Resistance,* pp. 318-337, 2012.

[11] E.Haruman, Y.Sun, H.Malik, A. Sutjipto, S.Mridha and K.Widi, "Low Temperature Fluidized Bed Nitriding of Austenitic Stainless Steel," *School of Materials Science and Engineering,* pp. 125-130, 2006.

[12] W. Liu, "Rapid MIC attack on 2205 duplex stainless steel pipe in a yacht," *Engineering Failure Analysis,* pp. 109-120, 2014.

[13] M. C. Pereira, J. W.J.Silva, H. A.Acciari, E. N.Codaro and L. R.O.Hein, "Materials Science and Application," *Morphology Characterization and Kinetics Evaluation of Pitting Corrosion of Commercially Pure Aluminium by Digital Image Analysis,* pp. 287-293, 2012.

[14] D. W.Hoeppner, "Pitting Corrosion:Morphology and Characterization," *NATO OTAN,* p. 16.

[15] R.A.Cottis, "Stress Corrosion Cracking," *Guides to Good Practice in Corrosion Control,* p. 11, 2000.

[16] T.Chirstiansen and M. Somers, "Low temperature gaseous nitriding and carburising of stainless steel," *Surface Engineering,* pp. 445-455, 2005.

[17] "Review of the Wear and Galling Characteristic of Stainless Steels," *A Designer Handbook Series,* p. 28.

[18] M. Bobadilla and A. Tschiptschin, "On the Nitrogen Disffusion in a Duplex Stainless Steel," *Material Research,* pp. 390-394, 2015.

[19] T.Bell and Y.Sun, "Low Temperature Plasma Nitriding and Carbirizing of Austenite Stainless Steel," *Heat Treatment of Metals,* pp. 57-64, 2002.

[20] T.Chen, K.Weng and J.Yang, "The effect of high-temperature exposure on the microstructural stability and toughness property in a 2205 duplex stainless steel," *Material Science and Engineering,* pp. 259-270, 2002.

APPENDICES

Figure A1: Temperature of alumina tube

Figure A2: Conical flask to ensure no leakage of gas during nitriding process

Figure A3: Untreated sample initial weight

Figure A4: Untreated sample final weight

Figure A5: Nitrided sample initial weight

Figure A6: Nitride sample final weight

Figure A7: Untreated sample after immersion test

Figure A8: Nitrided sample after immersion test