Variation of High Temperature Gas Nitriding Time on Duplex Stainless Steels

By

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CERTIFICATION OF APPROVAL

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Mechanical Engineering Programme
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Approved by,

(AP Dr Patthi Bin Hussain)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2011

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.

NURLIANAH BINTI ABDUL RASHID

ABSTRACT

This report presents the discussion on solution nitriding of duplex stainless steel. It consists of project's background, literature review, methodology, and all the relevant process and component related to this project. Nitriding is a surface-hardening heat treatment which introduces nitrogen into the surface of the duplex stainless steels at certain temperature range. The objectives of this project are to investigate the hardness and the changes on the surface microstructure of nitrided duplex stainless steel. During nitriding sample will exposed to a constant high temperature at 1100°C with varying the time which is at 1h, 2.5 h, 4.5h and 6 h. Metallographic study, XRD examination and assessment of the sample's hardness will be performed to examine the hardness of the treated sample. Scanning Electron Micrograph (SEM) and optical microscope will be used to do an assessment of the microstructure of the sample before nitriding and after nitriding process to be conducted. Weight of the nitrided sample at constant temperature 1100°C are increasing as the nitriding time increase. The microstructure observed for the nitrided sample shows that the grain course of austenite phases are increasing as longer time nitriding were conducted as compared to ferrite phases. It shows that austenite phases react more in nitrogen diffusion compared to ferrite. Highest value of hardness: 448.2HV is achieved from sample nitrided at 1100 °C for 6 hours. Diffusion of nitrogen content leads to higher hardness. XRD analysis also shows that the appearance of FeN increase the hardness of the material. Hence as a conclusion, the objectives of the project are achieved successfully. High Temperature Gas Nitriding at 1100°C has successfully improved the hardness of the material due to more nitrogen diffused in it.

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Mechanical Engineering Department

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ABBREVIATIONS AND NOMENCLATURES

DSS – Duplex Stainless Steel

FERR- Ferrite Stainless Steel

AUST- Austenitic Stainless Steel

LDX – Lean Duplex Stainless Steel

SEM – Scanning electron microscope

EDX – Electron Dispersion X-Ray

HTGN – High Temperature Gas Nitriding

CHAPTER 1

INTRODUCTION

1.1 Background of Project

Stainless steel (SS) is a common name for a number of different steels used primarily for their resistance to corrosion. Stainless steel has been developed to resist a number of corrosive environments. Stainless steel is always made using chromium. The minimum amount of chromium being used to make stainless steel is 10.5%. It is chromium that makes the steel stainless. Chromium also improves the corrosion resistance by forming the chromium oxide film on the steel. This very thin layer, when placed under the right conditions it can also be self repairing [1].

Stainless steels (SS) may be thermochemically treated to improve surface properties such as corrosion, erosion-corrosion and cavitations-erosion resistance [2]. *High Temperature Gas Nitriding* (HTGN) of these alloys has been performed since 1958 [3]. High temperature gas nitriding or solution nitriding is a new method for strengthening the stainless steel. It is performed by heating the material at high temperature under nitrogenous atmosphere. Nitrogen will diffuse into stainless steel and increase the hardness of the material during the treatment. Nitriding are being applied in improving the hardness of austenitic, ferritic, duplex and martensitic stainless steel [2].

1.2 Problem Statement

Duplex Stainless Steel is used since it has a two-phase microstructure consisting of grains of ferritic and austenitic stainless steel. It has a good corrosion resistance with high strength but it is also brittle. In order to maintain its hardness and toughness, nitriding method is chosen to overcome the problem. Hardness and toughness need to be improved so that the durability of the tools and the longer time frame in using it can be obtained. Nitriding will involve in heating the sample at a high temperature and sample will experience slow cooling instead of quenching.

1.3 Objective and Scope of Study

Objectives of this project are:

- To enhance the hardness of the material.
- To observe the change of microstructure on the nitrided sample

This project involves a study on the mechanical properties and physical properties of duplex stainless steel when involving in the variation of time on high temperature gas nitriding process at a constant time which is 1100°C. The author has done some literature review on the concept of the stainless steel, the concept of nitriding and standard and procedure in performing metallographic technique. It is a need to know the improvement of both properties by doing hardness, microstructure and X-ray diffraction test after nitriding process being done. For other relevant work, identification of sample hardness and chemical composition using SEM-EDX technique are also considered.

CHAPTER 2

LITERATURE REVIEW

Throughout chapter 2, the materials reviewed and the information related to the materials involved will be discussed deeper. It is important to know the details about materials being researched and the process involved from the beginning until the end.

2.1 An Overview of Stainless Steel

2.1.1 Definition

Stainless steels are the steel alloy with a minimum of 10% chromium content by mass. They are corrosion-resistance steel or known as CRES. They do not stain, *corrode, or rust easily [1]. There are 4 types of stainless steels that are usually used* in industry which are ferritic, austenic, martensitic and duplex stainless steels. Figure 1 shows a Scaffer diagram which is very useful to illustrate the different area of stability for stainless steels microstructure [4].

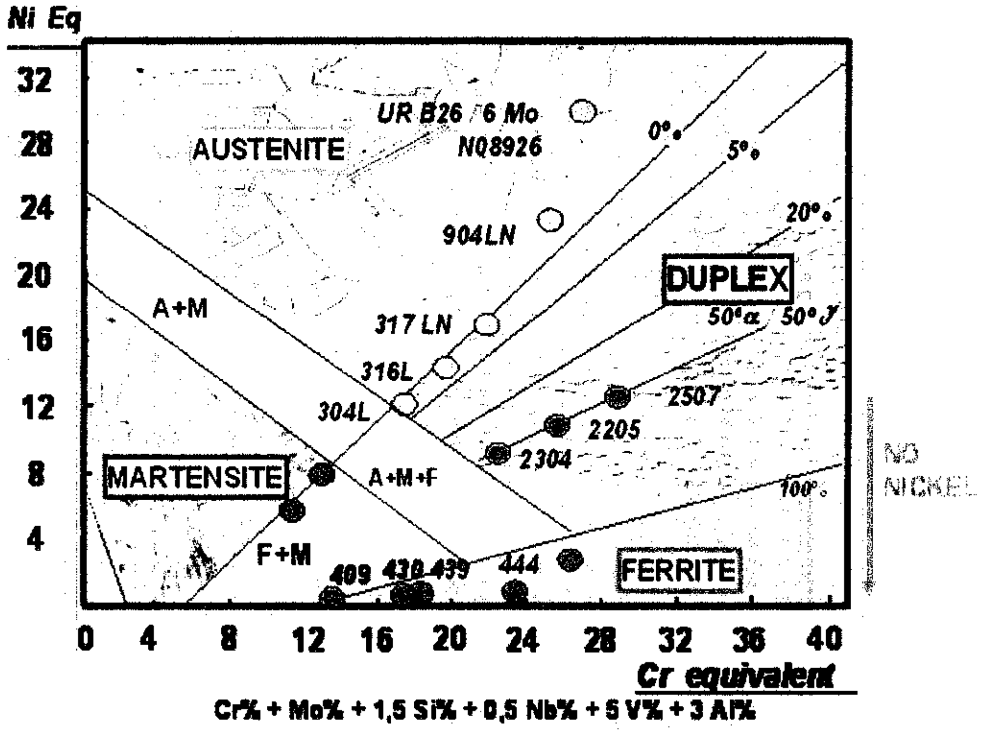


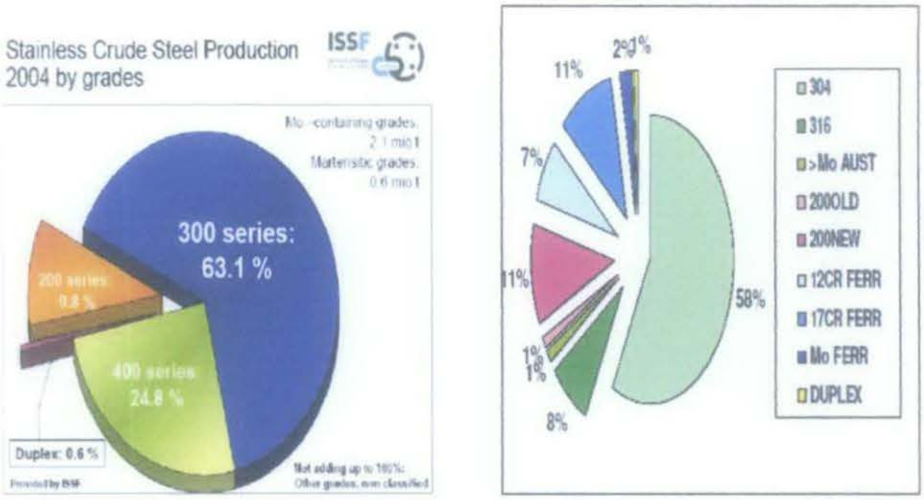
Figure 1: Schaeffler diagram [4]

As in **Figure 1**, the austenitic (300 series) contain a minimum amount of 9% to 10 % of Ni while the more alloyed grades in Cr or Mo, it will needs even more Ni to stabilize the austenitic phase [4]. Austenitic 304 is the most popular grades as it is the lowest alloying grade of austenitic phase.As for Ferritic stainless, it produced when Ni content is almost 0% and Cr minimum content is 12%. As in **Figure 1**, it shows that most of ferritic grades have a Cr content included in the 12% to 18% range [4].

A mixed of ferrite and austenite microstructure is observed in between the austenitic and the ferrite areas. Most of the duplex industrial grades have a typical 50% of ferrite and 50% of austenite microstructure. As observed, it is impossible to develop duplex grades having less than 19% without formation of martensite [4].

2.1.2 Status of Stainless Steels Worldwide

Stainless steels are central to a lot of application. Stainless steels may be appreciated by looking at the tonnage of its production and consumption in some major economies. According to **Figure 2(a) and (b)** , Austenitics remains the most popular grades thanks' to their unique combination of high ductility, high potential of strengthening, weld ability, toughness even at extra-low temperatures and of course corrosion resistance. Ferritics represent about 25% of the total production and due to welding aspects and toughness properties; they are restricted to thinner gauges even if they are often the cost saving grades. Duplex grades cover about 1% of the total production [4].



(a) (b)

Figure 2: (a) and (b); 2004 Stainless worldwide crude productions by grades [4]

2.2 Duplex Stainless Steels

2.2.1 Duplex Stainless Steels, the Past and Present

Duplex stainless steels have its history almost as long as stainless steels. Duplex catch a large attention from the industry although they represent less than one percent of the total volume of stainless steels [8].

Stainless steels were invented a century ago. Ferritic and Austenitic steels are the first grades were invented. Some ferritic into austenitic stainless casing being introduce for a better castability and to increase the resistance of sensitization and to improve the proof strength. This development of austenitic casing was the most probably start of duplex stainless steels around 1930 [8].

First duplex grades were relatively high content of carbon since efficient process techniques for decarburization were not available. Intentional nitrogen additions were not practiced and the phase balance was not optimized to present standard [8-9]. Ferralium was the first with the intentional addition of nitrogen for the first duplex alloy which in turn was developed from grade 26-5-1 casting but tended for both cast and wrought forms. By adding of nitrogen will reduced the problem with cracking during casting and welding. This will produce more ductile weld [9].

Currently, the development of duplex stainless steels has continued. Composition is an essential characteristic of stainless steel because it determines the alloy's corrosion resistance, microstructural phase balance, mechanical properties, and physical properties. Table 1 below shows the chemical composition and Pitting Resistance Equivalent Number (PREN) of common duplex stainless steels [15]

Table 1: Chemical composition and Pitting Resistance Equivalent Number (PREN) of common duplex stainless steels [15]

Common duplex stainless steels							
EN	**AISI**	**UNS**	**Cr**	**Mo**	**Ni**	**N**	**PREN**
Duplex grades							
1.4362	2304	S32304	23	0.3	4.8	0.1	25.6
1.4462	2205	S32205	22	3.1	5.7	0.17	35.0
1.4410	2507	S32750	25	4	7	0.27	42.5

2.2.2 Duplex stainless steels phases

Duplex Stainless Steels (DSS) offer an attractive combination of properties, including high strength, excellent resistance and good weldability [5]. Duplex Stainless Steels (DSS) is characterized by a dual phase structure comprising a mixture of ferrite (α) and austenite (γ) phases. The two phases is usually about 50% (by volume fraction) and it can vary between 30% and 70% and most regularly between 40% and 60% [6]. Shown below in **Figure 3** there are some examples of the micrographic that taken from SEM micrograph. The dark phase is ferrite where else the white phase is austenite [7].

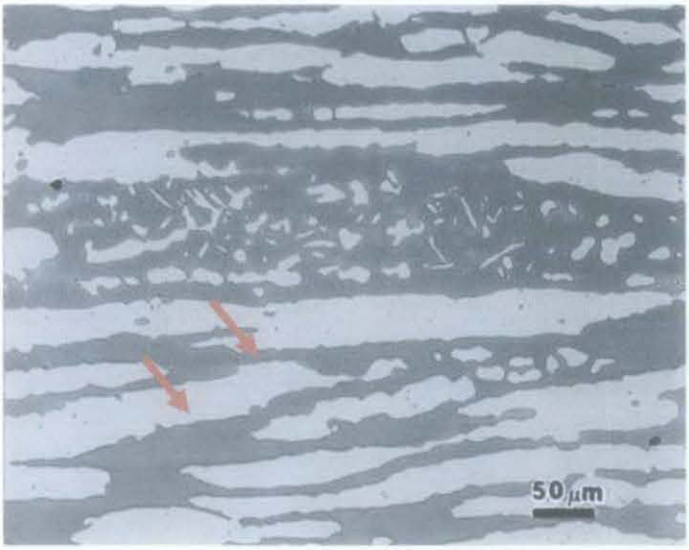


Figure 3: Duplex phase [7]

2.2.3 Duplex stainless steels application

Duplex stainless steels have been using worldwide. Duplex stainless steel is typically used in chemical processing, transport and storage, oil and gas exploration and offshore rigs, oil and gas refining, marine environments, pollution control equipment, pulp & paper manufacturing and chemical process plant.

2.2.4 Lean Duplex Stainless Steels (LDX)

The market today have four main types of duplex steels, lean duplex, standard duplex, super duplex and hyper duplex. The differences between them are the chemical analysis and their mechanical and corrosion properties. Their similarities are that they all have a ferritic solidification and that the austenite formation starts at application of 1420°C, at application of 800°C the austenite formation is finalized. In this project, Lean Duplex Stainless Steels (LDX 2101) will be used as the material. LDX 2101 is a recently developed low alloyed (lean) DSS with low addition of nickel in order to reduce and stabilize the cost [5]. Lean duplex is lean because it has only 1.5% nickel content. Nickel is an Austenite former in making stainless steels. In LDX, manganese replaces the expensive nickel without compromising any of the characteristics of the product [16]. Manganese ensures proper ferrite-austenite phase balance and allows the reduction in nickel content.

Lean duplex consist of equal amount of 50% austenite and 50% ferrite. This phase mix result in higher mechanical strength, and thus improved the resistance of stress corrosion cracking [14, 16]. As shown in **Table 3** below, LDX 2101 provide superior strength compared to 300 series stainless steels. It is also less prone to precipitation of intermetallic phases than other duplex as it is relatively low alloy content based on **Table 2** [12]. Due to all this factors, LDX 2101 priced competitively with 304L and 316L stainless steels.

Table 2 : Chemical Composition of LDX 2101, % [12]

Alloy	Min	Max
Chromium (Cr)	21.0	22.0
Nickel (Ni)	1.35	1.70
Manganese (Mn)	4.00	6.00
Molybdenum (Mo)	0.10	0.80
Nitrogen (N)	0.20	0.25
Carbon (C)	-	0.040
Silicon (Si)	-	1.00
Copper (Cu)	0.10	0.80
Phosphorus (P)	-	0.040
Sulfur (S)	-	0.030
Iron (Fe)	Balance	

Table 3 : Tensile Properties Cold Rolled Plate And Sheet ≤ 1/4" [12]

Alloy	Ultimate Tensile Strength, ksi (Min)	0.2% Yield Strength, ksi (Min)	Elongation, Percent (Min)	Hardness Brinell (Max)
LDX 2101	101	77	30	290
304/304L	75	30	40	201
316/316L	75	30	40	217
2205	95	65	25	293
2304	87	58	25	290
AL 2003	100	70	25	293

2.3 Nitriding

Nitriding is a thermochemical process by which the surface of a ferrous metal is enriched with nitrogen to improve the wear resistance of the component [18]. Nitriding will enhancing corrosion resistance on most steels and impairs it on stainless steels. This is because chromium, being a strong nitride-forming element, readily combines with diffusing nitrogen, thus depleting the steel matrix of its chromium content in solution, necessary for the formation of a protective film. Improvement of this affect can be obtained by nitriding at low temperatures, involving however a long processing times. Nitrided layers on precipitation-hardening steels exhibit similar features to those a martensitic stainless grades [2]

There is several type of nitriding which are:

- salt bath nitrocarburising
- gas nitriding and nitrocarburising
- plama and nitrocarburising

All of it involved different type of diffusion and procedure. The benefits of nitriding are the fatigue strength is increase as the development of surface compressive stress. The corrosion resistance of the metal also will be increased.

2.3.1 Nitrogen Alloying

Nitrogen has multiple effects on stainless steels by increasing pitting resistance, austenite content and strength [22]. Nitrogen partitions preferentially to the austenite due to the increase solubility in the phase and also concentrates at the metal-passive film interference. Nitrogen has also been noted to increase the crevice corrosion resistance [22]. Workers have proposed that this is due to nitrogen altering the crevice solution or by segregating to the surface, which is in keeping with the mechanism for enhancing pitting resistance. By reducing Cr-partitioning, nitrogen has the ability to stabilize duplex alloy against the precipitation of intermetallic phases such as sigma and chi. By increasing the nitrogen level actually can reduces the risk of nitride formation. This is due to an increase in austenite content and so a reduction in the distance between austenite islands.

2.3.2 High Temperature Gas Nitriding (HTGN)

Recently a chemical solid state nitrogen alloying technique was developed [19]. HTGN is one of chemical heat treatments to add nitrogen into stainless steel. It is well known that the nitrogen addition to stainless steel has many advantages including the tensile strength of the steels drastically increase without reducing the ductility too much, the corrosion resistance especially pitting corrosion resistance is improved and lastly nitrogen is considered to be harmless to the human body.

The schematic illustration of the gas nitriding equipment is shown in **Figure 4**. The process of HTGN involved the atomic nitrogen is absorbed at the surface of the steel and then diffuses into the near surface region [20]. Nitride case depth can range from as little as 0.05mm up to 0.7mm.

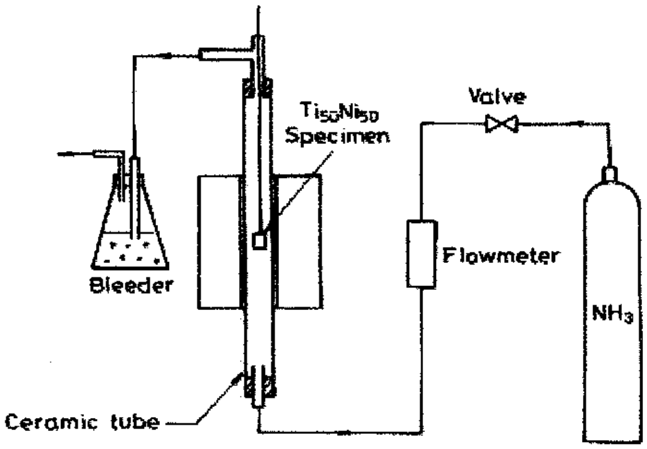


Figure 4: Schematic illustration of the gas nitriding equipment

2.3.2.1 Temperature above 1050°C

According to **Figure 5** below, for a standard grades and normal cooling rates, duplex stainless steels solidify completely in ferrite field. This is followed by solid state transformation to austenite [22]. Large increase in temperature e.g from 1050 °C to 1300°C will leads to an increase in ferrite content. Heat treatment in the temperature range 1100-1200°C can have a dramatic influence on the microstructure of a wrought product. The grains can be equiaxed by prolonged treatment at high temperature. A dual structure consisting of both coarse and fine austenite can be obtained by quenching [22].

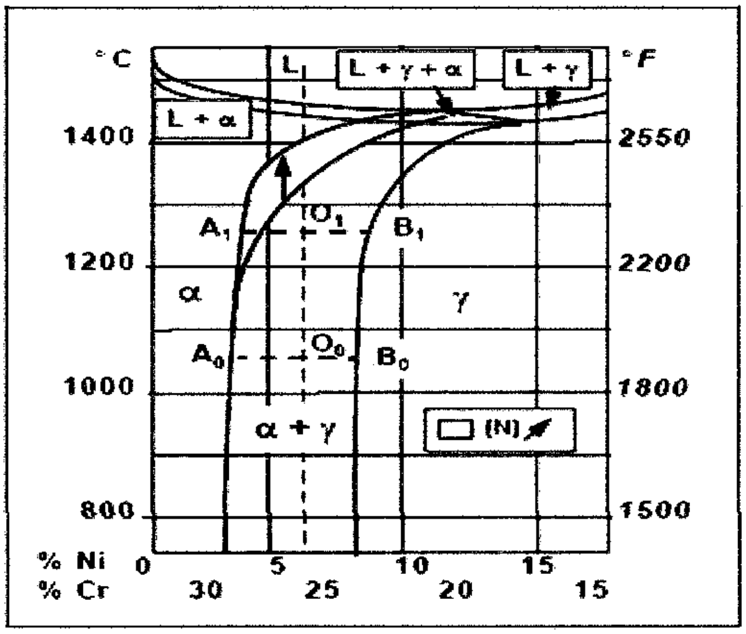


Figure 5: The schematic effect of nitrogen addition is shown in the concentration profile in the ternary Fe-Cr-Ni constitution diagram [22].

2.4 Previous study

2.4.1 Study done by C. M. GARZO´ N, A. P. TSCHIPTSCHIN on EBSD texture analysis of high temperature gas nitride duplex stainless steels [23]

The study involved UNS S31803 duplex stainless steel where it has been cut off into prismatic specimens with a dimension of 20mm x 20mm x 9mm). HTGN was carried out between 1423K and 1473K for times varying between 0.18kc and 86.4ks under nitrogen partial pressures varying between 0.03MPa and 0.2MPa.

First, the microstructure of the sample was examined by optical microscopy. Chemical microanalysis also was conducted through X-Ray wavelength-dispersive spectrometry (WDS). The grain boundary character distribution and the crystallite orientation distribution were studied using an electron back scattering diffraction TSL-EBSD system.

Results for as received sample are:

Figure 6 shows the microstructure was formed by alternalting ferritic (α) – austenitic (γ) grains. EBSD phase map gave 55% of ferrite and average grain diameters of 10 -12μm (ferrite) and 5-7μm (austenitic). **Table 4** shows the chemical composition of the sample.

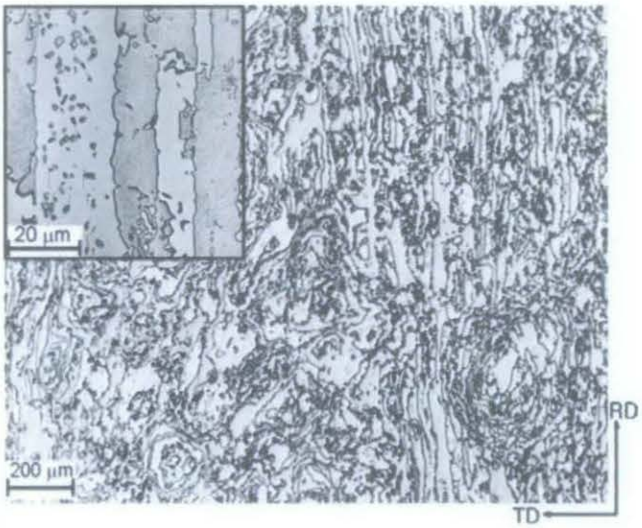


Figure 6 :Optical micrograph of the surface of the hot rolled plate. Austenite (γ) and ferrite (α). Etching: aqua regia. [23]

Table 4 :Chemical composition of the UNS S31803 duplex stainless steel (wt. %) [23]

Cr	22.5
Ni	5.4
Mn	1.9
Mo	3.0
C	0.019
Cu	0.14
N	0.16
S	<0.001

Results for after HTGN being conducted are:

Figure 7 shows EBSD grain maps, taken in the transverse section, of samples nitrided at 1423K for 0.9, 7.2 and 18 ks, under 0.065MPa nitrogen partial pressure. From the surface to the core of the specimens an austenitic layer and a 60/40 ferritic–austenitic inner region are observed.

During the earliest stages of nitriding, austenite growth toward the transition egion occurred mainly as side plates with tips of high mobility. The driving force to the $\gamma/(\gamma + \alpha)$ phase boundary migration is supplied by the nitrogen gradient, which is controlled by long-range nitrogen diffusion, and decreases while nitriding time is increased.

For intermediate times (10.8 ks) the tip's growth rate decreases and coarsening of the acicular grains occurs, although some grains with almost acicular morphology still remain.

For longer nitriding times (18 ks) a planar $\gamma/(\gamma + \alpha)$ boundary interface between the austenitic case and the transition region develops.

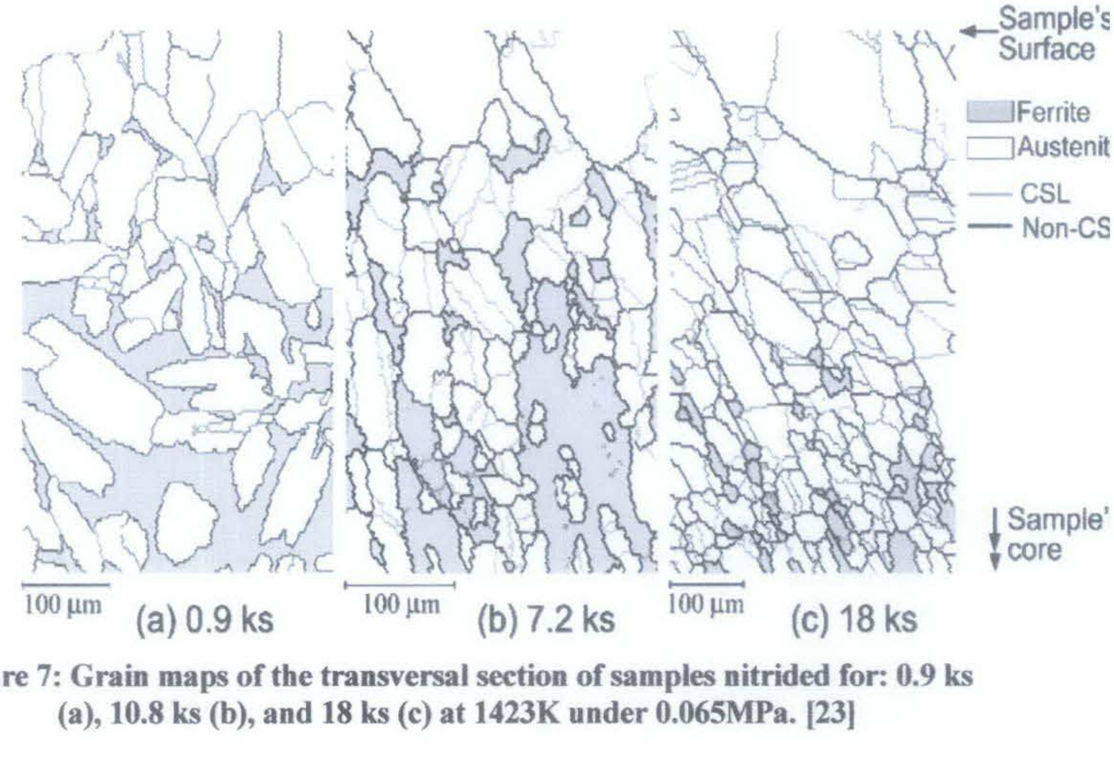


Figure 7: Grain maps of the transversal section of samples nitrided for: 0.9 ks (a), 10.8 ks (b), and 18 ks (c) at 1423K under 0.065MPa. [23]

The total length of each grain boundary character decrease as nitriding time is increased, tending to be asymptotic at lower limit value. The grain boundary character distribution mainly depended on nitriding time and nitrogen partial pressure, displaying a weak dependence on nitriding temperature. The friction of high-angle Coincidence-Site Lattice (CSL) grain boundaries increased as the nitriding was increase, tending to reach limit value (~0.65) and the fraction low-angle boundaries decrease and almost disappeared when nitriding time was increased. The relationship between CSL fraction and nitriding time can be reasonably attributed to kinetic differences of each type of grain boundary reduction rate as the nitriding time is increased.

2.4.2 Study done by J.Bielawski, J.Baranowska and K.Szczecinski on Protective Nitriided Layers on Ferrite-Austenite Chromium Steel [24]

Gas nitriding experiments were conducted in temperature range of 350°C to 550°C for 3 hours in ammonia atmosphere (100% NH_3) for austenitic-ferritic steel. Samples were activated by ion sputtering in the nitrogen or hydrogen atmosphere to make the gas treatment possible before nitriding. The morphology of the nitrided layers was investigated using light microscopy analysis and electron scanning microscope. The layers of micro hardness were measured with the load varying 10 to 100gf and cross section with load 5gf.

The appearance of the surface after nitriding was simi-lar for both sputtering gases but changed with temperature of the treatment. For samples nitrided at 350 °C – 450 °C the differences between ferritic and austenitic structures are clearly visible on **Figure 8** below. On the surface the characteristic relief was observed which becomes even clearer with temperature. For the samples nitrided at *500 °C* and *550 °C* it was no more differences between ferritic and austenitic grains, and the whole surfaces are uniformly rough.

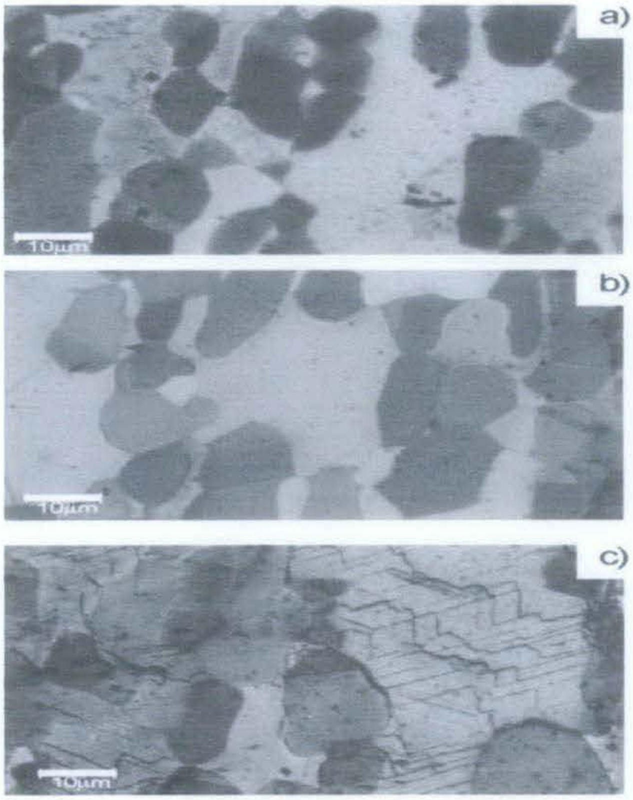


Figure 8: Surface of the samples sputtered in nitrogen after nitriding at: a – 350 °C , b – 400 °C, c – 450 °C [24]

The differences in morphology of the layers are observed on their cross section. The growth of the layers depends on the grain type. In the most cases the layer on the austenite was thinner than that one on ferrite which is shown in **Figure 9** below. The part of the layer produced on austenite has characteristic curvature being thicker in the near of the grain border and thinner in the central part of the grain.

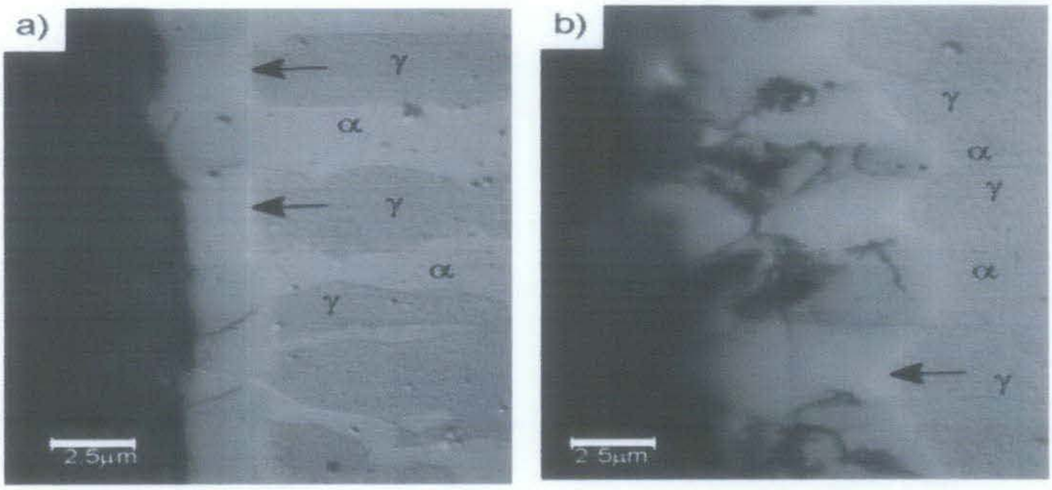


Figure 9: Cross sections of the layers on duplex steel after nitriding at: a – 400 °C; b – 450 °C. The arrows shows the curvature of the layer on austenitic grain [24]

The investigation of the layers by EBSD technique, have shown interesting relationship. The part of the layers produced on austenite was easily identified as austenite which is typical for "expanded austenite" produced on austenitic stainless steel are shown on **Figure 10**. The layer made on ferrite was not identified neither as austenite nor ferrite or nitrides. It could suggest that layer produced on ferrite has different nature from that produced on austenite.

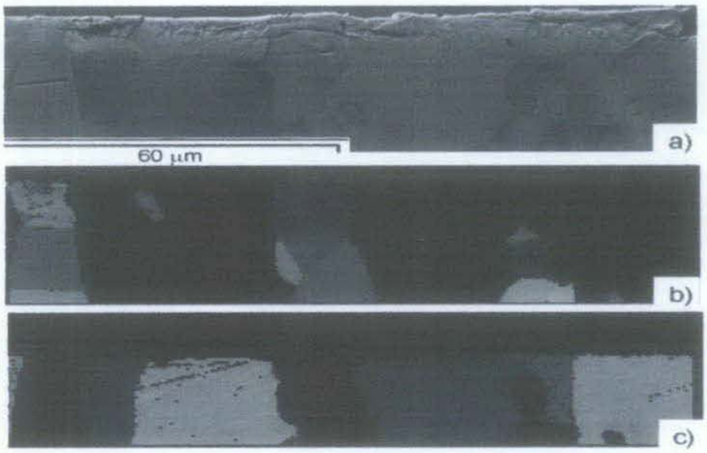


Figure 10: EBSD picture of the layer produced during nitriding at 450 °C: a – SEM picture of the layer; b – austenite; c – ferrite identification [24]

CHAPTER 3

METHODOLOGY

The project work can be divided into two parts which is for the first semester and work for the second semester. In the first semester, the project work focuses more on literature reviews and the material preparation. The experiment will be conducted during FYP 2 session due to time consuming. After some researches, the author makes the research flowchart to get more clearly about the sequence for this project. **Figure 11** show the research flowchart:

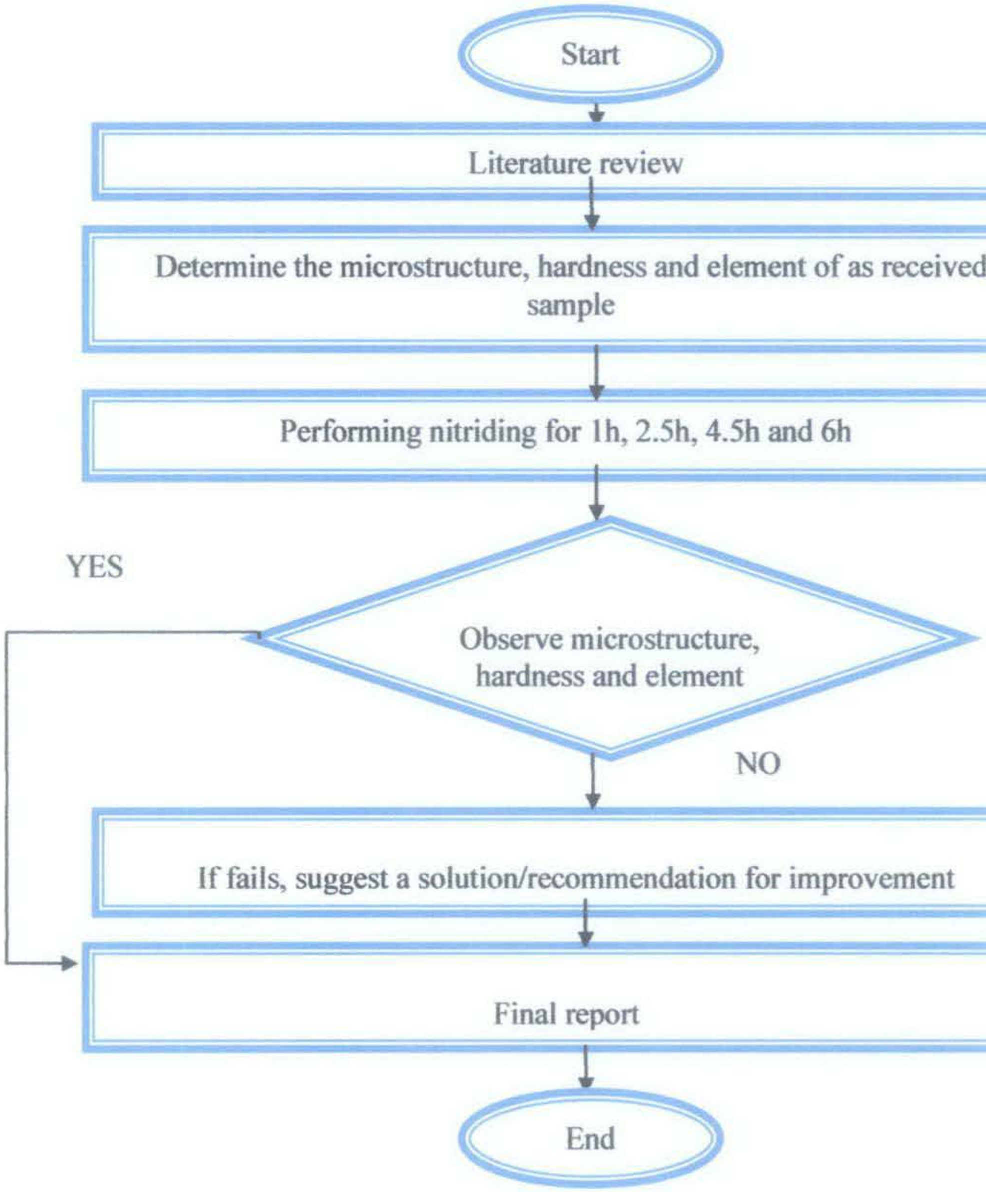


Figure 11: Project's flow chart

As of the research flowchart, the study into the concept of nitriding, limitation, and type of microstructure begin with researches. The author had read journals and articles to enhance the understanding on duplex stainless steels, its properties and microstructure, the concept of nitriding and all equipments that can be used on her project.

3.1 Procedures

In completing this project, few steps and procedures are taken to make sure that the objectives of the project are fulfilled.

3.1.1 Research Methodology

This project began with the study on discovering the project objective and study on the phases of duplex stainless steels and the nitriding process. There are several techniques used in performing the nitriding process which included gas nitriding, plasma and ion nitriding. For this project, high temperature gas nitriding was chosen. After confirming the technique to be used, further study on its effect on mechanical and physical properties of duplex stainless steel were done from previous papers. The study provides information on the microstructure, hardness, and phases of the nitrided duplex stainless steel. Literature review will be done continuously by referring to books, reference and some are from the previous papers and journal which are related to research area.

3.1.2. Material Acquisition

The material used in this project is LDX 2101 duplex stainless steels. The material was chosen because it is widely used as pipeline in oil and gas industry. Besides that, nitriding has potential to increase the surface properties of the material.

3.1.3 Sample preparation

The size of the material obtain is too big and need to be prepared to run this project. The author cut the duplex stainless steels to become pieces of specimens with a dimension of 20mm x 10mm x 5mm. Then, the surfaces of the samples need to be grind and polish until mirror image is obtained.

Step 1: Cutting the specimens

The material was cut by using Electrical Discharge Machine (EDM). The author choose to used EDM as a cutting machine to make a specimen because the Electrical discharge machining (EDM) is a machining method primarily used for hard metals or those that would be very difficult to machine with traditional techniques. In EDM wire cut a very thin wire serves as the electrode. Special brass wires are typically used where the wire is slowly fed through the material and the electrical discharges actually cut the work piece. **Figures 12** below shows the Electrical Discharge Machine and the product of the cutting process (Specimens).

Figure 12: Electrical Discharge Machine (EDM)

Step 2: Grinding

The specimen was ground using grinder shown in **Figure 13** below. It was ground on progressively finer SiC waterproof papers from 300 to 1200 grit, to produce a reasonably flat surface; it is lubricated with water to keep it cool and to remove the grinding products. If the sample is not flat, it might be necessary to remove some material on the lathe or grinding machine first. The sample should be moved forward and backward on the paper until the whole surface is covered with unidirectional scratches. It is then washed with running water to remove debris associated with the grade of paper used. It is then ground on the next finer paper such that the scratches produced are at right angles to those formed by the previous paper.

Figure 13:Grinder

Step 3: Polishing

Due to the very small depth of field obtained from an optical microscope it is essential that the surface is flat, in fact it needs to be optically flat, acting as a perfect mirror. The specimen therefore has to be "polished". This is done using rotating wheels covered with a cloth impregnated with a very fine abrasive compound. The compounds used are diamond. The 1 μm diamond wheel is used. The specimen is pressed down onto the lubricated rotating wheel. It is important not to hold the specimen in one orientation for an extended time as it will cause "dragging" of some microstructural components. After 20-30 seconds the specimen is removed and rotated through 90°in the hand, placed back on the wheel and then again oscillated. This process is continued until the fine scratches have been removed as shown in **Figure 14** below.

Figure 14: Sample that is free from scratches

3.1.4 Nitriding process

The nitriding process was done in a horizontal tube furnace as shown in **Figure 15**. The nitriding time was 1 hour, 2.5 hour, 4.5 hour and 6 hour with a constant temperature 1100°C. The gas compositions used was 100% nitrogen. The total gas flow rate was 120 mm^3 every time. The flow rate was control using flow meter as shown in **Figure 16**. Before starting the nitriding procedure, the furnace needs to be arranged properly. The samples must be cleaned using ultrasonic cleaner before putted inside the furnace. The weight of the samples was measured before and after nitriding.

Figure 15 :Horizontal tube furnace

Figure 16 : Flow meter

Step 1: Furnace arrangement

The furnace needs to be connected with nitrogen gas. The exhaust of the furnace must be connected with fume hood for safety reasons.

Step 2: Ultrasonic cleaning

Before putting the samples inside the furnace, it must be cleaned using ultrasonic cleaner. The purpose of this cleaning is to remove any debris that contain at the samples' surface. The samples were immersed with acetone inside a beaker. Then, the beaker was putted inside an ultrasonic cleaner. The cleaning time was 10 minutes. The ultrasonic cleaner can be seen in **Figure 17**.

(a) Front view of ultrasonic cleaner

(b) Top view of ultrasonic process

Figure 17 : Ultrasonic cleaner; (a) Front view (b) top view

Step 3: Nitriding

After cleaning the samples, the samples were putted in alumina boat. The alumina boat can be seen in **Figure 18**. The alumina boat will be placed at the center of the furnace. Steel wire was used to push the alumina boat to the center of the furnace. The furnace needs to be purged using nitrogen gas for 30 minutes to remove any gas *inside the furnace from previous experiments. Nitrogen composition inside the* furnace can be known by using oxygen indicator as shown in **Figure 19** below. After purging, the furnace will be heated. The heating rate was 5°C/min. During heating, nitrogen gas still flowing in the furnace. The nitriding time was 1 hour, 2.5 hour, 4.5 hour and 6 hour for a constant temperature 1100°C.

Figure 18 : Alumina boat

Figure 19 : Oxygen indicator for tube furnace

3.2 Microstructure Examination

The purpose of this test is to examine the microstructure changes subsequent to nitriding process. This test was conducted using optical microscope and scanning electron microscope. The chemical composition of the samples can be determined using energy-dispersive X-ray spectroscopy that attached together with the scanning electron microscope. The optical microscope is located at Block 17 as shown in **Figure 20** while the scanning electron microscope is located at Block P as shown in **Figure 21.**

Figure 20 : Microstructure examination using optical microscope

Figure 21 : Scanning electron microscope

Before conducting the microstructure examination, the samples need to be mounted, grinded, polished and etched.

Mounting of specimen is required so that it is more convenient during grinding and polishing. Specimen was mounted in a resin. Bakelite is commonly used. A further advantage of mounting is that the edges of the specimen will be reasonably well polished and not "bevelled" by the preparation process.

After mounting, the samples need to be grinded and polished. The method for this procedure has been discussed earlier.

For duplex stainless steels, the etchant used is fry reagent. The purpose of etching is to reveal the grain boundary. Firstly, the specimen was washed using alcohol and then dried. After that, fry reagent was applied at the surface of the specimen for 5 to 10 seconds as shown in **Figure 22**. Then the specimen was washed using water and alcohol. The specimen was dried and ready for microstructure examination. **Figure 23, Figure 24 and Figure 25** shows the step of etching that has been conducted.

Figure 22 : Etching solution; fry reagent

Figure 23 : Apply etching solution

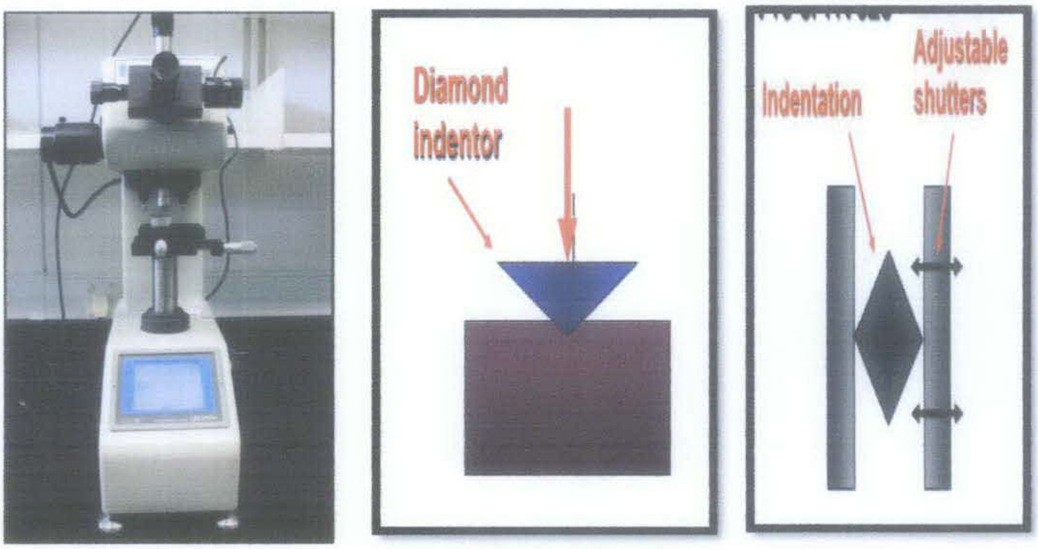
Figure 24 : Spray with Ethanol

Figure 25 : Dry the sample

3.3 Hardness Test

The hardness test was carried out by pressing a ball or a point with a predetermined force into the surface of the specimen. Three most commonly used methods are Brinell, Vickers and Rockwell hardness test. The measuring location on the specimens must have a bright, polished surface to prevent erroneous measurements due to rough grooves.

In this investigation, the method used for the hardness measurement is Vicker Hardness test as shown in **Figure 26**. Hardness is the measurement of material surface resistance to indentation from other material by static load. Indentation body is a square based diamond pyramid with 136 included angles. The average diagonal (d) from the adjustable shutters of the impression is converted to a hardness number. The indented image will be displayed in the calibrated Microscope screen. The load *used for this test was 25 gf. The dwell time was 15 second.*



(a) (b) (c)

Figure 26 : Hardness Measurement; (a)Vickers Hardness Equipment, (b) Diamond Pyramid Indentor, (c) Adjustable Shutters

3.4 X-Ray Diffraction Analysis

Generally, X-ray Diffraction is used to characterize the crystallographic structure and the technique that is commonly used is power method. In this technique a powdered specimen is utilized so that there will be a random orientation of many crystals to ensure that some of the particles will be oriented in the x-ray beam. It is also equipped with x-ray diffractometer that has a radiation counter to detect the angle and intensity of the diffracted beam. A recorder automatically plots the intensity of the diffracted beam as the counter moves on a goniometer cycle that is in synchronization with the specimen over a range of 2θ values. Commonly, the diffraction angles and intensities are plot simultaneously.

In the present investigation of nitriding of duplex stainless steel, the purpose of X-ray diffraction analysis is to determine the formation of alloying nitride subsequent to nitriding process. This will indicate the effectiveness of the process in collaboration with the hardness test and micrograph examination. The x-ray Diffraction machine used for this investigation was located at Block 17 as shown in **Figure 27**.

Figure 27: X-ray Diffraction Machine

3.5 Gantt Chart

For detail of project's planning and scheduling, refer **Table 5** *which is the Gantt* chart that shows the timeline allocate by the author to complete the task for FYP II.

Table 5 :FYP II Timeline Gantt Chart

Activities / Week	**1**	**2**	**3**	**4**	**5**	**6**	**7**		**8**	**9**	**10**	**11**	**12**	**13**	**14**	**15**
Project Work Continues	▨	▨	▨	▨	▨	▨	▨									
								Mid Semester Break								
Submission of progress report									●							
Project Worrk Continues									▨	▨	▨	▨	▨			
Pre-EDX												●				
Submission of Draft Report													●			
Submission of Dissertation (soft bound)														●		
Submission of Technical Paper														●		
Oral Presentation															●	
Submission of Project Dissertation (hard bound)																●

● Suggested Milestone

▨ Process

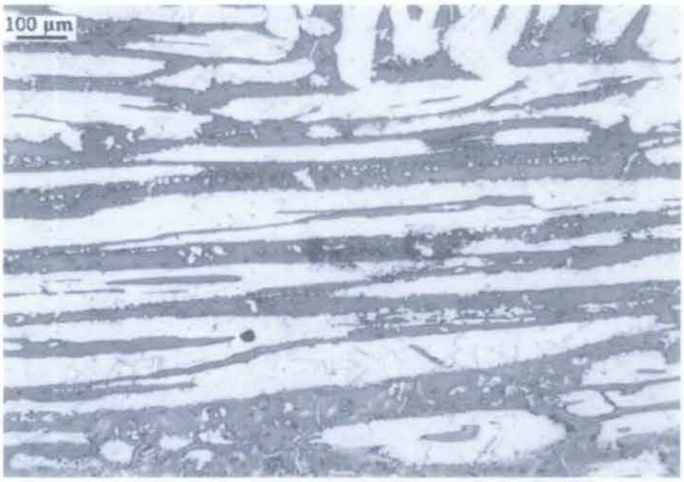
CHAPTER 4

RESULTS AND DISCUSSION

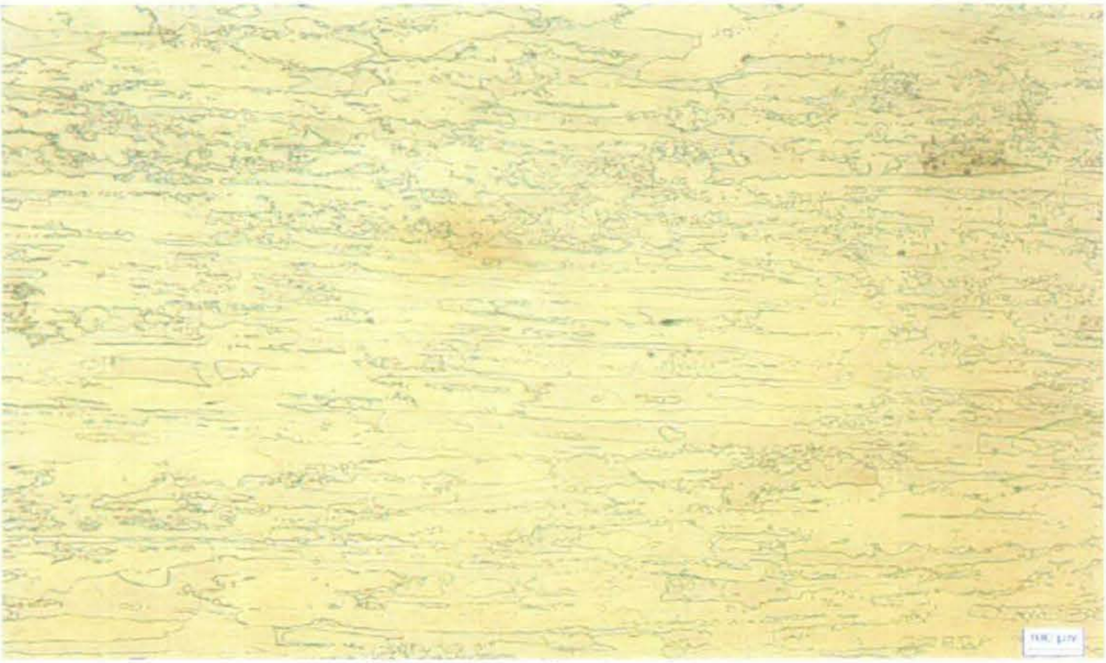
This chapter offers the experimental results of the untreated (as received) and heat treated LDX 2101 duples stainless steel through nitriding process. The results were obtained from the weight analysis, hardness test, microstructure test, edx analysis and x-ray diffraction analysis. The experiments were carried out in 1100°C for 1 hour, 2.5 hour, 4.5 hour and 6 hour.

4.1 Analysis on untreated duplex stainless steels

Figure 4.1 below shows an optical micrograph of the 'as received' (hot rolled) sample. The microstructures of the "as received" sample were analyzed using Optical Microscope (OM) and Scanning Electron Microscope (SEM). The microstructures that observed are compared with the reference microstructure with magnification of 100x by using Optical Microscope (OM) as in **Figure 28**. As for SEM, the microstructure with the reference of 500x and 1000x magnification are also shown in **Figure 29** below. The etching solution colors the ferrite dark and the austenite white. The typical ferrite-austenite duplex structure was observed. The austenite phase was evenly distributed as islands in the ferrite matrix and elongated along the rolling direction.



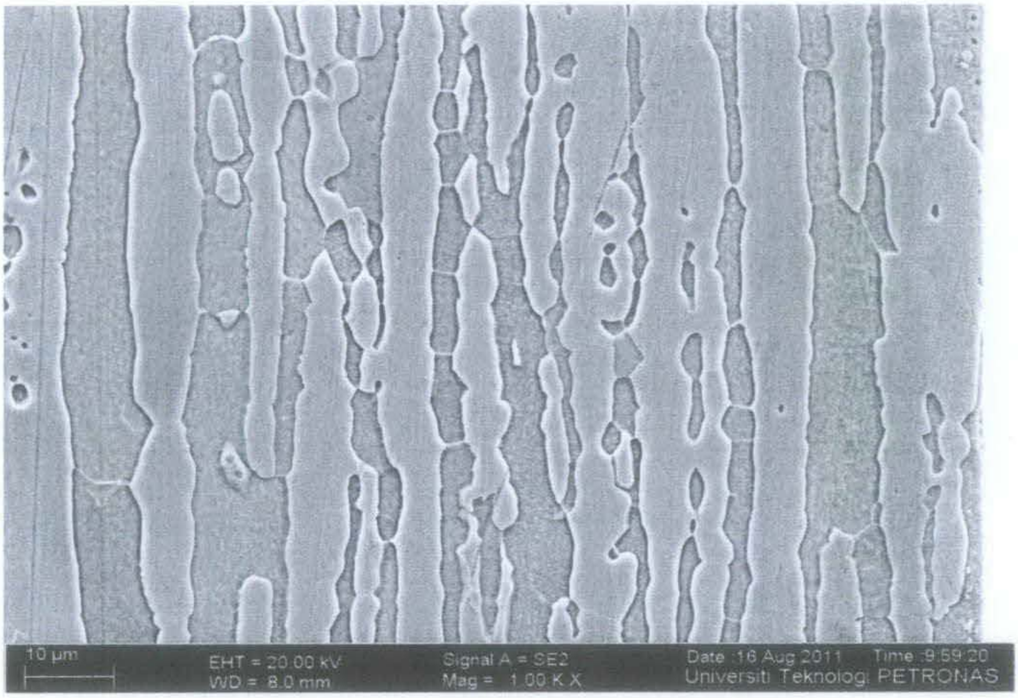
(a) reference microstructure of DSS [7]



(b) 100X magnification – I plane

Figure 28: DSS Microstructure by Optical Microscope; (a) Reference microstructure of DSS [6], (b) Microstructure of DSS under 100 x magnifications

(a) 500x Magnification



(b) 1000x Magnification

Figure 29 : DSS Cross section microstructure using SEM; (a) Microstructure under 500x magnification, (b) Microstructure under 1000x magnification

Table 6 below shows the surface hardness of untreated duplex stainless steel. The hardness measurement was taken at seven different points according to the distance from cross section surface. The load used was 25gf and the dwell time was 15 second. From **Table 6** shows the recorded hardness value for the sample at specific distance.

Table 6: Hardness for "as received' at specific distance

Distance from surface (µm)	0	50	100	150	200	250	300
Hardness (HV)	225.8	226.7	225.4	228.7	226.4	227.2	225.5

Area analysis on 'as received' has been conducted and the microstructure of the analysis is shown on **Figure 30** below. From area analysis, the compositions of the sample are tabulated as in **Table 7**.

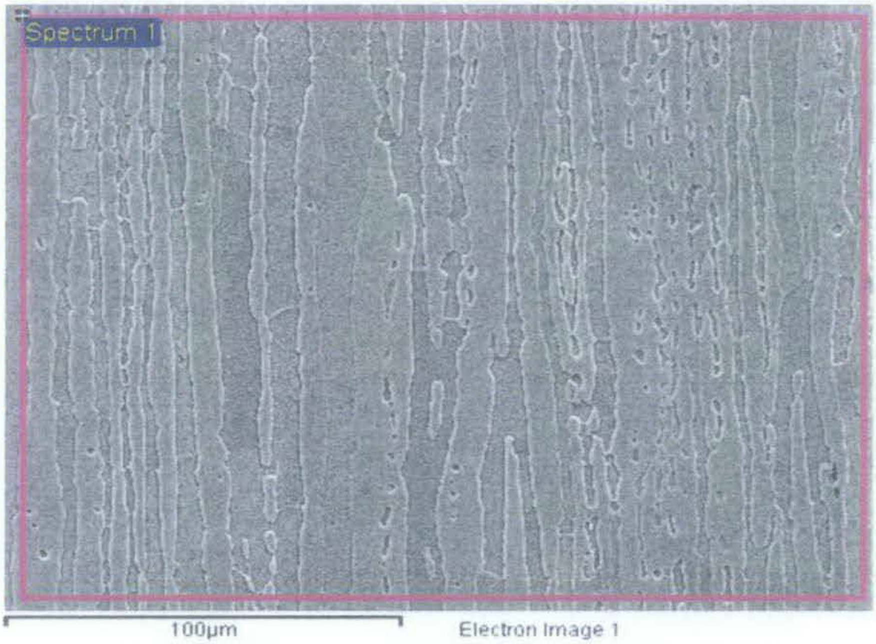


Figure 30: EDX Area analysis on 'as received' material

Table 7 : Overall chemical composition of as received sample

Element	Weight%	Atomic%
Cr K	22.74	26.62
Mn K	5.77	6.39
Fe K	72.17	78.66
Ni K	1.94	2.01
Mo L	0.10	0.06
Totals	100.00	

Spot analysis also has been conducted on 'as received 'sample for austenite and ferrite region. This has to be done in order to do a comparison between both regions after nitriding has been conducted. The results for both chemical compositions for austenite and ferrite region are tabulated in **Table 8** below.

Table 8 : Chemical compositions for austenite and ferrite region by spot analysis

Element	Weight %	
	Austenite	Ferrite
Cr K	21.91	24.04
Mn K	5.44	5.01
Fe K	71.43	70.78
Ni K	1.81	1.07
Mo L	0.26	24.04

From Table 7 and Table 8 above, EDX spot analysis has been conducted and the results for the as received material show that the percentages for elements Cr and Mo for ferrite region are higher than austennite. Where else, the weight for Mn, Fe, and Ni for ferrite region is slightly lower than austenite.

4.2 Weight of the samples before and after nitriding

Nitriding caused nitrogen to diffuse at the surface of the metal. The diffusion can increase the mass of the samples. If the mass of the samples increase after nitriding, it shows that nitrogen diffusion at the surface occurs. **Table 9** below shows the mass of the samples before and after nitriding process for 1 hour, 2.5 hour, 4.5 hour and 6 hour at constant temperature 1100°C.

Table 9 : mass of the samples before and after nitriding process

Sample parameters	Weight before nitriding (g)	Weight after nitriding (g)	Weight increase percentage (g) = weight after – weight before x 100% weight before
1.0 hour	7.281	7.284	0.04%
2.5 hour	7.350	7.355	0.07%
4.5 hour	7.351	7.360	0.12%
6.0 hour	7.466	7.484	0.24%

Based on **Figure 31** below, the increment of the weight percentage for nitrided sample for 1hour, 2.5 hour, 4.5 hour and 6 hour are consistent. So, it prove that nitriding do increase the weight of the nitride sample. Nitrogen diffusion do occur in the sample.

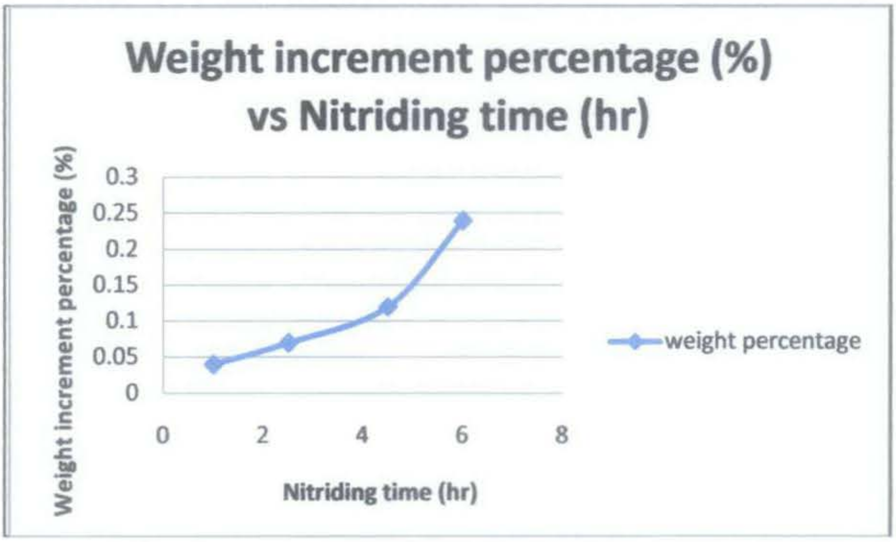


Figure 31: Graph of weight increment percentage (%) vs. Nitriding Time (hr)

4.3 Microstructural Development of Nitrided Duplex Stainless Steel

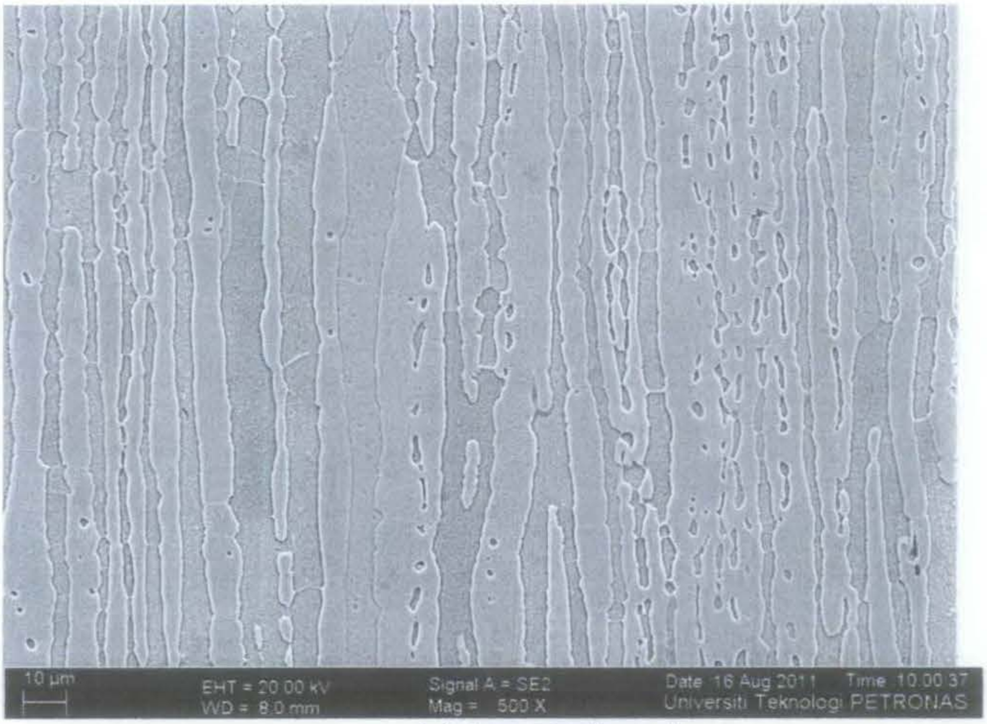
In this section, the microstructure of each specimen after nitriding was revealed in accordance with the processing parameters. The nitrogen composition is identified from the increment of nitrogen count per second (cps) at the cross section of the samples using energy-dispersive X-ray spectroscopy for each of the sample.

4.3.1 SEM analysis on Nitrided samples

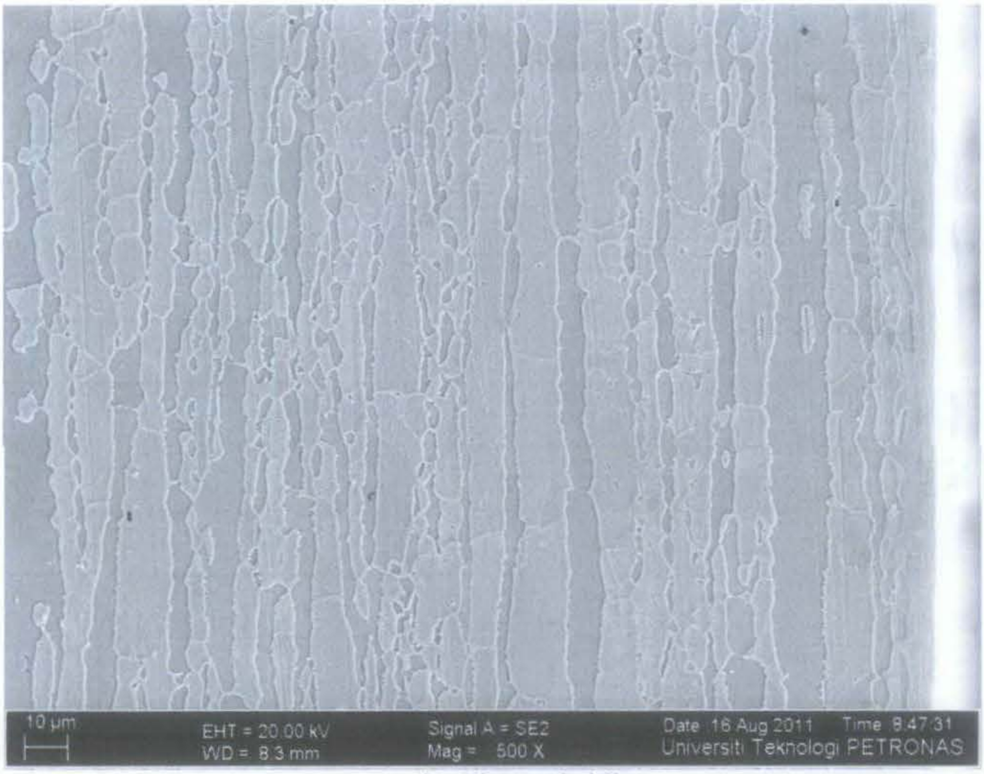
Microstructure of each specimen after nitriding was revealed in accordance with the processing parameters by using SEM. 500x magnification are used to observed the microstructural changes prior to nitriding time which is 1 hour, 2.5 hour, 4.5 hour and 6 hour for each specimens. Microstructural observations were based on the formation of austenitic phases subsequent to nitriding.

Figure 32 shows the microstructures of specimen's nitride at 1100°C for 1 hour, 2.5 hour, 4.5 hour and 6 hour. The typical ferrite-austenite phase was evenly distributed as islands in the ferrite matrix and elongated along the rolling direction. No visible precipitates were found in the nitrided specimens.

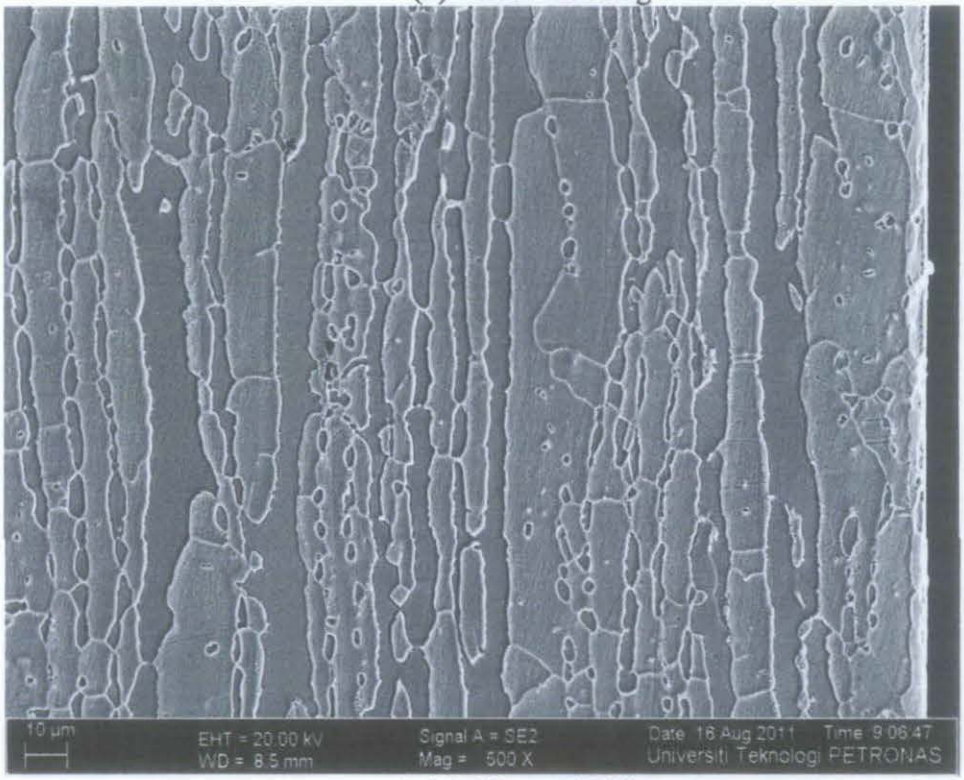
As can be seen from **Figure 32**, the austenitic volume fraction increase as the nitriding time is increased. During nitriding, nitrogen diffused to austenite and it leads to a decrease in ferrite region. For samples nitride at 1 hour, 2.5 hour, 4.5 hour and 6 hour the differences between ferritic and austenitic structures are clearly visible. It shows that austenite grain boundary becomes larger as the nitriding time is increasing compared to ferrite phases. This showed that austenite region are prolong as the time increase. It can be proved by microstructural analysis using SEM as shown in the **Figure 32** below.



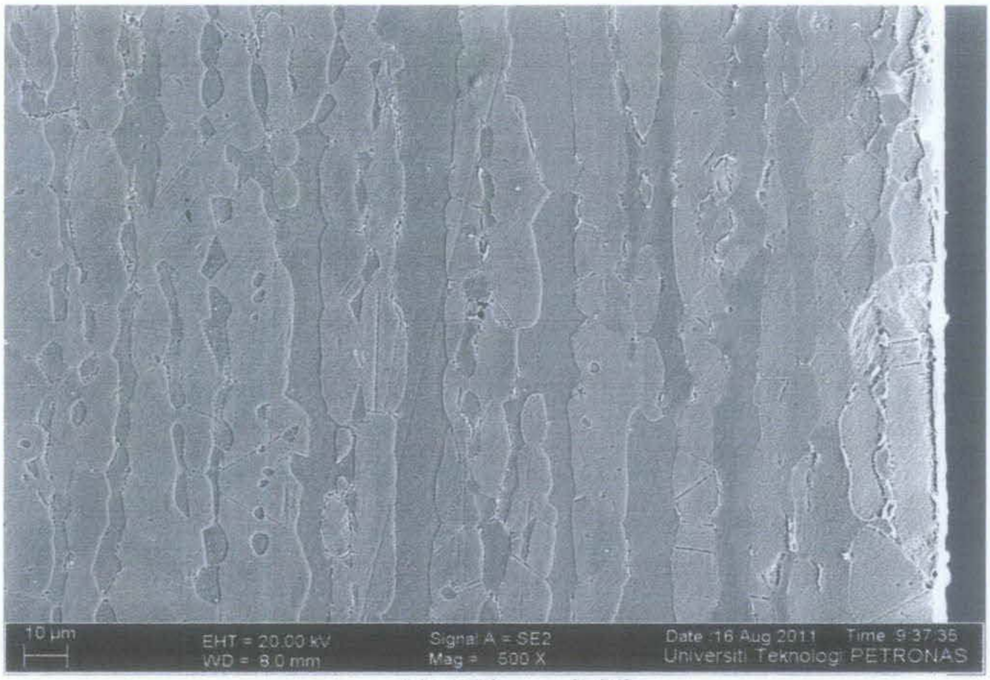
(a) As received sample



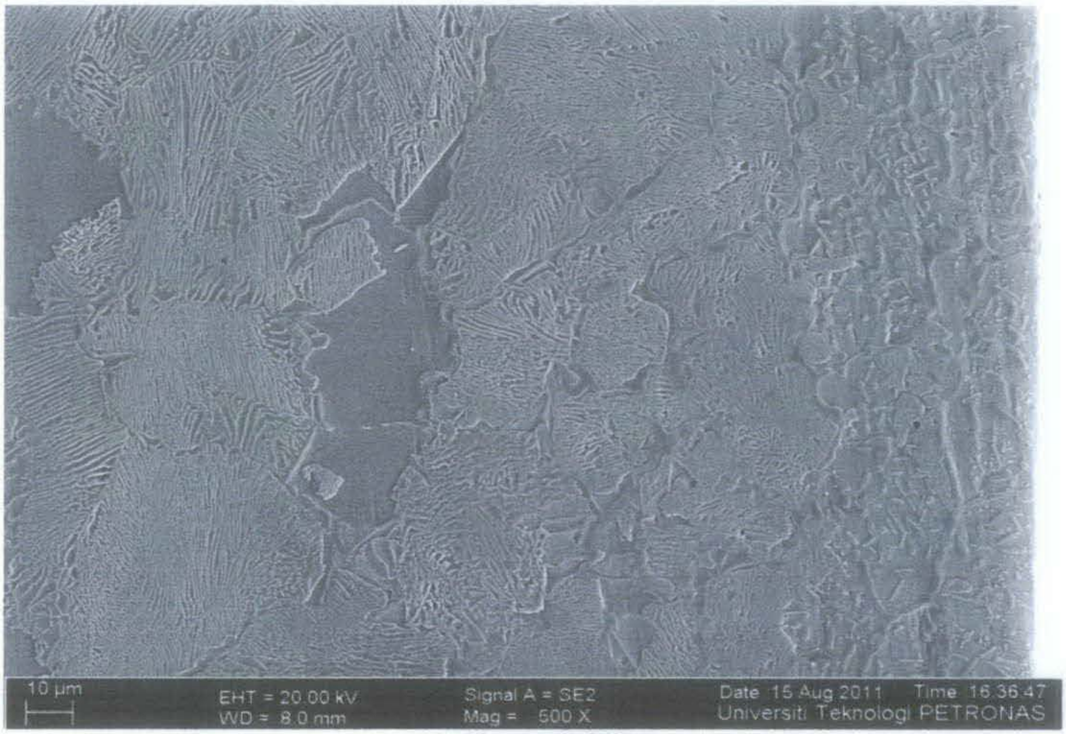
(b) 1 hour nitriding



(c) 2.5 hour nitriding



(d) 4.5 hour nitriding



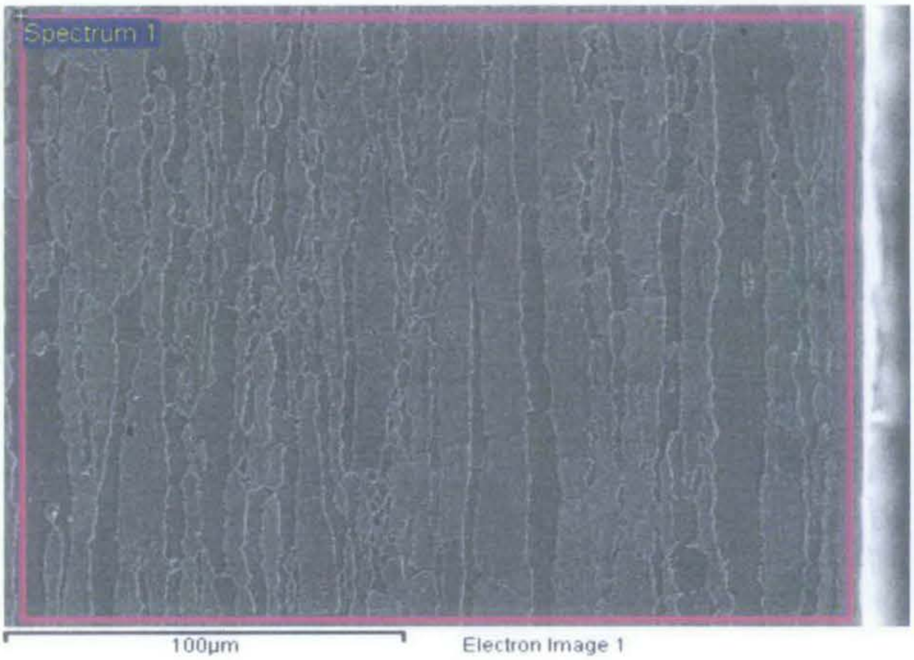
(e) 6 hour nitriding

Figure 32: Microstucture of DSS under variation of nitriding time using SEM with 500x magnification; (a) as received material, (b) 1 hour nitriding time, (c) 2.5 hour nitriding time, (d) 4.5 hour nitriding time, € 6 hour nitriding time

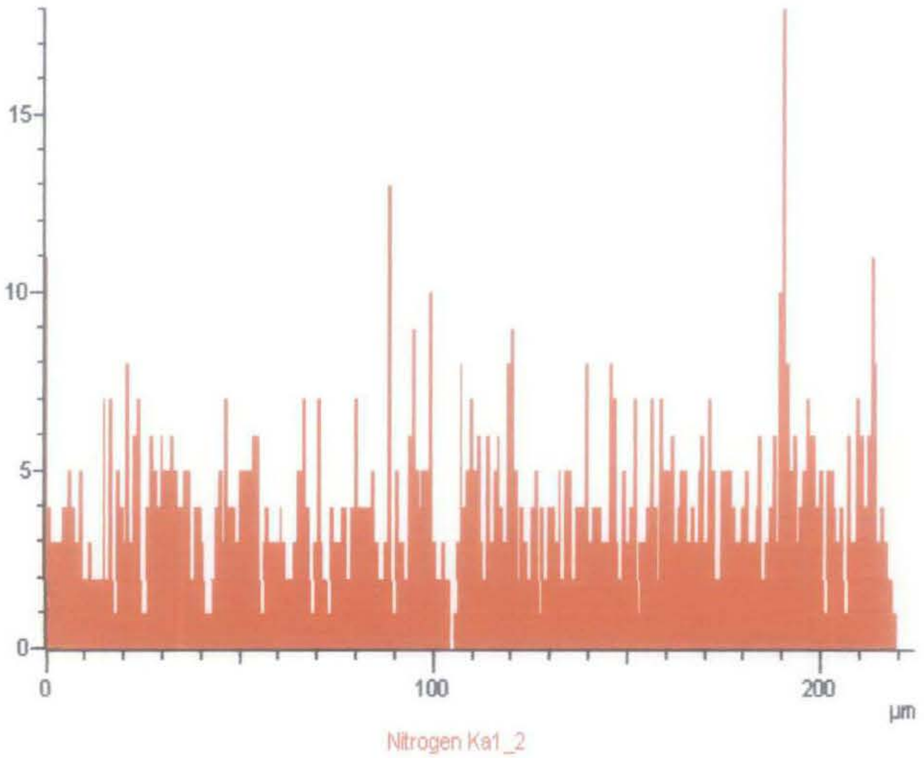
4.3.2 EDX analysis on Nitrided samples

Area analysis on treated samples have been conducted using SEM under 500x magnification and EDX analysis has been conducted after the nitriding at 1100°C for 1 hour, 2.5 hour, 4.5 hour and 6 hour. The nitrogen composition is identified from the increment of nitrogen count per second (cps) at the cross section of the samples using energy-dispersive X-ray spectroscopy for each of the sample.

Figure 33 (a) shows the micrograph of area analysis that has been conducted for nitride specimens at 1 hour under 500x magnification using SEM. Spot analysis also has been conducted on 1 hour nitride sample for austenite and ferrite region. This has to be done in order to do a comparison between both regions after nitriding has been conducted. The chemical compositions for austenite and ferrite region are shown in **Table 10. Figure 33 (b)** shows the nitrogen profile cross-sectional nitrogen count per second for 1 hour nitriding time.



(a) Micrograph of area analysis under 500x magnification



(b) Nitrogen profile cross-sectional nitrogen count per second

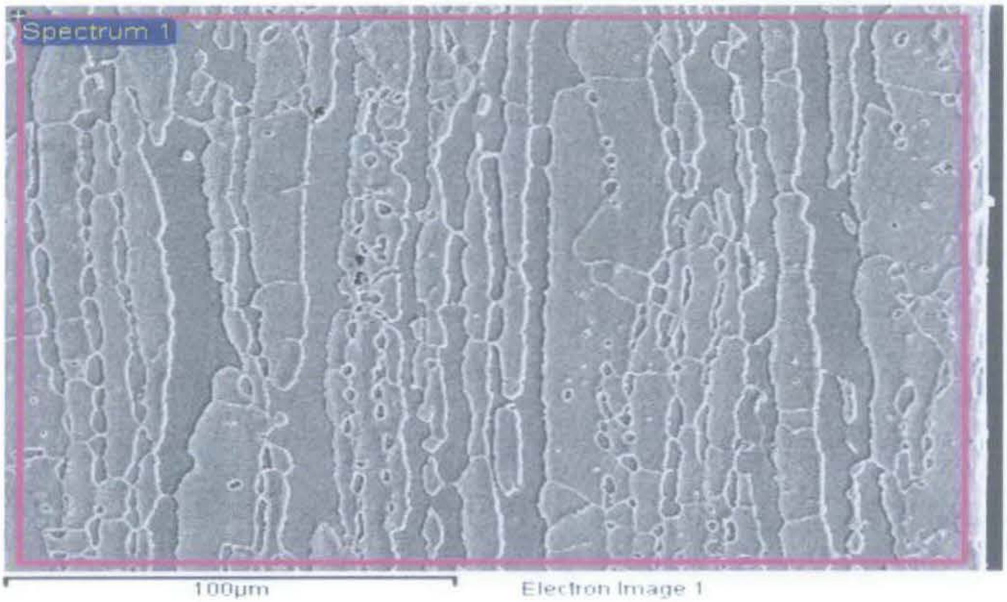
Figure 33: 1 hour nitriding time; (a) Micrograph of area analysis, (b) Cross section nitrogen profile counts per second

Table 10 : Chemical compositions for austenite and ferrite region for 1 hour nitriding time

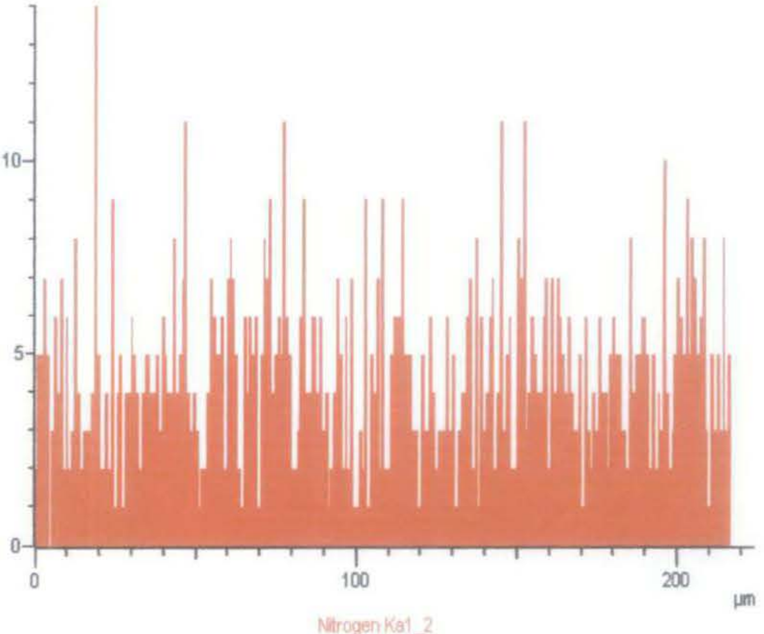
Element	Weight%	
	Austenite	Ferrite
N K	0.63	0.25
Si K	0.94	0.88
Cr K	21.56	24.27
Mn K	5.29	4.68
Fe K	70.49	69.79
Ni K	1.97	1.02

Figure 34 (a) shows the micrograph of area analysis that has been conducted for nitride specimens at 2.5 hour under 500x magnification using SEM. Spot analysis also has been conducted on 2.5 hour nitride sample for austenite and ferrite region.

This has to be done in order to do a comparison between both regions after nitriding has been conducted. The chemical compositions for austenite and ferrite region are shown in **Table 11**. **Figure 34 (b)** shows the cross-sectional nitrogen count per second for 2.5 hour nitriding time.



(a) Micrograph of area analysis under 500x magnification



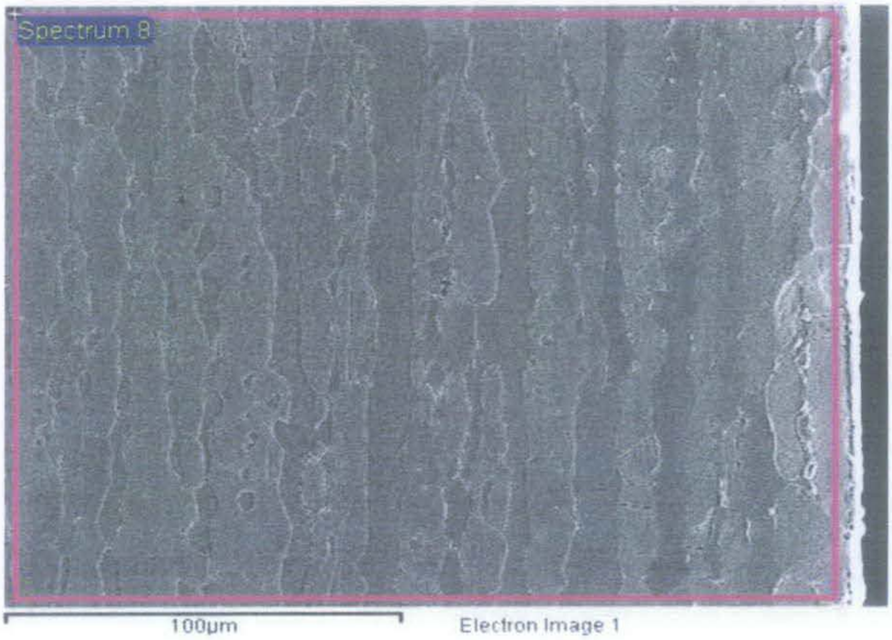
(b) Nitrogen profile cross-sectional nitrogen count per second

Figure 34 : 2.5 hour nitriding time; (a) Micrograph of area analysis, (b) Cross section nitrogen profile counts per second

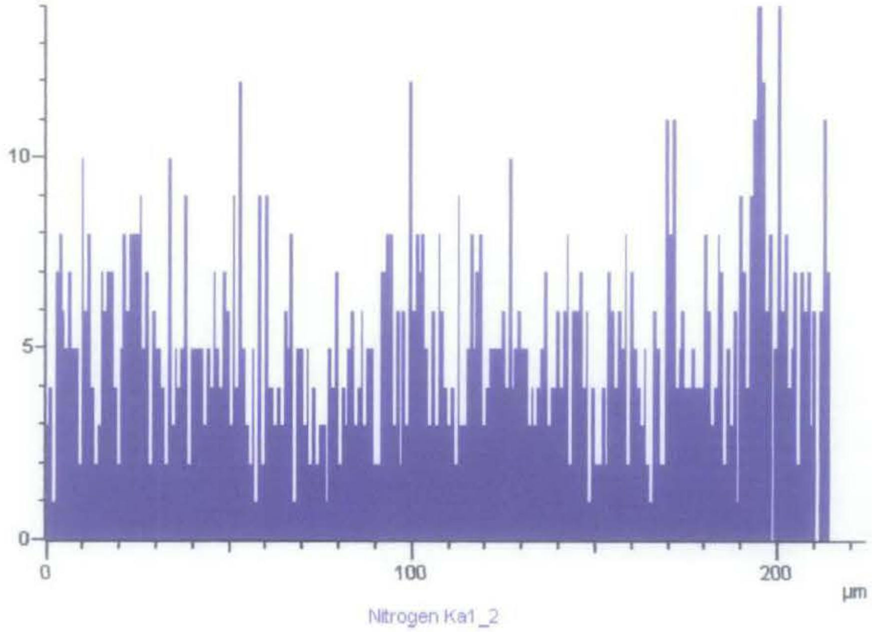
Table 11: Chemical compositions for austenite and ferrite region for 2.5 hour nitriding time

Element	Weight%	
	Austenite	Ferrite
N K	0.80	0.75
Si K	1.01	0.93
Cr K	23.24	22.73
Mn K	4.31	4.67
Fe K	64.75	65.95
Ni K	1.15	

Figure 35 (a) shows the micrograph of area analysis that has been conducted for nitride specimens at 4.5 hour under 500x magnification using SEM. Spot analysis also has been conducted on 4.5 hour nitride sample for austenite and ferrite region. This has to be done in order to do a comparison between both regions after nitriding has been conducted. The chemical compositions for austenite and ferrite region are shown in **Table 12. Figure 35 (b)** shows the cross-sectional nitrogen count per second for 4.5 hour nitriding time.



(a) Micrograph of area analysis under 500x magnification



(b) Nitrogen profile cross-sectional nitrogen count per second

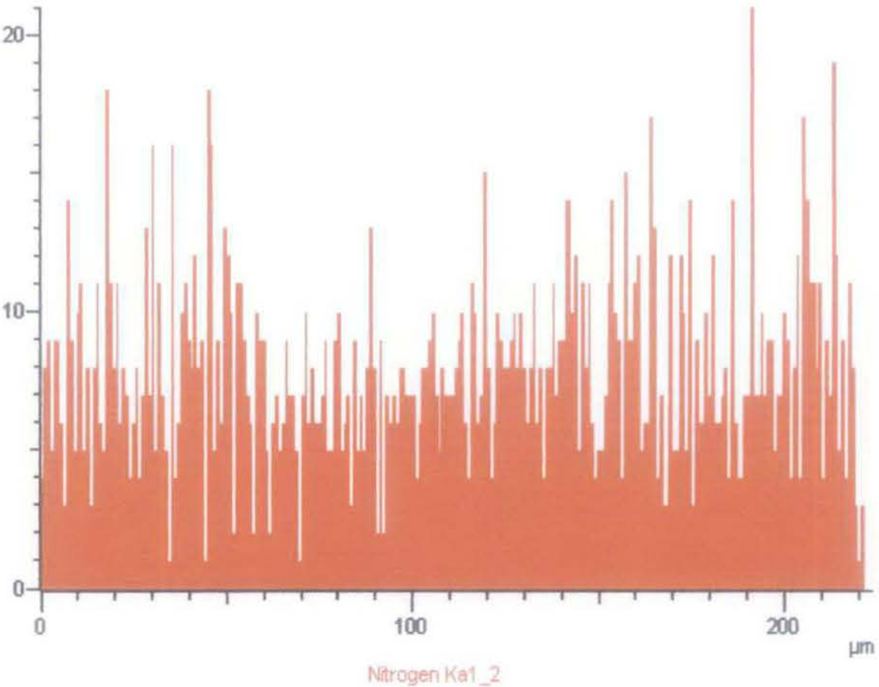
Figure 35 : 4.5 hour nitriding time; (a) Micrograph of area analysis, (b) Cross section nitrogen profile counts per second

Table 12: Chemical compositions for austenite and ferrite region for 4.5 hour nitriding time

Element	Weight%	
	Austenite	Ferrite
N K	1.28	1.27
Cr K	22.71	22.82
Mn K	5.30	5.21
Fe K	69.95	70.23
Ni K	1.32	1.72
Mo L	0.12	0.31

Figure 36 (a) shows the micrograph of area analysis that has been conducted for nitride specimens at 6 hour under 500x magnification using SEM. Spot analysis also has been conducted on 6 hour nitride sample for austenite and ferrite region. This has to be done in order to do a comparison between both regions after nitriding has been conducted. The chemical compositions for austenite and ferrite region are shown in **Table 13**. **Figure 36 (b)** shows the cross-sectional nitrogen count per second for 6 hour nitriding time.

(a) Micrograph of area analysis under 500x magnification



(b) Nitrogen profile cross-sectional nitrogen count per second

Figure 36: 6 hour nitriding time; (a) Micrograph of area analysis, (b) Cross section nitrogen profile counts per second

Table 13: Chemical compositions for austenite and ferrite region for 6 hour nitriding time

Element	Weight%	
	Austenite	Ferrite
N K	3.87	1.67
Si K	0.82	0.65
Cr K	22.59	16.71
Mn K	4.96	4.48
Fe K	61.45	69.04
Ni K	1.17	1.55

From the entire Figure above, nitriding do increases the amount of nitrogen diffuse in the sample. This is shown in **Figure 33 until Figure 36** the count per seconds for nitrogen amount for each specimen is increasing as the nitriding time is increase. **Table 14** below shows the comparison of nitrogen content in austenite and ferrite phases for each nitriding time. As shown in the table, more nitrogen diffuse in austenite phase compared to ferrite. These prove on why the grain boundaries for each nitride sample for austenite are larger than ferrite phases. More nitrogen diffuse in austenite make the phases become larger and the structural for the material will be improved as the hardness will increase.

Table 14 : Nitrogen content in austenitic and ferrite phases for nitride samples

Nitriding time	Nitrogen content (%)	
	Austenite	Ferrite
1 hour	0.63	0.25
2.5 hour	0.80	0.75
4.5 hour	1.28	1.27
6 hour	3.87	1.67

4.4 Hardness Profile of the Nitrided Duplex Stainless Steel

Hardness test was conducted to determine the characteristic of each specimen under the influence of the processing parameters such as nitriding time. Microhardness

Vickers test were conducted on the specimens from the distance of the bakelite or mounting. The load used was 25 g and the dwell time was 15 second. The results of the measurement are tabulated in **Table 15** as below:

Table 15 : Hardness of sample tested using Vickers Microhardness

Vickers Microhardness (HV)							
Distance (μm) from surface / Sample parameters	0	50	100	150	200	250	300
As received	225.8	226.7	225.4	228.7	226.4	227.2	225.5
1.0 hour	314.6	291.1	283.8	267.3	252.5	244.9	243.4
2.5 hour	336.8	326.3	310.4	298.9	286.7	285.5	284.7
4.5 hour	410.3	402.5	398.8	386.9	379.2	378.9	369.5
6.0 hour	448.2	434.9	423.5	405.8	398.2	393.8	387.4

The hardness of the surface of the samples prior to distance is given in **Table 15**. All samples undergone nitriding process show that their hardness are increased. Apparently nitriding as short as 1 hour has increased the hardness of the steel. As compared with the unnitrided sample, all nitriding applied to the samples show that a very high hardness was achieved.

The results given in **Figures 20** also illustrate that higher hardness is achieved by samples nitrided at longer time. Longer nitriding time is expected to diffuse more nitrogen into the steel. Thus it can be assumed that higher nitrogen content leads to higher hardness.

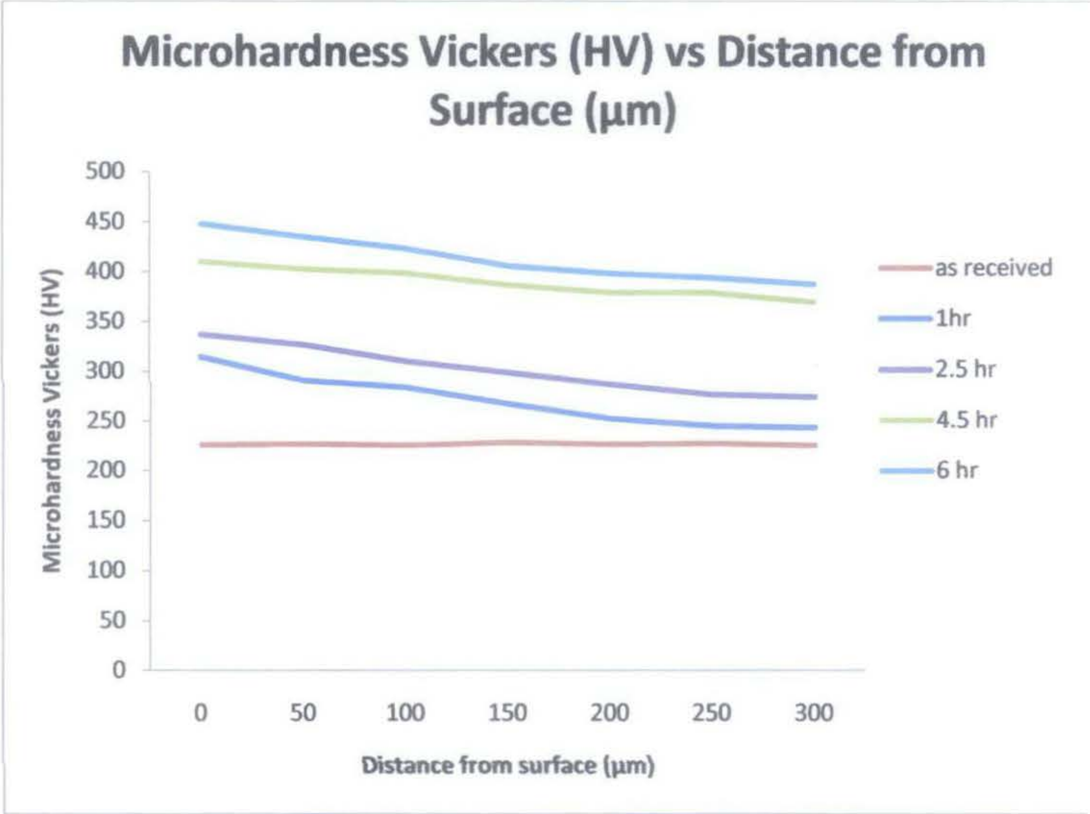


Figure 37 : Microhardness Vickers (HV) vs. Distance from Surface (µm)

Nitriding for 6 hour at 1100°C, the hardness profile is observed to have the highest hardness as compared to nitriding at 1 hour, 2.5 hour and 4.5 hour for the same temperature. From **Figure 37**, it is verified that the nitriding time affects the surface hardness significantly, in all of the samples.

The hardness for nitrided DSS is decreasing as it moves further from the surface. For nitrided DSS at 1 hour, the hardness of the outmost surface was 314.6 HVand decrease to 244.9 HV in the interior region. As for 6 hour of. It demonstrate that nitrogen just diffuse at the surface of the metal not until the core of the metal. **Figure 37** shows hardness profile of nitrided DSS.

4.4 X-Ray Diffraction Pattern of Duplex Stainless Steels

In order to clearly demonstrate which phases appeared at the surfaces of High Temperature Gas Nitriding (HTGN) treated and untreated specimens, XRD measurement was employed, as shows in **Figures 38**. Figure 38(a) shows the XRD patterns of the specimens treated with HTGN at 1100°C for 6 hour and followed by Figure 38(b) until Figure 38(d) the specimens treated at 4.5 hour, 2.5 hour and 1 hour. Figure 38(e) shows the XRD analysis of untreated material. At the surface of the specimens treated by HTGN, Cr_2N and FeN was observed along with the ferrite and austenite peak. It is believed that the appearance of these elements was due to the affinity between chromium and carbon/nitrogen.

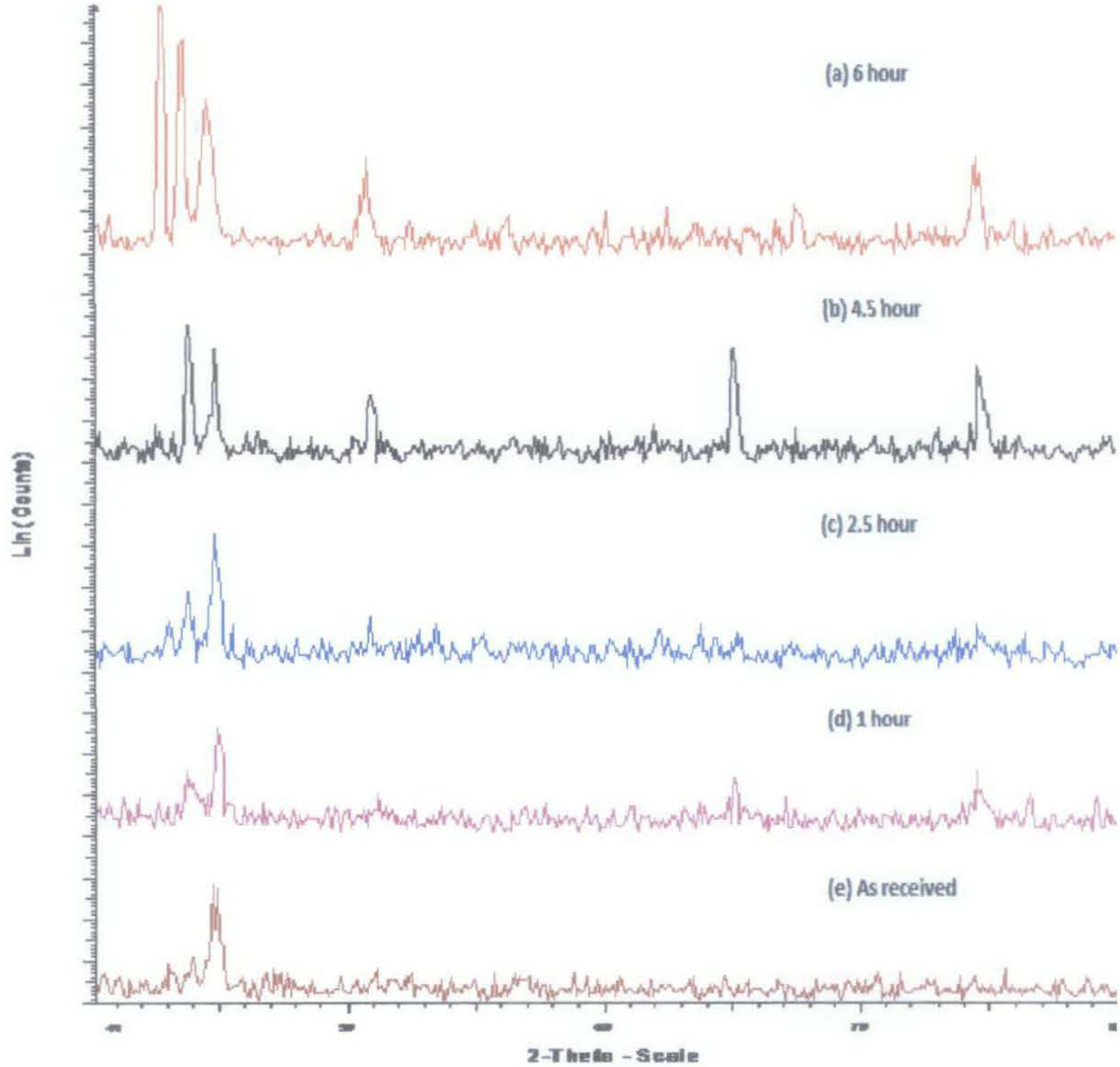


Figure 38 : X-Ray diffraction patterns of the specimens Duplex Stainless Steels at variation nitriding time

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As a conclusion, the objectives set up for this research has been accomplished which are basically to investigate the effect of High Temperature Gas Nitriding process towards the physical and mechanical properties of the duplex stainless steel. The high temperature gas nitriding has successfully improved the surface of duplex stainless steel. Longer nitriding time improves hardness of the steel due to the diffusion of nitrogen into the steel. Highest hardness; 448.2 HV is achieved by sample nitride at 1100 °C for 6 hours. It is expected that the formation of austenite will increase as the nitriding time increased. The nitrogen content affected the formation of the grains. Large austenite phases show the large increase of nitrogen content in it. As a result, as the nitriding time increased, the nitrogen content will increase and the austenite phases will be larger. Thus, the hardness of the metal will increased as well.

5.2 Recommendation

For future research, some improvements could be done. It is recommended for future investigations to:

i. Examine the elements and phases exist in nitride samples as quenching is done.

ii. Examination on nitrogen content at the treated samples is required to relate the hardness of the treated sample.

iii. Examine the corrosion resistance of the treated sample.

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