Nitriding of X-52 Carbon Steel: Mechanical Characterization

by

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
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Approved by,

(AP Ir. Dr. Mokhtar Che Ismail)

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.

MUHAMMAD SYAHIR BIN BASHARUDDIN

ABSTRACT

Carbon steel is the most cost effective material that being used in oil and gas industry. Although it is widely used, it has some limitation particularly in terms of corrosion resistance. Improving the surface properties can be beneficial to reduce the corrosion rate. Nitriding is one of the methods to improve the surface properties of carbon steel typically done at 495-595°C for 70 hours. Since corrosion resistance is related to the metal surface interaction with the corrosive environment, improving surface by nitriding could increase corrosion resistance of carbon steel. However, typical length of nitriding which is 70 hours is not economical. Only thin nitride layer required to improved carbon steel corrosion resistance. Thus, objective of this research is to conduct nitriding at 450°C, 480°C, and 520°C for 8 hours only. Metallography characterization, surface hardness measurement, and XRD characterization after the treatment were performed to examine the result of the treatment The surface hardness of nitriding at 8 hours is similar with the surface hardness of nitriding at 70 hours. Higher nitriding temperature produces higher surface hardness. Nitriding at 450°C produced surface hardness of 302HV. Surface hardness of 344HV is produced when nitriding at 480°C. Nitriding at 520°C produced the highest surface hardness which is 398HV. The only different is the case depth. 70 hours of nitriding can produced case depth around 25μm. Nitriding for 8 hours can only produced case depth of 3μm to 6μm. Phase transformation does not occur at the core metal due to low temperature heat treatment. X-ray diffraction pattern shows that alloying nitride is form due to nitrogen diffusion. The presence of alloying nitride increases the surface hardness. The conclusion of this project is nitriding is successful at shorter duration of 8 hours but lower nitriding thickness of 3-6 μm. The mechanical characteristic of the nitriding layer is comparable to the nitriding at 70 hours.

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CHAPTER 1

INTRODUCTION

1.1 Project Background

Carbon steel is widely used in industry. It is the most cost effective material in oil and gas sector. However, carbon steel has some limitation in terms of corrosion resistance. Corrosion resistance is related with the corrosive environment. This limitation will required a lot of inspections to maintain the material working conditions. Corrosion resistance of carbon steel can be increase by improving the surface properties of carbon steel. Nitriding is one of the methods that can improve surface properties of carbon steel. Nitriding procedure usually takes around 70 hours to improve metal surface properties and to produce case depth. The process time is very long and not economical. The process cost can be reduced significantly by reducing nitriding time. The effect of shorter nitriding time for carbon steel is unknown.

Nitriding is a heat treatment process which involves altering the microstructure of material to obtain desired properties such as mechanical properties, physical properties and corrosion properties with the application of series of thermal cycle. Nitriding is performed to improve wear resistance, fatigue strength, surface hardness and also corrosion resistance. Its basic principle is diffusion of nitrogen into the surface of a material. It is enormously utilized in the automotive, mechanical and aeronautical engineering. Crankshaft, gears, valve parts, die-casting tools, forging dies and extruder screws are some parts that undergoes the metallurgical process.

Nitriding involves the diffusion of nitrogen into the surface layers of low carbon steel at elevated temperature. The formation of nitrides in the nitrided layer provides the increased hardness. Nitriding is typically carried out in the temperature range of 500 - 575°C, This is in the ferritic state rather than the austenitic used for carburising. This is possible since ferrite has a much higher solubility for nitrogen than it does for carbon.

The advantage of nitriding in the ferritic state is that any previous heat treatment of the steel component is not disrupted and there is little / no distortion of the final component shape. Nitriding can be carried out using solid, liquid or gaseous media but the most common is gas nitriding using ammonia (NH3) gas as the nitrogen carrying species. To get a hardening effect on nitriding the steel must contain strong nitride forming elements such as Al, Cr and / or V.

The characteristic of nitrided X52 carbon steel is unknown. The author will perform nitriding on X52 carbon steel. Low temperature nitriding and short nitriding time is used. There is no research on metallography of nitrided X52 carbon steel. The author will conduct metallography characterization, surface microhardness measurement and XRD characterization on the nitrided X52 carbon steel. The characterization will be performed by using optical microscope, SEM, XRD and Vickers Microhardness.

1.2 Problem Statement

Nitriding is a surface heat treatment to increase the surface properties of metal. The effectiveness of nitriding not only depends on temperature but it is also depends on the process duration. No extensive study on effect of shorter duration in nitriding for carbon steel.

1.3 Objective and Scope of Study

The objectives of the project are to conduct nitriding on X52 carbon steel at shorter duration and to perform metallography characterization, XRD characterization, and surface hardness measurement. Nitriding is being conducted at 450°C, 480°C, and 520°C for 8 hours.

CHAPTER 2

LITERATURE REVIEW

2.1 Material Selection for Oil and Gas Pipeline

Pipeline for oil and gas transportation are very significant components of national as well as global economic infrastructures. API 5L has set specification to provide standards for pipe suitable for use in conveying gas, water, and oil in both the oil and natural gas industries. (API, 2000)

The current API 5L edition is an adopted back ISO 3183 specification that contains both API and ISO requirements melded together to result in a single international standard. API 5L was maintained by Subcommittee 5 / Task Group on Line Pipe. Quality management system must be performed by manufacturer to meet the requirement of Spec 5L. (Baniak, 2008)

The European gas pipeline network plays very important role for national economies as well as global. In 2004, X52 carbon steel is the most type of steel that being used in European gas network. The distribution of different grades of steel in European gas network can be seen in Figure 2.1 below.

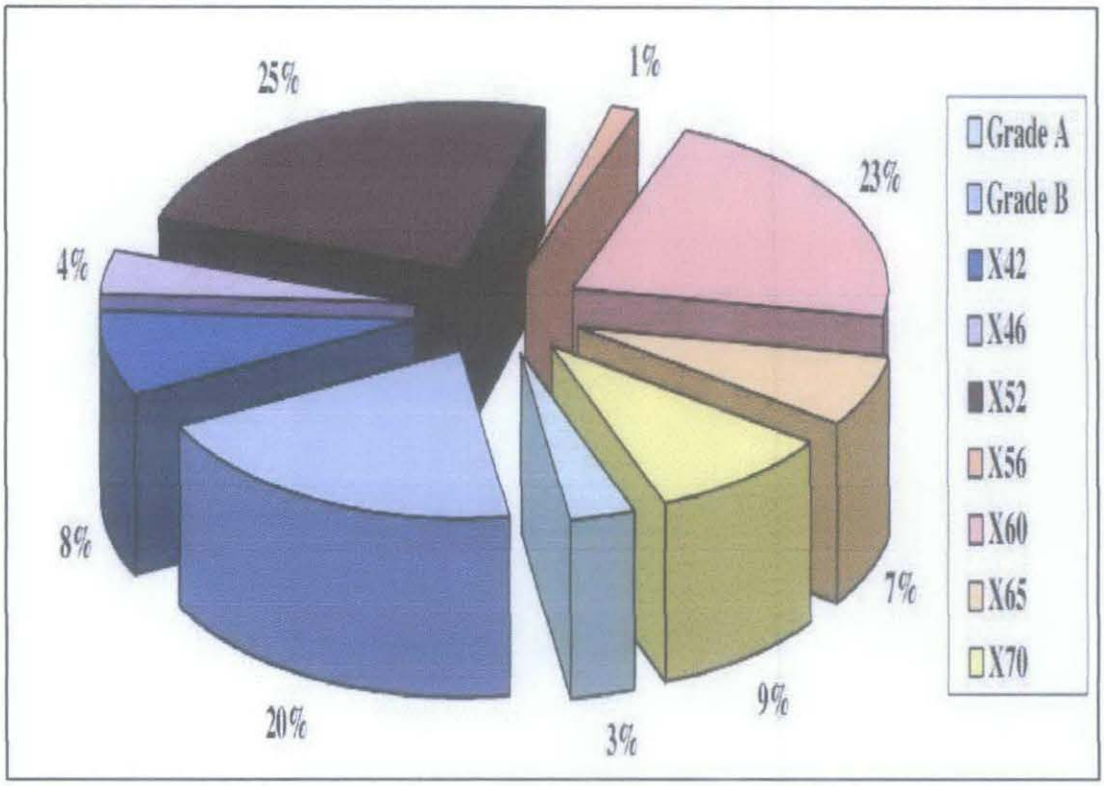


Figure 2.1: Distribution of different grades of steel in European gas network in 2004 (6th Report of the Europeon Gas Pipeline Incident Data Group 1970-2004, 2005)

2.2 Nitriding Process

In nitriding, nitrogen is introduced into the surface of the steel while it is in ferritic condition. This surface hardening heat treatment is similar to carburizing but nitrogen is added into the ferrite instead of austenite. The secret of the nitriding process is that it does not require a phase change from ferrite to austenite, nor does it require a further change from austenite to martensite. In other words, the steel remains in the ferrite phase (or cementite, depending on alloy composition) during the complete procedure. This means that the molecular structure of the ferrite (body-centered cubic, or bcc, lattice) does not change its configuration or grow into the face-centered cubic (fcc) lattice characteristic of austenite, as occurs in more conventional methods such as carburizing. Furthermore, because only free cooling takes place, rather than rapid cooling or quenching, no subsequent transformation from austenite to martensite occurs. Again, there is no molecular size change and, more importantly, no dimensional change, only slight growth due to the volumetric change of the steel surface caused by the nitrogen diffusion. What can produce distortion are the induced surface stresses being released by the heat of the process, causing movement in the form of twisting and bending.

Principal reasons for nitriding are:

- To obtain high surface hardness
- To increase wear resistance and antigalling properties
- To improve fatigue life
- To improve corrosion resistance (except for stainless steels)
- To obtain a surface that is resistant to the softening effect of heat at temperatures up to the nitriding temperature

In nitriding, the steel is heated in the furnace and the transfer of nitrogen to the furnace will produce nitride layer. The nitride layer generally will improve the hardness of the surface. Nevertheless, the nitriding parameter is extremely important to ensure that the surface has high surface hardness with sufficient thickness layer but without the formation of brittle white layer that can be seen in Figure 2.2. (Pye, 2007)

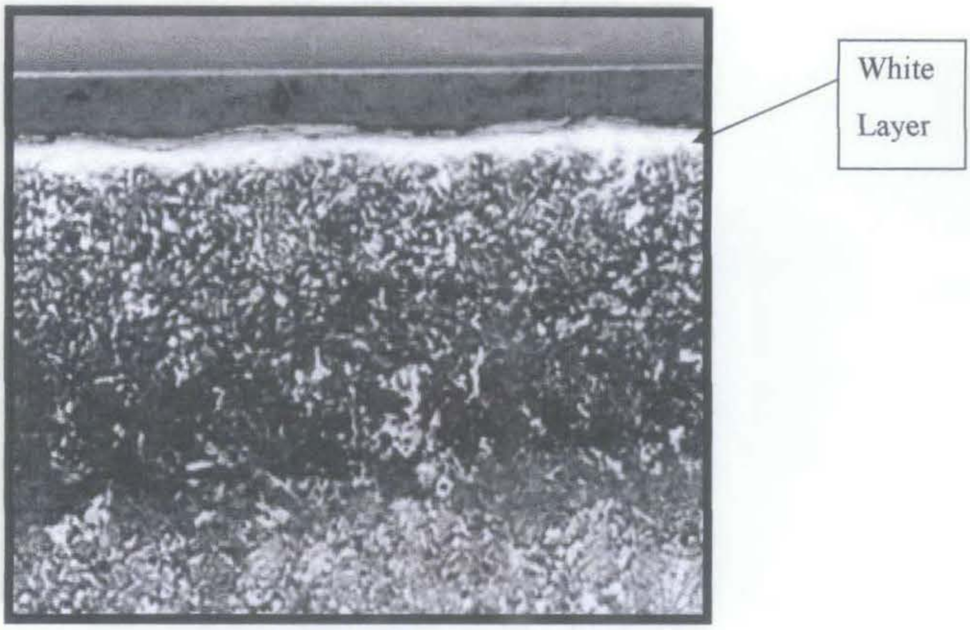


Figure 2.2: Brittle White Layer

The properties of the compound layer, also known as the white layer, have generated much interest among engineers and metallurgists. The formed phases within the surface layer are known as:

- The epilson phase
- The gamma prime phase

Epilson Phase

During the gas nitriding process the compound layer is formed and it has been previously stated that the compound layer comprises the two metallurgical phases that are mixed together. Generally each of the two phases is present on the surface. The value of each phase is approximately 50%. The epsilon phase is strongly influenced by the presence of carbon in the steel, and if carbon is present in the gas flow. A compound layer of predominately epsilon phase will create a surface with good wear characteristics, but it will have no impact strength. To create a dominant phase of epsilon in the compound layer it can be accomplished simply by raising the process temperature to 570°C (1060F) and adding methane to the gas flow.

Gamma Prime Phase

The gamma prime phase is a phase that is present in the compound layer and it will give reasonably good impact strength without surface fracture, provided that the compound layer is not excessively thick. To accomplish this, one would simply maintain a process temperature of 500°C (930F) and reduce the nitriding potential of the process gas. Control of the thickness of the compound layer is simply accomplished by process temperature and gas flow manipulation for the process of gas nitriding.

Gas Nitriding

In gas nitriding process, the gas used is usually Ammonia (NH_3). The Ammonia disassociates into nitrogen and hydrogen when it comes into contact with the heated workpiece. Figure 2.3 shows the dissociation of ammonia and nitrogen pick-up in steel during gas nitriding. Below is the balanced chemical equation for the disassociation process:

$$2NH_3 \rightleftharpoons 2N + 3\,H_2$$

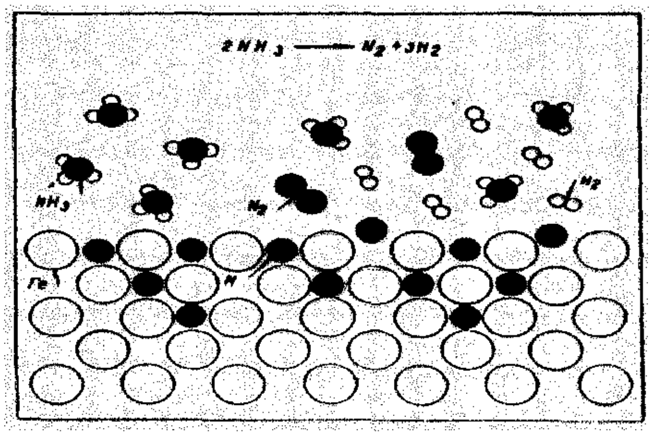


Figure 2.3: Dissociation of ammonia and nitrogen pick-up in steel during gas nitriding

Several advantages of this process include minimum distortion and deformation. In addition, the equipment cost for gas nitriding is relatively low as compared to Plasma nitriding. However, gas nitriding has limitations too. Since the nitriding medium is ammonia, it must be handled with good care especially when heating with the presence of oxygen. This is to reduce the risk of explosion. Besides, oily surface will give poor results because the reaction kinetic is highly influenced by the surface condition.

Gas Nitriding is a case-hardening process whereby nitrogen is introduced into the surface of a solid ferrous alloy by holding the metal at a suitable temperature (below Ac1, for ferritic steels) in contact with a nitrogenous gas, usually ammonia. Quenching is not required for the production of a hard case. The nitriding temperature for all steels is between 495 and 565 °C (925 and 1050 °F)

Because of the absence of a quenching requirement, with attendant volume changes, and the comparatively low temperatures employed in this process, nitriding of steels produces less distortion and deformation than either carburizing or conventional hardening. Some growth occurs as a result of nitriding, but volumetric changes are relatively small.

Aluminum, chromium, vanadium, tungsten, and molybdenum are beneficial in nitriding because they form nitrides that are stable at nitriding temperatures. Molybdenum, in addition to its contribution as a nitride former, also reduces the risk of embrittlement at nitriding temperatures. Other alloying elements, such as nickel, copper, silicon, and manganese, have little, if any, effect on nitriding characteristics. (ASM, Volume 4 Heat Treating, 1991)

2.3 X52 Characteristic

Understanding microstructure and grain size of steels is an important aspect for the understanding of properties such as strength, ductility, hardness and toughness. There are some researches made to determine the microstructure of API-X52. The study of the microstructure of this low carbon steel by means of scanning electronic microscopy (SEM) and X-ray diffraction (XRD) had been undergone.

Figure 2.4 present the X ray diffraction patterns of the API5L-X52 steel samples. Five samples being used in this experiment. The peaks represent the crystalline planes (110), (200), (211) and (220), they correspond with the body centered cubic (bcc) structure of the α-Fe phase, with a lattice parameter value of 2.8664 angstroms. The JCPDS-ICDD 6-0696 card was used in determining this. (Peña-Rodríguez, Flores-Macías, Díaz Góngora, Muñoz-Hernández, & Calderón, 2005)

The chemical composition for X52 carbon steel is listed in Table 2.1. (Wang, Atrens, Cousens, & Kinaev, 1999)

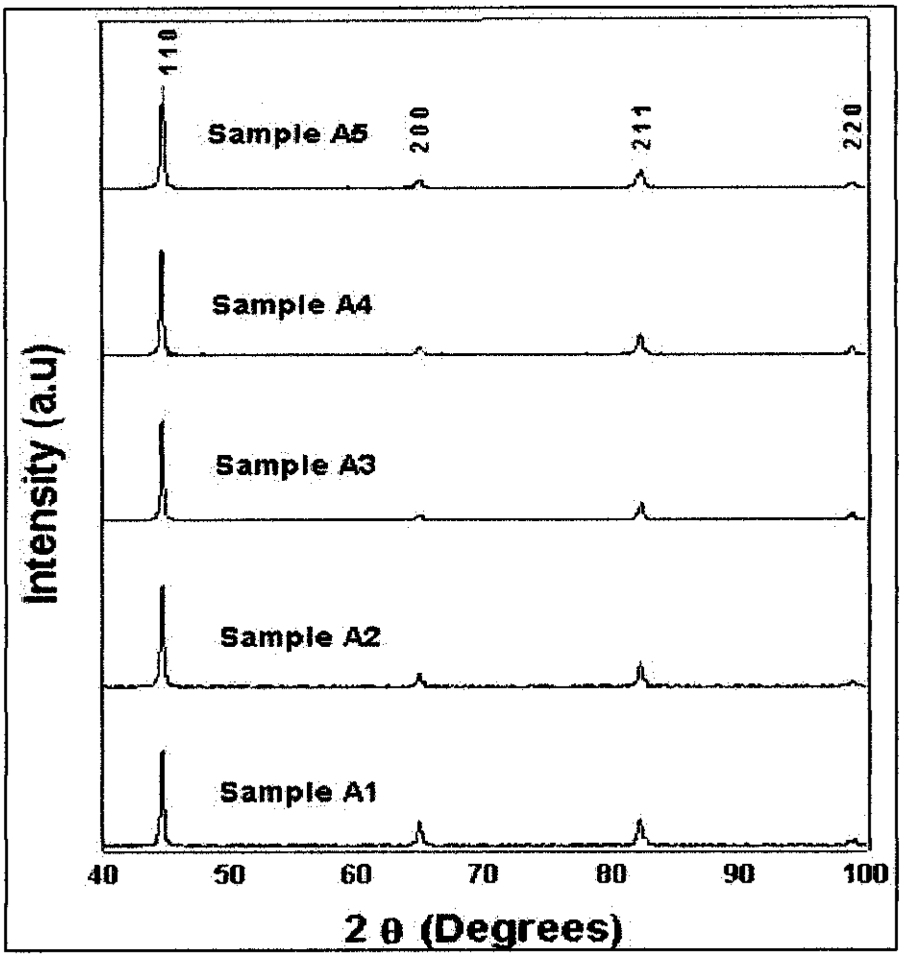


Figure 2.4: XRD patterns for API5L-X52 carbon steel samples

Table 2.1: X52 Chemical Composition (in wt %)

C	Mn	Si	S	P	Ni	Cr	Nb	Al
0.16	1.32	0.31	0.006	0.017	0.01	0.01	0.02	0.03

A decrease in the grain size of ferrous steel with a low carbon concentration give an increase in mechanical of the material and thus provide better resistance to fracture. SEM and XRD results are consistent and show the main phase in API5L-X52 steel is the α-Fe or ferrite. The SEM analysis also shows lamellar areas of the pearlite phase and solid inclusions as can be seen at Figure 2.5. The main elements of these inclusions are Al (33%), Fe (30%), and O (17%) and smaller quantities of Mn (8%),S (6.4%), Mg (2.6%), and Ca (2.3%). The ASTM E112-96 method shows 6.084 and 3.027μm for the α-Fe phase and the inclusions grain sizes, respectively. (Peña-Rodríguez, Flores-Macías, Díaz Góngora, Muñoz-Hernández, & Calderón, 2005)

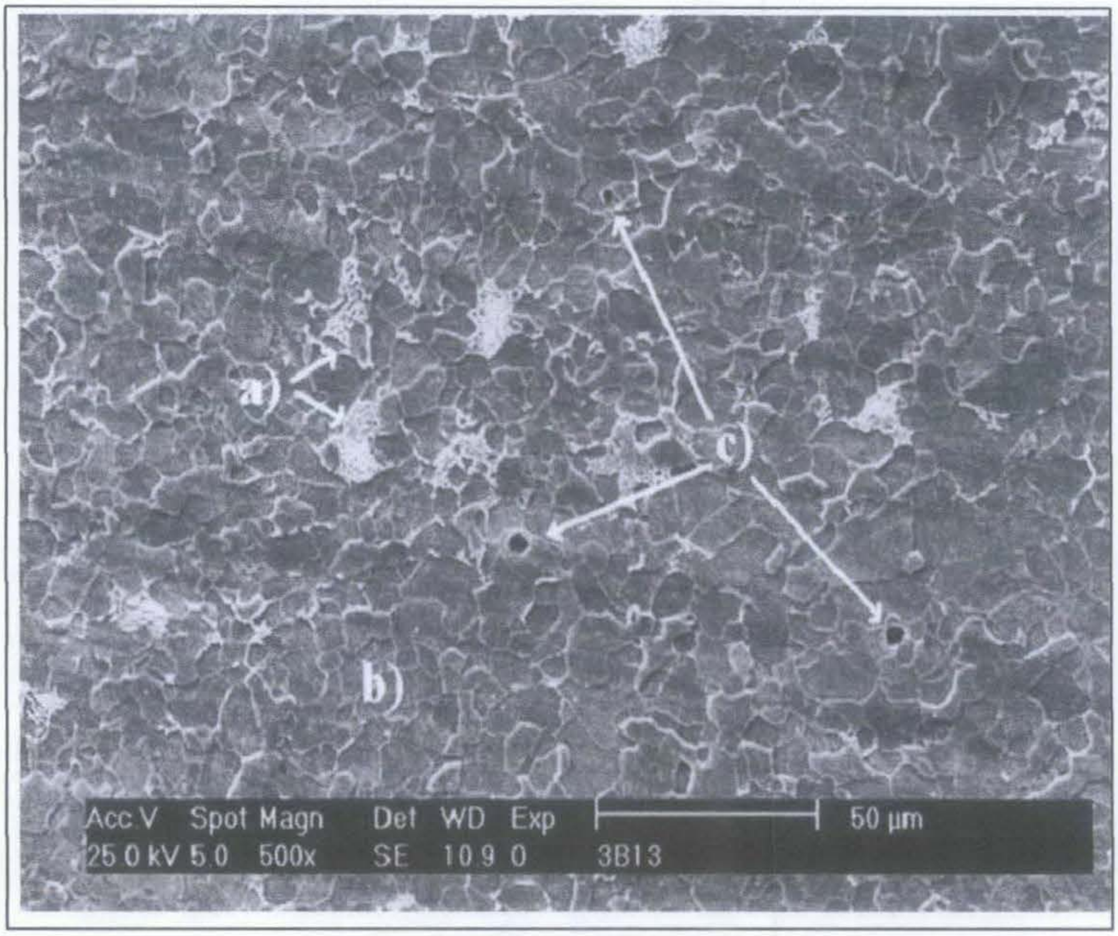


Figure 2.5: SEM image showing the microstructure of the API5L-X52 carbon steel by 500×magnification: (a) pearlite, (b) ferrite, and (c) solid inclusion particles in the structure

The microstructure of X52 pipeline steels shows banding of pearlite rich and ferrite rich areas. The grains were about 10 µm in size with curved grain boundaries. There was carbide at the ferrite grain boundaries for X52 steel, and circumstantial evidence to suggest carbon segregation at the boundaries. (Wang, Atrens, Cousens, & Kinaev, 1999)

From the previous research on microstructure of X52, it is confirmed that the main phase of X52 carbon steel is ferrite. This proof that nitriding is suitable to be performed on X52 carbon steel because nitriding is a process that introduced nitrogen to the surface of the steel while it is in ferritic condition.

2.4 Previous Nitriding Research

Nitriding of Ferritic Steel

According to research that being made by Hudiyo Firmanto, nitriding AISI 430 ferritic stainless steel has successfully enhanced the surface hardness of the steel. The microstructure of the nitride samples consist of martensite and ferrite which is coarser than the ferrite at the original material. The existence of the martensite contributed the hardness of the steel. Longer nitriding also improves the hardness of the martensite.

Martensite transformation started from the outer layer. The martensite grows deeper when the nitriding time is lengthened. The martensite transformation also started at the core at a sufficient nitriding time. This is initiated at the ferrite grain boundary.

Analysis of the phase transformation and metallographic examination reveals that the nitrogen diffusion yields the martensite formation. Therefore the existence of martensite indicates the nitrogen diffusion into the steel. This fact convinces that longer nitriding time diffuses more nitrogen into the steel. The work confirms that nitrogen has a significant role in the transformation of ferrite to martensite during the solution nitriding of ferritic stainless steel.

Solution nitriding was carried out on 1.2 mm thickness sheet of AISI 430 ferritic stainless steel. Samples were prepared in the size of 20 mm x 30 mm. Nitriding was carried out in Carbolite horizontal tube furnace. Samples were washed with acetone before each process was carried out. For each treatment sample was placed in the boat and inserted into the heating zone. Before the samples were heated, the air in the furnace was purged with nitrogen for 15 minutes at a flow rate of 1000cm3/min to prevent oxidation of the sample. Heating at 5°C/minute was started immediately after the purging was completed. Nitrogen was introduced into the furnace with the flow rate of 1000 cm3/min when the temperature reached 1200°C. At the end of the process, the samples were removed from the furnace and directly quenched into water. (Firmanto, Hussain, & Mamat, 2009)

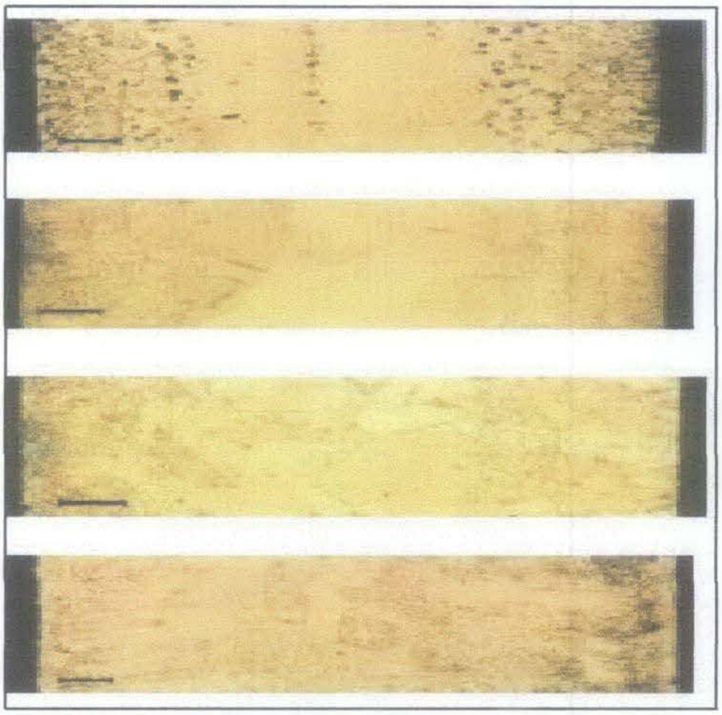


Figure 2.6: Optical micrograph image of the cross section of AISI 430 steel samples nitrided at 1200°C for (a) 15, (b) 30, (c) 60 and (d) 240 minutes

Mechanical and Structural Properties of AISI 1015 Carbon Steel Nitrided after Warm Rolling

Based on research that being made by C. Medrea and G. Negrea, warm rolling can improve mechanical properties by refining the ferrite-pearlite microstructure. This microstructure is stable to later heating up to 550°C. The stability of the microstructure makes possible the thermal treatment of the steel in this temperature range. Nitriding of the steel after warm rolling gives a hard surface layer. Nitriding of steel after warm rolling leads to increased wear resistance of parts made from low carbon steel. In the same time, the core preserves its fine grain microstructure with improved tensile properties as compared to untreated pieces.

The rolling was performed in the following conditions: temperature 670 – 550°C, rolling speed 1.39 s^{-1} and deformation ratio 36.4%. After rolling, the samples were reheated to 550°C for a duration varying from a few minutes to 10 hours. The microstructural changes were assessed by light microscopy and quantitative microscopy analysis. Warm rolled samples were ion nitrided at 510-520 °C in dissociated ammonia. The microstructure was analyzed by scanning electron microscopy and the mechanical properties were evaluated by tensile testing, surface hardness and friction coefficient measurements. Table 2.2 shows the mechanical properties of the ion nitrided samples after warm rolling. (Medrea & Negrea, 2008)

Table 2.2: Mechanical properties of samples after warm-rolling and in normalized condition

AISI 1015	Yield strength (MPa)	Tensile strength (MPa)	Elongation (%)	Reduction in area (%)	HV_5	Friction coefficient μ
Warm rolled	359	493	24.7	59	188	0.342
Nitrated after warm rolling	398	538	18.6	49.5	304	0.206

Influence of laser parameters on the nitriding of low carbon steel

Nitriding treatments were performed on low carbon steel using a XeCl excimer laser (308 nm) and a Nd:YAG laser (1064 nm) in N2 atmosphere. The presence of different nitride phases is detected in almost all irradiated samples (ά-Fe(C, N), γ-Fe(C, N) and/or ε-Fe_x(N, C)) regardless of the laser wavelength. (Copola, et al., 2002)

Figure 2.7 below shows the XRD spectra of the UV-irradiated samples grouped by energy density of the 308 nm laser beam. The peak at about 44.7° in all the spectra corresponds to the (1 1 0) plane of the α-Fe phase. A slight shift of the position of the peak towards larger angles can be observed as the nitrogen pressure is increased. This shift can be caused by the stress in the top nitride layers that results to the opposite stress formed in the underlying layers, or to the formation of the martensitic ά-Fe(C, N) phase. The shift is also more evident in the samples treated at higher N_2 pressure. In all the samples, additional peaks around 42.3–43.2 and 50.5° appear that indicates the formation of nitride or carbonitride phases. (Copola, et al., 2002)

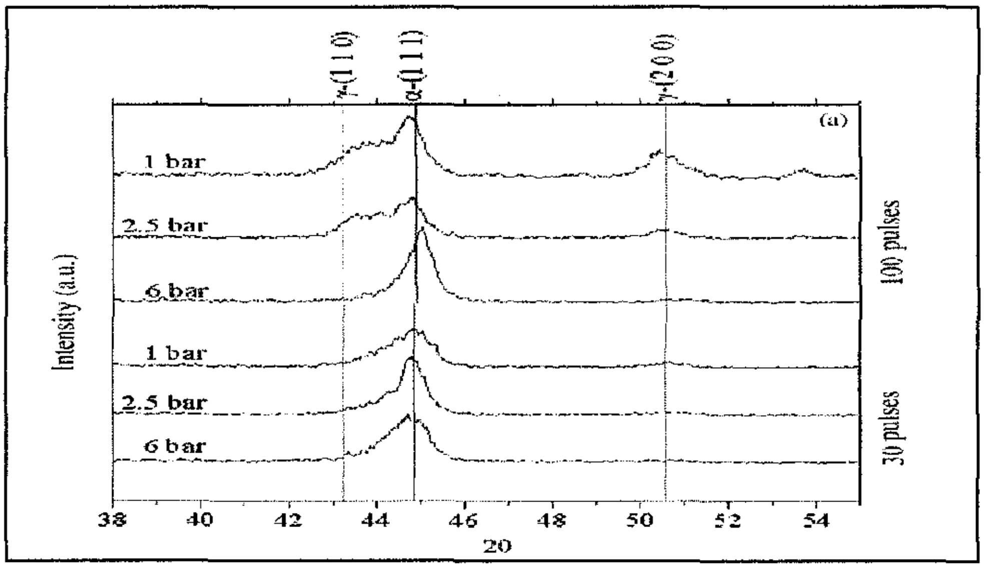


Figure 2.7: The XRD spectra of the UV-irradiated samples grouped by energy density of the 308 nm laser beam at 1.5 J/cm^2

Influence of plasma and gas nitriding on fatigue resistance of plain carbon (CK45) steel

Based on research made by F. Ashrafizadeh, nitriding can increase the surface hardness of carbon steel. Nitriding of CK45 steel had been conducted in a sealed quenched furnace under industrial conditions for 70 hours. 25μm of case depth had been produced in this process. The surface hardness after the treatment is 470HV. The core hardness of the metal is 280HV. Table 2.3 below shows the hardness of CK45 steel after nitriding for 70 hours. (Ashrafizadeh, 2003)

Table 2.3: Hardness and nitriding depth

Steel(Treatment)	Core Hardness (HV)	Case Hardness (HV)	Case Depth
CK45 (gas nitriding)	280	470	25μm

CHAPTER 3

METHODOLOGY

3.1 Research Methodology Flowchart

A proper planning is very important before starting experiments. The author prepared a well structured flowchart before starting the experiment so that the experiment can run smoothly. The project flowchart can be shown at Figure 3.1 below.

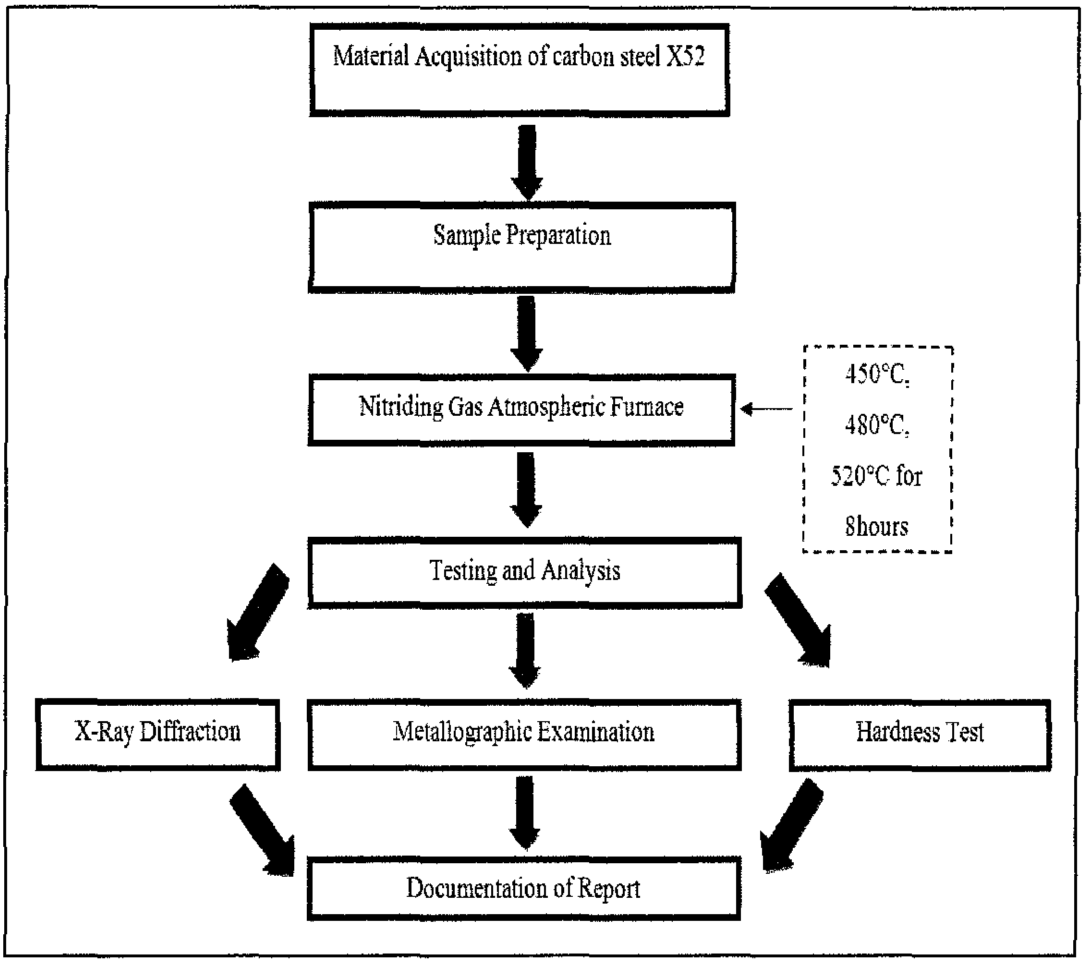


Figure 3.1: Project methodology flowchart

3.2 Material Acquisition

The material used in this project is API5L-X52 carbon steel. 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 low carbon steel. Nitrided X52 will have good properties compare to untreated X52 thus can increase its performance in industry application.

3.3 Sample Preparation

The size of the material obtain is too big and need to be prepared to run this project. The materials need to be cut to rectangular shape 20mm X 10mm X 10mm. The samples need to be annealed after cutting to remove any residue stress from the sample. After annealing, the surfaces of the samples need to be grind and polish until mirror image is obtained.

Step 1: Cutting of specimen

Pieces of steel were cut from a section of pipe. The cutting was performed using linear hack saw machine as shown in Figure 3.2 below. The sample size that needs to be cut must be around 10mm to 20mm for convenience during grinding and polishing. Twelve specimens were prepared for this project. The size of the sample after cutting is around 20mm X 10mm X 10mm.

Figure 3.2: Linear hack saw machine

Step 2: Annealing of specimen

The purpose of stress relief annealing is to reduce the inherent stresses in the work piece which have occurred as a result of cold shaping, microstructural transformation, thermal strain or machining. The samples were annealed at 900°C for 1hour. The heating and cooling rate is 5°C/min.

Step 3: Grinding

The specimen was ground using grinder shown in Figure 3.3 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 3.3: Grinder

Step 4: 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.

3.4 Nitriding Process

The nitriding process was done in a horizontal tube furnace as shown in Figure 3.4. It is located at Nano Technology Lab at Block N. The nitriding temperature was 450°C, 480°C, and 520°C. The nitriding time for all temperature was 8hours. The gas compositions used was 50% ammonia and 50% nitrogen. The total gas flow rate was 2 SLPM. The flow rate was control using digital flow meter as shown in Figure 3.5. 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 3.4: Horizontal tube furnace

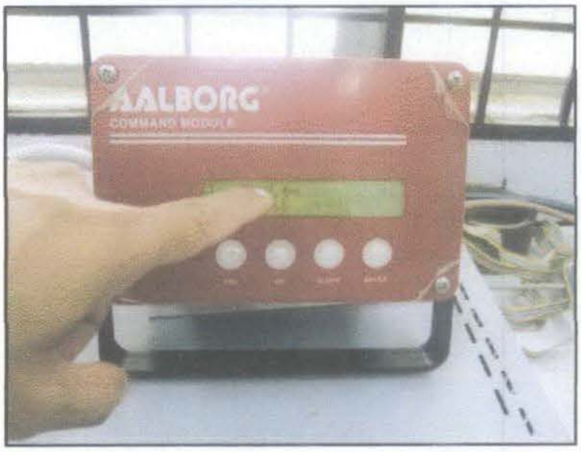


Figure 3.5: Digital flow meter

Step 1: Furnace arrangement

The furnace needs to be connected with ammonia and nitrogen gas. The exhaust of the furnace must be connected with fume hood for safety reasons. Ammonia and nitrogen will be mix in a mixing chamber before entering the furnace. The schematic diagram of the furnace arrangement can be seen in Figure 3.6.

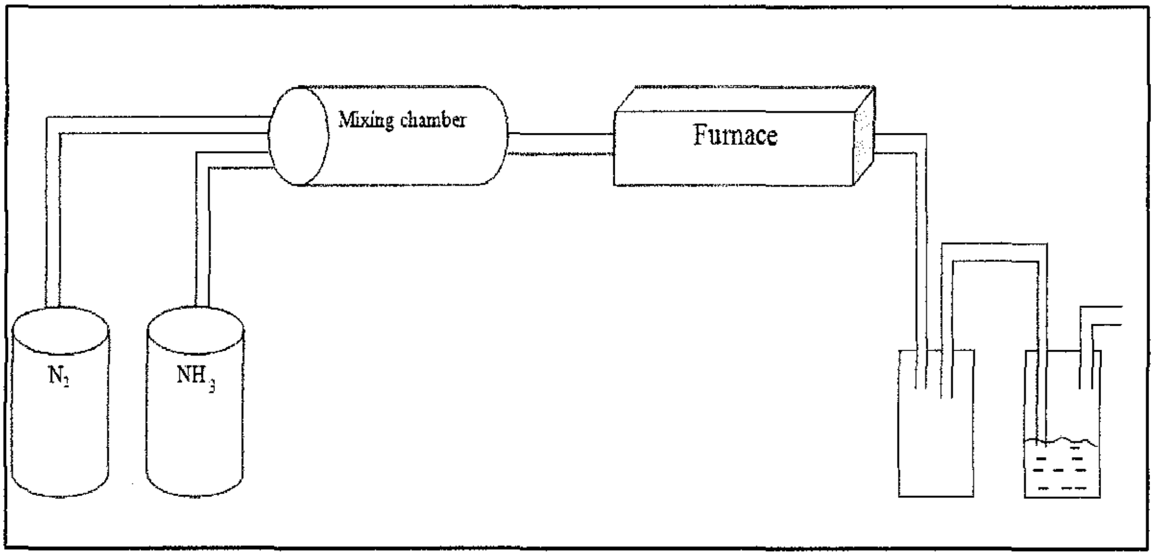


Figure 3.6: Furnace arrangement

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 3.7.

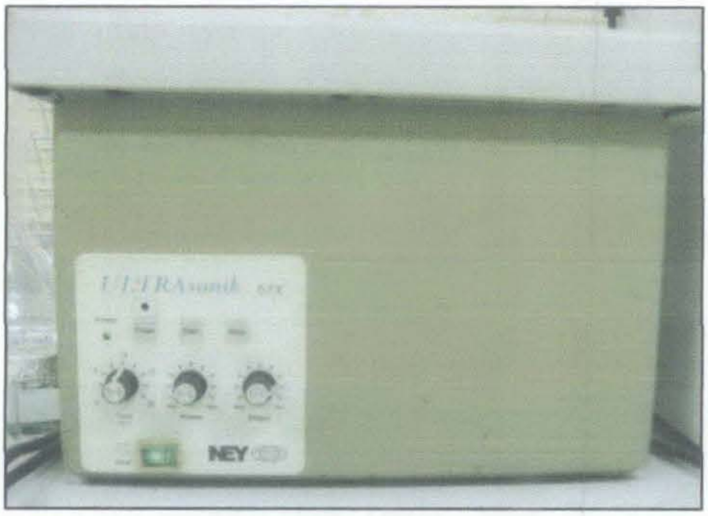


Figure 3.7(a): Ultrasonic cleaner

Figure 3.7(b): Ultrasonic cleaner top view

Step 3: Nitriding

After cleaning the samples, the samples were putted in alumina boat. The alumina boat can be seen in Figure 3.8. 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 shown in Figure 3.9. The furnace needs to be purged using nitrogen gas for 30 minutes to remove any gas inside the furnace from previous experiments. After purging, the furnace will be heated. The heating rate was 5°C/min. During heating, nitrogen gas still flowing in the furnace. When the temperature reached the nitriding temperature (450°C, 480°C, and 520°C), ammonia will start flowing in the furnace. The nitriding time was 8 hours for each temperature. The cooling rate was 30°C/min.

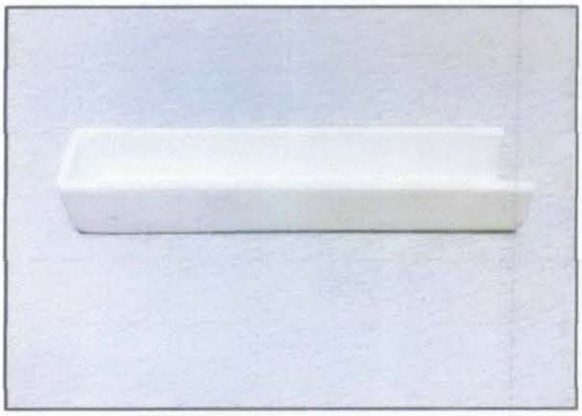


Figure 3.8: Alumina boat

Figure 3.9: Placing the alumina boat at the center of the furnace using steel wire

3.5 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.

Since the wavelength of some x-rays are about equal to the distance between planes of atoms in crystalline solids, reinforced diffraction peaks of radiation of varying intensities can be produced when a beam of X-rays strikes a crystalline solid. A monochromatic beam of X-rays are to be incident on a crystal. If the reflected wave patterns of the beam leaving the various planes are in phase, then reinforce of the beam or constructive interference occurs as shown in Figure 3.10.

Consider the incident x-rays 1 and 2 as indicated in Figure 3.10. For these rays, the extra distance of travel of ray 2 is equal to MP + PN, which must be an integral number of wavelength λ. Thus,

$N\lambda = MP + PN$ where $n= 1,2,3....$ and is called the order of the diffraction.

Since both MP and PN equal d_{hkl} where d_{hkl} is the interplanar spacing of the crystal planes of indices (hkl), the condition for constructive interference must be:

$$n\lambda = 2\, d_{hkl} \sin\theta$$

The equation is known as Bragg's law and in most cases, the first order of diffraction where n=1 is used. Therefore, Bragg's law takes the form

$\lambda = 2\, d_{hkl} \sin\theta$

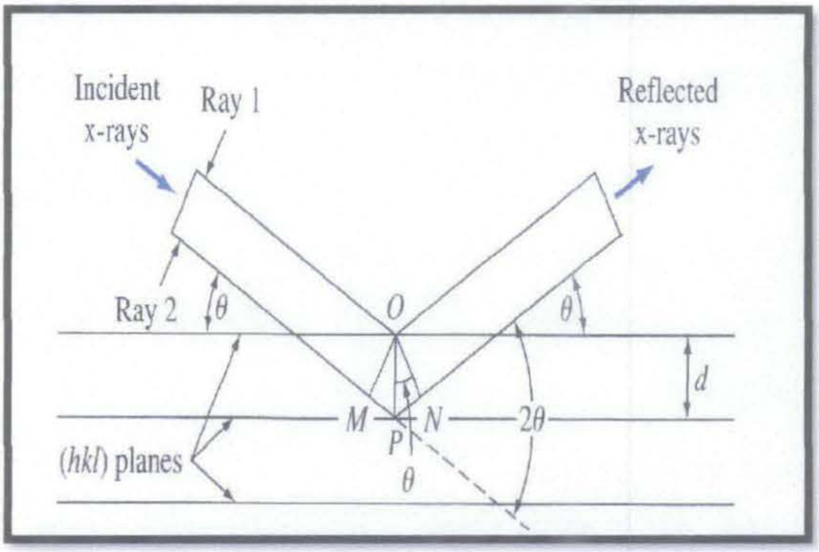


Figure 3.10: The reflection of an X-ray beam by the (hkl) planes of a crystal

In the present investigation of nitriding of carbon 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 3.11.

Figure 3.11: X-ray Diffraction Machine

3.6 Microstructure Examination

The purpose of this test is to examine the formation of nitride layer 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 being attached together with the scanning electron microscope. The optical microscope is located at Block 17 as shown in Figure 3.12 while the scanning electron microscope is located at Block P as shown in Figure 3.13.

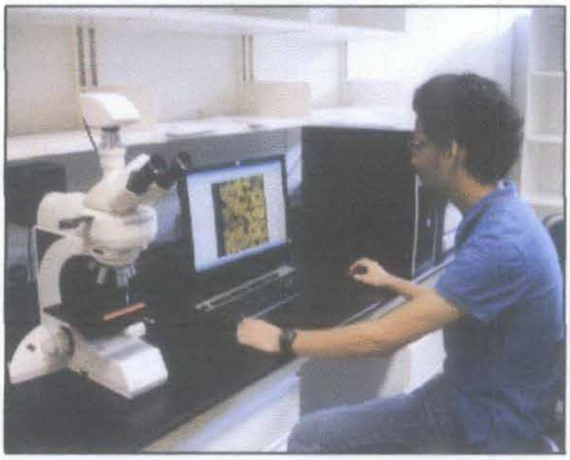


Figure 3.12: Microstructure examination using optical microscope

Figure 3.13: 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 X52 carbon steel, the etchant used is nital 2%. The purpose of etching is to reveal the grain boundary. Firstly, the specimen was washed using alcohol and then dried. After that, nital 2% was applied at the surface of the specimen for 5 to 10 seconds as shown in Figure 3.14. Then the specimen was washed using water and alcohol. The specimen was dried and ready for microstructure examination.

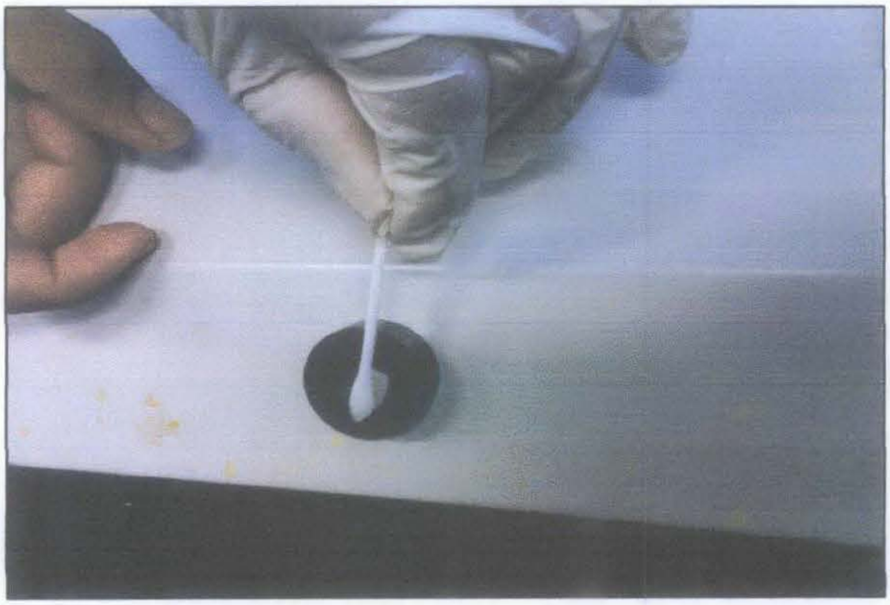


Figure 3.14: Etching on X52 surface

3.7 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 3.15. Hardness is the measurement of material surface resistance to indentation from other material by static load. Indentation body is a square based diamond pyramid (Figure 3.16) with 136 included angles. The average diagonal (d) from the adjustable shutters (Figure 3.17) 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 10gf. The dwell time was 15 second.

Figure 3.15: Vickers Hardness Equipment

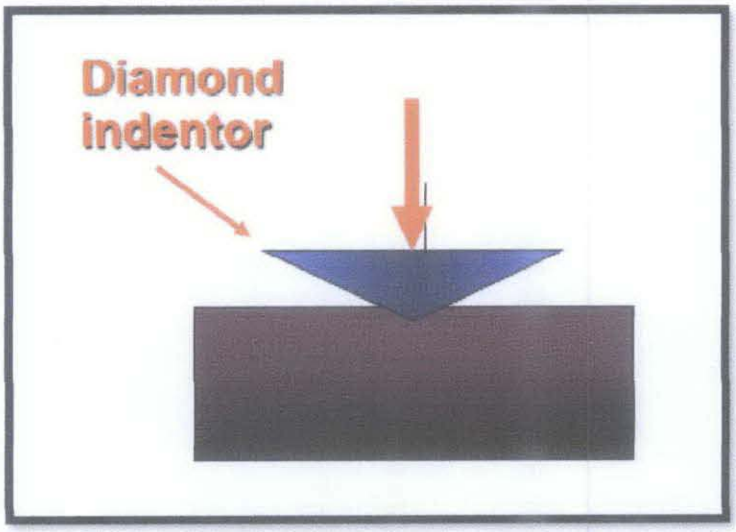


Figure 3.16: Diamond Pyramid Indentor

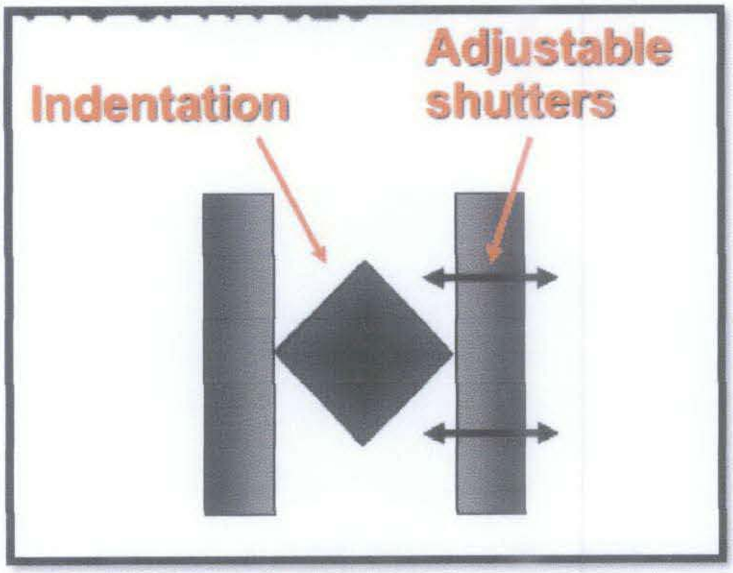
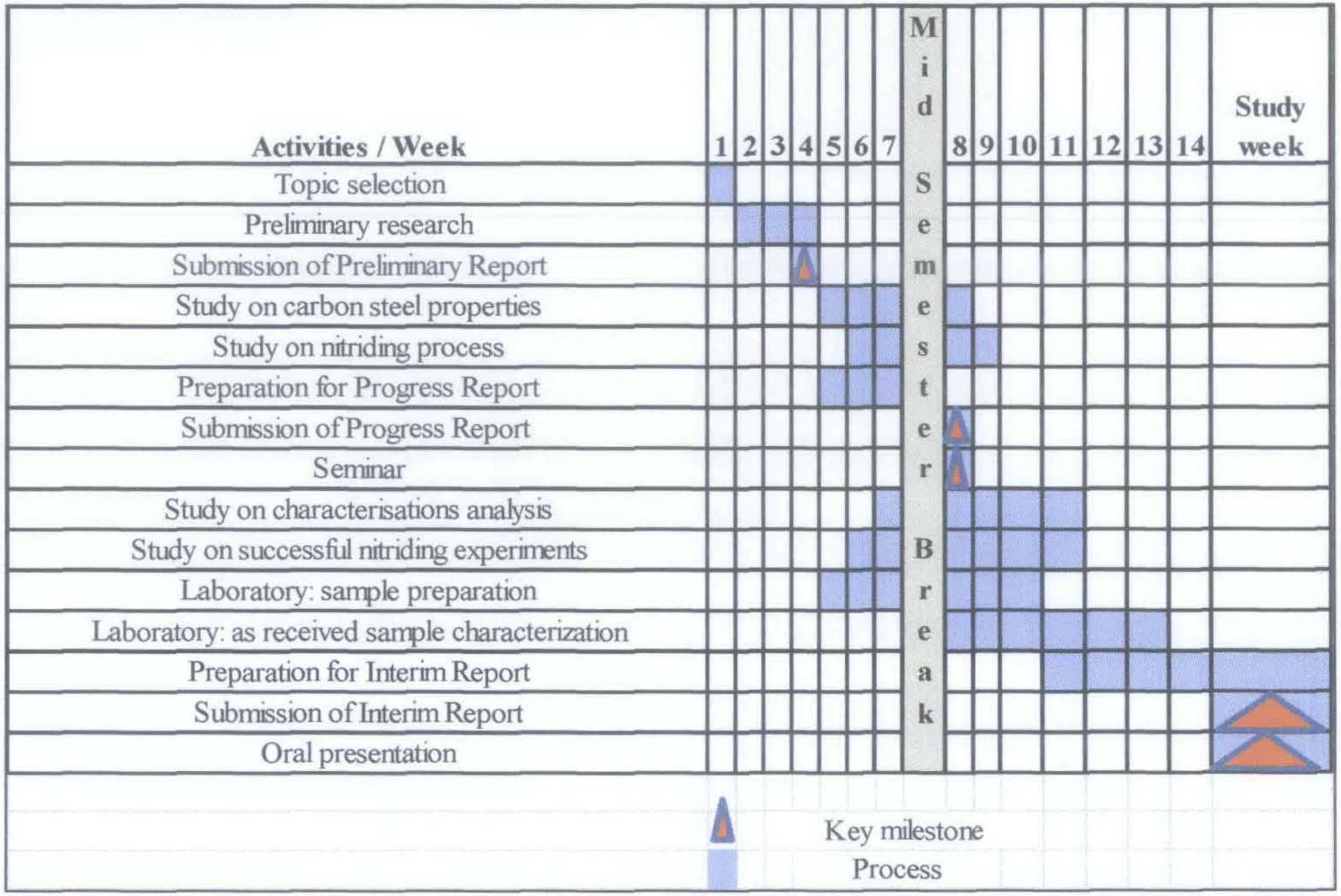


Figure 3.17: Adjustable Shutters

3.8 Project Gantt Chart



Activities / Week	1	2	3	4	5	6	7	Mid	8	9	10	11	12	13	14	Study week
Topic selection	▨							S								
Preliminary research		▨	▨	▨				e								
Submission of Preliminary Report				▲				m								
Study on carbon steel properties					▨	▨	▨	e	▨							
Study on nitriding process						▨	▨	s	▨	▨						
Preparation for Progress Report					▨	▨	▨	t								
Submission of Progress Report								e	▲							
Seminar								r	▲							
Study on characterisations analysis							▨		▨	▨	▨	▨				
Study on successful nitriding experiments						▨	▨	B	▨	▨	▨	▨				
Laboratory: sample preparation					▨	▨	▨	r	▨	▨	▨					
Laboratory: as received sample characterization								e	▨	▨	▨	▨	▨	▨		
Preparation for Interim Report								a				▨	▨	▨	▨	▨
Submission of Interim Report								k								▲
Oral presentation																▲

▲ Key milestone

▨ Process

Figure 3.18: FYP I Gantt Chart

Activities/Weeks	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Arranging furnace	🟦	🟦	🟦												
Nitriding process				🟦	🟦	🟦									
Metallography characterization							🟦	🟦							
XRD characterization								🟦	🟦						
Submission of progress report								▲							
Surface hardness testing									🟦	🟦					
Pre-EDX											▲				
Submission of draft report												▲			
Submission of dissertation (soft bound)													▲		
Submission of technical paper													▲		
Oral presentation														▲	
Submission of dissertation (hard bound)															▲

▲ Key Milestone

🟦 Process

Figure 3.19: FYP II Gantt Chart

CHAPTER 4

RESULT & DISCUSSION

4.1 Introduction

This chapter offers the experimental results of the untreated (as received) and heat treated X52 low carbon steel through nitriding process. The results were obtained from the hardness test, microstructure test and x-ray diffraction analysis. The experiments were carried out in 450°C, 480°C, and 520°C for 8 hours.

4.2 Analysis of the Untreated Steel

Figure 4.1 below shows the microstructure of untreated X52 carbon steel. From the picture of the microstructure, the main phase of X52 carbon steel is ferrite. X52 also contain some pearlite colonies in the microstructure. Some of the pearlite is connected with each other and some of them are isolated.. The magnification used was 500x.

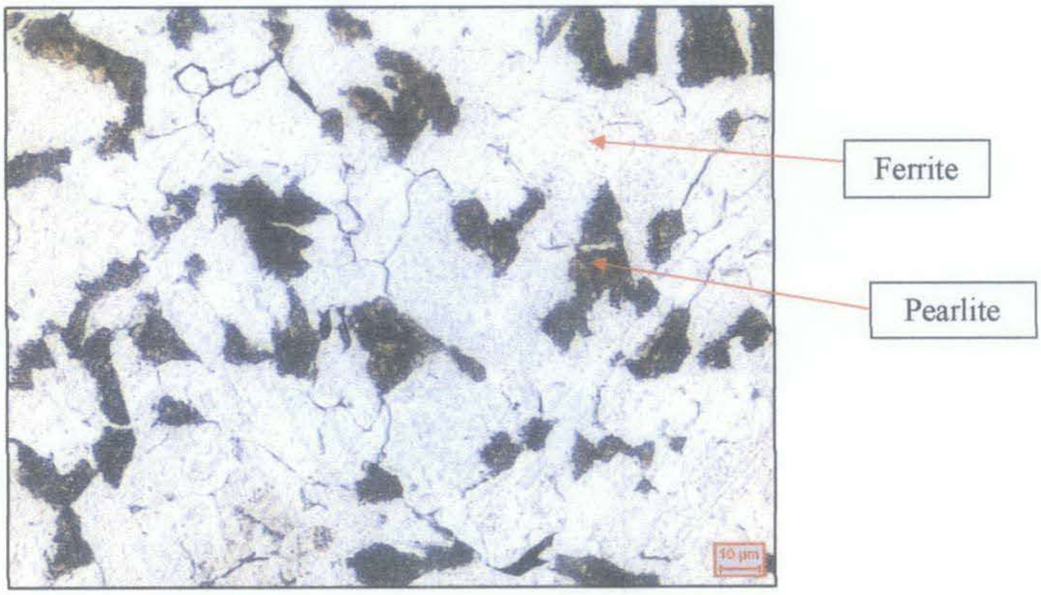


Figure 4.1: X52 microstructure at 500x

Table 4.1 below shows the surface hardness of untreated X52. The hardness measurement was taken at five different points. The load used was 10gf and the dwell time was 15 second. From Table 4.1, we can get the average hardness of untreated X52 carbon steel. The average hardness is 143.9 HV.

Table 4.1: Surface hardness of untreated X52

	HV
Point 1	142.3
Point 2	146.3
Point 3	137.7
Point 4	140.0
Point 5	153.1

4.3 Mass of the samples before and after nitriding

Nitriding will cause 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 4.2 below shows the average mass of the samples before and after nitriding process for 450°C, 480°C, and 520°C.

Table 4.2: Average mass of the samples

Temperature	**Before Nitriding**	**After Nitriding**	**% mass increase**
450°C	19.385g	19.387g	0.010%
480°C	16.857g	16.860g	0.017%
520°C	14.166g	14.169g	0.021%

Figure 4.2 below shows the percentage of mass increase of the samples after nitriding process for 450°C, 480°C, and 520°C. The percentage of mass is increase when higher nitriding temperature is used. This is due to more nitrogen diffusion occurred at the surface when using higher nitriding temperature.

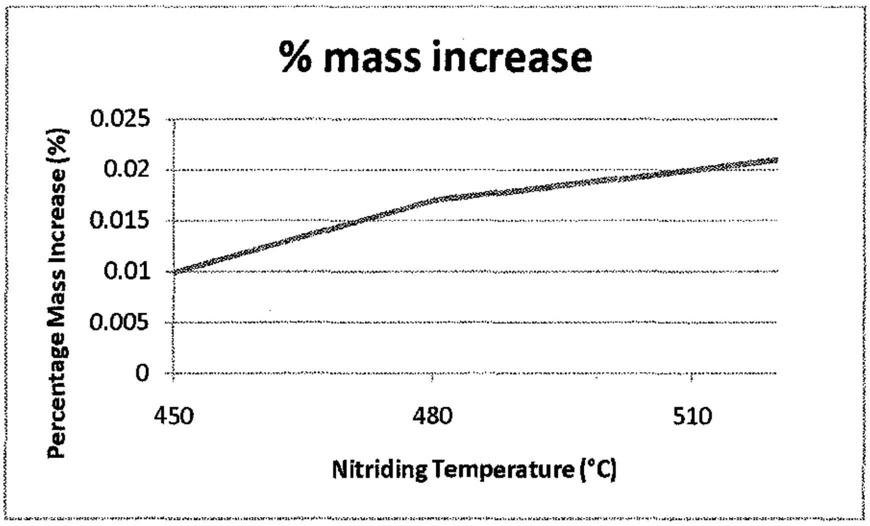


Figure 4.2: Percentage of mass increase after nitriding

4.4 Morphology of Nitrided Steel

In this section, the morphology of each specimen after nitriding was revealed in accordance with the processing parameters. Microstructural observations were based on the nitrided layer subsequent to nitriding. The nitride layer is identified from the increment of nitrogen count per second (cps) at the cross section of the samples using energy-dispersive X-ray spectroscopy.

Figure 4.3 shows that the case depth produced after nitriding at 450°C with a 2000x magnification. It produced the thinnest case depth from all the other nitriding conditions. The thickness of the nitride layer is 3.5μm. This is mainly due to the nitriding temperature of 450°C which is the lowest temperature employed during the nitriding process. Figure 4.4 shows the cross-sectional nitrogen count per second (cps) for 450°C of nitriding.

An improvement is shown when nitriding temperature was increased to 480°C. Figure 4.5 shows the formation of nitride layer with a 2000x magnification. The case depth is thicker than nitriding temperature 450°C. The thickness of the nitride layer is 6.9µm. Figure 4.6 shows the cross-sectional nitrogen count per second (cps) for 480°C of nitriding.

Figure 4.7 shows the formation of nitride layer at 520°C with a 5000x magnification. The formation of nitride layer is similar with nitriding at temperature 480°C. The thickness of the nitride layer is 6.3µm. Figure 4.8 shows the cross-sectional nitrogen count per second for 520°C of nitriding.

Nitriding carbon steel for 8 hours produced about 3µm to 6µm of case depth. Comparing with longer nitriding time about 70 hours that being made from previous research, the case depth that being produced is about 25µm. Nitriding for 70 hours can produced very thick case depth because a lot of nitrogen diffusion occur at the surface.

Phase transformation does not occur at the core metal after nitriding process for all temperature. The main phase of nitrided X52 is ferrite. Nitrided X52 also contain some pearlite. Figure 4.10, Figure 4.11, and Figure 4.12 show the cross sectional view of nitrided X52 at 450°C, 480°C, and 520°C at 500x.

Figure 4.3 shows the cross-sectional nitrogen count per second for 450°C of nitriding. The intensity of the nitrogen is bigger compare to nitriding at 480°C and 520°C because of the scan time using for nitrided 450°C is longer compare to 480°C and 520°C.

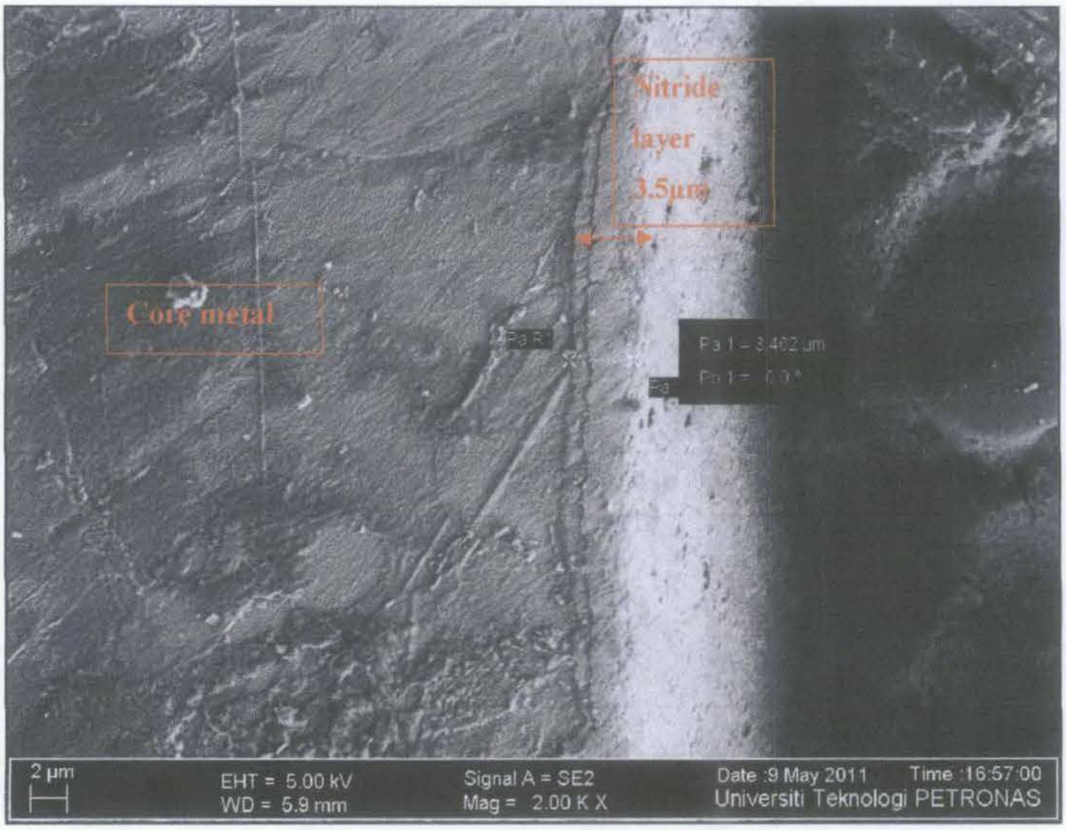


Figure 4.3: Microstructural development of 450°C of nitriding

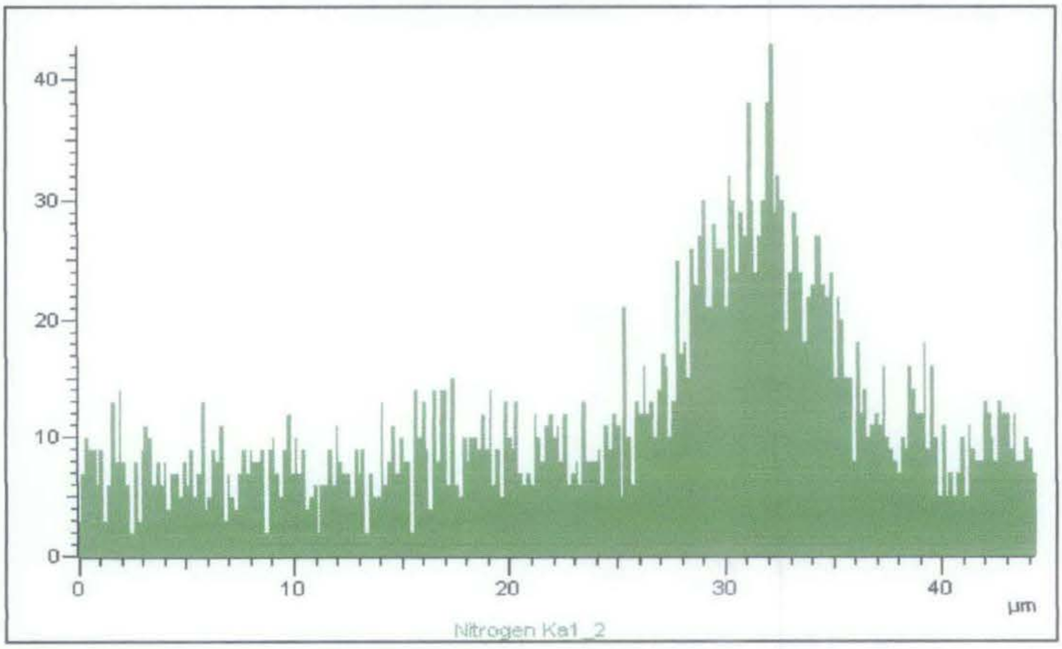


Figure 4.4: Cross-sectional nitrogen count per second (cps) for 450°C of nitriding

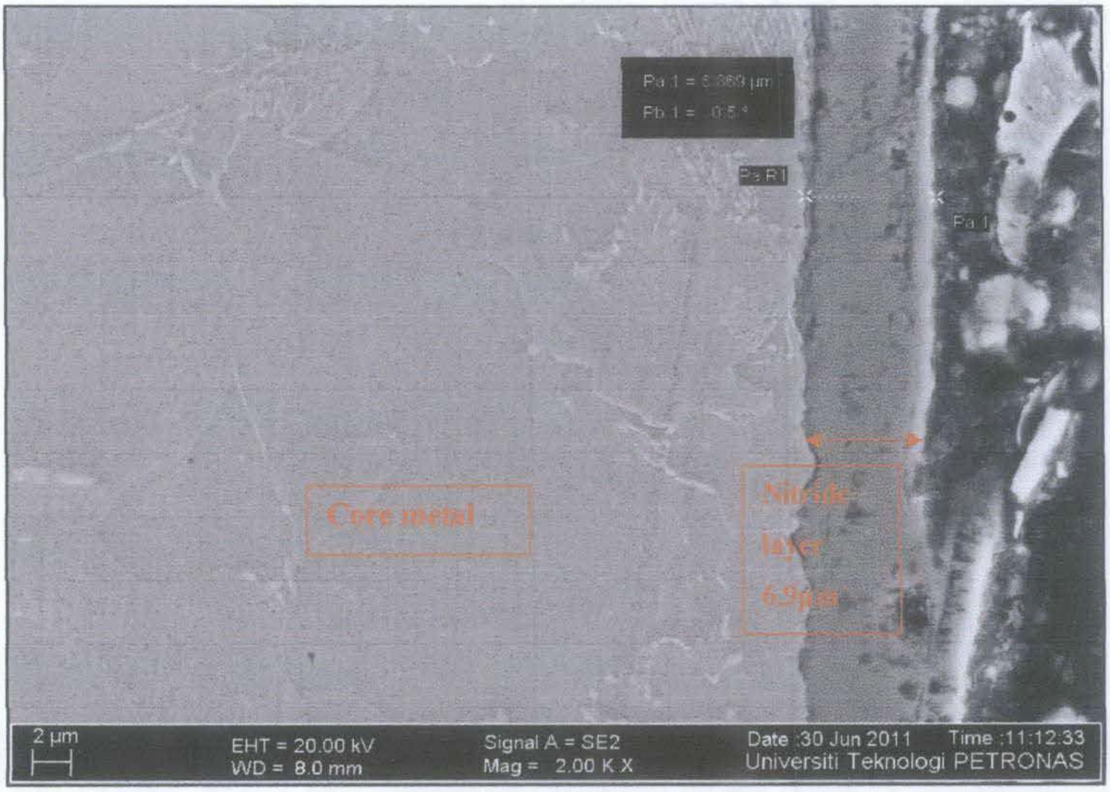


Figure 4.5: Microstructural development of 480°C of nitriding

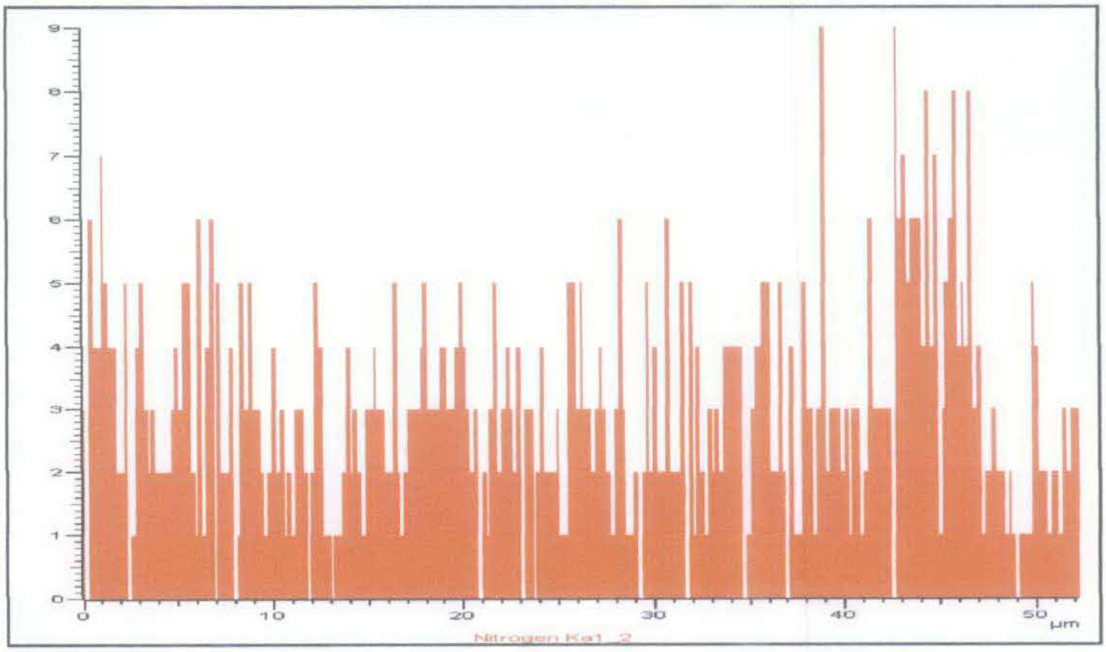


Figure 4.6: Cross-sectional nitrogen count per second (cps) for 480°C of nitriding

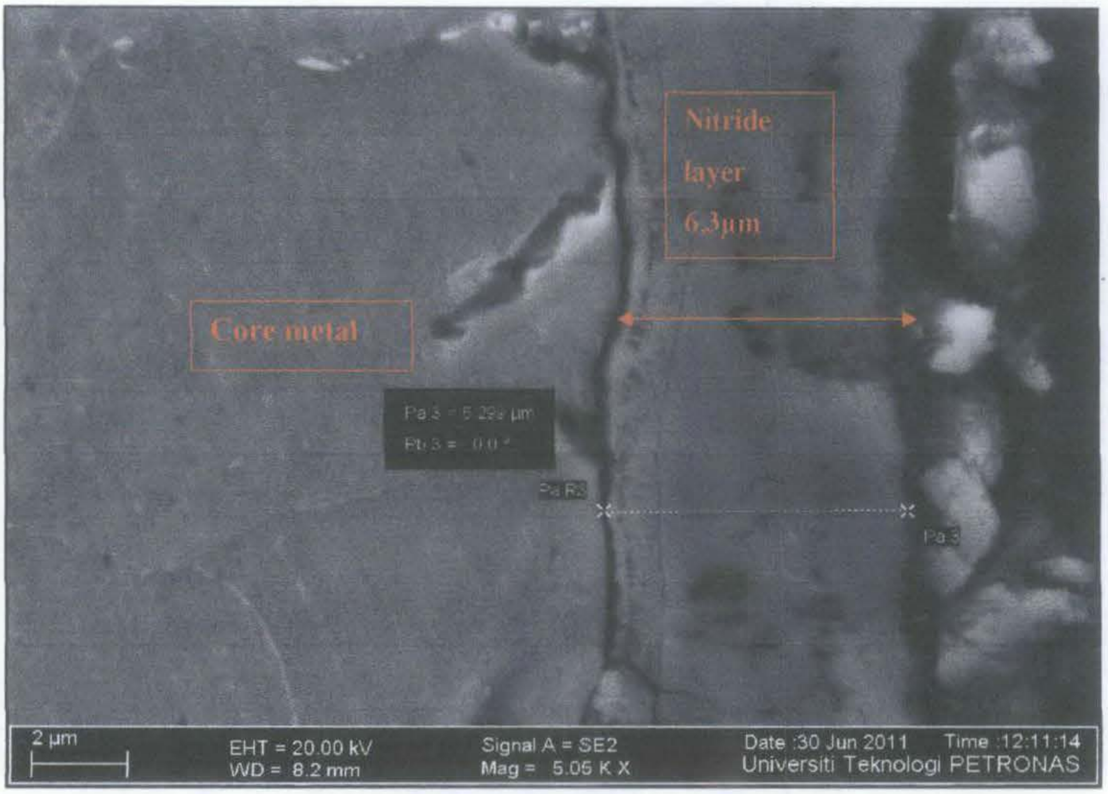


Figure 4.7: Microstructural development of 520°C of nitriding

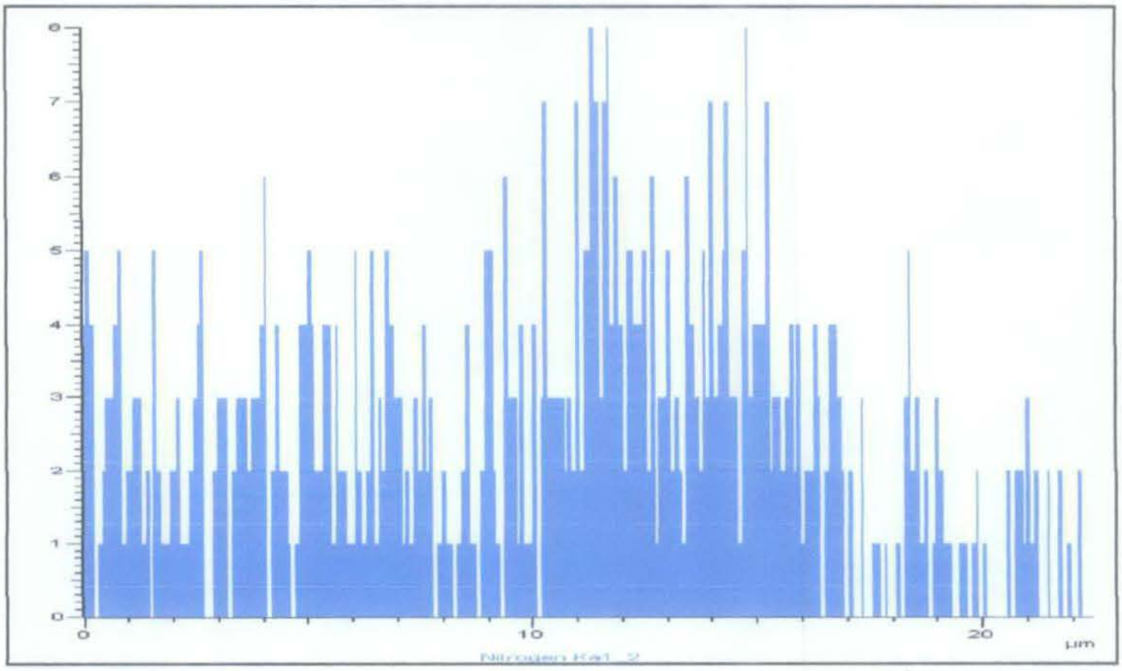


Figure 4.8: Cross-sectional nitrogen count per second (cps) for 520°C of nitriding

For EDX line scan mode analysis, the SEM electron beam is scanned along a preselected line segment across the sample while x-rays are detected at discrete positions along the line. Analysis of the resulting x-ray energy spectrum at each position provides plots of the relative elemental concentration variance for each element as a function of those position-point values along the given path. As shown from the figure above, the highest nitrogen concentration gradient is indicating the formation of nitride layer. However, for the lowest temperature which is at 450°C, the overall intensity of nitrogen which is measured in counts per second shows the highest value which at about 40 cps compared to others parameters. This is because, measuring the xray intensity of any particular element is depends on the number of frames measured and the time of scanning takes places. Due to the high and different of numbers of frames measured and longer time of scanning compare to other temperatures, the intensity of nitrogen for this temperatures give highest value whereas these two factors should be constant and fix in order to determine the trend of intensity variance of nitrogen for each temperatures. However, it is sufficient enough to show that there is significance concentration of nitrogen at this temperature although it is in the difference range of frames measured and time of scanning compared to other temperatures.

Figure 4.9 below shows the comparison of the case depth that being produced using different temperature.

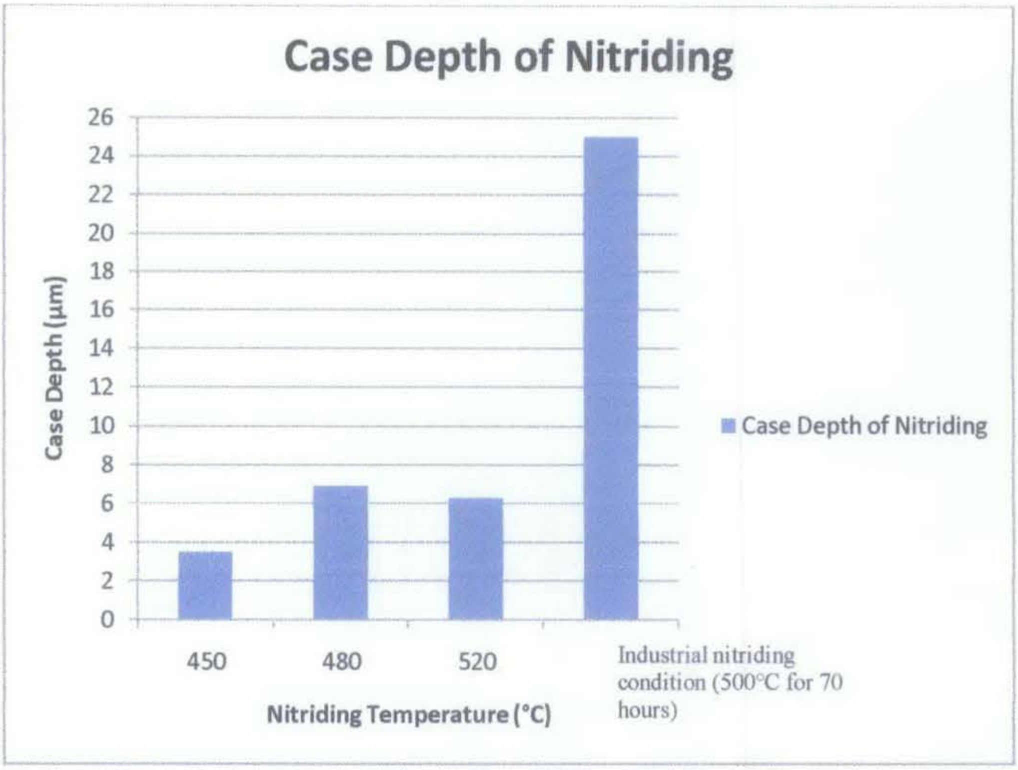


Figure 4.9: Case depth of nitriding

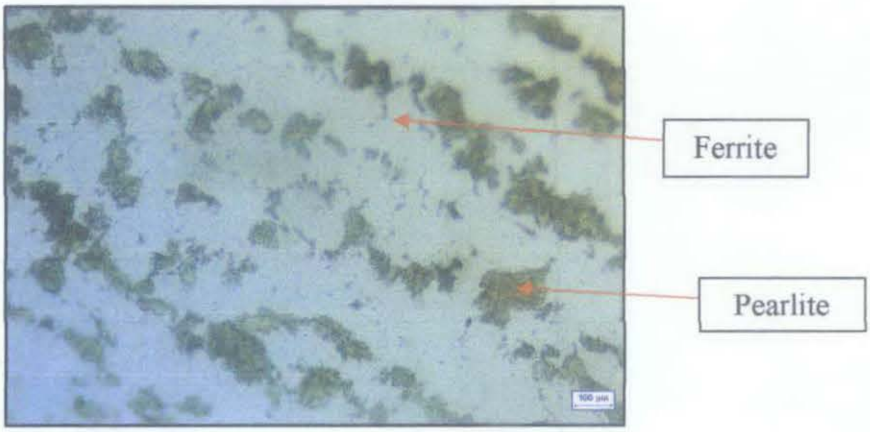


Figure 4.10: Cross sectional view of nitrided X52 at 450°C

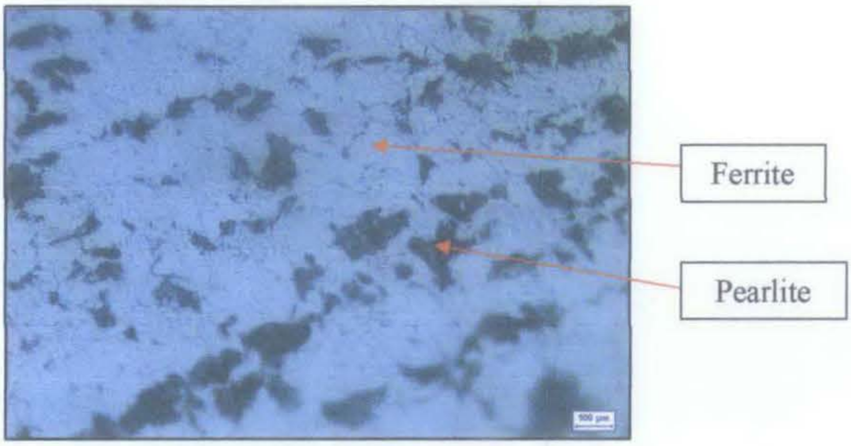


Figure 4.11: Cross sectional view of nitrided X52 at 480°C

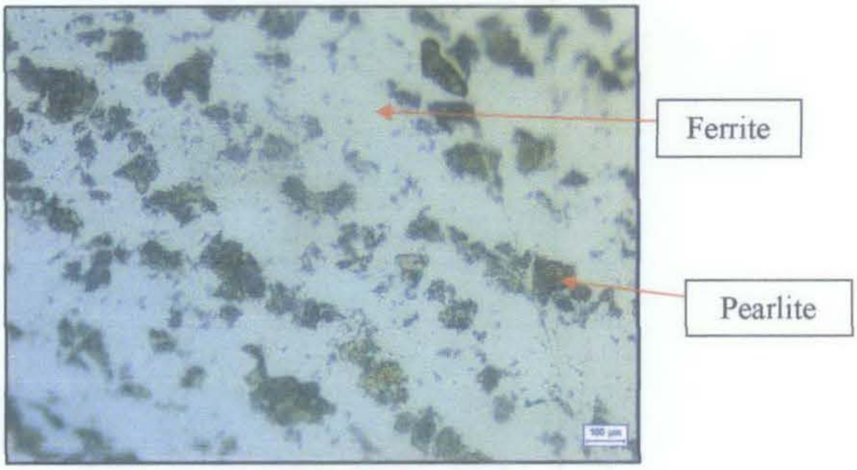


Figure 4.12: Cross sectional view of nitrided X52 at 520°C

4.5 Hardness Profile of the Nitrided X52 Carbon Steel

Hardness test was conducted to determine the characteristic of each specimen under the influence of the processing parameters such as nitriding temperature. Microhardness Vickers test were conducted to the specimens from the distance of the bakelite or mounting. The load used was 10gf and the dwell time was 15 second.

The surface hardness for nitrided X52 at 450°C is 302HV. The hardness of the specimen is decreasing as it moves further from the surface. The surface hardness starts to increase when the nitriding temperature is increased. The surface hardness for nitrided X52 at 480°C is 344HV. Nitriding at 520°C produce the highest surface hardness. The surface hardness for nitrided X52 at 520°C is 398HV.

The hardness for nitrided X52 is decreasing as it moves further from the surface. The hardness of nitrided X52 becomes constant at average of 143HV. This value is the same as untreated X52. It demonstrate that nitrogen just diffuse at the surface of the metal not until the core of the metal. Figure 4.13 below shows hardness profile of nitrided X52.

Nitriding carbon steel for 70 hours produced case depth hardness of 470HV. Nitriding for 8 hours at 520°C produced case depth hardness of 397.5HV. The case depth hardness when nitriding for 70 hours is similar with the case depth hardness when nitriding for 8 hours.

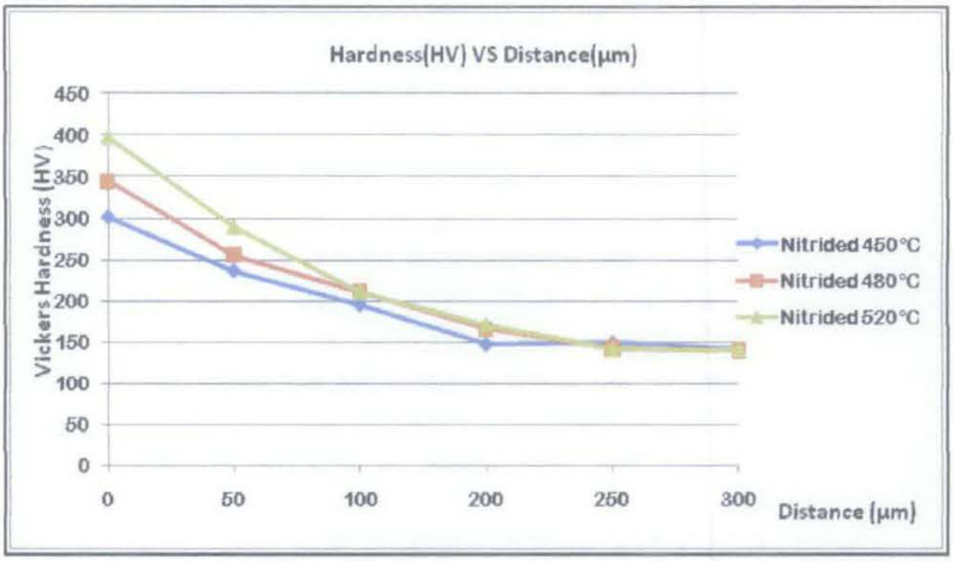


Figure 4.13: Hardness profile of nitrided X52

4.6 X-Ray Diffraction Pattern of Nitrided X52 Carbon Steel

The X-ray diffraction test determines the compound present in X52 carbon steel. The compounds are ascertained by the peaks in the graph of the intensity versus the angle 2θ.

The X-ray diffraction patterns in Figure 4.14 X52 shows the main compound of the untreated steel is alpha iron which has the highest pick. X-ray diffraction pattern for nitrided 450°C shows that there is formation of iron nitride, Fe_3 N. No other alloying nitride can be detected in this pattern. This proved that the steel only experienced minor improvement in the hardness and case depth

Besides the alpha iron phase, there were also iron nitride, Fe_3 N and chromium nitride, CrN detected as shown in the X-ray diffraction pattern in for nitrided 480°C and 520°C. This shows that the steel improved in terms of hardness and case depth. The presence of chromium nitride proves that the steel has improved in hardness. The formation of alloying nitride indicates that nitrogen diffusion occur at the surface.

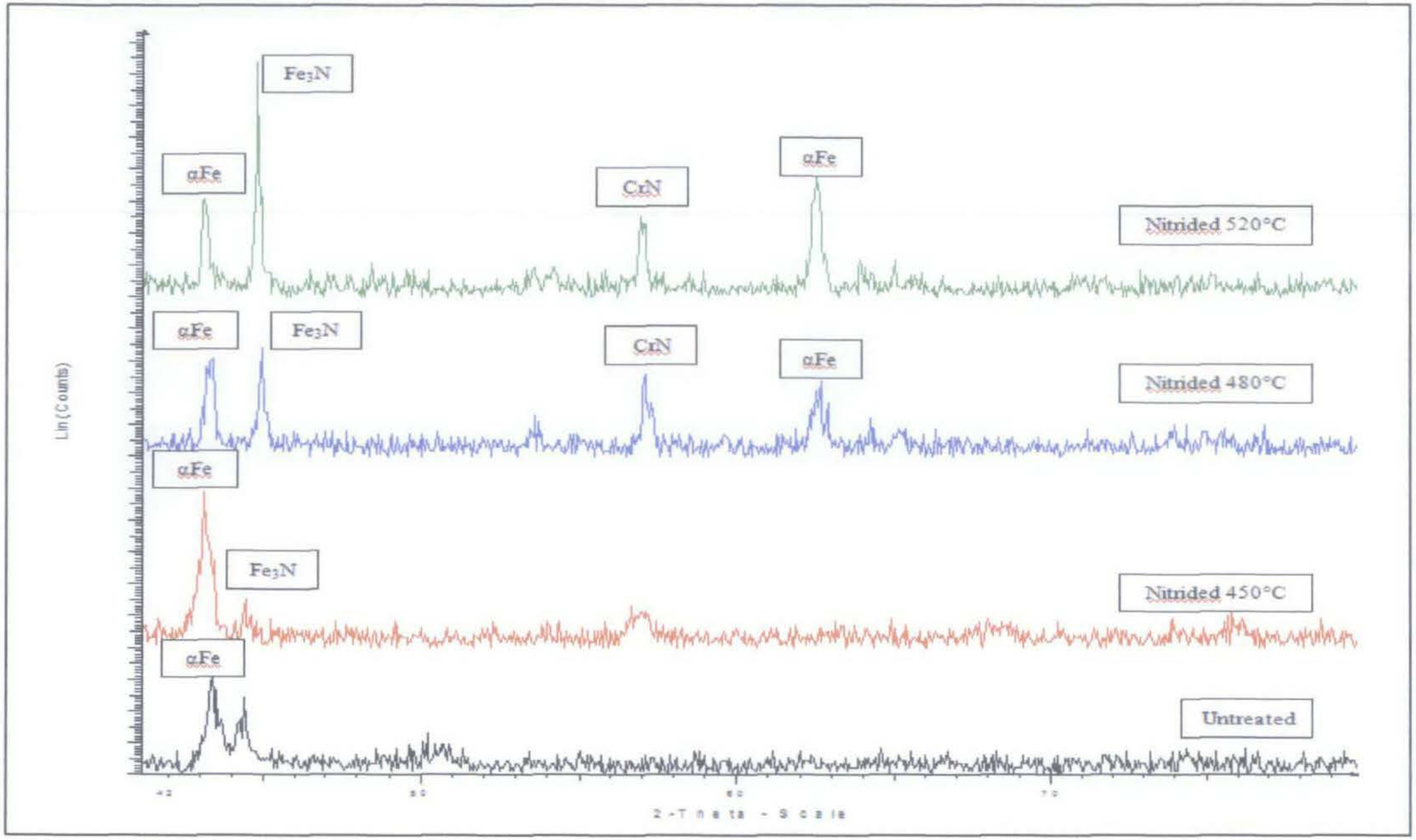


Figure 4.14: X-ray diffraction pattern for nitrided X52

CHAPTER 5

CONCLUSIONS & RECOMMENDATIONS

From the result that had been obtained, it is possible to produce nitrided X52 using short nitriding time compare to industrial condition which is usually around 70 hours. The surface hardness of nitriding at 8 hours is similar with the surface hardness of nitriding at 70 hours. The only different is the case depth. 70 hours of nitriding can produced case depth around 25µm. Nitriding for 8 hours can only produced case depth of 3µm to 6µm.

From the morphology observation, it shows that higher nitriding temperature will gave thicker nitride layer proven in Figure 4.3, Figure 4.5, and Figure 4.7. Nitriding at 450°C produces nitride layer with thickness of 3.5µm. The thickness of nitride layer for nitriding at 480°C is 6.9µm. For nitriding at 520°C, the thickness of nitride layer is similar with nitriding at 480°C. The thickness is 6.3µm. Phase transformation does not occur at the core metal after nitriding process.

From the hardness test result, nitiriding at 520°C showed the highest surface hardness among all the specimens which has reached to the surface hardness of 398HV. It is then followed by nitriding t 480°C and 450°C. Therefore, it is undeniable that the longer the nitriding time, the higher the hardness it will produce. The hardness is decreasing as it moves further from the surface. The hardness becomes constant when the hardness value reaches average of 143HV. This value is the same as untreated X52.

The presence of alloy nitrides in the X-ray diffraction analysis shows the improvement of the steel in terms of the hardness as well as the case depth. Some of the alloy nitrides detected such as iron nitride (Fe_3N), and chromium nitride (CrN). However, alloy nitride such as manganese nitride, molybdenum nitride and other alloy nitrides were not detected in the X-ray diffraction analysis.

In conclusion, this study has managed to meet and achieve its objective; to study the characteristics of nitriding treatment on X52 carbon steel associated with the hardness improvement and the microstructural changes produced by different nitriding temperature. Nitriding temperature is directly proportional to the surface hardness of X52 carbon steel. In this study, nitriding at 520°C achieved the highest surface hardness. The surface hardness is 398HV.

To encourage improvements and findings of this study, it is recommended that the processing parameter should be further extended. Different gas compositions of the Nitrogen and ammonia should be applied for instance, 30% of ammonia and 70% of nitrogen. This could not be performed in this investigation due to the insufficient time.

Some improvement can be made to get good results. The X-ray diffraction data from this experiment contain a lot of noise. This is due to very fast scan speed. To get smooth data, slower scan speed must be used. The lab technician have to use faster scan speed because there are a lot of people want to used the X-ray diffraction machine. The faculty should add more X-ray diffraction machine so that more samples can be analyzed using slower scan speed and get smooth results.

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