Nitriding of AISI 316L Austenitic Stainless Steel at Low Temperature for the Enhancement of Surface Properties and Corrosion Properties

by

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Project Dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Mechanical Engineering Programme
Universiti Teknologi PETRONAS
In partial fulfilment of the requirement for the
BACHELOR OF ENGINEERING (Hons)
(MECHANICAL ENGINEERING)

Approved by,

____

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May 2013

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.

BADRULZZAMAN BIN MOHAMMED

ABSTRACT

Austenitic stainless steel (ASS) makes up over 70% of total stainless steel production and has been used widely in many industrial fields such as automotive, oil & gas, chemical, medical and food industries due to their excellent corrosion resistance. However, the applications of this material are severely limited by very poor surface hardness as well as wear resistance. Many investigations have been conducted to improve surface hardness of ASS and thus enlarging their possibility of wider application, but led significant loss of its corrosion resistance. This tendency occurs due to the sensitivity effect. The objectives of this investigation are to improve the surface hardness as well as corrosion properties of AISI 316L austenitic stainless steel. Theoretically, the low temperature treatment is to avoid the formation of nitride and carbide precipitation which can reduce the corrosion resistance of stainless steel. AISI 316L stainless steel has been treated by surface hardening technique, which is low temperature gas nitriding treatment (LTGN) in quartz tube furnace. The variable of nitriding temperature of this treatment is at 400°C, 450°C and 500 °C with constant 8 hours of nitriding time. The morphological changes, structural phase and elemental profile of the treated samples were observed by optical microscope (OM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX). From the results, the microstructure and phase composition depend on the nitriding temperatures. X-ray diffraction (XRD) has been used to confirm the formation of nitrides on the surface layer of the samples. The surface microhardness was investigated using Vickers hardness tester. The results showed that the surface microhardness values increased as the treatment temperature increased which has close relationship with elemental depth profile. The corrosion properties of unnitrided 316L austenitic stainless steel and nitrided 316L austenitic stainless steels at low temperature, e.g: 400^{o}C and high temperature e.g: 500^{o}C were evaluated by measuring polarization curves in 3.5% NaCl solution in CO_2 environment. From the result, gas nitriding at a low temperature significantly improved the corrosion properties of sample. However, when gas nitriding is carried out at a high temperature of 500^{o}C , chromium nitrides form in the nitrided case so that the bulk of the nitrided case had very poor corrosion resistance.

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Badrulzzaman Bin Mohammed

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CHAPTER 1

INTRODUCTION

1.1 Background of Study

In mechanical engineering industry, the protection of material surfaces from destructive operating conditions and unfavorable environments is associated with excellent technical awareness and economic necessity. This is due to the surface and subsurface properties of materials which establish their performance. Thus, the requirements of high hardness, as well as improved wear, corrosion and fatigue properties can be achieved by surface modifications using nitriding process. Nitriding is one of the surface engineering treatments applied to the surface of machine tools, parts and other metallic objects to improve their surface hardness and enhance the mechanical properties.

For this investigation, the author has performed low temperature gas nitriding treatment (LTGN) of austenitic stainless steel at different temperatures. In this process, nitrogen is diffused into the surface of a solid ferrous alloy by treated the material at three different temperatures (400^{o}C, 450^{o}C and 500^{o}C) with constant treatment time and pressure in contact with a nitrogenous gas. Austenitic type AISI 316L stainless steel has been used as the sample for this project. Types 316L is a low carbon version of chromium-nickel-molybdenum alloy austenitic stainless steel. This type of alloy is largely used in corrosive industrial environment, such as in the oil and gas, chemical and food industries due to its excellent corrosion resistance. Unfortunately, its wear and hardness characteristics are relatively poor and therefore, its use in applications that require these characteristics is limited.

In order to identify all these samples evolutions, the author was using quartz tube furnace to conduct the gas nitriding process, x-ray diffraction meter (XRD), field emission scanning electron microscope with energy dispersive x-ray spectroscopy (FESEM-EDX), optical microscope (OM) and Vickers microhardness tester. In addition, flat cell has been used to perform corrosion test.

1.2 Problem Statement

Stainless steels have been classified by their crystalline structure and for austenitic stainless steel, it has austenite as their primary phase (face centered cubic crystal). The use of austenitic stainless steel is widespread throughout many industrial fields. This alloy is selected for a range of applications because of its excellent corrosion resistance primarily due to the presence of chromium. However, due to its inherent austenitic structure, this material has relatively low hardness. This problem seriously limits their applications in which hardness as well as wear resistance are needed and required.

Many investigations have been performed to improve surface hardness of austenitic stainless steel and therefore enlarging their possibility of wider application, but led significant loss of its corrosion resistance. It is well known that resistance to corrosion is a crucial factor that has to take into account in selecting a material especially for highly corrosive environments. In oil and gas industry, corrosion of equipment, pipeline and pipes become the most common issues facing by offshore as well as onshore infrastructure. This problem leads to numerous consequences such as maintenance and operating cost, plant shutdowns, contamination of products, loss of product and effect of safety and reliability. Austenitic stainless steel (ASS) especially AISI 316L is widely used for surface piping, vessel cladding and clad line pipe, are must be taken to ensure the application is completely deaerated. In the presence of oxygen, 316L will pit, for example, if exposed to even cold seawater. In conditions containing H2S, the performance of AISI 316L is very sensitive to the presence of chloride ions. In chloride-free environments (<50ppm chloride), 316L has given reliable service in sour gas handling facilities, but pitting is readily initiated when chloride ions are present.

Thus, conducting this project is very significant research to produce a high surface hardness as well as high wear resistance austenitic stainless steel any reduction in corrosion resistance. In fact, the corrosion resistance might even be improved based on past researches that have been done.

1.3 Objective

The objective of this project is divided into two significant purposes which are:

- To investigate the effect of low temperature gas nitriding treatment (LTGN) on surface hardness as well as corrosion resistance of AISI 316L austenitic stainless steel.
- To determine and compare microstructure changes in the nitrided samples.

1.4 Scope of Study

Scope of study of this project is mainly in the form of laboratory experiments. This project cover on the conducting the gas nitriding surface treatment at low temperature on AISI 316L austenitic stainless steel, identify the effect of nitriding temperatures on the hardness as well as corrosion resistance and microstructure behaviour of the samples before and after nitriding. Non treated 316L austenitic stainless steel specimen was used as a reference material.

For this project, the low temperature gas nitriding process (LTGN) has been conducted in a quartz tube furnace for three different temperatures, 400^{o}C, 450^{o}C and 500^{o}C. Besides, Vickers microhardness tests have been done as following and referring to the standard of ASTM E-92, Standard Test Method for Vickers Hardness of Metallic Materials. Although empirical in nature, it can be correlated to tensile strength for many metals, and is an indicator of the material's hardness profile. Corrosion tests have been conducted by using a flat cell which is a three-electrode set-up with the tested sample as the working electrode, a silver chloride (AgCl) electrode as the reference electrode, and a platinum electrode used as the auxiliary electrode. The corrosion resistance of unnitrided and nitrided samples will be evaluated by measuring polarization curves in 3.5% NaCl solution at 25^{o}C.

Therefore, the mechanical properties (included hardness and physical properties) as well as corrosion resistance of the material are expected to be improved.

Besides, the morphological changes, structural phase and elemental profile of the treated samples were observed by optical microscopy (OM), field emission scanning electron microscopy (FESEM) and energy dispersive X-ray (EDX). For other relevant work, X-ray diffraction (XRD) has been used to confirm the formation of nitrides on the surface layer of the samples. Not to forget, all these observation and identification highlighted the significance relationship of utilizing variations of nitriding temperatures which could affect the result compiled.

1.5 Relevancy of Project

From this project, nitriding treatment as a surface hardening technique may bring the significance as a scientific reference to heat treatment industries in improving their process design and lifetime. This project may provide a wider application to the austenitic stainless steel users because of significant enhancement in surface hardness as well as corrosion resistance.

1.6 Feasibility of Project

This project is analyzed to be feasible where the laboratory equipment is all provided in the university. The implementations of the experiments follow the theories, which become the fundamental to complete the project. The allocation of financial cost is sufficient for this project. Moreover, the project is conducted with postgraduate student where this become the medium to share some data and information in order to achieve the project completion successfully. Therefore, author could ensure the feasibility of this project within the given period.

CHAPTER 2

LITERATURE REVIEW

2.1 Stainless Steel

Alloy steel is defined as carbon-iron solid solution with additional elements added to change properties of the metal. The most common alloying elements are chromium and nickel (Newell, 2009). When an iron based alloy containing at least 10.5% chromium and a maximum of 1.2% carbon, the metal is classified as stainless steel. (European standard EN 10088, 2010).

The alloying elements, depending on percentages, give stainless steel their physical, chemical and mechanical properties. Stainless steel still confers great corrosion resistance with the chromium content beyond the minimum of 10.5%. Corrosion resistance may be further enhanced, and a wide range of properties provided, by the addition of 8% or more nickel. The addition of molybdenum further improves corrosion resistance (in particular, pitting corrosion resistance), while nitrogen increases mechanical strength and enhances resistance to pitting. (The stainless steel family, 2009)

2.2 Austenitic Stainless Steel

Austenitic stainless steel is a group of stainless steel, which is an alloy material principally, contains iron (Fe) and minimum of chromium (Cr) and nickel (Ni). Due to the present of minimum chromium compositions 10.5%, this material becomes the better corrosion resistance (International Stainless Steel Forum, 2011). The existing of chromium will form the passive layer which is known as chromium oxide (Cr_2O_3) when reacts with oxygen in the environment. This protection layer brings the steel surface prevented from corrosion mechanism to the environment (Fontana, 1987).

Moreover, by adding the molybdenum (Mo), it can increase corrosion resistance in particularly to the pitting corrosion (International Stainless Steel Forum, 2011).

Nickel with minimum of 8% in the austenitic stainless steel composition can stabilize the austenitic structure of iron where the steels become non-magnetic and less brittle at low temperature (Callister, 2007).Austenitic stainless steel is in the face-centered cubic (F.C.C) atomic structure. The formation of this atomic structure is initially from the adding of nickel into the ferrite stainless steel, which is formerly in the atomic structure of body-centered cubic (B.C.C) (International Molybdenum Association, 2011).The formation of F.C.C atomic structure gives more planes for the flow of dislocations and low level of interstitial elements which provides the austenitic stainless steel good ductility (Dyson, 2011)

In order to distinguish the different between the steel and cast iron, this could be referred on the Iron Carbon Equilibrium Diagram. In the austenitic structure, the carbon contains are lower which compare to the cast iron. Carbon becomes an essential alloying addition in steel. The increasing of carbon will increase the hardness and strength of the steel (TATA Steel, 2011). However, as mention before, austenitic stainless steel 316L, which is low carbon content, need to maintain below 0.03%. This is the reason why the inherent austenitic structure is not good in wear and surface hardness because of less carbon content.

2.2.1 Grades of Austenitic Stainless Steel

Austenitic, or 200 and 300 series, stainless steels have an austenitic crystalline structure, which is a face-centered cubic crystal structure. For 300 series, there are several grades such as Type 316 and Type 304. These grades differ in the physical and chemical properties. However, there is also different in straight grades, L grades, and H grades.

Straight grades define the content of austenitic stainless steel that have maximum of 0.08% carbon (Tverberg, 2011). For example Type 316. However, for L grades, for instance Type 316L, this grade indicates low carbon of austenitic stainless steel. The percentage of carbon is maintained maximum up to 0.03% (Roll, 2011). This is because to avoid carbide precipitation or known as sensitization effect. At high temperature, carbon could react with chromium and gather at grain boundaries. This could reduce the formation of passive layer (chromium oxide) as the corrosion resistance to the surface. This is why the amount of carbon needs to be controlled for type 316L (Stainless Steel Processing, Inc, 2011). Moreover, the lower carbon content for this type of steel possesses a good weldability because sensitization effect could be prevented at high temperature of welding process.

For H grades, the range of carbon content is minimum 0.04% and maximum 0.10%. This grade is used for extreme temperature where the high carbon could give some strength to the stainless steel. The example grade is Type 316H (Stainless Steel Processing, Inc, 2011).

2.2.2 Enlarging application of Austenitic Stainless Steel

Starting from the mid of 1980’s, investigations have been performed to improve surface hardness of ASS and thus enlarging their possibility of wider application, but led significant loss of its corrosion resistance. This tendency occurs due to the sensitivity effect. Sensitization is a common problem in austenitic steel where precipitation of chromium carbides ($Cr_{23}C_6$) occurs at the grain boundaries at elevated temperatures, typically between 450^oC to 850^oC; diffusional reaction in forming chromium nitride/carbide leads to the depletion of Cr in the austenitic solid solution and consequently unable to produce Cr_2O_3 passive layer to make stainless feature. As a result, it reduces the corrosion resistance property of the stainless steel. This phenomenon causes reduction in ductility, toughness and aqueous corrosion resistance (Clark & Varney, 1962).

The efforts have been made in the past decades to modify the surfaces of these materials to improve their surface hardness, wear resistance as well as corrosion resistance which are shown in Figure 1.

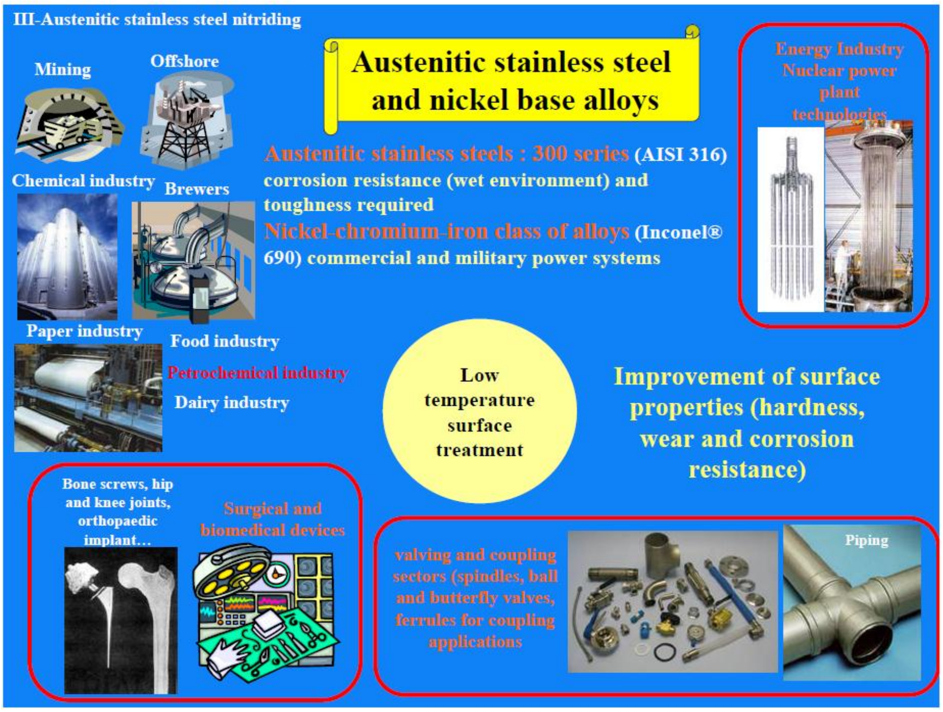


Figure 1: Enlarging application of Austenitic Stainless Steel (Czerwiec, 2010).

Bell et al. (T. Bell, 2001) suggested that a low temperature nitriding can eliminate the formation of chromium nitrides but at the expense of strengthening effects made by CrN precipitates. Alternatively, the strengthening effect will be replaced by supersaturation of interstitial species in austenite matrix which leads to the hardening of the surface region several tens micro meter thick. This precipitation-free nitride layer not only exhibits high hardness but also possesses good corrosion resistance due to the availability of retaining chromium in solid solution for corrosion protection.

In relation with the functional properties of a part, such as fatigue and static strength, or wear and corrosion resistance, are the basis for specifying the proper process and steel as illustrated in Figure 2 (T. Bell, 2005). The functional part properties that essentially depend on the compound layer are wear resistance, tribological properties, corrosion resistance and general surface appearance. Both abrasive and adhesive wear resistance increase with hardness and with minimized porosity of the compound layer. Porosity can be positive in lubricated machinery parts as the pores act as lubricant reservoirs. The compound layer depth has to be deep enough not to be worn away. The diffusion layer (depth, hardness and residual stress) determines surface fatigue resistance and resistance to surface contact loads.

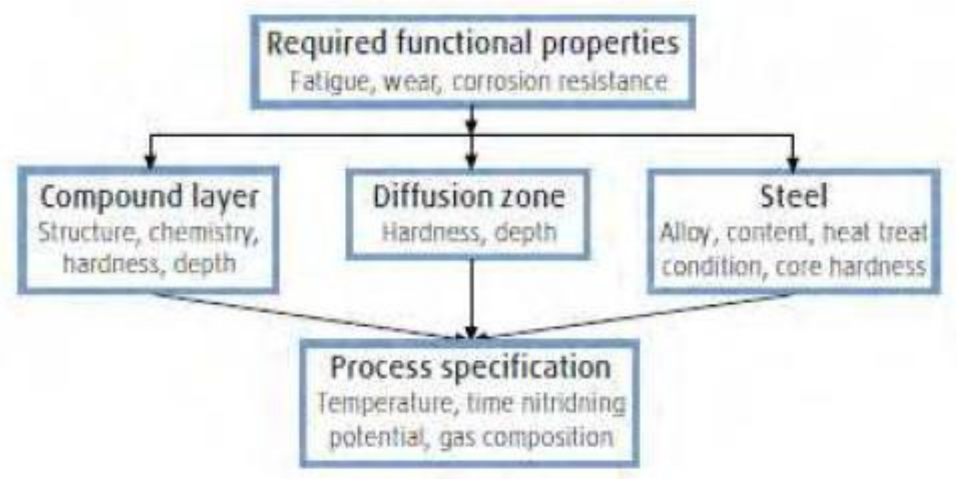


Figure 2: The steps to process specification starting from required part properties.

2.3 Concept of Nitriding

Nitriding is a surface hardening technique by the diffusion of nitrogen into the surface layers and the change of chemical compositions of the steel (Elgun, 1999). There are several advantages by nitriding treatment, which are to improve mechanical properties, tribological properties and corrosion properties. These improvements are due to the structural changes and high dimension stability by nitriding treatment on the steel. (Leppänen et al, 1999, Subbiah et al., 2005).

There are different methods of nitriding process. Salt-bath nitriding is a method with the nitrogen in the cyanide salt as medium for nitriding (Hamdy et al, 2011). While the method of plasma or ion nitriding is involved with diffusion of nitrogen atoms into the metal surface in the presence of plasma environment. For this project, author will utilize the gas nitriding methods, which the equipment facilities are provided in the university laboratory. Ammonia gas will be used to become the medium for denoting nitrogen.

2.4 Gas Nitriding Process

In early 1920’s, gas nitriding process had begun to be used in the industry. The treatment is conducted where the gases accumulate in the furnace and diffuse to the tempered surface product with a gas atmosphere control. The nitriding gas resource that could be used is pure nitrogen, nitrogen/argon gas mixture, nitrogen/hydrogen gas mixture or ammonia gases. There are some advantages from this process where hardness is achieved without the oil, water or air quench. Another advantage is surface hardening is accomplished in a nitrogen atmosphere and could prevents scaling and discoloration (Elgun, 1999). This process also can easily form a hardened layer on the surface of material and it is not expensive as those newly developed technologies (Triwiyanto et al, 2009).

For this project, author will use ammonia as the gas resource for nitriding. Nitrogen is introduced into the surface steel by holding the metal at a suitable temperature in contact by ammonia. Thus, ammonia will disassociate into gas into hydrogen and nitrogen on the surface steel (Mridha, 2006). Nitrogen then diffuses from the surface into the core of the material at the certain temperature range, which could bring the formation of alloy nitrides in nitrogen diffusion zone (Haruman et al, 2006).

In order to accelerate diffusion on austenitic stainless steel, the steel will be treated at relatively high temperature, about 570 °C (Bell et al, 2002). However, the formation of chromium nitride/carbide could occur during the diffusion at high temperature. As the results, chromium nitride/carbide might be precipitated into the grain boundary and the passive layer which is chromium oxide (Cr2O3) will unable to be produced and reduced the corrosion resistance property of stainless steel (Triwiyanto et al, 2009). This phenomenon is known as sensitization effect.

2.5 Low Temperature Nitriding Gas Treatment

The efforts to avoid the sensitization effect relatively with high temperature treatment have done by Zhang and Bell (2002).They have investigated the low temperature nitriding technique where it was found that a nitrided layer is formed in AISI 316L with plasma nitriding technique. The thickness of the layer could be formed up to 20μm at temperature around 400 °C. The characteristics of the layer show that it has very high hardness and excellent wear resistance, as well as very good corrosion resistance.

This gives strong evidence that the nitrogen layer could be produced at low temperature and the term for the nitrogen layer is an expanded austenite (γN) (Haruman et al, 2006). Besides that, the nitriding layer formed containing a new type nitrite phase with new phase composition is also known as S-phase (Toshkov et al, 2007). This phase is characterized with its good mechanical properties and acceptable corrosion resistance (Hamdy et al, 2011).

Even though the formation of chromium nitride as strengthening effects is eliminated under the low temperature nitriding, super saturations of the interstitial nitrogen species in austenite matrix become the alternative ways to give the strengthening effects. (Triwiyanto et al, 2009)

In previous research, some variables could be controlled to investigate the effects. For temperature variables, the different in temperature treatment could give the indications on how nitrided stainless steel surface possess the susceptibility to the corrosion attack relates with the sensitivity effect produces by the particular material (Haruman et al, 2006).

Time variables of treatment also could be analyzed in this low temperature nitriding treatment. The case depths of the nitriding layer become the relation with the time variables (Subbiah et al, 2005). There are different case depth could be identified under the nitrided layer morphology. Moreover, the time variables may bring us to have the understanding in the improvement of surface hardness for each different time of treatment.

2.6 Previous studies

There are some investigations regarding the microhardness and corrosion resistance on nitrided AISI 316L stainless steel with difference low temperatures of treatment by several investigators. Y. Li et al., (2011) has completed the investigation with plasma nitriding on AISI 316L at temperatures ranging from 450 to 540°C for 4 hours in a gas atmosphere of ammonia. The results obtained bring the significance improvement on surface hardness of ~680 HV at 450°C nitriding temperature. Meanwhile, for the sample nitrided at 480°C, the surface hardness also increased to 960 HV. The higher hardness value (1340 HV) obtained in the sample nitrided at 540°C. The improvement can be explained due to the combined hardening effect by S-phase and formation of chromium nitride (CrN). Whereas, for 450°C and 480 450°C, the improvement was due to the formation of mono S-phase layer on the surface.

On the other hand, according to the research made by C.X.Li et al. (2003), on his paper in title "*the corrosion properties of active screen plasma nitrided 316L austenitic stainless steel*", he carried out the experiments for two nitriding temperatures which are 420 ^{o}C and 500 ^{o}C. From his discovery, he stated that when nitriding temperature is sufficiently low, a nitrogen expanded austenite, also known as S-phase can be produced on the surface of an austenitic stainless steel. Due to the superb properties of the S-phase, the low temperature nitrided austenitic stainless steels possess not only significantly increased surface hardness and wear resistance, but also much improved corrosion resistance. The figures 3 and 4 below show the result from his investigations.

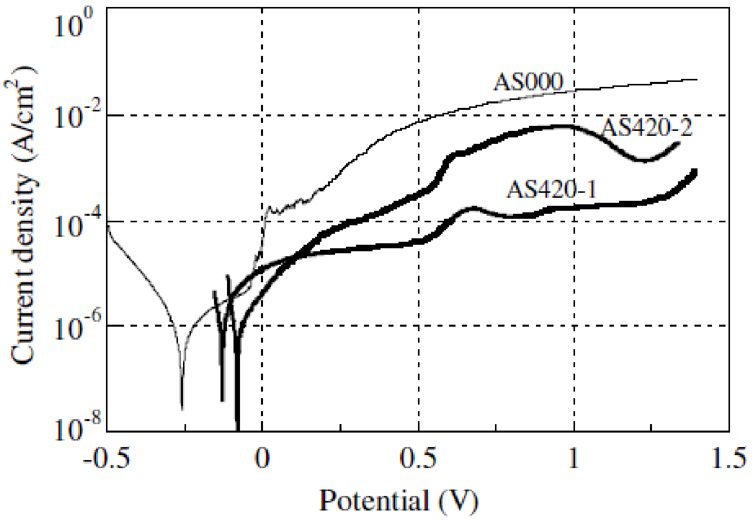


Figure 3: Comparison of polarisation curves of the low temperature AS plasma nitrided (AS420 series) and untreated 316 steel in 3.5% NaCl water solution (C.X.Li et al, 2003)

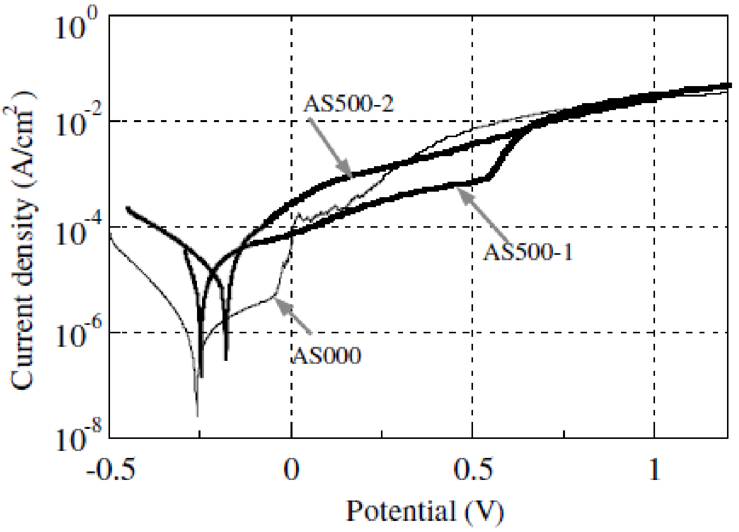


Figure 4: Polarisation curves for the untreated and 500 C AS plasma nitrided 316 steels (C.X.Li et al, 2003)

According to his results, he identified that AS plasma nitriding at low temperature (420 ^{o}C) produced a single phase nitrided layer of nitrogen expanded austenite (S-phase), which considerably improved the corrosion properties of the 316 austenitic stainless steel. In contrast, AS plasma nitriding at a high temperature (500 ^{o}C) resulted in chromium nitride precipitation so that the bulk of the nitrided case had very poor corrosion resistance.

Another investigations was done by Triwiyanto et al, (2009)by using the same material termochemical treatment furnace with Haruman et al., (2006) experiments, but the treatments conducted are nitriding, carburizing, nitrocarburizing and hybrid treatments at 450°C (2, 5 and 8 hours) . However, only nitriding treatment results obtained will be highlighted in order to relate with author’s project. From the nitrided layer morphology conducted by Field Emission Scanning Electron Microscopy (FESEM), the nitrided specimen has a thickness nitrided layer between 3.26 to 8.35 µm for 450°C (2, 5 and 8 hours). From the depth profiles of microhardness obtained by the investigation, the surface hardness for 450°C (8 hours) decreasing moderately from 0 to 10 µm which is from 1600 to 1400 HV respectively. This result could relate to the thickness nitrided layer obtained from FESEM and the nitrogen diffusivity characteristic, where the density of atomic nitrogen supersaturated into the surface decreasing moderately through the distance from the surface.

CHAPTER 3

METHODOLOGY

3.1 Research Methodology

At the beginning, the author did certain research and read some journals for the literature review in order to enhance the understanding on hardness profile, corrosion properties, microstructure changes and mechanical properties of the nitrided samples. In this study, AISI 316L austenitic stainless steel is used as a material for analysis. This material will undergo low temperature gas nitriding treatment (LTGN) in different treatment temperature and constant time. Temperature of treatment varies at 400 ^{o}C, 450 ^{o}C and 500 ^{o}C. Meanwhile, the time is set 8 hours. Corrosion resistance analysis has been analyzed by conducting corrosion test using flat cell. For nitrided layer morphology and surface morphology, Field Emission Scanning Electron Microscopy (FESEM) instrument has been utilized. The flow chart in Figure 5, which is the iterative process of the experiment and the investigation, will be described accordingly. Data analysis and final result section are discussed later in the next chapter.

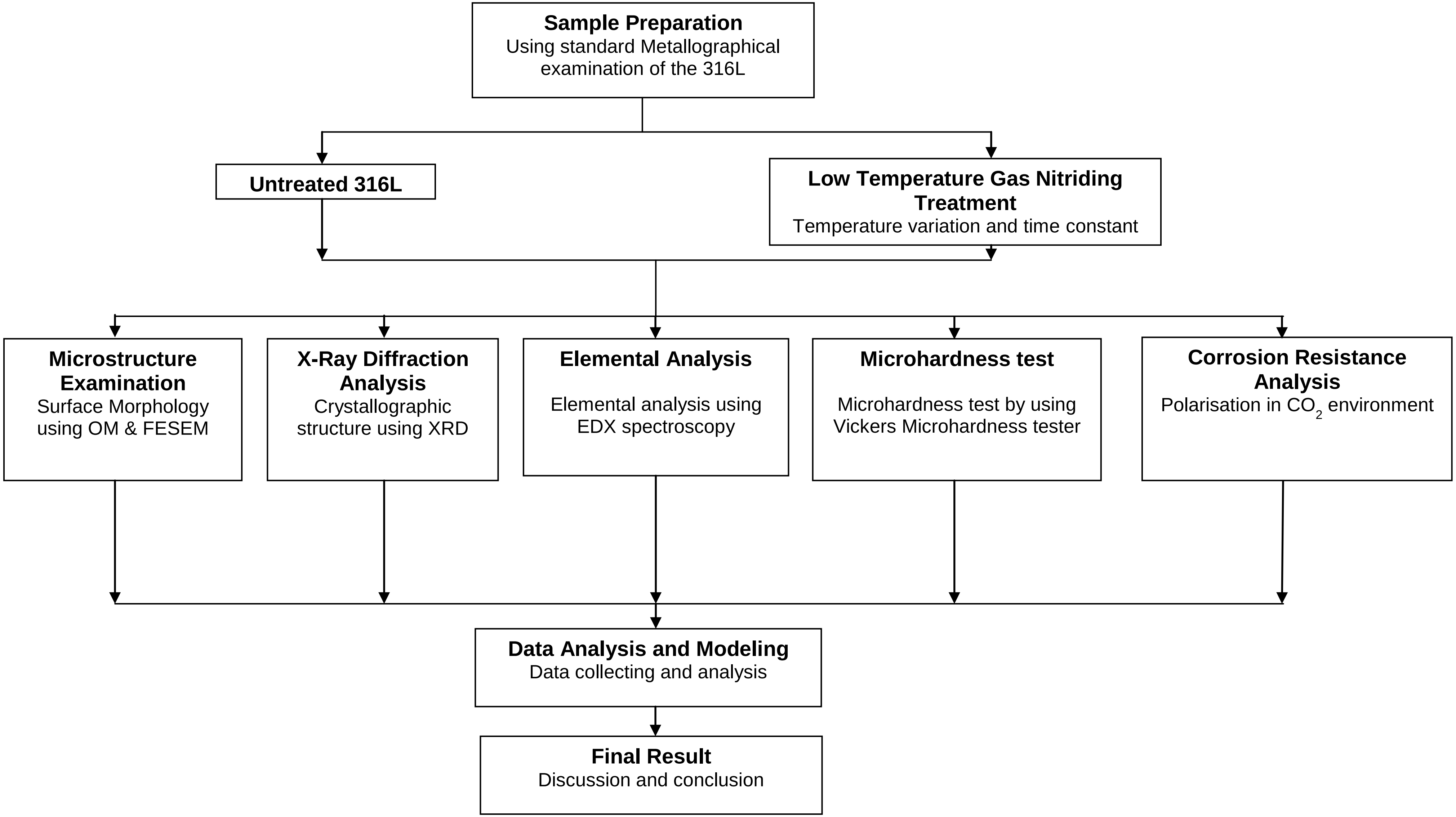


Figure 5: Flowchart of iterative process for experimental work

3.2 As Received Sample

The sample used in this project was AISI 316L austenitic stainless steel with following chemical compositions (wt %): C (0.03), Cr (17.50), Ni (10.10), Mo (2.16), and Fe balance. The material obtained by the author at the first time is in the plate pattern and need to be cut in order to prepare for this project. After cutting the first sample, the sample was prepared for analysis of as received sample which then will be recorded to compare with the nitrided samples.

3.3. Metallographic Sample Preparation for Grains Observation

Metallographic sample preparation is done to observe the grains of the 316L Austenitic Stainless Steel before nitriding process. The grains and grain boundaries is observed using Optical microscope (OM).

3.3.1 Sectioning

Sectioning is a step in sample preparation where the specimen is cut into the desired dimension and shape which is a rectangular shape 15mm X 10mm X 5mm. This step involves cutting action that can change the microstructure due to heating and work hardening. The degree of damage varies with techniques used and type of sample material. For this experiment, sectioning has been done by using abrasive cutter as shown in Figure 6 below.

Figure 6: Water abbrasive cutter for sectioning

3.3.2 Mounting

Mounting is a step in specimen preparation where the specimen in encapsulated in polymeric matrix. The purpose of mounting is to provide protection for the specimen and ease handling during microscopic examination. Figure 7 shows the equipment used for mounting.

Figure 7: Hot mounting machine for mounting

3.3.3 Grinding

The purpose of grinding is to remove damage introduced by previous operation such due to heating or work hardening. Instead of that it is also remove the saw marks and clean the encapsulant and specimen surfaces. The goal of grinding is a plane surface with minimal damage. Grinding is performed on SIC abrasive paper that mounted on a motor driven wheel. Grinding is done in wet medium with water as lubrication. Grinding sequence follows a series of descending grain size from 120, 320, 600, 800 and 1200 grit.

3.3.4 Polishing

The purpose of polishing is to produce scratch free surface with mirror-like finish. Washing and cleaning between steps are critical. Polishing involve two steps which are the rough polishing and fine polishing. Rough polishing is performed using diamond paste on a wheel covered with Naples cloth. It is involve diamond suspension size range from 6 – 3 μm. For fine polishing, it is performed using 1μm grain diamond suspension on a wheel covered with napped cloth or polishing cloth. Figure 8 below shows the equipment used for grinding and polishing.

Figure 8: Grind/Polish machine for grinding and polishing.

3.3.5 Etching

Etching is functioned to reveal the microstructure of the 316L Austenitic Stainless Steel under microscope inspection. This process involves chemical reaction between the sample and etchant under controlled condition. For 316L Austenitic Stainless Steel, the etchant that used in etching the sample is Marble's Region (Figure 9). The compositions of Marble's reagent are 10g of $CuSO_4$, 50 ml HCl and 50 ml H_20. Sample was swapped by the etchant to create clear view on different microstructure. Table 1 below shows the details of Marble's Reagent etchant.

Table 1: Marble's reagent etchant

Etchant	Composition	Conc.	Conditions
Marble's Reagent	Copper (II) sulphate,CuSO4	10 grams	Immerse or swab for 5-60 seconds.
	Hydrochloric acid	50 ml	
	Water	50 ml	

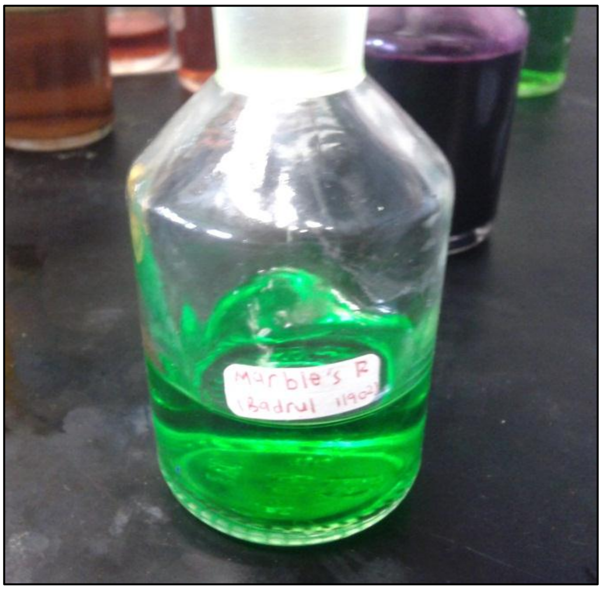


Figure 9: Marble's reagent for etching

3.4 Low Temperature Gas Nitriding Treatment

3.4.1 Nitriding equipment: Model OTF-1200X-3CLV

As shown in Figure 10, OTF-1200X-3CLV is cover split-able single zone tube furnace with three channels gas flowing system. As Figure 10 showing below, this nitriding equipment is divided the whole system into two sub-systems: (1) OTF-1200-2-80mm dual zone tube furnace and (2) 3 channels gas mixing system.

OTF-1200-2-80mm is split-able two zones tube furnace, which can achieve faster heating up to 1200 ^{o}C and create a different thermal gradient by adjust two zone temperature. The furnace includes one 50 mm diameter fused quartz tube for immediate use. Two precision temperature controllers are installed, which can provide 30-segments heating and cooling steps with +/- 0.5 ^{o}C accuracy.

3 channels gas mixing system is a mixer system which is specified for mixing up to two gases or continuously supplying one gas, under small gas flowing rate and low pressure. The air cannot get in whenever users switch the different gas into use. Gas flowing rate and pressure can be exactly displayed in one screen for an efficient control.

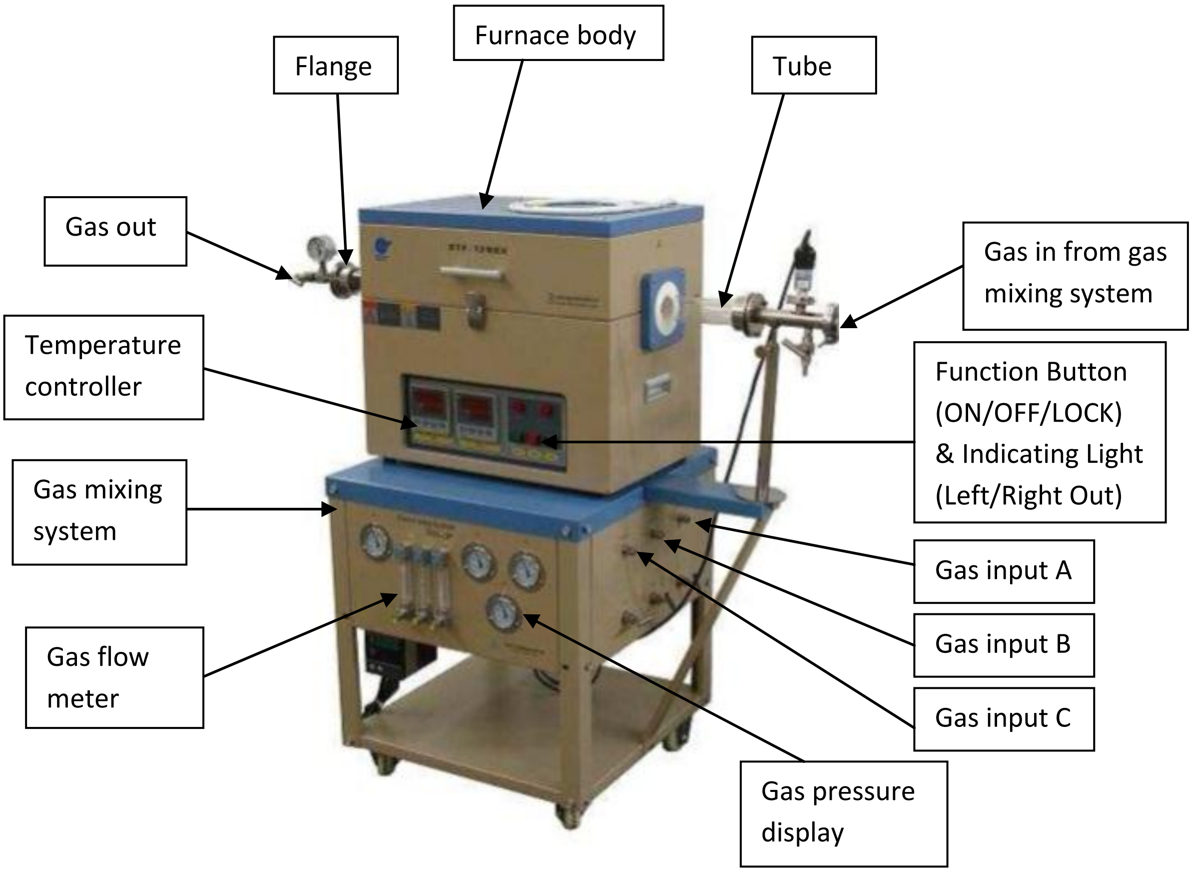


Figure 10: OTF-1200X-3CLV

3.4.2 Preparation of equipment and furnace

First, the inner and outer surface of the quartz tube is cleaned by using a special chemical solution in order to remove any contaminants and debris that will affect the nitriding reaction. After that, the fitting system is set up to allow gas flow from gas tank to the quartz tube furnace. For this purpose, nitrogen tank is directly connected to the quartz tube while ammonia tank and methane tank are connected to gas mixing system. Then, a connection is prepared between the output of the gas mixing system and the quartz tube. An alumina boat is placed at the end side of the quartz tube.

3.4.3 Nitriding temperature setup

Figure 11 shows the panel of temperature controller and function button (ON/OFF/LOCK). When power is on, the controller's version will show up on panel for a few seconds, then controller enter a normal state, and blinking "stop" sign means the program is in stop status. After the normal state, the desire parameters such as temperature and time can be set on the temperature controller. For this investigation, the desire nitriding temperatures are 400 ^{o}C, 450 ^{o}C and 450 ^{o}C (nitriding temperature variation of treatment). In order to avoid mistake, it is better to make a drawing and table based on the desire temperature profile before key in the data to controller. For the first experiment, the target temperature is set to be 400 °C from the room temperature with the heating rate of 10 °C/min. Figure 12 shows temperature profile to be set for 400^{o}C nitriding temperature and Table 2 shows the data table to be entered based on temperature profile in Figure 12.

Figure 11: Temperature controller and function button (ON/OFF/LOCK)

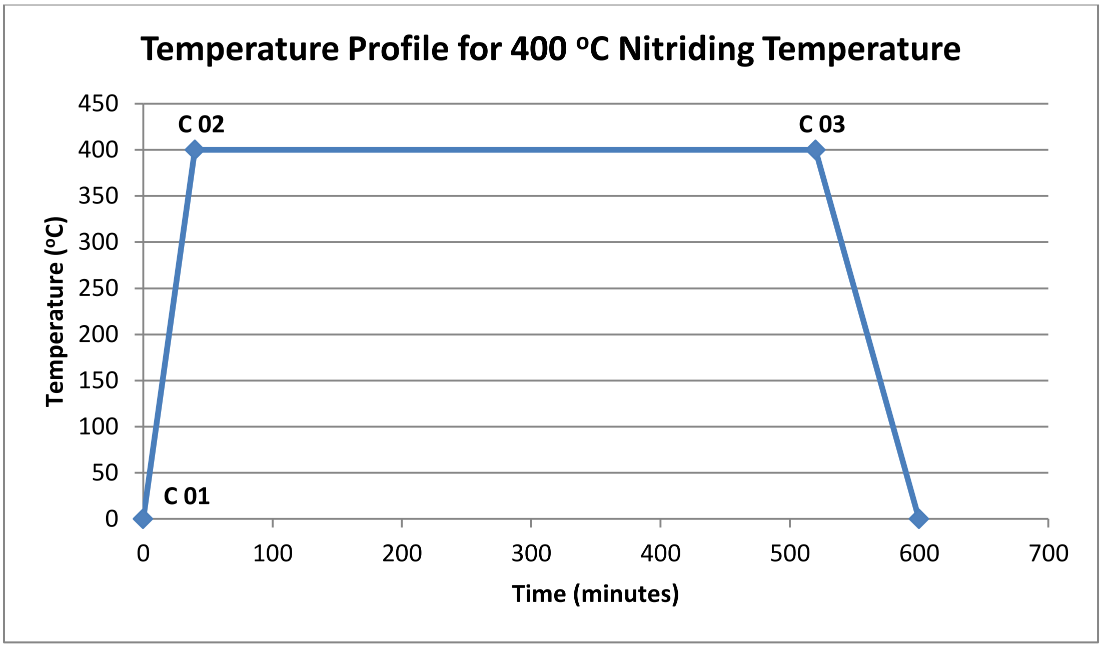


Figure 12: Temperature profile to be set for 400oC nitriding temperature

Table 2: Data table to be entered based on temperature profile in Figure 11

Segment	Input Data	Details
C 01	0	Initial Temperature. It can be leaved as '0'
T 01	40	Running time in the first segment. Ramping time to reach temperature C 02 (450°C) which is 40 minutes
C 02	400	Temperature to be reached within T 01 which is 400°C
T 02	480	Holding time for treatment in the second segment which is 480 minutes or 8 hours
C 03	400	Temperature to be reached in the second segment. If C 02 is same value as C 03, it means dwell time in second segment
T 03	121	It means program finish and stop. The furnace will cold naturally.

3.4.4 Low Temperature Gas Nitriding Treatment

Before start the nitriding treatment, all the samples are cleaned using ultrasonic cleaning to remove any debris that contain at the sample's surface. The samples that will undergo nitriding treatment will be immersed in Hydrochloric Acid solution, HCl, (2 M) for 15 minutes to remove the native oxide layer that can affect the nitrogen diffusion into the sample's surface**.**

Nitriding treatment will be conducted in quartz tube furnace model OTF-1200X-3CLV. This furnace has 3 channels gas mixing system and accurate vacuum measuring meter. After being immersed in HCl solution for 15 minutes, the sample that will undergo nitriding treatment is quickly positioned on the alumina boat. Then, the alumina boat is pushed carefully by using steel rod into the middle of the furnace. The cycle of nitriding is set through the temperature controller. For the first experiment, the target nitriding temperature treatment is set to be 400 °C from the room temperature with the heating rate of 10 °C/min. Then, push the 'Turn-on' button to start run the experiment. Nitrogen will be purged into the furnace to maintain the environment inert, where the oxidation of samples and furnace component can be prevented. Moreover, nitrogen purging also prevent potentially explosive mixture when the ammonia begin to purge into the furnace. Flow meter is calibrated to ensure the right flow of nitrogen into the furnace. Observation is made on the appearance of gas bubble in water-contained conical flask to ensure the nitrogen is flowing through the furnace. When the temperature reaches 400°C, the valves for ammonia tank and methane tank is opened to flow the gases into the gas mixing system before it flow to the tube furnace. The process is maintained for 480 minutes (8 hours) with additional time 10 minutes. After the nitriding process is done, the valves for ammonia tank and methane tank are closed and let the furnace to cool down naturally until it reaches room temperature. Then, the furnace is opened and the samples are taken out carefully. This experiment is repeated for nitriding temperature of 450 ^{o}C and 500 ^{o}C (temperature of variation of treatment). Table 3 shows the details for 450 ^{o}C and 500 ^{o}C nitriding temperature experiments.

The flow rate for each gas is set up based on the flow meter reading on the control panel; Nitrogen gas (150ml/min), Ammonia Gas (40ml/min) and Methane Gas

(10ml/min). Ammonia gas and Methane gas will mix in the mixing chamber before purge together into the tube furnace.

Table 3: Details for 450 ^{o}C and 500 ^{o}C nitriding temperature experiments

Segment	Details	Experiment 1 400 ^{o}C	Experiment 2 450 ^{o}C	Experiment 3 500 ^{o}C
C 01	Initial Temperature. It can be leaved as ‘0’	0	0	0
T 01	Ramping time to reach temperature C 02 with heating rate of 10^{o}C/min	40 minutes	45 minutes	50 minutes
C 02	Temperature to be reached within T 01	400 ^{o}C	450 ^{o}C	500 ^{o}C
T 02	Holding time for treatment in the second segment.	480 minutes or 8 hours	480 minutes or 8 hours	480 minutes or 8 hours
C 03	Temperature to be reached in the second segment. If C 02 is same value as C 03, it means dwell time in second segment	400 ^{o}C	450 ^{o}C	500 ^{o}C
T 03	It means program finish and stop. The furnace will cold naturally.			

3.5 X-Ray Diffraction Analysis

Generally, X-Ray Diffraction analysis will be 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 angle and intensity of the diffracted beam [14]. 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 austenitic stainless steel, the purpose of X-Ray Diffraction analysis is to determine the formation of alloying nitride subsequent to nitriding process. The X-Ray Diffraction machine that will be used for this project is located at Block 17.

3.6 Microstructure Analysis

The purpose of this test is to determine the formation of nitride layer subsequent to nitriding process and the microstructure analysis of untreated AISI 316L austenitic stainless steel. This test will be conducted using Optical Microscope (OM) and Scanning Electron Microscope (SEM). Before conducting the microstructure examination using Optical Microscope (OM), 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 will be mounted in a resin. Bakelite is commonly used. A further advantage of that the edges of the specimen will be reasonably well polished and not “beveled” by the preparation process. After mounting, the samples need to be grinded and polished.

Then, the samples need to be etched by using etchant. The purpose of etching is to reveal the grain boundary. Firstly, the specimen will be washed by using ethanol and then dried. After that, etchant will be applied at the surface of the specimen for 5 to 10 seconds. Then the specimen needs to be washed using water and ethanol. The specimen will be dried and ready for microstructure examination.

3.7 Elemental Analysis

The chemical composition of the samples can be determined by using Energy-Dispersive X-ray (EDX) Spectroscopy that being attached together with the Scanning Electron Microscope (SEM). This equipment is located at Block P.

3.8 Corrosion Resistance Analysis

The corrosion resistance of unnitrided 316L austenitic stainless steel and nitrided 316L austenitic stainless steels at 400^oC and 500^oC in CO^2 environment will be evaluated at room temperature by measuring polarization curves in 3.5% NaCl. The flat cell, as schematically shown in Fig. 8, was a three electrode set-up consisting of the specimen as the working electrode, a silver chloride (AgCl) as the reference electrode, and a platinum electrode used as the auxiliary electrode. CO^2 gas will be purged during the experiment. Sample to be tested will be placed against a Teflon ring at one end of the flat cell, leaving a theoretical circle area of 0.35 cm^2 on the sample surface in contact with the testing solution through a round hole in the Teflon ring. Test control, data logging and data processing will be achieved by a ‘‘Sequencer’’ computer software. The scanning potential is in the range of -0.8 to + 1.2 V, and the scan rate was 1 mV/s.

3.9 Vickers Microhardness Analysis

The hardness of particular material sample could be obtained by Vickers microhardness test technique as follow the standard requirement test. (Instron, 2011)

- ASTM E384 – micro force ranges – 10g to 1kg
- ASTM E92 – macro force ranges - 1kg to 100kg
- ISO 6507-1,2,3 – micro and macro ranges

The Vickers hardness test method consists of indenting the test material with a diamond indenter, in the form of a pyramid with a square base and an angle of 136 degrees between opposite faces subjected to a test force of between 1g and 100kg. The full load is normally applied for 10 to 15 seconds (material.co.uk, 2011). The advantages of the Vickers hardness test are that extremely accurate readings can be taken, and just one type of indenter is used for all types of metals and surface treatments. The Vickers method is capable of testing the softest and hardest of materials, under varying loads (Indentec, 2011).

For this project, microhardness assessment by Vickers hardness test is performed to examine the results surface hardness for each different treatment. The instrument used is Model HV-1000A Micro Hardness Tester (Figure 13) with 10gf load and 15 s dwell time. The surface hardness of nitrided steel will be tested from the edge nitrogen diffusion surface in the range from 0 to 50 μm depth. This is to obtained depth profile of microhardness. According to the investigation by (Triwiyanto et al., 2009), the surface hardness for 450°C (8 hours) decreasing moderately from 0 to 10 μm which is from 1600 to 1400 HV0.5. The results of this investigation guide author to apply the same technique in order to relate the thickness of nitrided layer and the surface hardness improvement.

Figure 13: Vickers hardness test instrument; Model HV-1000A Micro Hardness Tester

3.9 Tools Required

Raw material:

i. AISI 316L austenitic stainless steel plate

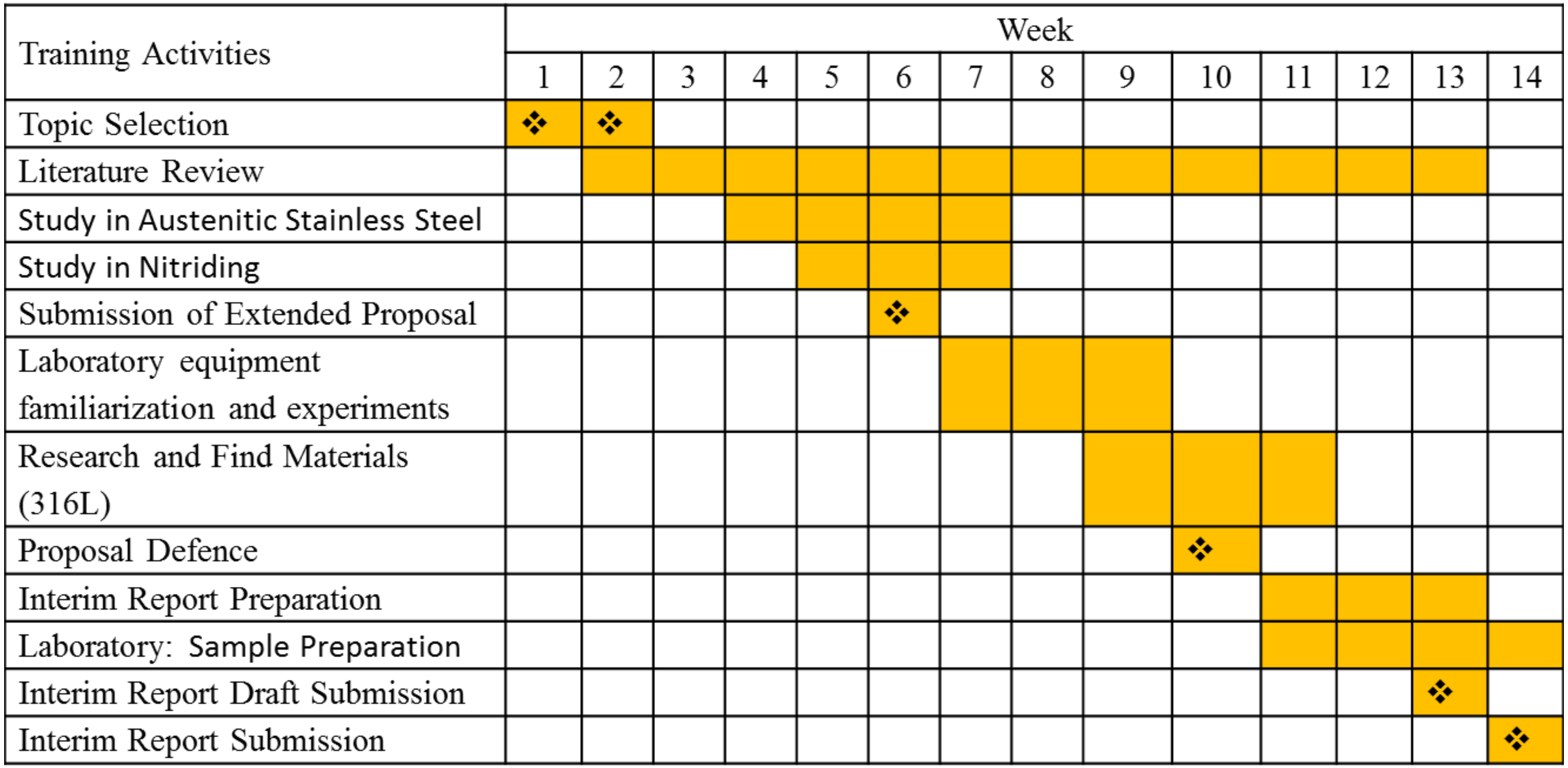
Tools:

i. Water Abrasive cutter machine
ii. Hot mounting machine
iii. Grinding/polishing machine
iv. Silica carbide abrasive grit paper
v. Polisher and Aluminum oxide/diamond paste
vi. Etchant (Marble's Region)
vii. Ultrasonic cleaning bath
viii. HCl (2 M) solution
ix. Quartz tube furnace
x. Ammonia, methane and nitrogen gas tanks
xi. Vickers Microhardness Testing Machine
xii. Optical Microscope (OM)
xiii. Field Emission Scanning Electron Microscope (FESEM)
xiv. Energy-dispersive X-ray (EDX) spectroscopy
xv. X-Ray Diffraction (XRD) machine
xvi. Flat Cell

3.10 Gantt- Chart and Key Milestones

3.10.1 Final Year Project (FYP) 1

Table 4: Gantt-chart and key milestones for FYP1



Training Activities	Week													
	1	2	3	4	5	6	7	8	9	10	11	12	13	14
Topic Selection	❖	❖												
Literature Review		🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	
Study in Austenitic Stainless Steel				🟨	🟨	🟨	🟨							
Study in Nitriding					🟨	🟨	🟨							
Submission of Extended Proposal						❖								
Laboratory equipment familiarization and experiments							🟨	🟨	🟨					
Research and Find Materials (316L)									🟨	🟨	🟨			
Proposal Defence										❖				
Interim Report Preparation											🟨	🟨	🟨	
Laboratory: Sample Preparation											🟨	🟨	🟨	🟨
Interim Report Draft Submission													❖	
Interim Report Submission														❖

❖ Milestone
🟨 Progress

3.10.2 Final Year Project (FYP) 2

Table 5: Gantt-chart and key milestones for FYP2

Training Activities	Week														
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15
Sample Preparation	🟨	🟨													
Microstructure Examination - OM		🟨													
Arranging Furnace			🟨	🟨											
Nitriding Process				🟨	🟨	🟨									
Microstructure Examination - FESEM						🟨	🟨								
Elemental Analysis - EDX						🟨	🟨								
Submission of Progress Report						🟨	🟨	❖							
X-Ray Diffraction Analysis								🟨	🟨						
Microhardness Test								🟨	🟨						
Corrosion Test									🟨	🟨					
Pre-SEDEX											🟨 ❖				
Submission of Draft Report									🟨	🟨	🟨	❖			
Submission of Technical Paper												🟨	🟨 ❖		
Submission of Dissertation (Soft cover)												🟨	🟨 ❖		
Oral Presentation													🟨	❖	
Submission of Dissertation (Hard-bound)															🟨 ❖

❖	Milestone
🟨	Progress

CHAPTER 4

RESULT AND DISCUSSION

4.1 Weight differences before and after nitriding

Nitriding will cause diffusion of nitrogen into the metal. The diffusion can increase the weight of the samples. If the weight of the samples increases, it shows that nitrogen diffusion at the surface successfully occured. Besides, the diffusion of nitrogen is greatly influenced by the temperature. Table 4 below shows the mass recorded before and after the nitriding process for 400 ^{o}C, 450 ^{o}C and 500^{o} C nitriding temperature.

Moreover, nitrogen flux control is important for optimizing nitriding parameters. The flux values measured from the weight differences are shown in Table 6. Weight differences indicated the weight gain for each nitrided sample after the nitriding process. Equation 1 is used in which; J- flux, A- surface area and t- nitriding time, to find the nitrogen flux from weight gain (Wei, 2013).

$$J = \frac{weight\ gain}{A.t} \qquad (1)$$

Table 6: Flux values measured from the weight differences

Nitriding Temperature (^{o}C)	Mass before nitriding (g)	Mass after nitriding (g)	Weight Difference (g)	Percentage of weight difference (%)	Flux (g/cm^{2}/s) from weight gain
400	3.138	3.140	0.002	0.064	2.29 (10^{-8})
450	3.140	3.144	0.004	0.127	4.59 (10^{-8})
500	3.142	3.147	0.005	0.159	5.74 (10^{-8})

From the results in Table 6, nitriding at 500 °C brings about a 2.5 times higher nitrogen uptake than nitriding at 400°C. It is understood that weight difference increased when the temperature increased in nitriding process. Besides, it is agreed that the nitrogen flux is influenced by the temperature of the nitriding process. Based on the result, it shows that increase in the nitriding temperature will increase the rate of nitrogen diffusion per unit area of the treatment.

Based on Figure 14, the graph shows that the percentage of weight difference of samples before and after nitrided increase gradually with temperature. Thus, it can be concluded that increasing the nitriding temperature will increase the nitrogen diffusion into the sample. Besides, from the result, it also shows that nitriding process was successfully took place to all the samples.

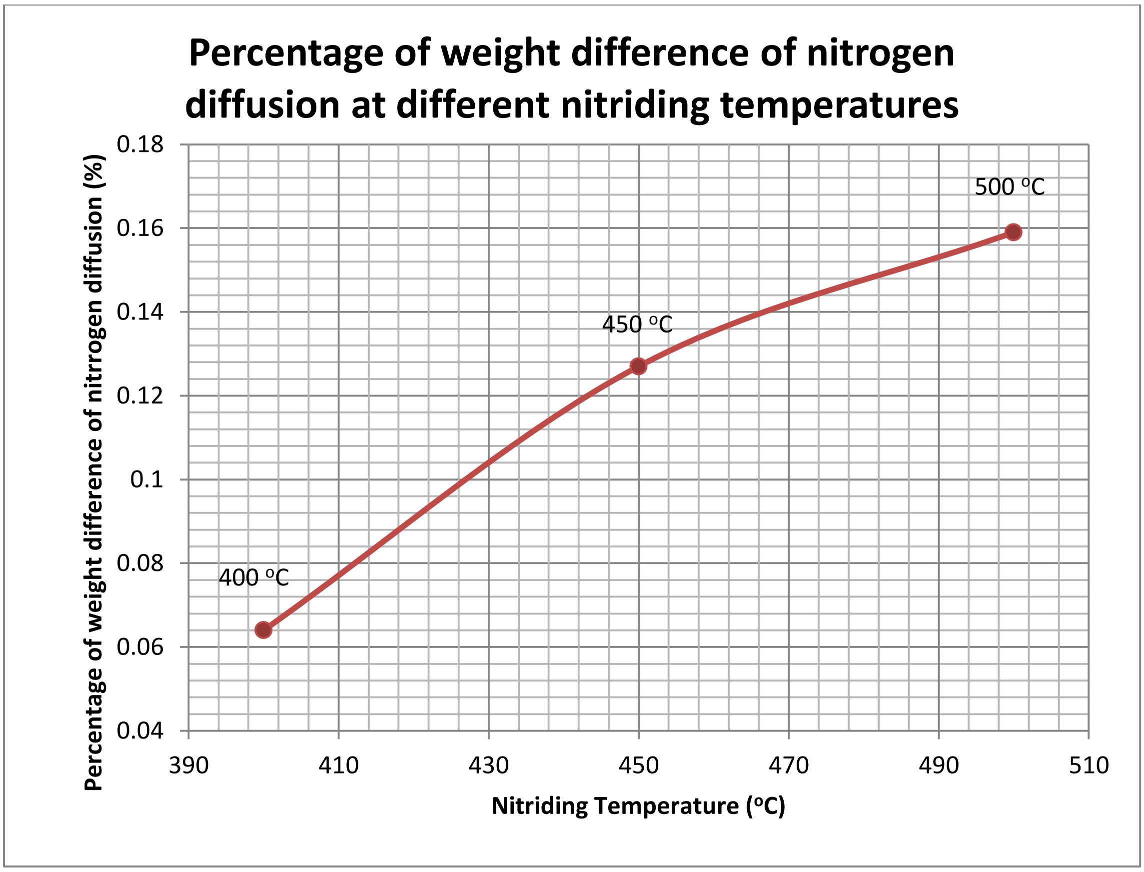


Figure 14: Percentage of weight difference of nitrogen diffusion at different nitriding temperatures

4.2 Microstructure and Morphology

4.2.1 Microstructure Images by Optical Microscope (OM)

Most metallurgical features are microscopic in size, thus they cannot be seen or analyzed without optical magnification of at least 50 X and as much as 1000 X when using light microscopes. In order to analyze planar features such as grain boundaries, a metallic sample must be polished to a very fine mirror-like finish. Then, to create contrast between the elements of the metal's microstructure, chemical solutions known as etchants are used to selectively corrode some of those elements, which show up as darker regions. This is possible because differences in the composition, structure or phase of a metal will create electrochemical potentials that alter the relative rates of corrosion when exposed to an etchant. For this investigation, etchant that have been used is Marble’s reagent.

Figure 15 shows the microstructure of as received AISI 316L austenitic stainless steel under optical microscope with magnification of 500 X. It is noticed that the bond zone of several µm widths consists of a mixture of stainless steel and low carbon steel. Each component metal is composed of small crystal grains size. Many of the grains contain annealing twins. The dark region indicates the presence of chromium in material. Furthermore, it is observed that the stainless steel had the anticipated austenitic structure with a grain size of estimated 10–20 microns. Austenitic grains, in turn, are divided into sub grains by dislocation walls with different size ranging. Theoretically, Austenitic steels have a Face Centered Cubic (F.C.C) atomic structure which provides more planes for the flow of dislocations, combined with the low level of interstitial elements (elements that lock the dislocation chain), gives this material its good ductility. This also explains why this material has no clearly defined yield point, which is why its yield stress is always expressed as a proof stress.

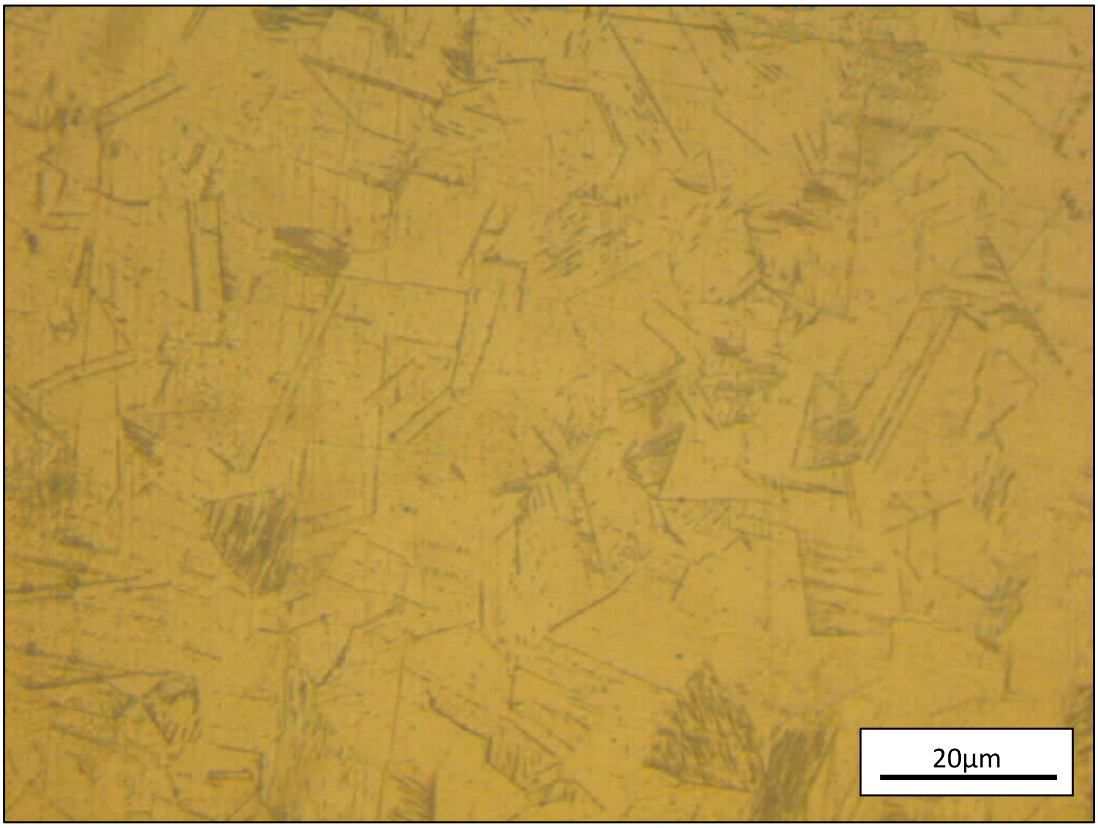


Figure 15: Microstructure of as received AISI 316L stainless steel

4.2.2 FESEM – Microstructure and nitrided layer thickness

Figures 16 to 18 show the microstructure on the cross-section of 400 °C, 450 °C and 500 °C nitrided 316L austenitic stainless steel that were measured by field emission scanning microscopy (FESEM) with magnification of 500 X to 2500 X. As seen in Figures 16, 17 and 18, three distinct regions (1) a 'bright' or 'white' layer having nitrides (2) a transition or interface layer below the nitrided layer and (3) a substrate or base material which is not affected by diffusion of nitrogen atoms can be observed from FESEM examinations. It is believed that the nitrided layer partially consists of metallic nitrides (M_xN_y) depending on steel constitution elements and their percentage.

From Figures 16 and 17, the nitrided layers were measured to be about 2µm and 8µm for the sample nitrided at 400°C and 450°C respectively. It also showed that nitrided layer formed on both samples was not uniform. This might be due to the characteristic of gas nitriding technique. Theoretically, during the ammonia purged into the furnace, the gas that in contact with tempered steel will disassociate into nitrogen and diffuse into the surface (Mridha, 2006). Besides, irregular diffusion also can be occurred due to the gas that accumulating near to the surface instead of accelerating directly onto the surface for diffusion. As seen in Figure 18, sample nitrided at 500°C formed the highest thickness of nitrided layer with 30µm and the layer formed were more uniform. The nitrided layer thickness increases from 2 µm to 30 µm as the nitriding temperature is increased indicating that the nitrogen flux into the metal core is larger due to the larger diffusion rate at elevated temperature. These results support the discussion in the Section 4.1. It is understood that the hardness on the top surface of the nitrided layer is higher than the hardness on the interface and substrate. This effect leads to enhancement of surface hardness of the nitrided samples.

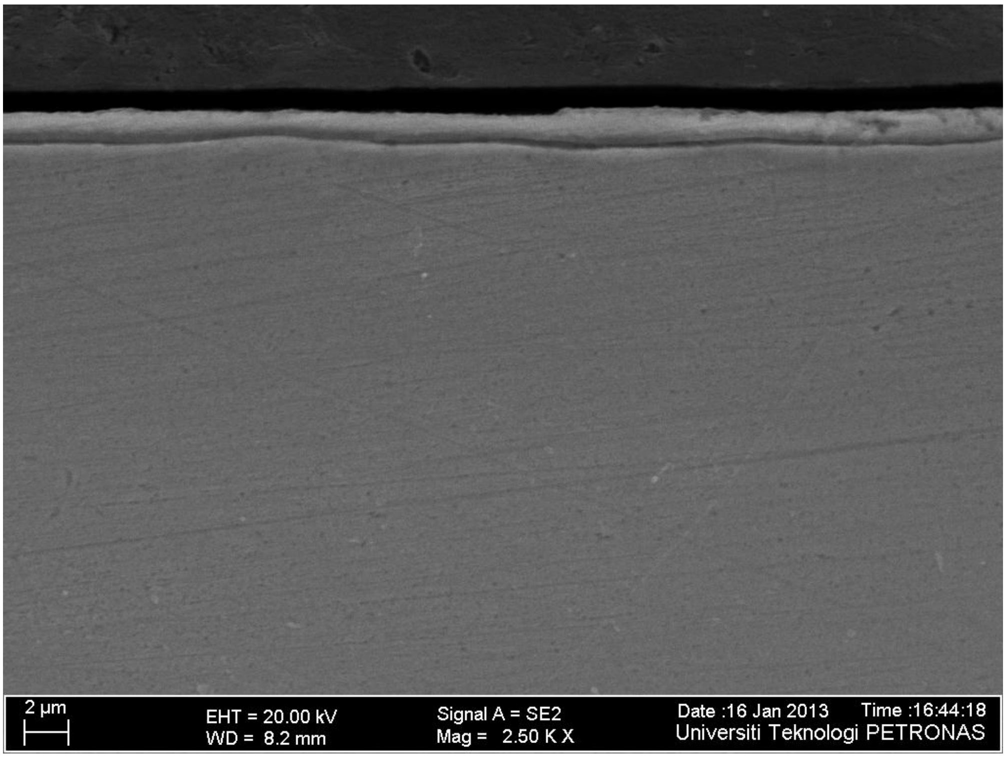


Figure 16: Nitrided layer morphology of sample at 400 °C with 2500 X magnifications

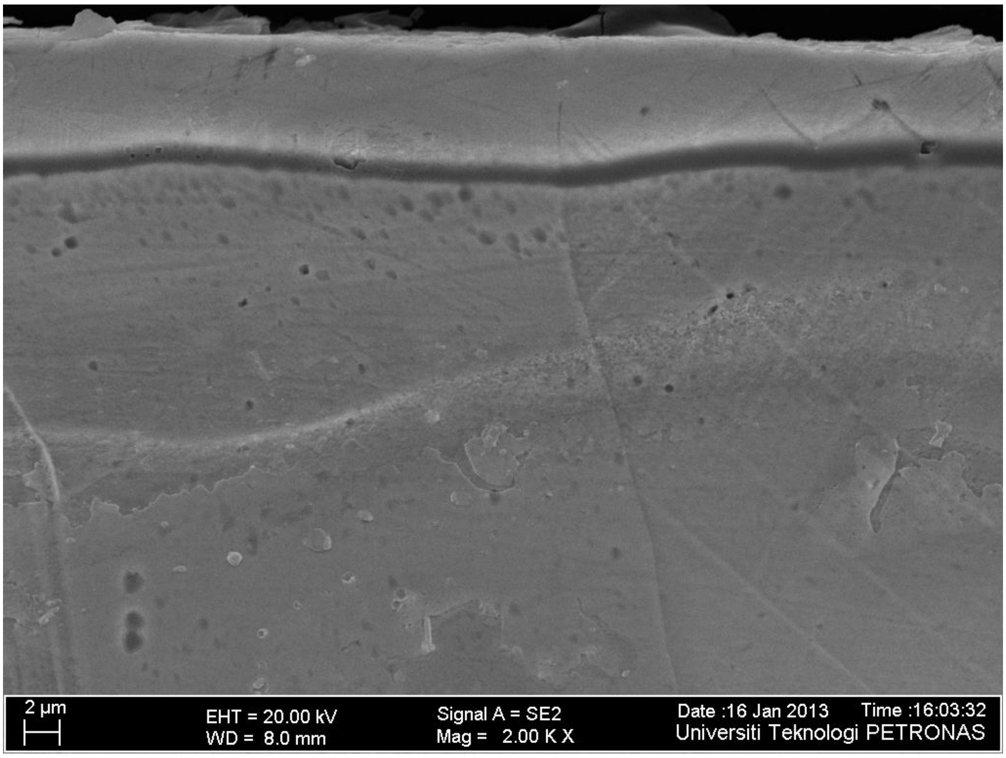


Figure 17: Nitrided layer morphology of sample at 450 °C with 2000 X magnifications

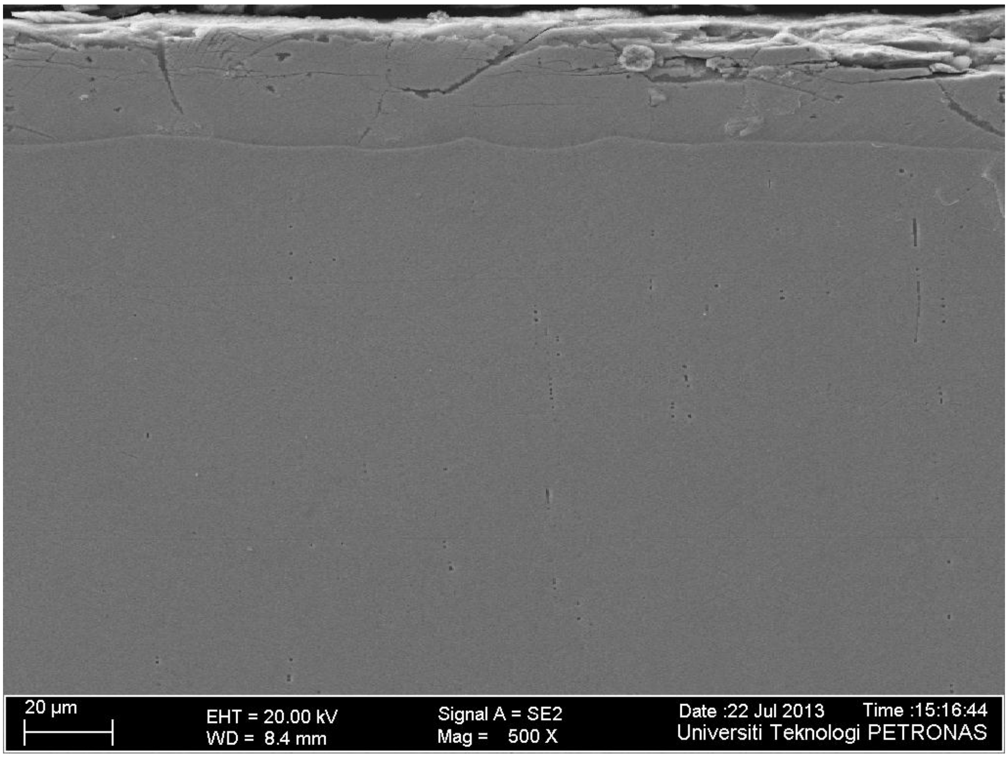


Figure 18: Nitrided layer morphology of sample at 500 °C with 500 X magnifications

4.2.3 EDX – Microanalysis of Nitrided Layer

The EDX microanalyses of the nitrided layer of the sample nitrided at 500 ^oC are shown in Figure 19 and as a result, a 3-zones structure was formed. Table 7 summarizes the results corresponding to the different elements detected by the EDX analysis and their weight percentages. Zone 1 (spectra 1 and 2), which is located at the external surface of the materials, is composed of a homogeneous thin layer. This layer could be possibly associated with the formation of oxide compounds. In the thin outer layer, the presence of oxygen atoms clearly shows the formation of oxides, associated with chromium (spectrum 1). While the sample was nitrided, some dark spots became visible in the nitrided layer. Zone 2 is characterized by the presence of these dark spots, which can be associated with the formation of iron nitrides, chromium nitrides, and/or chromium carbides. The analysis of the dark dots indicated in zone 2 (spectrum 5) revealed the presence of oxygen and chromium, as well as a significant decrease in iron and nickel. This result is possibly due to the formation of nitrides associated with chromium atoms. Zone 3 (spectrum 9), adjacent to the interface, is quite homogeneous. In this zone, nitrogen atoms are also present, confirming the existence of the typical white layer. Close to the interface (spectrum 7), the presence of nitrogen in a small amount can be observed, which confirms the diffusion of nitrogen atoms from the surface to the core of the alloy. Finally, the composition of the substrate (spectrum 8) is in a good agreement with typical microstructure that characterizes 316L austenitic stainless steel. Small deviations are expected due to the experimental measurements correspond to discrete point analysis.

Based on Figure 20, as expected, nitrogen content is gradually reducing with increasing distance from surface. There are no nitrogen content in the substrate which revealed that no diffusion of nitrogen atoms until the substrate.

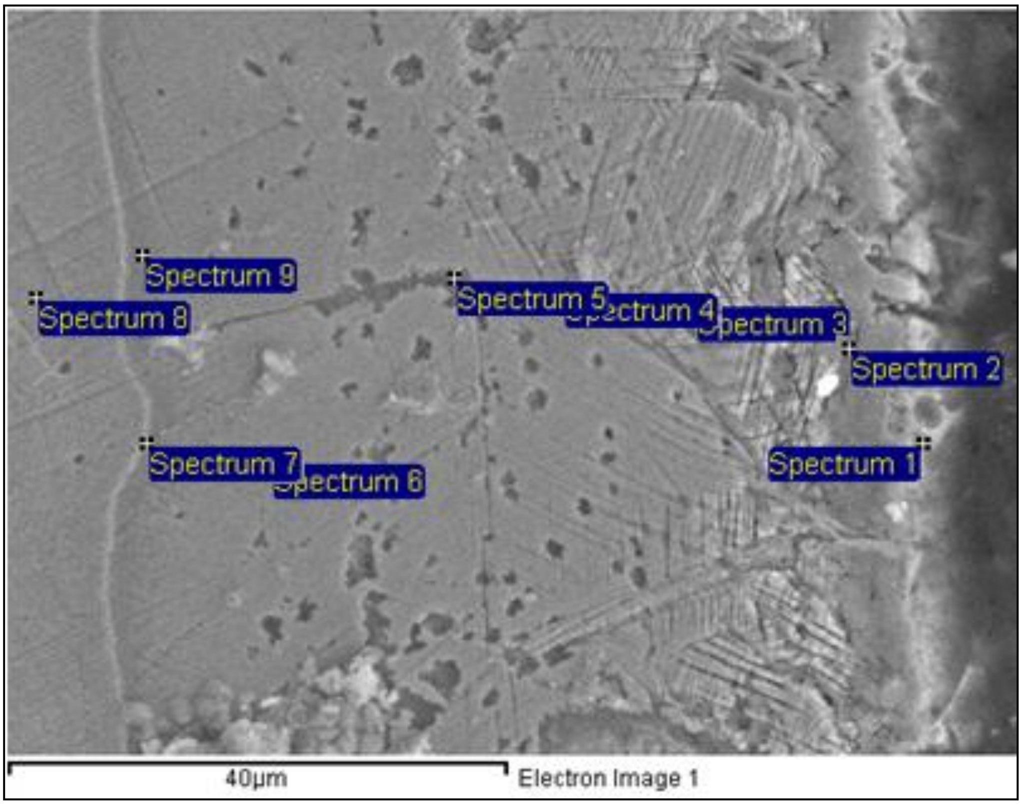


Figure 19: SEM cross-section image of the AISI 316L stainless steel nitrided at 500°C and EDX microanalysis of nitrided layers

Table 7: Different elements detected by the EDX analysis and their weight percentages

Zone	Spectrum		Weight %					
		N	O	Cr	Fe	Ni	Mo	Balance
1	1	-	18.7	33.23	29.82	3.87	-	14.38
	2	-	18.1	25.81	27.53	3.72	1.91	22.93
2	3	11.38	-	18.01	58.12	8.50	2.14	1.85
	4	9.79	-	17.81	57.74	10.46	2.29	1.91
	5	8.24	4.6	37.55	40.46	3.37	3.67	2.11
	6	5.23	-	18.57	61.27	10.07	2.48	2.38
3	9	2.47	-	18.65	64.08	10.13	2.40	2.27
Interface	7	1.03	-	18.33	66.39	10.19	2.62	1.44
Substrate	8	-	-	18.16	69.10	8.92	2.65	1.17

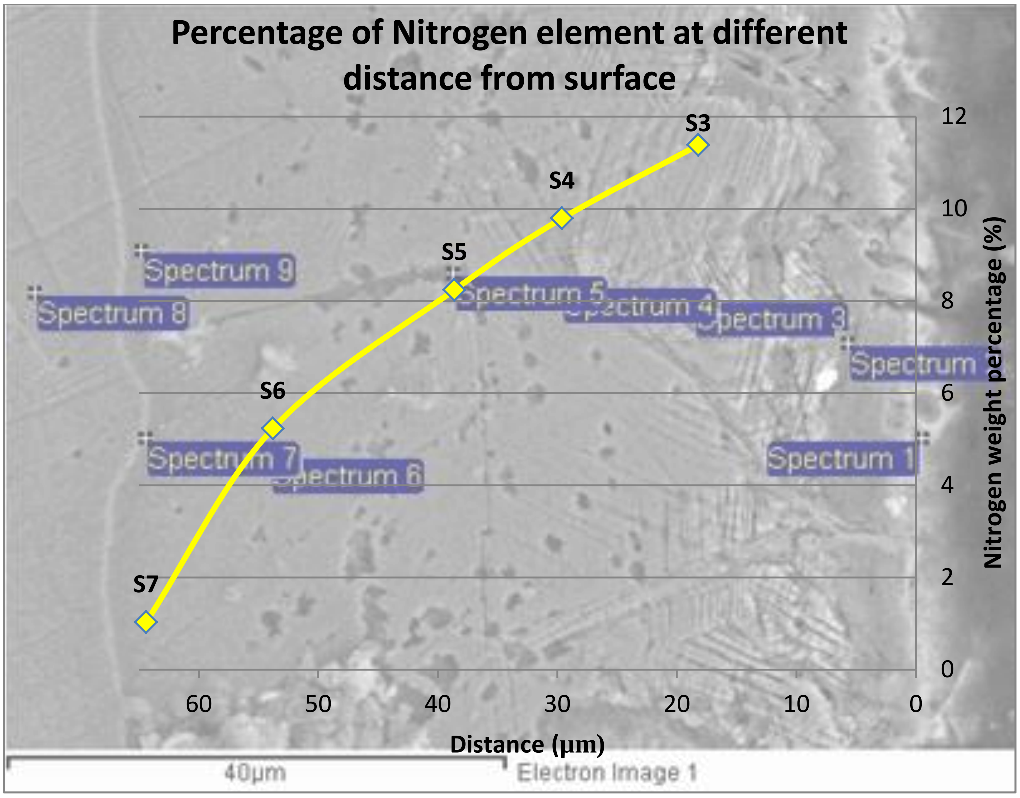


Figure 20: Percentage of Nitrogen element at different distance from surfaces

4.3 X-Ray Diffraction (XRD) Analysis

Figure 21 displays XRD patterns of the samples unnitrided and nitrided at 400 °C, 450 °C, and 500 °C for 8 hours. In the case of untreated sample the diffraction pattern showed γ and α peaks. For all the nitrided samples, XRD patterns showed that the γN(111) and γN(200) peaks from the hybrid layer were broadened and shifted to a lower angle compared with the γ(111) and γ(200) peaks from the untreated substrate. This behavior was associated with the nitrogen and carbon supersaturation in the austenite lattice. These supersaturation of nitrogen and carbon are responsible to enhancement of treated layers hardness values as confirm with Vickers and elemental analysis measurement. Besides two main γN peaks, the weak peaks of CrN were visible for the sample nitrided at 500 °C.

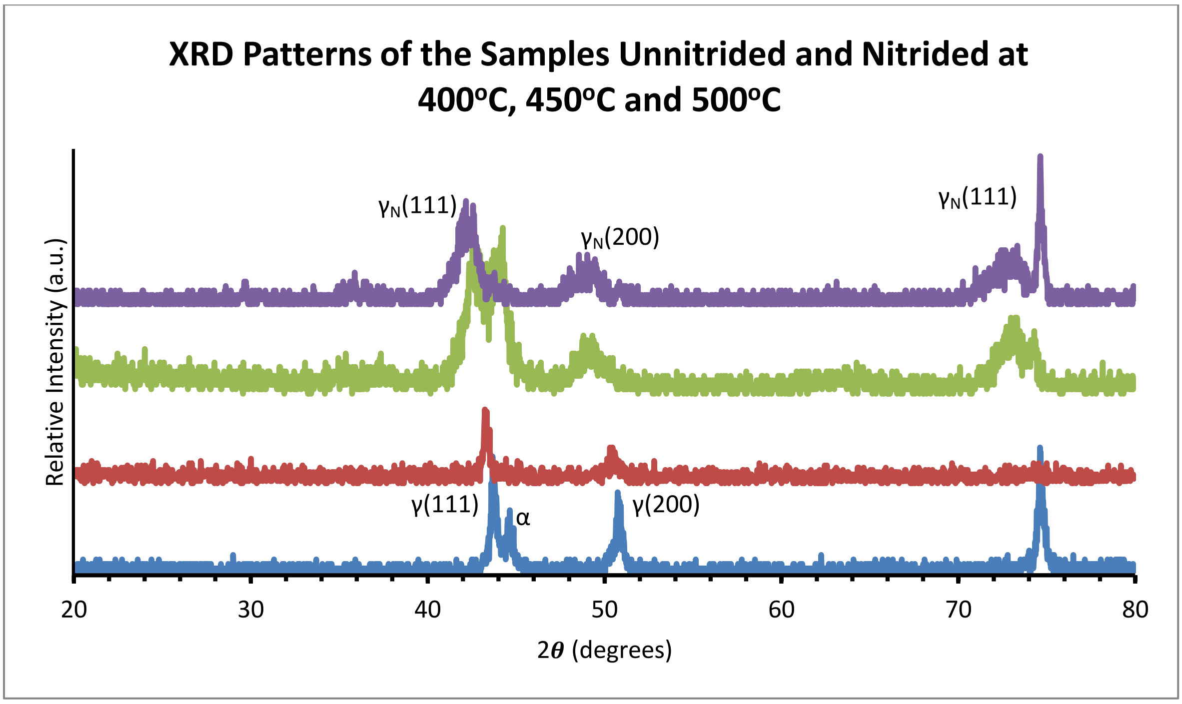


Figure 21: XRD patterns of the samples unnitrided and nitrided at 400°C, 450°C and 500°C

4.4 Microhardness Analysis

The depth profiles for thermochemically hardened stainless steel typically show a trend of increasing depth with higher temperatures and longer process variations. Microhardness test was performed to determine the characteristics of each specimen under the influence of the nitriding temperatures. Microhardness Vickers tests were conducted to the samples start from the surface and along on the cross section of the nitrided samples (400 °C, 450 °C and 500 °C). The load used was 10gf and the dwell time was 15s. Therefore, the data collected for the unnitrided and nitrided samples was tabulated in Table 8.

The surface microhardness of nitrided layers as a function of temperature is shown in Figure 22. The surface microhardness value of the sample nitrided at 400°C was 728.9 HV showing as 3.3 times as the surface microhardness of the unnitrided sample (220.0 HV). For the sample nitrided at 450°C, the surface microhardness value was 1291.3 HV, which was about 5.9 times harder than that of the unnitrided sample. The highest hardness value (1475.6 HV) for this investigation is obtained in the sample nitrided at 500°C. This high surface microhardness value can be related to the presence of hard chromium nitride/carbide precipitates in the nitrided layer (Li et al, 2011).

The microhardness profiles of the samples unnitrided and nitrided at 400 °C, 450 °C, and 500 °C are shown in Figure 23. All the nitrided samples were found to be harder that the unnitrided sample. A 6 μm hardened layer with hardness around 720 HV was achieved on the sample nitrided at 400 °C. As nitrided temperature increased, higher hardness values and thicker hardened layers were obtained. For the sample nitrided at 500 °C, the microhardness value (1500-400 HV) remained higher than the untreated sample throughout the thicker hardened layer (about 30 μm). The microhardness profile shows that the nitriding temperature influences the hardness of the nitrided samples. The effectiveness of the treatment to increase the hardness of the steel was verified. On the other hand, the hardness of the nitrided samples maintained at a high level and at a certain distance, it decreased gradually from modified layer to the metal core.

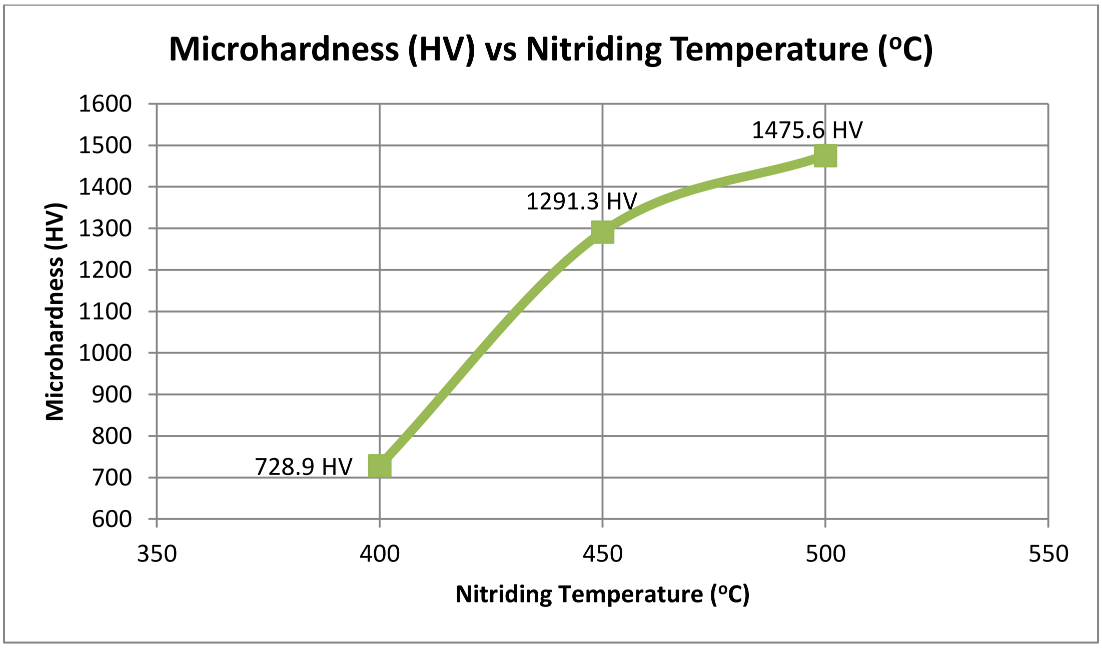


Figure 22: Microhardness data as a function of nitriding temperature

Table 8: Microhardness data of unnitrided sample and nitride samples

Distance (μm)	Vickers Hardness (HV)			
	Unnitrided	400°C	450°C	500°C
2	220.0	728.9	1291.3	1475.6
4	200.7	721.2	1225.9	1453.7
6	190.5	700.4	1255.4	1469.3
8	180.7	301.4	892.2	1458.1
10	198.1	220.02	620.2	1442.2
12	215.1	321.3	300.3	1288.1
14	198.9	220.6	290.1	1072.6
16	212.8	215.3	238.6	819.8
18	182.0	208.8	254.1	744.7
20	204.8	198.1	250.6	692.7
25	185.0	209.03	253.5	407
30	220.0	211.4	239.7	367.5
35	210.1	206.7	228.9	254.8
40	216.0	208.6	236.5	253.6
45	224.4	211.7	227.1	260.7
50	204.4	203.2	226.06	225.3

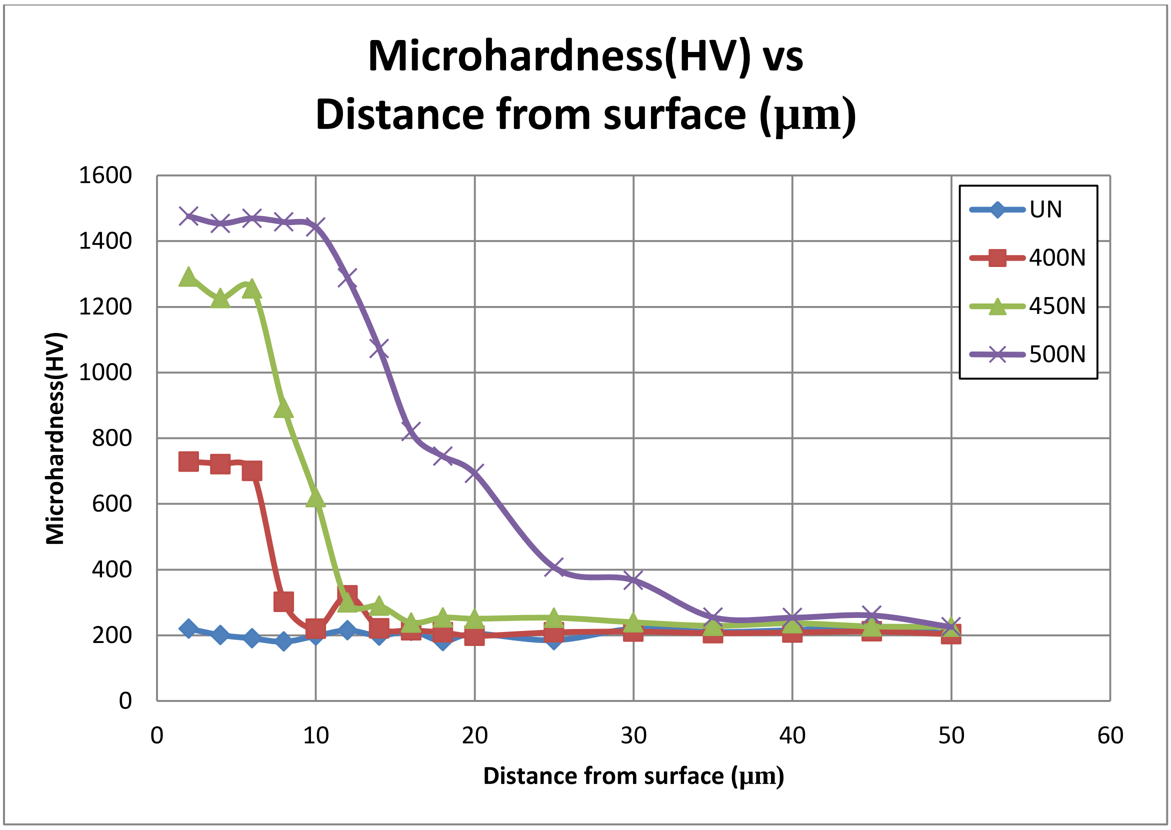


Figure 23: Microhardness profiles of unnitrided sample and samples nitrided at different temperature

4.5 Corrosion Resistance Analysis

Nitriding, carburizing and nitrocarburizing as a class of processes when performed above the nitride/carbide formation temperatures generally decreases the corrosion resistance of stainless steels. Nitriding treatment of austenitic stainless steel at elevated temperatures, typically above 450 ^{o}C, increased the surface hardness of the steel, but led to significant loss of its corrosion resistance due to the sensitization effect (Li et al, 2011; Triwiyanto et al, 2012). Thus, an experiment has been performed by the author to investigate and analyze this problem. The corrosion resistance of unnitrided 316L austenitic stainless steel and nitrided 316L austenitic stainless steels at 400^{o}C and 500^{o}C was evaluated by measuring polarization curves in 3.5% NaCl solution. The flat cell which is a three-electrode set-up consists of the specimen as the working electrode, a silver chloride (AgCl) as the reference electrode, and a platinum electrode used as the auxiliary electrode. The area exposed to the solution was 0.35 cm^2. The scanning potential was in the range of −0.8 to 1.2 V, and the scan rate was 1 mV/s.

The potentiodynamic curves of anodic polarization of samples unnitrided and nitrided at 400^{o}C and 500^{o}C in 3.5% NaCl solution are presented in Figure 24. It can be seen that the current density for the untreated 316 steel initially is low, but it rapidly increases to high values at a potential of around -0.45 V. It is well known that this sudden increase in current density is caused by the ‘‘break-through’’ of the passive film on stainless steel surface (Y. Li et al, 2011).

From Figure 24 and Table 9, nitriding at a low temperature (400 ^{o}C) has changed the polarisation properties of the 316L steel and also, shifted the corrosion potential (Ecorr) to a higher value, from -544.34 mV (for unnitrided) to -330.22 mV (for nitrided at 400^{o}C). Besides, the current density of the steel is reduced, from 0.022 mA/cm^2 (for unnitrided) to 0.009 mA/cm^2 (for nitrided at 400^{o}C), demonstrated an improvement in corrosion resistance. This result displays an enhancement in corrosion resistance by several orders of magnitude and indicates the excellent corrosion resistance of the nitrided sample at 400 ^{o}C as compared to that for the unnitrided sample. The much enhanced corrosion resistance observed for the nitrided sample at 400^{o}C may be attributed to the supersaturation of the upper part of the nitrogen-enriched layer without precipitation of chromium nitride/carbide. Thus, chromium is retained in solid solution for corrosion protection (Sun et al, 1999; Thaiwatthana et al, 2002). Moreover, the enhancement of its corrosion resistance may be related with the layer formed at 400 ^{o}C has new phase composition, containing a new type of nitrite (S-phase). This layer would contribute to the observed higher hardness and better corrosion resistance as compared to unnitrided sample (Hashemi et al, 2011).

It is generally believed that nitriding at such a high temperature of 500 ^{o}C would adversely affect the corrosion resistance of austenitic stainless steel, so that after nitriding, the steel will lose its ‘‘stainless’’ feature. From the result in Figure 24 and Table 9, the corrosion potential (Ecorr) of nitrided sample at 500^{o}C was moved to -775.01 mV, and the corrosion density (Icorr), 0.068 mA/cm^2, obviously higher than the unnitrided sample. These results indicated that the corrosion resistance of the nitrided sample at 500^{o}C is reduced as compared with the unnitrided sample. This behavior was mainly due to the formation of CrN in the compound layer. This effect leads to depletion of chromium from the adjacent matrix and consequently unable to produce Cr_2O_3 passive layer to make stainless feature. Therefore, the corrosion resistance property of the stainless steel is reduced (Y. Li et al, 2011).

Table 9: Results of the corrosion resistance test in AISI 316L stainless steel electrodes in 3.5% wt.% NaCl solution

	Unnitrided	Nitrided at 400°C	Nitrided at 500°C
E_{corr} (mV)	-544.34	-330.22	-775.01
I_{corr} (mA/cm^2)	0.022	0.009	0.068

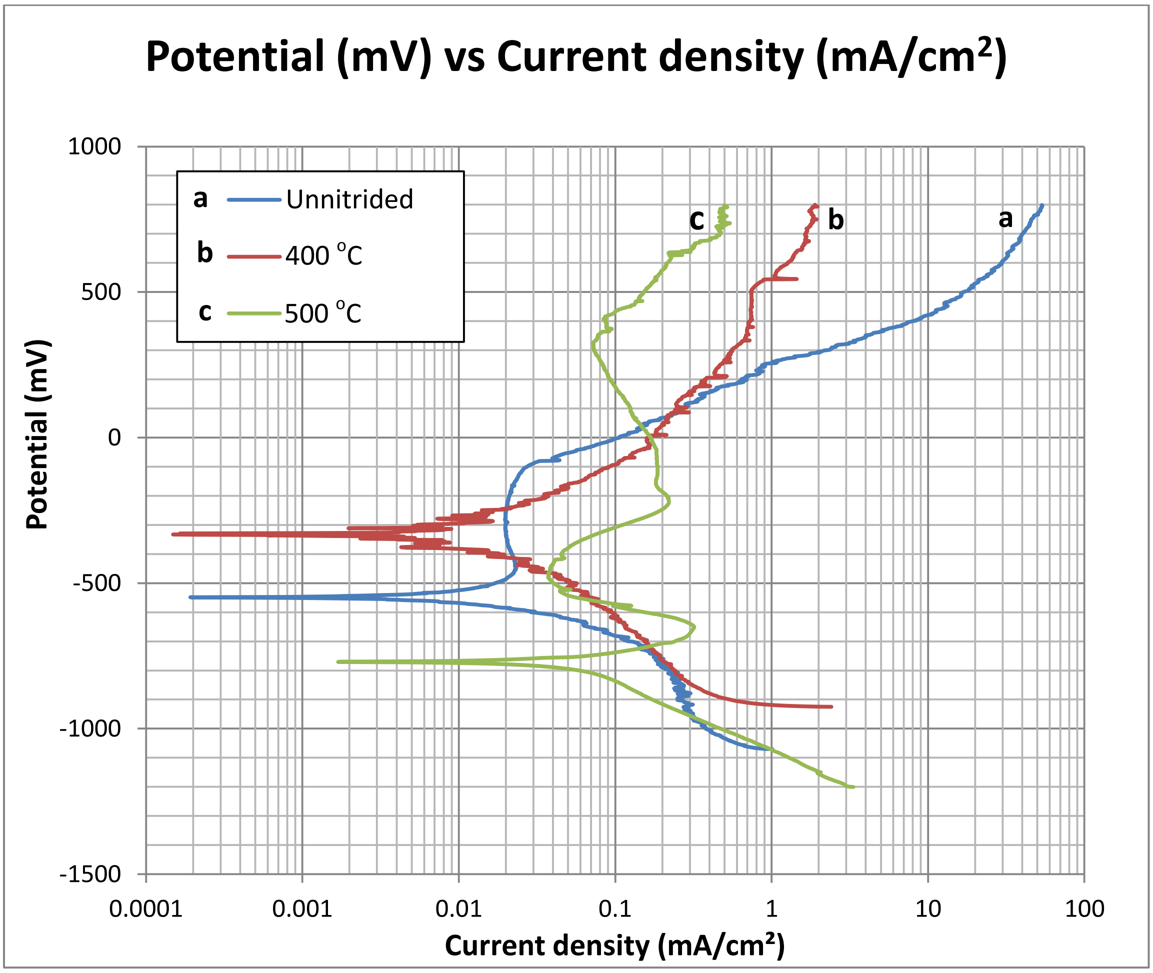


Figure 24: Polarization curves of unnitrided and nitrided samples in 3.5% water solution at different temperatures

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

As a conclusion, the objectives set up for this research has been accomplished which are basically to investigate the effect of low temperature gas nitriding treatment (LTGN) on surface hardness as well as corrosion resistance of AISI 316L austenitic stainless steel. Besides, any microstructure changes of the nitrided samples also have been observed and compared. Based on microscopic examination results, it is observed that nitriding process formed three distinct regions (1) a ‘bright’ or ‘white’ layer having nitrides (2) a transition or interface layer mostly composed of a solid solution with nitrogen and partially metallic nitrides, which has a higher hardness value than the base metal and (3) a substrate or base material which is not affected by diffusion of nitrogen atoms.

The surface microhardness values and the thickness of the nitrided layers increased as the nitriding temperature increased. For all the samples, nitrided samples showed better surface hardness compared with the unnitrided sample. Nitrided sample at 500^oC achieved maximum surface hardness (1475.6 HV), which was about 6.7 times harder than that of the unnitrided sample. These improvements are due to the formation of nitrided layer on the treated steel that successfully formed during low temperature gas nitriding treatment. Besides, the thickness layer formed for this sample was the highest with thickness of ~30 μm which could be attributed to high rate of nitrogen diffusion per unit area at high temperature treatment. It is concluded that the nitriding of 316L stainless steel increases the surface hardness of the steel as well as increases the nitrided layer thickness, and presumably shows a great resistance to wear.

Gas nitriding introduces high amount of nitrogen into the 316 austenitic stainless steel surfaces. When gas nitriding is carried out at a low temperature, e.g. 400^{o}C, the nitrided layer is a single phase of nitrogen expanded austenite (S-phase), which considerably improved the corrosion properties of the 316 austenitic stainless steel. However, when gas nitriding is carried out at a high temperature, e.g. 500^{o}C, chromium nitrides form in the nitrided case so that the bulk of the nitrided case had very poor corrosion resistance.

Last but not least, with all the results that the author obtained, it can be concluded that, the low temperature gas nitriding treatment did gave the major effects to the hardness measurement, corrosion resistance and microstructural changes of this type of austenitic stainless steel. As the temperature increased, the surface hardness values of samples were also increased. Besides, conducting gas nitriding at low temperature improved the corrosion properties of this material. Not only that, when temperature increased, the microstructure also experienced major changes from the nitriding process. Therefore, the objectives of this work have been achieved successfully.

5.2 Recommendations

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

i. Conduct tensile tests to prove and achieve the expectation of enhancing the ductility.
ii. Identify the optimum parameters such as the compaction pressure and most suitable temperature and time to improve the properties of the steel without affecting or even improving the corrosion resistance.
iii. Conduct Nano-indentation hardness test in order to obtain the value of hardness along the nitrided layer. This can give the best understanding regarding the relation of increasing of thickness layer with the increasing of surface hardness.

Finally, the surface properties and corrosion properties analysis on low temperature gas nitriding treatment have much significance in various aspects. The investigations in many areas can lead to more understanding on how the improvement can be achieved. Thus, this analysis can give great impact to the industrial applications.

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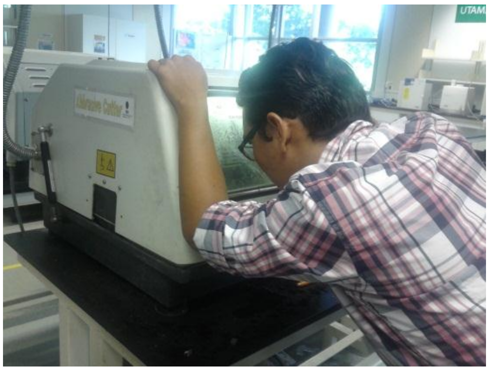
APPENDICES

A. Metallographic Sample Preparation



Sectioning and cutting by using water abrasive cutter

Apparatus needed to prepare Marble's Reagent etchant

Mounting by using hot mounting machine

Microstructure examination by using Optical Microscope (OM)

Polishing by using Grinding/polishing machine

B. Low Temperature Nitriding Treatment


Cleaning process of quartz tube


Immersion of sample in HCl (2M) for 15 minutes

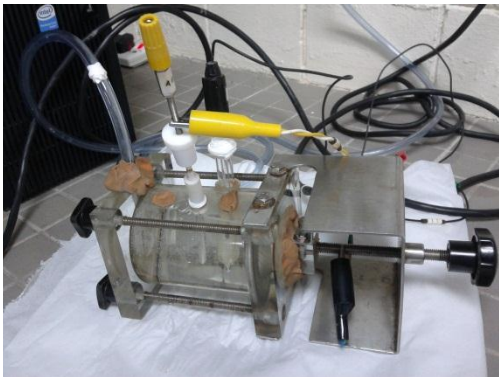

Pulling out the alumina boat after the nitriding process is done


Key in the data at the temperature controller


Fitting system at the quartz tube furnace


Gas tanks used for nitriding process

C. Corrosion Test


Flat cell

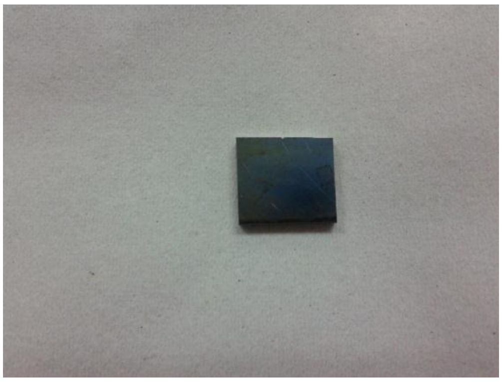


Image of Sample before the corrosion test

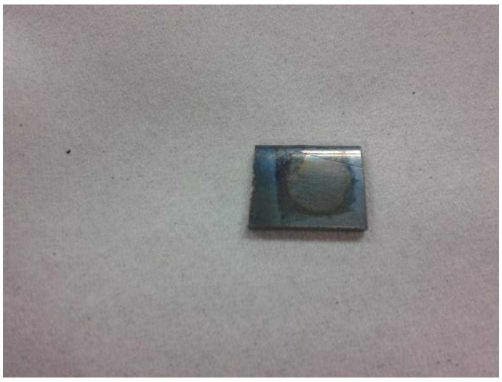


Image of sample after the corrosion test