THE EFFECTIVE DURATION OF GAS NITRIDING PROCESS OF AISI 316L

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A dissertation submitted in partial fulfilment of
the requirements for the
Bachelor of Engineering (Hons)
(Mechanical Engineering)

SEPTEMBER 2013

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CERTIFICATION OF APPROVAL

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CERTIFICATION OF ORIGINALITY

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

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ABSTRACT

The gas nitriding process has been proven as one of the most successful and economical ways to overcome the poor wear resistance and low surface hardness of the stainless steel. The main problem identified is the lack of information on the effective duration of the nitriding process on stainless steel 316L. The objective of this project is to develop an equation to relate the thickness of nitrided layer of AISI 316L to time duration of the nitriding process.

The high temperature gas nitriding process was subjected on AISI 316L austenitic stainless steel at the temperature of 1200°C with nitrogen and ammonia gas for different duration of times which are 2, 4, 8 and 24 hours. The samples are undergoing the metallography process to see the growth of the microstructure of treated AISI 316L. Based on optical microscopy, the formation of twins is observed and can divide into two patterns which is suspended twin and transgranular twin. In addition the size of grain is increasing with increasing time of heat treatment. The grain size of austenite tends to be enlarged while increasing the gas nitriding time, but the austenite single phase structure is maintained even after the long-time solution nitriding. The microhardness testing is done and shows that the hardness values drop to the centre of the samples. The surface hardness increase is due to the high nitrogen concentration at or near the surface in solid solution. At 245HV, the graph of the effective duration of nitriding process is plotted to see the maximum depth of nitrogen diffuse below the surface. The best fit lines of the experimental result are plotted and extrapolated by using SigmaPlot software to develop an equation of thickness of nitrided layer of AISI 316L to time duration of the nitriding process. Based on this equation of the effective duration of nitriding process, the duration of high temperature gas nitriding process can be estimated to produce the desired thickness of nitrided layer.

ACKNOWLEDGEMENT

First and foremost, I would like to express my greatest gratitude to Allah S.W.T for His blessings during my strenuous times and for His gift of the health and the ability for me to complete this Final Year Project. In these two semesters, I have been received generous supports from several persons who contributed in different ways to the process of completion of this project.

I would like to take this opportunity to express my profound gratitude and deep regard to my supervisor, Mr. Azman B. Zainuddin and my co-supervisor, Assoc. Prof. Dr. Patthi b Hussain for his exemplary guidance, monitoring and constant encouragement throughout the course of this project. The blessing, guidance and help given by him time to time shall carry me a long way in the journey of life on which I am about to embark.

I would like to thank the entire technical staff; Dr. Syuaib b Mohamed (nitriding), Mr. Danial (metallography), and Mr. Kamarul (hardness) for their kind assistance during the work. This project would not have been completed without receiving help from them. My deep appreciation also goes to Dr. Azmi Abdul Wahab for his co-operation and willingness to evaluate my project works. I highly appreciated their invaluable criticism and guidance.

I would like to express my sincere thanks to my loving family for their patience, encouragement and their understanding to enable me to complete this work.

Lastly, my special thanks to my colleagues and friends for their constant encouragement without which this project would not be possible.

TABLE OF CONTENTS

CERTIFICATION ……………………………………………………….ii
ABSTRACT ……………………………………………………………….iv
ACKNOWLEDGEMENT....………………………………………………v

CHAPTER 1: INTRODUCTION

1.1 Background of Study……………………………………………….1
1.2 Problem Statement………………………………………………….2
1.3 Objectives of Project………………………………………………..2
1.4 Scope of Study……………………………………………………...2
1.5 Significant of the Project…………………………………………....3

CHAPTER 2: LITERATURE REVIEW

2.1 Austenitic Stainless Steel 316………………………………………4
2.2 Gas Nitriding………………………………………………………..5
2.3 Depth of Nitrogen Diffusion………………………………………..8

CHAPTER 3: METHODOLOGY

3.1 Project Flow Chart........……………………………………………10
3.2 Tools and Equipment....……………………………………………11
3.3 Materials.……………………………………………………………13
3.4 Samples Preparation...14
3.5 Gas Nitriding Process……………………………………………15
3.6 Metallography……………………………………………………16
3.7 Hardness Test.………….....……………………………………18
3.8 Key Milestone and Gantt chart……………………………………...19

CHAPTER 4: RESULT AND DISCUSSION

4.1 Metallography Analysis……………………………………………….……21
4.2 Microhardness of AISI 316L………………………………………….24
4.3 Curve Fitting……………………………………………………………..26
4.4 Effective Duration of Gas Nitriding…………………………………..29

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion…………………………………………………………….31
5.2 Recommendation……………………………………………….……..31

REFERENCES……………………………………………………….………….32
APPENDICES………………………………………………………………...34

LIST OF FIGURE

Figure 2.1: Stainless steel 300 Series……………………………………………4
Figure 2.2: The formation of nitride layer………………………………………….6
Figure 2.3: The sub-layer of nitride on surface of material……………………...7
Figure 2.4: (a) N-concenttration vs. Depth (b) Microhardness vs. Depth………….9
Figure 3.1: The flow chart of the project…………………………………………..10
Figure 3.2: Sample size……………………………………………………………14
Figure 3.3: The setting for gas nitriding experiment...……………………………15
Figure 3.4: Optical Microscope…………………………………………………...17
Figure 3.5: Micro Hardness Testing Machine……………………………………..18
Figure 4.1: The microstructure of as-received sample…………………………….21
Figure 4.2: Microstructures of nitrided AISI 316L at (a) 2 hours (b) 4 hours...…..22
Figure 4.3: Microstructures of nitrided AISI 316L at (c) 8 hours (c) 24 hours…...22
Figure 4.4: The graph of Hardness Vs. Depth……………………………………24
Figure 4.5: Depth Vs. Nitriding Time……………………………………………..26
Figure 4.6: Graph of effective duration of nitriding………………………………29
Figure A1: Hardness value of As-received sample of AISI 316L………………...35
Figure A2: Hardness value of AISI 316L nitrided at 1200°C for 2 hours………...36
Figure A3: Hardness value of AISI 316L nitrided at 1200°C for 4 hours………...36
Figure A4: Hardness value of AISI 316L nitrided at 1200°C for 8 hours………...37
Figure A5: Hardness value of AISI 316L nitrided at 1200°C for 24 hours……….37

LIST OF TABLE

Table 3.1: Equipment and their function………………………………………….11
Table 3.2: Physical properties of AISI 316L……………………...………13
Table 3.3: Key milestone………………………………………………………….19
Table 3.4: The Gantt chart and key milestone…………………………………….20
Table 4.1: Experimental result at hardness value 245HV……………………...…26
Table 4.2: Result of Curve fitting using SigmaPlot…………………….………27
Table 4.3: Value of effective duration of nitriding………………………………..30
Table A1: Experimental data of hardness value…………………………………..34

CHAPTER 1

INTRODUCTION

1.1 Background of Study

The iron-chromium-nickel alloys known as stainless steels are widely used in applications requiring corrosion resistance and good elevated temperature strength. Stainless steel is considered to be more of a specialist material, and only used where essential. This is because it can be difficult to machine compared with carbon steels and aluminium, and more costly to purchase. On the other hand, for some applications, such as those in the food, pharmaceutical and chemical industries, the use of stainless steel is all but essential because of its corrosion resistance. Stainless steels are often classified in terms of their crystal structure and are commonly divided into 3 groups which are austenitic, ferritic and martensitic. In this study, the AISI 316L austenitic stainless steel is used. AISI 316L is the standard molybdenum-bearing grade with low carbon contains, second in importance to 304 amongst the austenitic stainless steels. The molybdenum gives AISI 316L better overall corrosion resistant properties than Grade 304, particularly higher resistance to pitting and crevice corrosion in chloride environments. The disadvantages of the AISI 316L are having a poor wear resistance and low surface hardness. The gas nitriding process will be subjected to the AISI 316L to overcome this problem.

Gas nitriding process is a case-hardening process whereby nitrogen is introduced into the surface of stainless steel by holding the metal at a suitable temperature in contact with nitrogen gas. The diffusion of nitrogen into surface layers of steel promotes the formation of hard nitrides, which in turn could improve the wear resistance and the surface hardness of the material. So the depth of the nitrogen diffuse below the surface of the material will be analyzed by conducting the hardness test to get the effective duration of nitriding process of the AISI 316L austenitic stainless steel.

1.2 Problem Statement

The gas nitriding process has been proven as one of the most successful and economical ways to overcome the poor wear resistance and low surface hardness of the stainless steel when compared with carbon steels. The main problem identified is the lack of information on the effective duration of nitriding process on stainless steel 316L. Most of the previous studies only focus on the effects on surface hardness at the certain duration of the nitriding process, effect on strength of coating thickness, corrosion resistance but did not state about the effective duration of nitriding process on the SS316L. In this paper, the author attempt to study the relationship between the gas nitriding process on austenitic stainless steel 316L and the degree of improvement of hardness when subjected to 50% nitrogen gas and 50% ammonia gas at the temperature 1200°C.

1.3 Objectives of Project

The three main objectives of this project are:

- To investigate the effects on the microstructure of austenitic stainless steel AISI316L when subjected to nitriding at high temperatures
- To determine the hardness increase below the surface of AISI 316L when nitrided at 1200°C
- To develop an equation to relate the thickness of nitrided layer of ASS 316L to the time duration of the gas nitriding process.

1.4 Scope of Study

This project is on high temperature gas nitriding only with operating temperature of 1200℃ with gas composition of 50% of ammonia gas and 50% of nitrogen gas. The material study is austenitic stainless steel 316L.

1.5 Significance of Project

This project is very beneficial and important when the effective duration of gas nitriding process of stainless steel 316L at 1200°C is determine because it will help and guide others to produce desire depth of nitrided layer below surface. Besides that, the outcome of this project is to create an equation of the effective duration of nitriding process for SS316L at 1200°C when subjected to the 50% of nitrogen gas and 50% of ammonia gas. The outcomes of this project will save the energy used and save time consumed by referring to the equation of effective duration of nitriding process. So this project will provide important information and knowledge to the others and especially to the industries.

CHAPTER 2
LITERATURE REVIEW

2.1 Austenitic Stainless Steel 316L

Austenitic grades are those alloys which are commonly in use for stainless applications. The most common austenitic alloys are iron-chromium-nickel steels or known as stainless steel. The austenitic grades are not magnetic and known widely as 300 series. Stainless steel in this series have minimum of 12% chromium that would impart corrosion and oxidation resistance to steel [1]. Based on their crystalline structure, stainless steels are classified into three basic groups such as austenitic, ferritic and martensitic [2]. The austenitic is a face-centered cubic (fcc) structure which is very tough and ductile down to absolute zero temperature besides do not lose its strength at elevated temperature as rapidly as ferritic (bcc, body-centered cubic) iron base alloys [3].

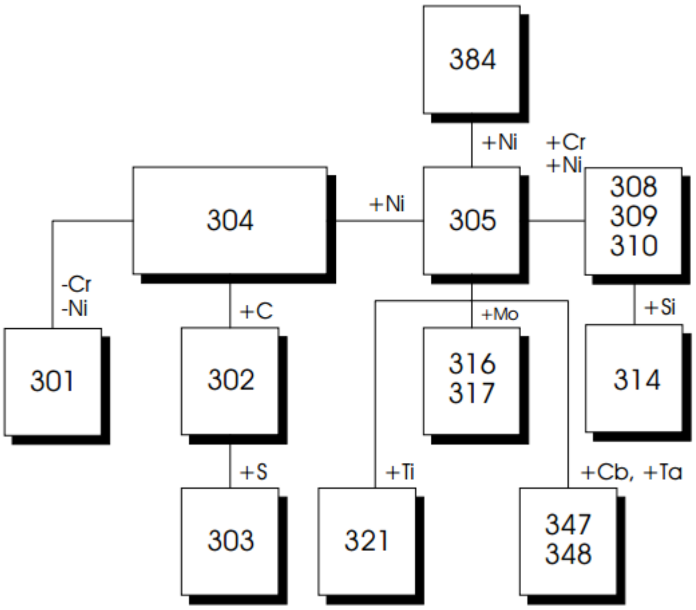

Figure 2.1: Stainless Steel 300 Series

Stainless steels with their excellent corrosion properties have a very broad application range. This extends to chemical plants, dairy and food processing industries, nuclear power plants, heat exchangers, laboratory benches and equipment. The reason for the good corrosion resistance of stainless steels in oxidizing environments is the thin passive oxide film. Stainless steel 316 contains 16% to 18% chromium, 11-14% nickel and 2-3% molybdenum added to the nickel and chrome of the 304 stainless steel. As chromium is added to steel, a rapid reduction in corrosion rate is observed to around 10% because of this protective film or passive layer [2]. The salient feature of austenitic alloys is that as chromium and molybdenum, nickel or other austenite stabilizers must be added if the austenitic structure is to be preserved [3].

2.2 Gas Nitriding

Stainless steels have a good combination of strength and corrosion resistance, low hardness and poor tribological properties of these materials can shorten the life of components subject to wear. There exist several established processes such as gas nitriding, carburizing and carbonitriding or cyaniding, form a surface coating which improves the characteristic of stainless steel components [2]. These processes operate at elevated temperatures necessary to obtain treatment depths of several tens of micrometres in a reasonable time.

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 in contact with nitrogenous gas usually ammonia [4]. Gas nitriding is a class of low temperature thermo chemical treatment which is the temperatures between 400°C and 590°C. During nitriding process, the nitrogen supplied diffuses into the work piece surface to a depth depends on time and temperature. There are two types of nitriding phase which are ferritic phase nitriding and Austenitic phase nitriding. As the name indicates, is done in the ferritic phase at around 500 – 650°C while for austenitic phase is done at temperature around 800-1000°C [2]. The figure 2 below has shown how the formation of the nitride layer occurred on the surface of the material.

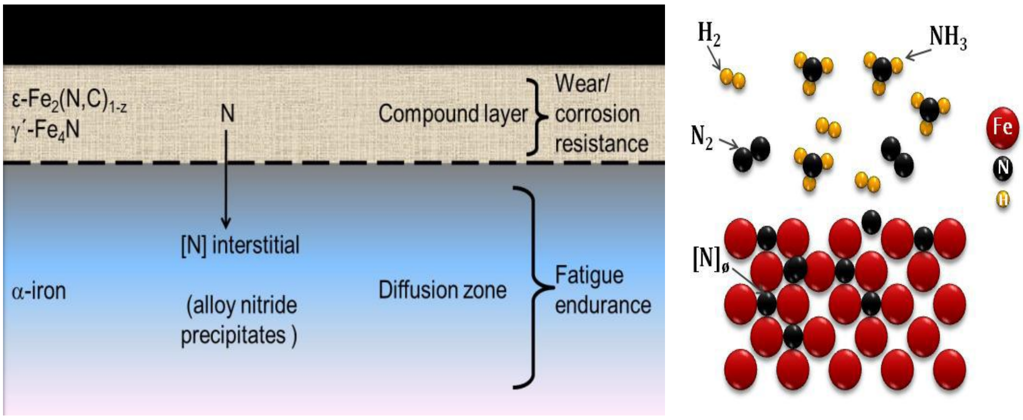

Figure 2.2: The formation of nitride layer

Gas nitriding is accomplished with the ammonia gas that dissociates on the surfaces of the steel during heating, according to the following reaction:

$NH3 \rightarrow 3H + N$ [Eq.1]

$2N \rightarrow N2$ [Eq.2]

$2H \rightarrow H2$ [Eq.3]

The atomic nitrogen and hydrogen components shown in Eq 1 are unstable and unite with other like atoms to form molecules as shown in Eq 2 and Eq 3. It is while they are in the atomic state that diffusion takes place. Nitriding atmosphere are in non-equilibrium while at the process temperature, which means that at the steel surface a high degree of nitrogen activity takes place from the ammonia [4].

The solubility limit of nitrogen in iron is temperature dependent, and at 450 °C the iron-base alloy will absorb up to 5.7 to 6.1% of N. A number of operating process parameters which are furnace temperature, pressure, gas flow and time must be adhered to and controlled in order to successfully carry out the nitriding process [5]. The study shows however that the gas nitriding of austenitic stainless steels at conventional nitriding temperatures (500–650 °C) resulted in the formation of chromium-nitrides leading to a deterioration of its corrosion property, although it significantly improved the wear properties of steels [6]

The nitride-layer consisting of the four sub-layers, the first layer is pores and micro-cracks were often observed. The second sub-layer was not so distinctively recognizable at this temperature. The third sub-layer showed a short lamellar structure intermixed with round particles and the fourth sub-layer displayed a typical coarse lamellar structure [6].

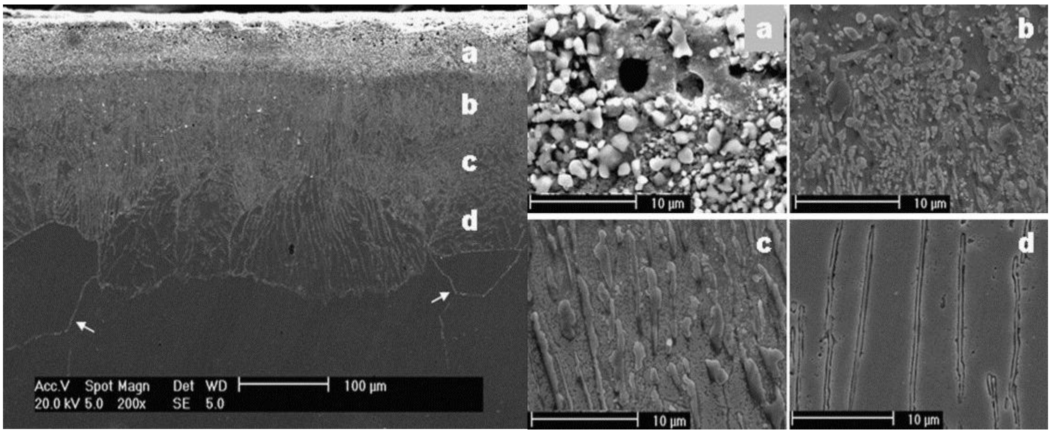

Figure 2.3: The sub-layer of nitride on surface of material

The Figure 3 above is shown all the four sub-layer in the nitrided coat. Nitriding processes conducted at temperatures above approximately 490 °C take effect on creation of the layers of this type of structures are satisfactory tough (900–1300 HV), however their corrosion resistance seems to be worse than the base material corrosion resistance. The layers obtained at lower temperatures than 490 °C takes an effect of smaller layer thickness, however excellent hardness (1700 HV) and predicted good corrosion resistance qualify this temperature range as more perspective [7].

The hardness increased with the increase of nitriding time is due to the increase of nitrided layer thickness and high nitrogen content in the layer. The micro hardness increased with time, while for nitriding times in excess of 7 h at 420 -C the value of hardness did not change much [8]. However, some defects and chromium nitride precipitation appeared in the nitrided layer after longer nitriding time. Maximum value of hardness was established at the surface and then it gradually decreased to core value. However it still has a small increment of hardness up to 800 µm in depth [9]. This observation evidences that some nitrogen atoms were able to interstitially diffuse to that depth.

Nitriding has a number of advantages compared to the other surface coating process which is produces the hardest cases. No heat treatment is required after hardening and corrosion resistance of nitrided parts is better than that of carburized parts. Besides the nitrided part have good elevated-temperature resistance, reheating parts to 540 to 595°C for short periods does not affect their hardness, while long-term exposures to 315 to 425°C will affect carburized but not nitrided parts [10].

2.3 Depth of nitrogen diffusion.

Nitriding is a well-known process to improve the mechanical properties of a steel surface. The introduction of nitrogen in the steel improves the hardness, wear resistance, and fatigue strength of the surface of steel. In industrial practice, a model that predicts the nitriding depth from nitriding conditions and steel composition would be useful, because with such a model optimum nitriding conditions for a given steel type could be calculated instead of inferred from a trial and error approach [11].

The effects of nitriding process on hardness and nitrogen diffusion was done at different nitriding temperature and treatment times on En40B steels. The observation shows that the maximum surface hardness increases from 875 VHN in 10% NH3 to around 1025 VHN in 80% NH3 [12]. It means the hardness of the samples is influences by the nitrogen gas supplied at the surrounding during nitriding process.

Besides that, at 570 °C the hardness build up was insignificant with very shallow profiles in 10% NH3; the increase of ammonia content increased the maximum surface hardness and it is about 850 VHN in 80% NH3. The build-up of hardness up to a certain depth is established rapidly and remains constant with time. In addition, the maximum surface hardness remains constant for any length of treatment time at this temperature and the hardness profiles remain constant under all conditions. [12]

A series of plasma nitriding experiments has been conducted on AISI 304L austenitic stainless steel at temperatures ranging from 375 to 475°C using pulsed-DC plasma with different pulse duty cycles, N2–H2 gas mixtures and treatment times shows that the nitrogen concentration of the layers is between 23 and 17 at.%, with a slight decrease inside the layer. We observed a sudden drop of nitrogen at the interface, which correlated well with the hardness profiles [Fig. 6(b)]. The sudden drop of the nitrogen content is additional evidence for the occurrence of a new phase. A simple expansion of c-austenite due to randomly dissolved nitrogen would be expected to lead to a gradual decrease of the nitrogen concentration across the interface. The decrease of nitrogen observed inside the layer may be due to a gradient of interstitially dissolved nitrogen within the modified layer. [13]

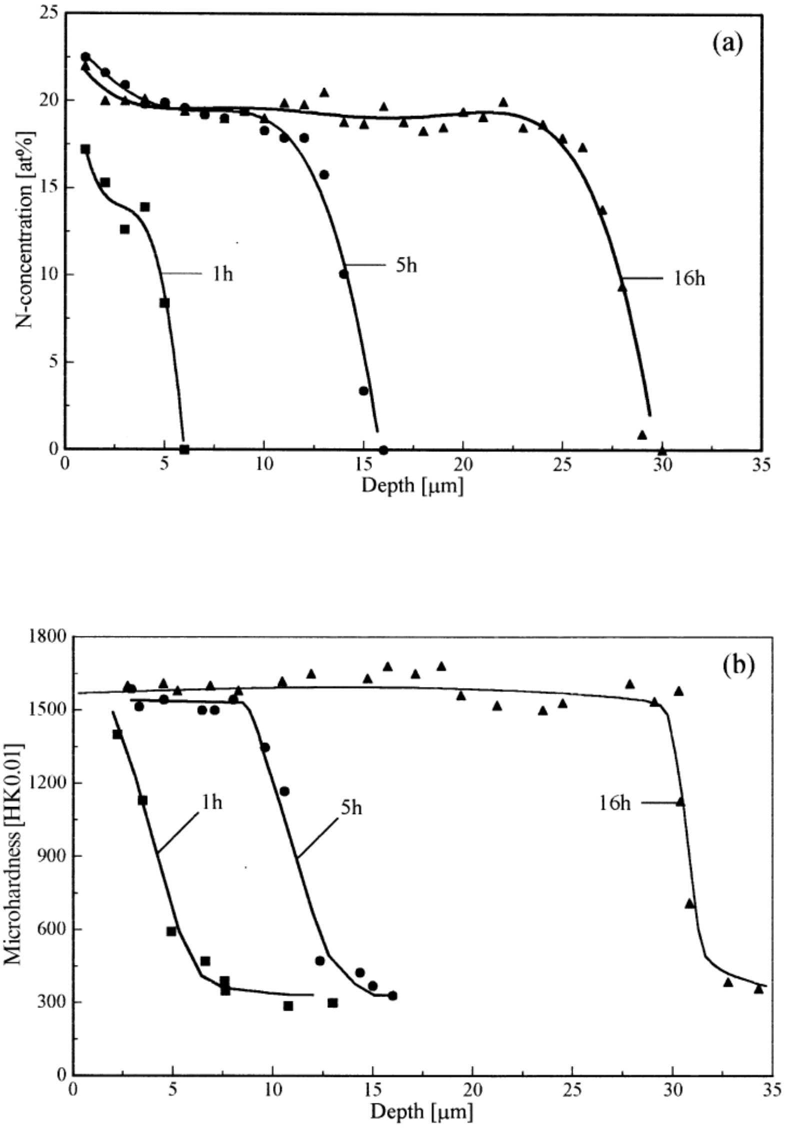

Figure2.4: (a) N-concentration vs Depth (b) Microhardness vs Depth

Besides that, a lower partial pressure of nitrogen leads to a lower nitrogen concentration inside the layer, and hence the layer thickness is reduced. Lower nitrogen content leads also to a lower layer [13].

CHAPTER 3
METHODOLOGY

3.1 Project Flow Chart

The overall planning for this project is as shown in figure 3.1 below.

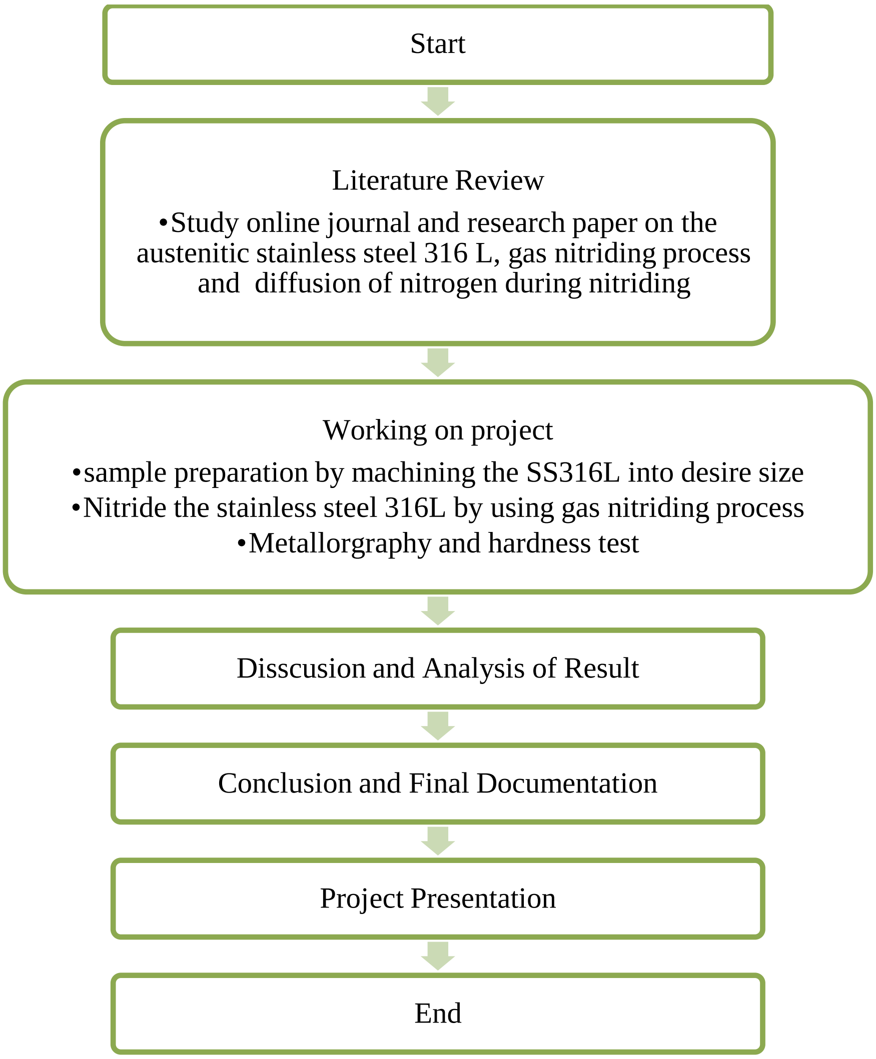

Figure 3.1: The flow chart of the project

3.2 Tools and Equipment

These are tools and equipment required to carry out the experiments. All the equipment is available in Block 17, UTP. Table 3.1 shows the summary of equipment and their functions.

Table 3.1: Equipment and their functions

Equipment	Function
Buehler Delta Non-Ferrous Abrasive Cutter 	Sectioning or cutting machine to produce desire dimension. Sectioning should be flat and cut close to the area of interest by minimize microstructural damage.
Nitriding Machine 	The high temperature furnace to hold the samples at specific temperature with nitrogen and ammonia gas flow into the furnace.
Simplimet 1000 Automatic Mounting Press 	Mount the samples by using phenolic powder to protect the samples and make it easy to handle.
Metaserv 2000 Grinder and Polisher 	Remove the damage produced area during cutting process by grinding and polishing.

Leica Optical Microscope 	Use to magnify and resolve the image of the microstructure. Able to magnify the image up to 500X.
LECO LM247AT Vickers's Hardness Testing Machine 	To hardness testing machine is used to record the hardness value of the sample. The load use is 50g.
METTLER TOLEDO Electronic Balance 	Electric balance is used to weight the Cupric Chloride before mixed with concentrated Hydrochloric acid.
Measuring Cylinder, Beaker, Petri dish 	The equipment for the etching process. The measuring cylinder is used to measure the solution needed and mixed in the beaker. The etchant used is Marble's solution.

3.3 Materials

The austenitic stainless steel AISI 316L was obtained from TSA Industries Sdn. Bhd, Ipoh, Perak. The materials received in form of the square bar with dimension of 12.9mm X 12.9mm.

The composition of this material is 0.02%C, 0.42%Si, 1.7%Mn, 0.03%P, 0.002%S, 17.19%Cr, 2.06%Mo, 11.54%Ni, 0.31%Co and balance Fe. The physical properties of the AISI316L are shown in the table below.

Table 3.2: Physical properties of AISI 316L

Properties	**Value**	**Unit**
Density	8.027	g/cm3
Melting point	1390-1440	°C
Modulus of Elasticity	200	GPa
Modulus of Shear	82	GPa

3.4 Sample Preparation

The square bar of AISI 316L was cut by using abrasive cutter to the desire dimension which is 12.9 mm X 12.9 mm X 6.0 mm as shown in the figure below.

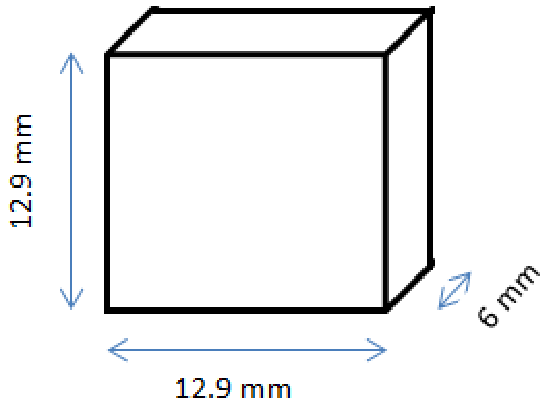

Figure 3.2: Sample size

Prior to nitriding process, the samples were ground and polished, so that after nitriding only polishing was required to produce a good surface finish without removing too much nitrided layer.

There are three experiments will be conducting for completing this project which are gas nitriding process, metallography and hardness test.

3.5 Gas Nitriding

The procedure of high temperature of gas nitriding process is shown as below.

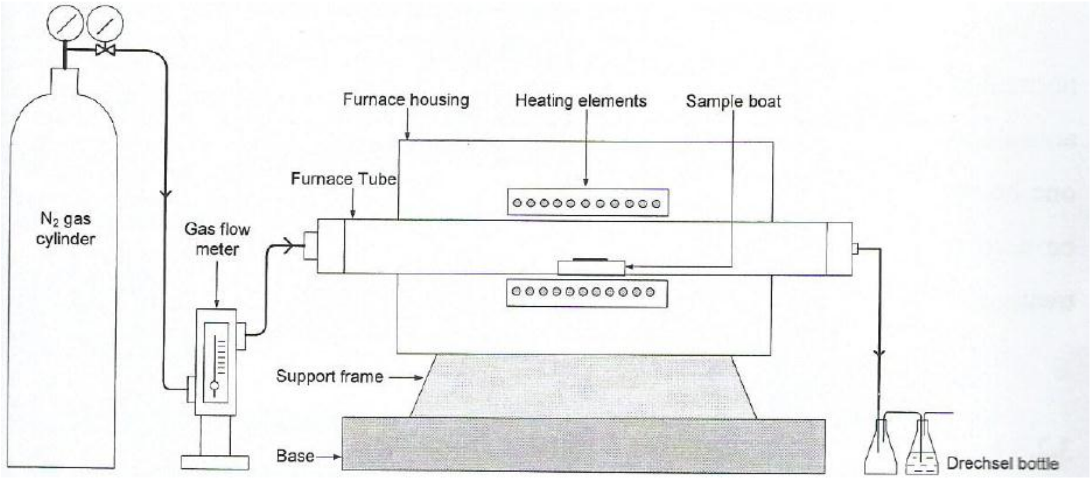

Figure 3.3: The setting for gas nitriding experiment

1. The gas flow rate meter is attached to the tube furnace to adjust the flow rate of the nitrogen gas
2. Gas outlet tube is connected to drechsel bottle
3. 5 mm of the outlet tube length was inserted into the bottle to increase the pressure in furnace
4. Samples were washed with acetone before the experiment started.
5. Samples were placed in alumina boat and inserted into heating zone
6. Before heating, air in the furnace was purged with the nitrogen gas for 15 minutes at a flow rate of 200 cm3/min to prevent oxidation of the samples. Nitriding was carried out at temperature 1200°C in gas mixture of 500cm3/min of N2 and 500cm3/min of NH3.
7. Heating at 5°C/min was started immediately after purging completed until temperature reached 1200°C for 2 hours
8. At the end of the process, nitrogen flow was stopped and the samples were removed from the furnace and quench into the water
9. The steps 4 until 8 are repeated for the duration of 4, 8 and 24 hours.

3.6 Metallography

Metallography is the study of a materials microstructure by preparing, interpreting, and analyzing microstructures to understand material behavior. The basic steps for proper metallographic specimen preparation include sectioning and cutting, mounting, grinding, polishing, etching and microscopic analysis [15].

Mounting

The nitrided samples are prepared for the mounting process by using the phenolic powder as a mounting compound. The molding process was set up for 3 minutes during molding with pressure of 4000 psi and 2 minutes for cooling process. The mounting operation accomplishes three important functions which is to protects the specimen edge and maintains the integrity of a materials surface features, fills voids in porous materials and improves handling of irregular shaped samples, especially for automated specimen preparation.

Grinding

After molding process is finished, the samples were proceeding to the next process which is grinding process. This grinding process is to clean the surface of the molded sample, produce the flat surface and reduce the damage created by sectioning. The grinding step is accomplished by decreasing the abrasive grit/ particle size sequentially to obtain surface finishes that are ready for polishing. Care must be taken to avoid being too abrasive in this step, and can create greater damage. The abrasive paper used in this process is 800, 1200, 1500 and 2400 grit to produce fine surface.

Polishing

The purpose of the polishing step is to remove the damage produced during cutting and grinding. Proper rough polishing will maintain specimen flatness. The polishing process is accomplished with 1 micron diamond abrasive and polycrystalline diamond.

Etching

The purpose of etching is to optically enhance microstructural features such as grain size and phase features. Etching selectively alters these microstructural features based on composition, stress, or crystal structure. The etchant used for the etching process is Marble's Reagent and applied it on the sample surface for 30 seconds

Optical Microscopy

The optical microscopy is a process to examine the microstructure after the etching process. The procedure of using optical microscope is shown as below.

Figure 3.4: Optical Microscope

Optical microscope with DinoCapture software is used to examine the microstructure. Metallography microscope is conducted based on the following procedure:

i. Take the sample previously prepared to the optical microscope.
ii. Start focusing with the objective lens with the smallest magnification, and using the coarse focus controller until an image appear in the eye pieces.
iii. Focus it. Change to the fine focus controller to get the better resolution as possible.
iv. Change to the next objective lenses with the next larger magnification. Focus the image.
v. For this and the next objective lenses do not use the coarse focus control. Use only the fine focus controller.
vi. Observe the features you are interested in. If it was necessary, go to higher magnifications.
vii. Take a photograph of each specimen at the optimal magnification and save it.

3.7 Hardness Test

The hardness value of the samples needs to be recorded and the procedure is shown below.

Figure 3.5: Micro Hardness Testing Machine

Vickers hardness test determines the hardness by measuring the amount of force required to indent the specimens over the size of the indenter. A diamond in the form of a square-based pyramid will act as the indenter and the ratio of the force use to indent the specimen would give the hardness value, HV. Vickers hardness testing can be used to all metals.

Hardness testing is conducted based on the following procedure:

i. Switch on the power supply and move the indenter to forward position nearest to the operator.
ii. Place the specimen and raise it until the test surface is touching the indenter tip.
iii. Bring the specimen into contact with the indenter by turning the hand wheel clockwise.
iv. Use the microscope to confirm that the point is reached.
v. Press the indenter into the sample by an accurately controlled test force.
vi. Maintain the force for a specific dwell time between 10 to 15 seconds. Remove the indenter once dwell time completed.
vii. Record hardness reading for the specimen.
viii. Release the specimen by turning the hand wheel counter-clockwise.
ix. Repeat the procedure for the next reading at different spot.

3.8 Key Milestones and Gantt chart

The key milestone and the Gantt chart to complete this project are shown in the table 3.3 below.

Table 3.3: Key milestone

Milestones	Week
Early Research Development • Research background • Scope of studies and assumptions • Information gathering • Identify tools and materials needed	1-9
Middle Research Development • Detailed research • Developing the procedure • Data gathering • Conducting the experiment and testing	10-19
Final Research • Analyzing the result of experiment and testing • Finalizing the result • Completing the documentation	20-26

Gantt chart and Milestone

Table 3.4: Gantt chart and Milestone

Project Activities	Week																											
	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24	25	26	27	28
Selection of FYP title		🟨	🟨																									
Literature review and theory				Literature review on austenitic stainless steel, gas nitriding process and depth of nitrogen diffusion	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨	🟨														
Extended proposal submission							●																					
Experiment procedure development							Procedure of gas nitriding, metallography, hardness test	🟨	🟨	🟨	🟨	🟨	🟨	🟨														
Sample preparation								Buying, machining the material	🟨	🟨	🟨	🟨	🟨	🟨														
Proposal defense									●																			
Interim report submission														●														
Lab experiment															Gas nitriding, metallography and hardness testing	🟨	🟨	🟨	🟨	🟨	🟨							
Analysis the findings and result																				Analysis the result of the experiment and testing	🟨	🟨	🟨	🟨	🟨			
Documentation																									🟨	●	🟨	
Final report submission																												●

🟨	progress
●	suggested milestones

CHAPTER 4

RESULT AND DISCUSSION

4.1 Metallography Analysis

The AISI 316L austenitic stainless steel were nitrided with NH_3 and N_2 at different duration of time which are 2, 4, 8 and 24 hours at 1200°. The equipment used and procedure for nitriding are as in 3.5.

Nitrided specimens were sectioned perpendicular to the surface, polished and etched with Marble's Solution to reveal the microstructure of the specimen.

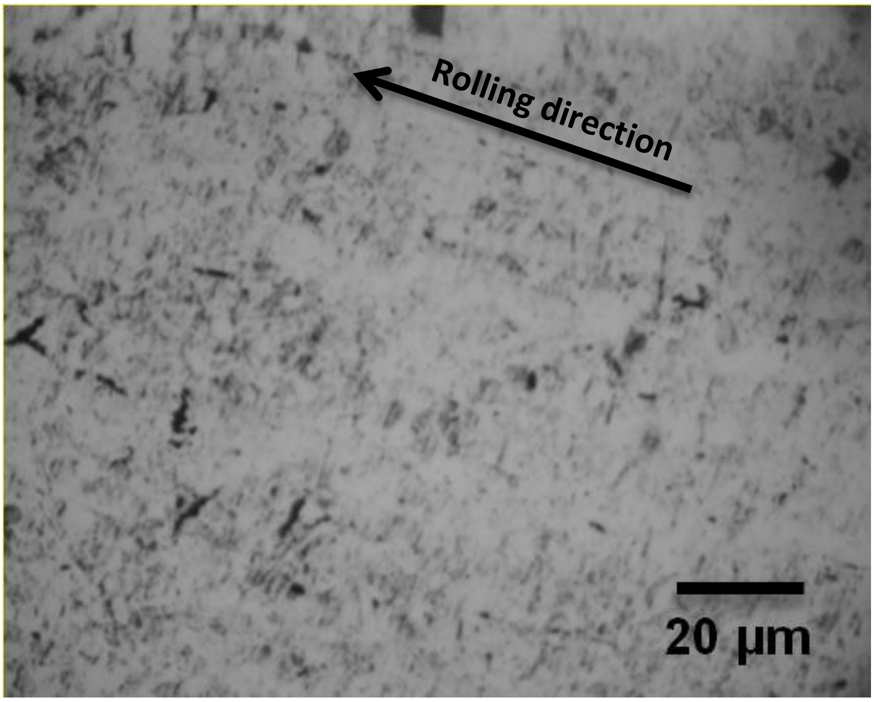

Figure 4.1: The microstructure of as-received sample

The figure above is a microstructure of as-received sample of AISI 316L. The rolling effect of cold working can be seen and due to the poor surface preparation, the optical microscopy failed to reveal the microstructure of as-received sample. The cold work means to mechanically deform a metal at a temperature below the recrystallization temperature to reduce in cross-sectional area or thickness of the metal by processes such as rolling [16].

The microstructure of AISI 316L austenitic stainless steel with different duration of nitriding process at 1200 °C. Etched with Marble’s Solution, the magnification of 100X by using optical microscopy.

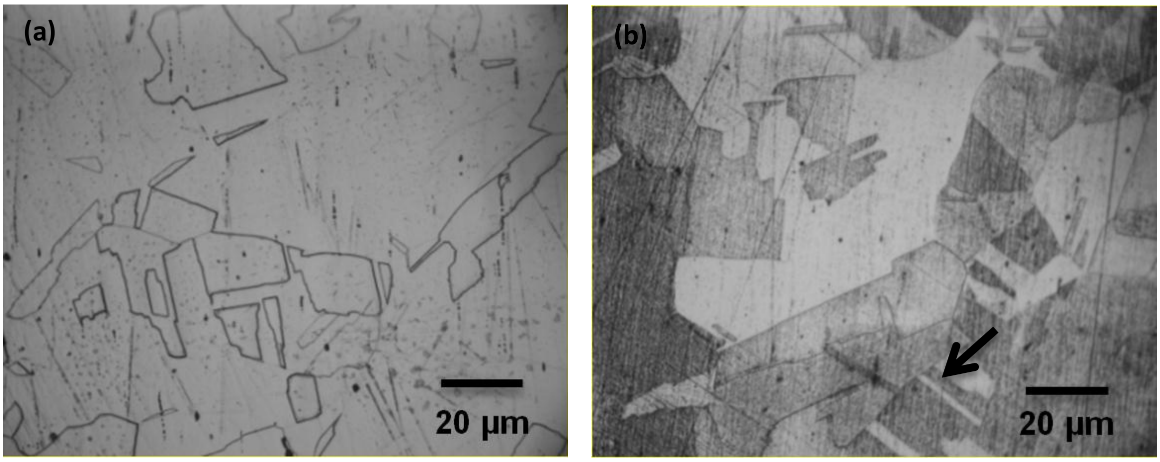

Figure 4.2: Microstructures of nitrided AISI 316L at (a) 2 hours (b) 4 hours

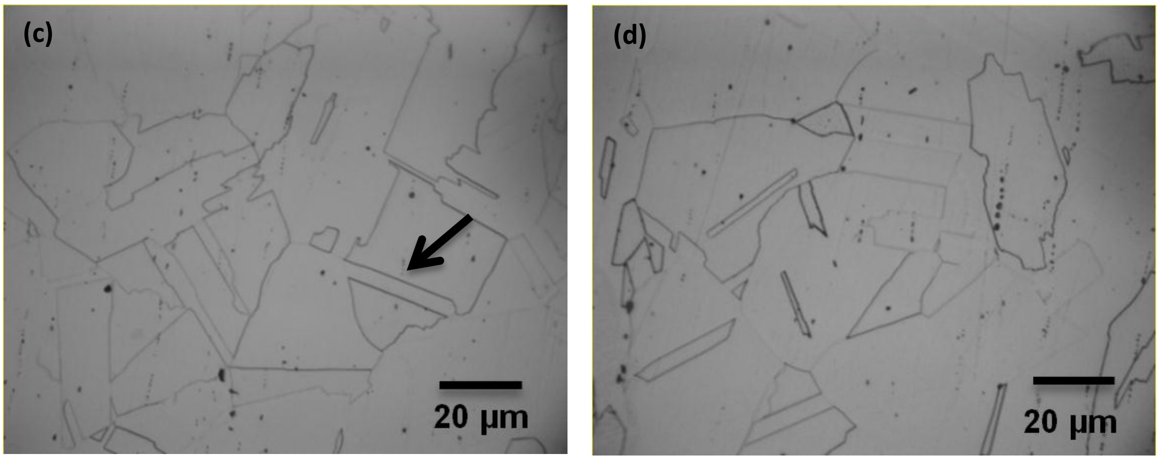

Figure 4.3: Microstructures of nitrided AISI 316L at (c) 8 hours (c) 24 hours

The microstructure of the nitrided AISI 316L shows that the typical structure for austenitic stainless steel when treated in this manner can be seen in figure above. The twin formation is observed in the microstructure of the austenitic stainless steel. The formation of twinning is observed in multiple slip systems especially in low stacking fault energy (SFE) faced centered cubic metal like AISI 316L [18]. Twinning is generally considered as a deformation mechanism for the low SFE metals such as ASS or TWIP steel. Grains without mechanical deformation twins contain a high density of planar dislocation structures [17].

In this study, according to the shape of twins in 316L ASS, twins can be divided into two patterns: suspended twin and transgranular twin [18]. The characteristics of optical microscopy of these two patterns twins are shown in Fig. (b) and Fig. (c). It can be seen that the suspended twin is consists of four parts: two sides are the coherent twin planes, the head is the incoherent twin plane and the end is grain boundary, which stops in original austenite grain after growth of a section as can be seen in Fig. (b). Otherwise, Fig. (c) shows the morphology of the transgranular twin which consists of four parts: two sides are the coherent twin planes and two ends are the grain boundary.

Besides the twin formation, based on the microstructure of the samples with different duration of nitriding time, the size of grain is increasing with increasing time of heat treatment. The grain size of austenite tends to be enlarged while increasing the gas nitriding time, but the austenite single phase structure is maintained even after the long-time solution nitriding. This means all of nitrogen absorbed into the specimen is in solid solution of austenite without precipitating any nitrides. Similar phenomena were reported by S. R. Bo et al. (2011) when the size of grain increase from 21μm to 33μm after undergoing solution treatment at 1050°C for 6 minutes. On heating steel through its critical range, transformation to austenite takes place. The austenite grains are extremely small when first formed, but grow in size as the time and temperature are increased. Grain size can be measured using an optical microscope on a transverse metallographic mount (because rolling elongates the grains) by counting the number of grains within a given area, by determining the number of grains that intersect a given length of a random line, or by comparison with reference pictures [19]

4.2 Microhardness of AISI 316L

The Vickers hardness test was carried out to measure the microhardness of both the as-received and nitrided specimens. The result of the test is plot in the graph of Hardness vs. Depth as shown in the figure below.

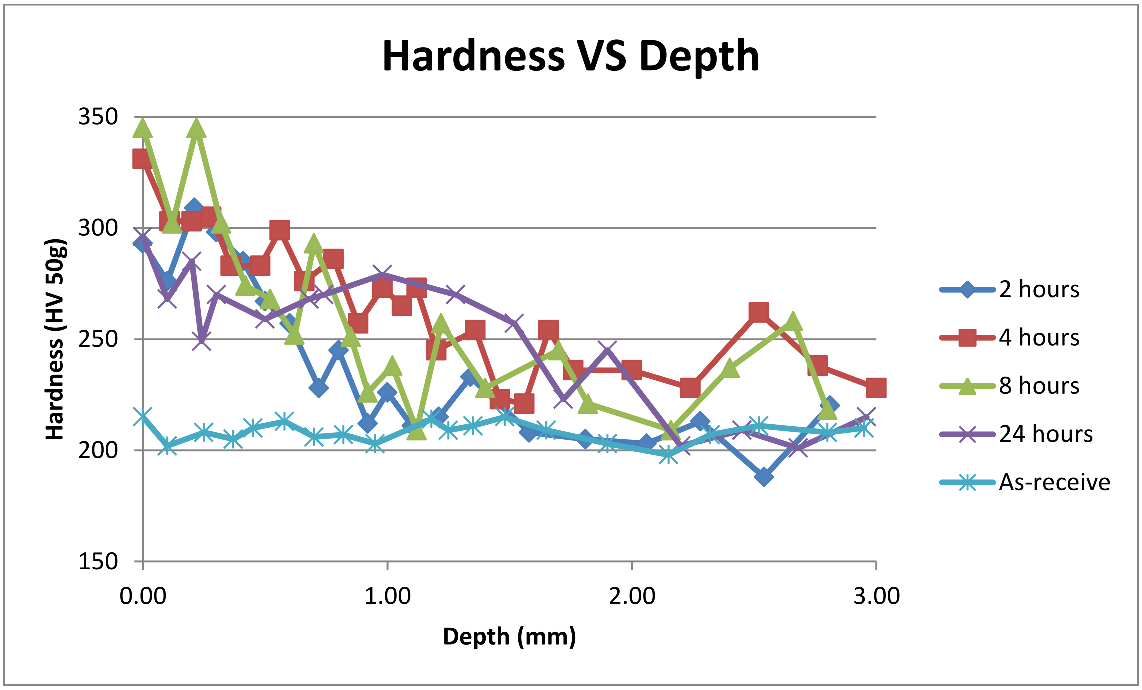

Figure 4.4: The graph of Hardness Vs. Depth

Microhardness measurements were performed across these nitrided specimens. The microhardness of nitrided specimen is larger than original AISI 316L. From the graph, the hardness is decreases gradually as the depth increases until reaching values similar to those of the original material. Hardness measurement method is the most suitable way to check the thickness of the nitrogen layer in the solid solution below the surface. The surface hardness increase is due to the high nitrogen concentration at or near the surface in solid solution. Nitrogen has a strong solid solution hardening effect [20].

Both hardness and nitrogen content decrease monotonically with the distance from the surface. The high nitrogen contents, ~0.5–1.0 wt. %, are dissolved in austenite, in the 1273–1473K temperature range, in which intense chromium nitride precipitation occurs, greatly increasing the hardness, but impairing the corrosion resistance of stainless steels [21].

The pattern of the graph is clearly can be seen when the hardness value drop toward the center of the specimen. Based on A. Fader et al. (2003), the increase in hardness in the surface layers could be related to (1) a larger concentration of nitrogen present in such regions, (2) a larger grain size, and (3) the presence of transformed phase (t'-phase).

In addition, it should be noticed that the hardness at the surface for 24 hours is smaller than for 8 or 4 hours. This could be related to an increase in the size of tetragonal (t') domains in the nitrided specimen [22]. Besides that, from the graph above, the highest hardness value recorded is about 345 HV which is increasing 58% compare to the as-received specimen.

4.3 Curve Fitting

The hardness value of specimen with different durations of gas nitriding process is randomly selected to plot the graph. Based on the experimental result, the hardness value of 245HV is selected; the curve fitting is done by using the SigmaPlot Software. The data of the experimental result is tabulated and the graph of depth vs. nitriding time is plot as shown below.

Table 4.1: Experimental result at hardness value 245HV

Nitriding Time (hours)	Nitrided layer below surface (mm)
0	0
2	0.8
4	1.2
8	1.7
24	1.9

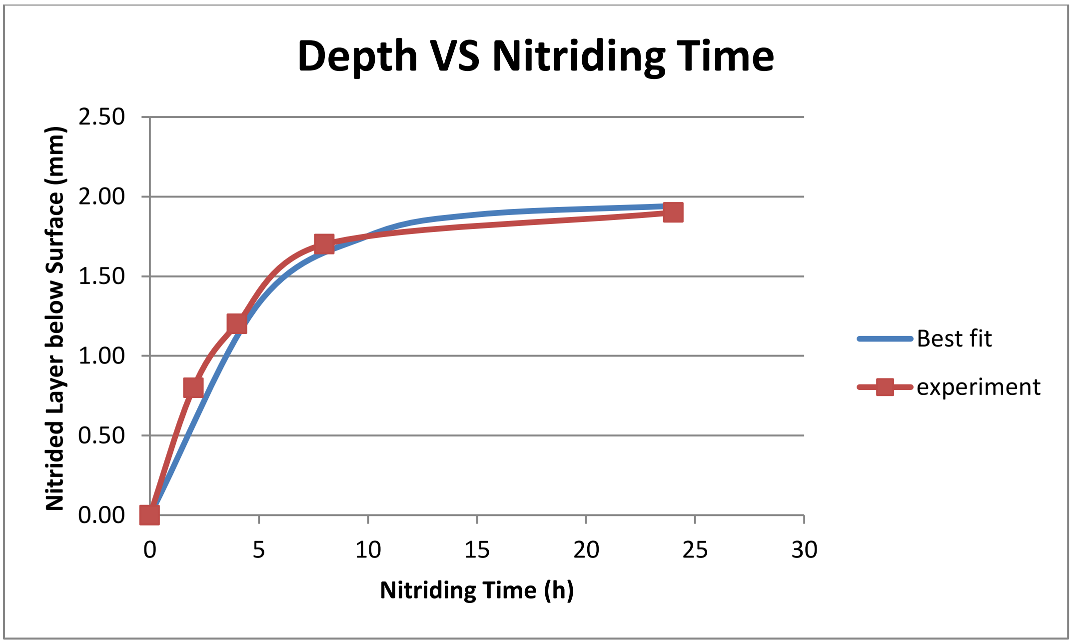

Figure 4.5: Depth Vs. Nitriding Time

The curve fitting is a capturing the trend in the data by assigning a single function across the entire range. The goal of curve fitting is to find the parameter values that most closely match the data. The models to which data are fitted depend on adjustable parameters for examples the coefficients ‘a’ and ‘b’ such that f(x) ‘fits’ the data well [23]. The result obtained by the curve-fitting software is tabulated as shown in the table below.

Table 4.2: Result of Curve fitting using SigmaPlot

R	**R^2**	**Adj R^2**	**Standard Error of Estimate (SEE)**
0.9853	**0.9709**	**0.9636**	**0.1512**

Corrected for the Mean of the observation					
	DF	**SS**	**MS**	**F**	**P**
Regression	**1**	**3.0499**	**3.0499**	**133.4705**	**0.0003**
Residual	**4**	**0.0914**	**0.0229**		
Total	**5**	**3.1413**	**0.6283**		

The ‘R’ value above is referred to the strength of the linear association between two variables is quantified by the correlation coefficient which is 0.9853. The R^2 is the square of the correlation coefficient, the value R^2 quantifies goodness of fit. It is computed as the fraction of the total variation of the Y values of data points that is attributable to the assumed model curve, and its values typically range from 0 to 1. The R^2 for this curve fitting is 0.9709 which is the values close to 1 indicate a good fit.

The adjusted R-squared is a modified version of R-squared that has been adjusted for the number of predictors in the model. The adjusted R-square is 0.9636 which is decrease compare to the R-square. The adjusted R-squared increases only if the new term improves the model more than would be expected by chance. It decreases when a predictor improves the model by less than expected by chance. Normally the adjusted R-square is lower than R-square [24]

The standard error of the estimate (SEE) is a measure of the accuracy of predictions. Recall that the regression line is the line that minimizes the sum of squared deviations of prediction (also called the sum of squares error). The standard error of the estimate is closely related to this quantity and is defined below:

$$\text{SEE} = \sqrt{\frac{\sum (Y - Y')^2}{N}}$$

Where SEE is the standard error of the estimate, Y is an actual score, Y' is a predicted score, and N is the number of pairs of scores. The SEE for the nitrided layer below surface and duration of nitriding time is 0.1512. In a scatterplot in which the SEE is small, one would therefore expect to see that most of the observed values cluster fairly closely to the regression line. When the SEE is large, one would expect to see many of the observed values far away from the regression line which means the model with the smallest standard error of estimate (SEE) is the best fit for the sample [25]

The equation obtained from the curve fitting by using SigmaPlot software is $F=1.9491\ (1 - 0.7947^{X})$, where F is nitrided layer below surface and X is duration of nitriding time. The curve obtained is the best fitting graph when the value of R^2 recorded is 0.9709 which is the values close to 1 indicate a good fit. Besides that, the value of Standard Error of Estimate (SEE) obtained also show the best fit for the sample when value recorded is 0.1512 which is the smallest value achieved by the curve-fitting software.

4.4 Effective Duration of Nitriding

The equation of effective duration of gas nitriding process obtained from the curve fitting by using SigmaPlot software which is F=1.9491 $(1 - 0.7947^{X})$, where F is nitrided layer below surface and X is duration of nitriding time. The equation is extrapolated until 48 hours as shown in the figure below.

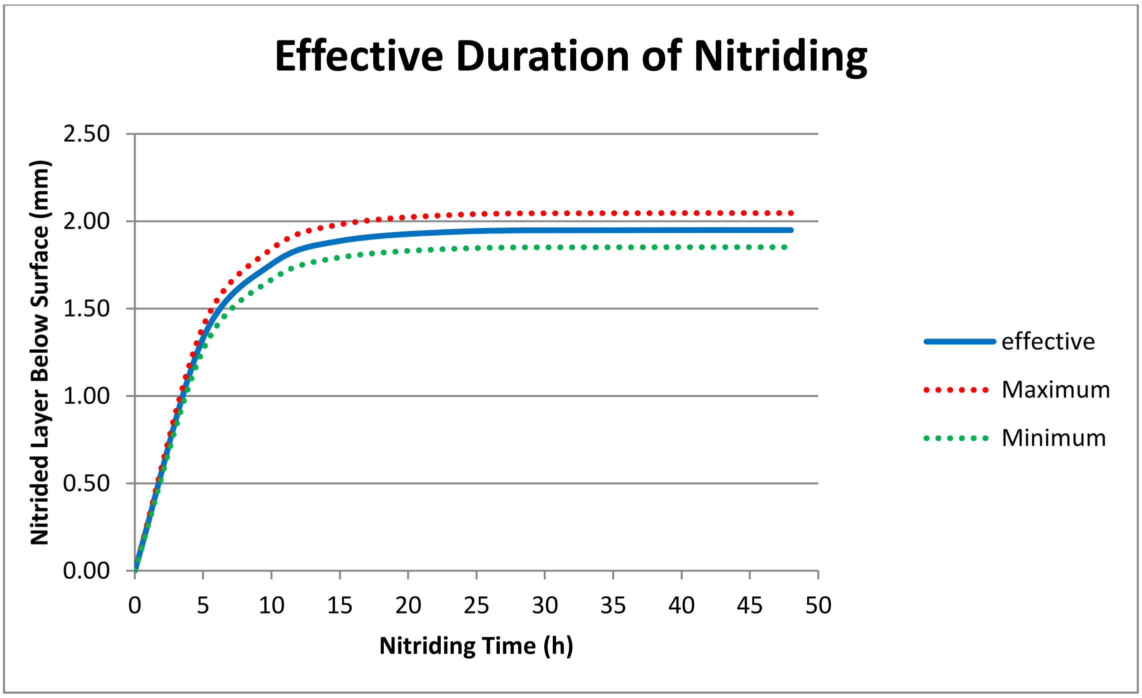

Figure 4.6: Graph of effective duration of nitriding

The depth of nitrogen penetration in AISI 316L austenitic stainless steel nitrogenized at 1200°C can be obtained by case depth method and it shown in the figure above. From the graph, the rate of diffusion of nitrogen into the samples is increasing rapidly from 0 to 5 hours. However, it start to decrease after 5 hours and when the duration of gas nitriding process approaches 18 hours, the depth of nitrogen penetration below the surface is unchanged although with increasing the duration of nitriding process. The same case is observed by L. Ge (2013) on the titanium alloy when subjected to gas nitriding at 950°C, longer nitriding time cause the thicker nitrided layer and higher surface hardness. The data of effective duration of gas nitriding is shown in the table below.

Table 4.3: Value of effective duration of nitriding

Nitriding Time (hour)	Nitrided layer below surface (mm)
16	1.9
17	1.91
18	1.92
19	1.93
20	1.93
21	1.93

From the table above, we can say that the nitrided layer below the surface is not expanding with the nitriding time equal to 20 hours. The nitrogen content seems to reach it limit to produce 245HV at 20 hours of nitriding time. Hence, there are no point to extend the gas nitriding process by using same parameter to achieve have desire thickness of nitrided layer.

The effective duration of gas nitriding process can be achieved based on this equation, F=1.9491 $(1 - 0.7947^{X})$ to produce desire thickness of nitrided layer with hardness value 245HV.

CHAPTER 5
CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The nitrided AISI 316L austenitic stainless steel have a good surface hardness compare to the as-received samples. From the Vicker's microhardness at the surface of the nitrided sample, the highest value recorded is 345HV which is higher about 58% compared to the original samples. The increasing the surface hardness is due to the high nitrogen concentration at or near the surface in solid solution. Besides that, the grain size of the microstructure of the AISI316L tends to be enlarged when the gas nitriding time is increased and formation of twins is observed. The twin formation can divide into two patterns which are suspended twin and transgranular twin. Based on the experimental result of the hardness value at 245HV, the effects of duration of gas nitriding process can be predicted by applying the equation $Y=1.9491(1-0.7947^X)$, where Y is the thickness of nitrided layer below the surface and X is duration of nitriding process. By using this equation the, the duration of gas nitriding process can be predicted for the desire thickness of nitrided layer.

5.2 Recommendation

The recommendations for this project are as follow:

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

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

III. The number of the samples should be increased by using more than 1 parameter.

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APPENDICES

Table A1: Experimental data of hardness value

As-Received sample of AISI 316L					
	Depth	Hardness		Depth	Hardness
1	0	215	11	1.25	209
2	0.1	202	12	1.35	211
3	0.25	208	13	1.48	215
4	0.37	205	14	1.65	209
5	0.45	210	15	1.9	203
6	0.58	213	16	2.15	198
7	0.7	206	17	2.32	207
8	0.82	207	18	2.52	211
9	0.95	203	19	2.8	208
10	1.18	214	20	2.95	210
AISI 316L Nitrided at 1200°C for 2 Hours					
	Depth	Hardness		Depth	Hardness
1	0.00	293	11	1.00	226
2	0.10	276	12	1.10	211
3	0.21	309	13	1.21	215
4	0.30	298	14	1.34	233
5	0.41	285	15	1.58	208
6	0.50	267	16	1.81	205
7	0.60	257	17	2.06	203
8	0.72	228	18	2.28	213
9	0.80	245	19	2.54	188
10	0.92	212	20	2.81	220
AISI 316L Nitrided at 1200°C for 4 Hours					
	Depth	Hardness		Depth	Hardness
1	0	331	13	1.12	273
2	0.11	303	14	1.2	245
3	0.2	303	15	1.36	254
4	0.28	305	16	1.46	223
5	0.36	283	17	1.56	221
6	0.48	283	18	1.66	254
7	0.56	299	19	1.76	236
8	0.66	276	20	2	236
9	0.78	286	21	2.24	228
10	0.88	257	22	2.52	262
11	0.98	273	23	2.76	238
12	1.06	265	24	3	228

AISI 316L Nitrided at 1200°C for 8 Hours

	Depth	Hardness		Depth	Hardness
1	0	345	11	1.02	238
2	0.12	302	12	1.12	209
3	0.22	345	13	1.22	257
4	0.32	302	14	1.4	228
5	0.42	274	15	1.7	245
6	0.52	268	16	1.82	221
7	0.62	252	17	2.16	209
8	0.7	293	18	2.4	237
9	0.85	251	19	2.66	258
10	0.92	226	20	2.8	218

AISI 316L Nitrided at 1200°C for 24 Hours

	Depth	Hardness		Depth	Hardness
1	0	296	10	1.28	270
2	0.1	268	11	1.52	257
3	0.2	285	12	1.72	223
4	0.24	249	13	1.9	245
5	0.3	270	14	2.2	202
6	0.5	259	15	2.45	209
7	0.68	268	16	2.68	201
8	0.74	270	17	2.96	215
9	0.98	279			

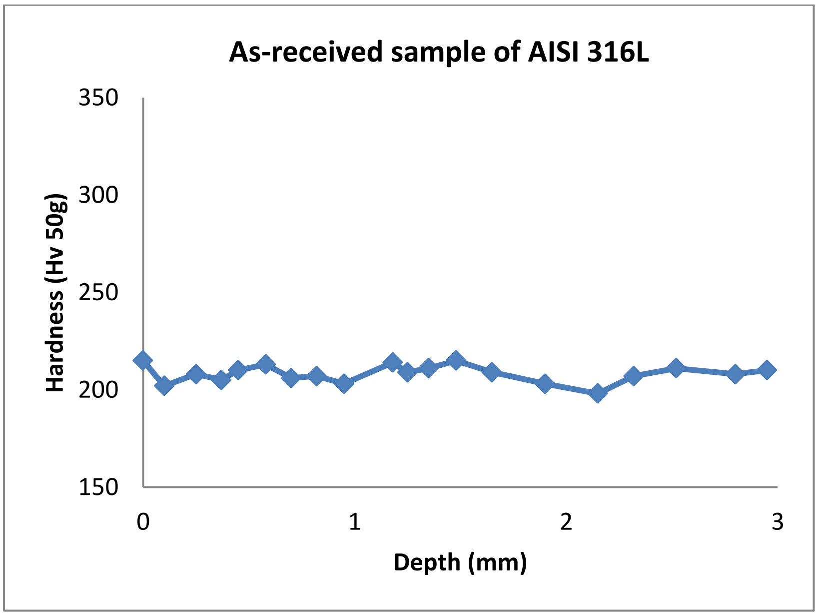

Figure A1: Hardness value of As-received sample of AISI 316L

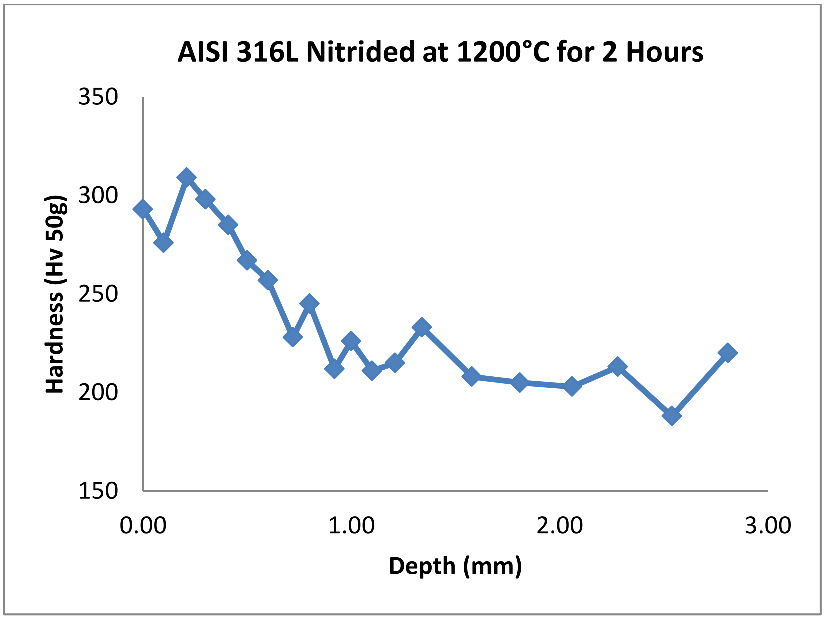

Figure A2: Hardness value of AISI 316L nitrided at 1200°C for 2 hours

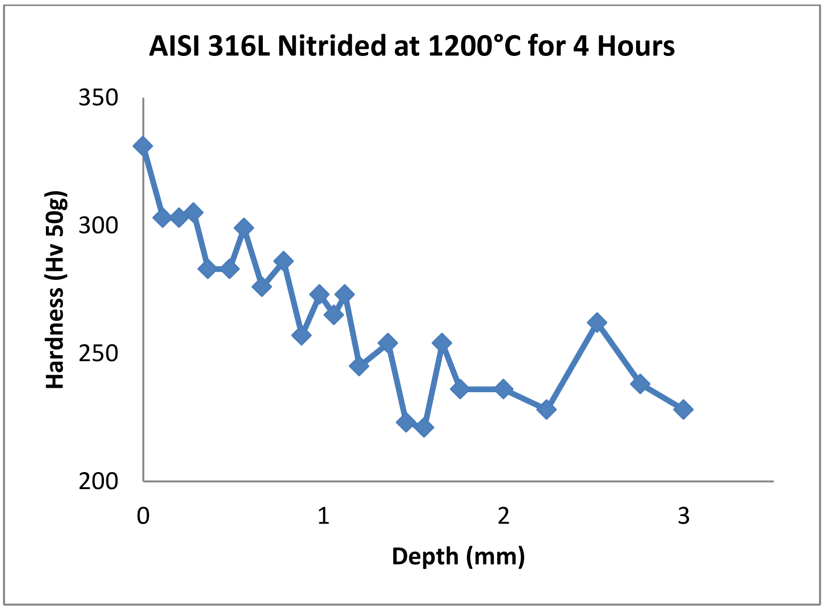

Figure A3: Hardness value of AISI 316L nitrided at 1200°C for 4 hours

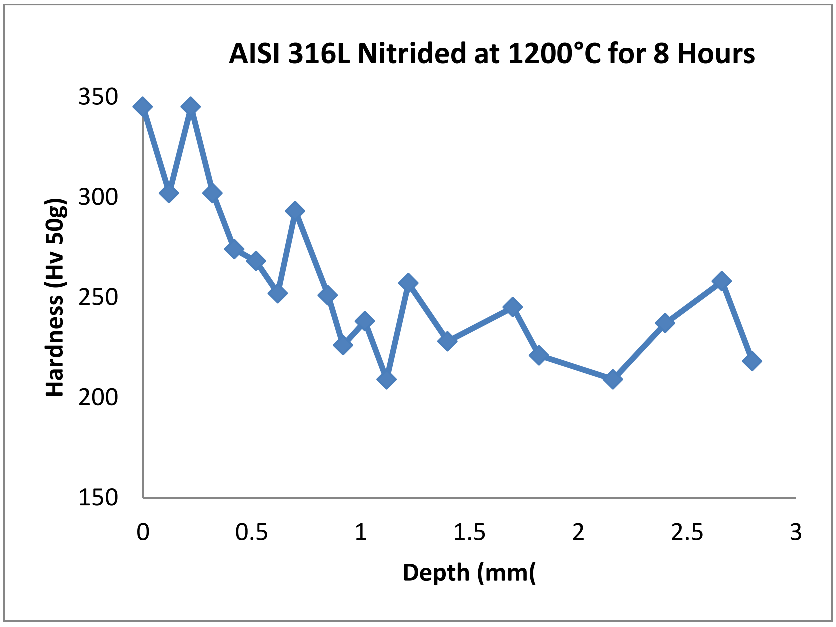

Figure A4: Hardness value of AISI 316L nitrided at 1200°C for 8 hours

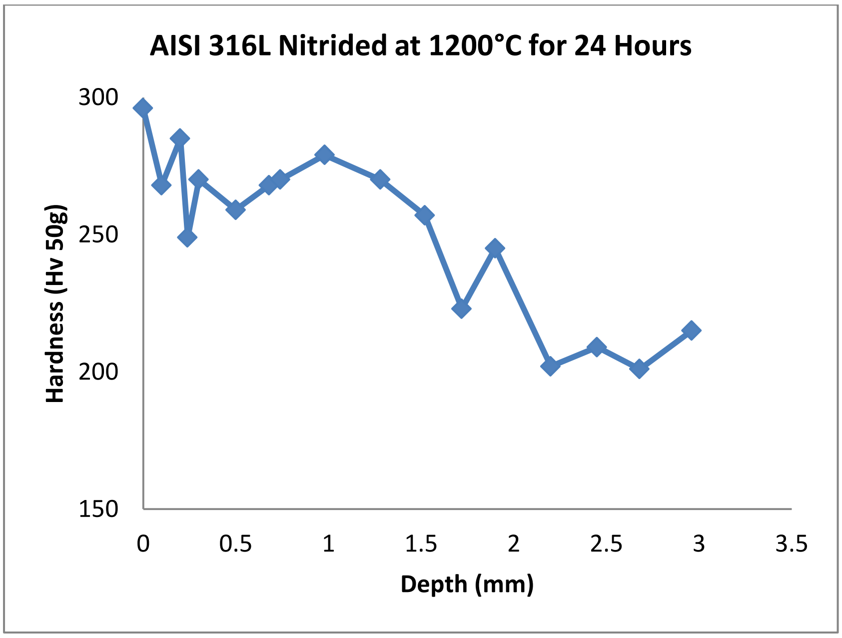

Figure A5: Hardness value of AISI 316L nitrided at 1200°C for 24 hours