A study of hardness and the sensitization of nitrided martensitic stainless steel during cooling down process

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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
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Approved by,

(Hj. Kamal Ariff b. Zainal Abidin)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
SEPTEMBER 2011

CERTIFICATION OF ORIGINALITY

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

NURFATIN EZZUNI BT ADNAN

ABSTRACT

This report presents the discussion on the sensitization of nitrided martensitic stainless steel grade AISI420 during cooling down process. It consists of project's background, literature review, methodology, and all the relevant process and component related to this project. Basically, nitriding is one of the surface treatments where it involved diffusion of nitrogen into the grain boundaries. For this project, martensitic stainless steel is exposed to high temperature (above 1200°C) and low temperature (below 600°C) for 4 hours and 10 hours. The objectives of this project are to determine the effect of the gas nitriding process on the hardness and the microstructure of the AISI420 Martensitic Stainless Steel. Besides that, is to determine and compare the microstructure and sensitization of nitride martensitic stainless steel with different holding time. Metallography or microstructure of all the samples is observed by using Light Optical Microscope (LOM). Meanwhile for hardness, Vickers Hardness Testing is used and was plot in graph. Energy Dispersion X-Ray (EDX) examination and Scanning Electron Microscopy (SEM) are carried out to prove about the microstructure and new entities contain in the samples such as carbide chromium precipitation. The microstructure observed for the nitride sample show that high temperature of nitriding has more sensitization compared to low temperature. The precipitate along the grain boundaries can be seen clearly. At high temperature, the grain boundaries getting expand and bigger compare to as received samples and also low temperature samples. But low temperature of nitriding, the grain boundaries getting closer, dark and compact to each other. Highest value of hardness: 424.1HV is achieved from sample nitride at 1200°C. Diffusion of nitrogen into the samples content leads to higher hardness. EDX show analysis shows that the appearances of N increase the hardness of the material. Thus, as a conclusion, the objectives of the project are achieved successfully. Low temperature of nitriding shows less sensitize compare to high temperature.

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Thank you,
Nurfatin Ezzuni bt Adnan
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CHAPTER 1 : INTRODUCTION

1.1 Background of study

Surgical stainless steel is a very specific type of stainless steel, basically used in medical applications, which includes alloying elements of molybdenum, chromium and also nickel. Back to real world, the word ‘surgical’ is actually refers to the fact that these types of steel are well-suited for making surgical instruments. This is mainly because they are very easy to clean and sterilize strong and very good corrosion-resistant. In some cases today, titanium is used instead in procedures that require metal implant which will be permanent in the body. Titanium is a reactive metal, where the surface will quickly oxidizes on exposure to air, creating a microstructure stable oxide surface. Thus, steel may be used for temporary implants and the very expensive titanium for permanent implant.

However, although these typical martensitic stainless steel is used temporary implant, it properties must always maintain to be in very good condition. Same goes to any surgical equipment. For further information, in our world nowadays, most surgical equipment is made out of martensitic stainless steel. This is because; it is much harder than austenitic steel, and easier to keep sharp.

In that case, these types of material really need to have a very good hardness and also have a good corrosion resistance. So far, nitriding is the one the heat treatment where the hardness can be increase. But, the only reason lead to limitation is because at certain high temperature of nitriding can lead to formation of carbide precipitation where the corrosion resistance will be lower.

Low hardness sometimes limits its uses in industrial applications [1]. For many years of these applications, an increase in surface hardness by nitriding can be beneficial for improving the performance and longer service life. Besides, nitriding is well known as the most an effective technique to improve the surface hardness of steel, including stainless steel, and has been developed for many years ago. As said by Wu, Liu et al. 2010[2], nitriding allows them to have much higher surface hardness and anti-fatigue strength, better resistance to abrasion and other superior properties.

Basically, for nitriding process, they are divided by three types, first is plasma nitriding, second is gas nitriding and the last but not least is salt-bath nitriding. Plasma nitriding is one of the most versatile nitriding processes (Tsuchiyama, Tobata et al. 2012) with many advantages over the others. Since in UTP, the only available for nitriding process is gas nitriding process, so the experiment later shall be gas nitriding. Since, not much different between plasma nitriding and gas nitriding, the discussion will be both include.

This nitriding process has been well demonstrated in nitriding of austenitic stainless steel but in contrast only limited studies have been carried out so far regarding martensitic stainless steels. Alphonsa et al. [21], and Pinedo and Monteiro[22],have investigated the microstructures of nitride AISI420 martensitic stainless steels. All these studies, have demonstrated that martensitic stainless steels can be nitride like austenitic stainless steels to improve hardness. In this study, SUS420 martensitic stainless steel will be gas nitrided following methodologies generally used for nitriding austenitic stainless steel.

Numerous failures of stainless steels have occurred because of intergranular corrosion. This happens in environments where the alloy should exhibit excellent corrosion resistance. When these steels are heated in approximately at certain temperature range, they become sensitized or susceptible to intergranular corrosion. Here sensitizing means that chromium precipitates as chromium carbide leaving the grain boundary areas with less chromium.

In a martensitic stainless steel, carbide dissolution processes can change chemical composition of its austenite phase during heating. In this process, heating parameters will play critical roles in the transformation of austenite phase. Similarly, cooling rates have considerable influences on the austenitic decomposition and transformation. Solid-solution treatments are performed to obtain austenite and then dissolve carbides, followed by cooling to transform austenite into martensitic and often cause carbide precipitation. The amount of carbides in the quenched microstructure affects an important influence on the mechanical and corrosion characteristics of this material [6].

1.2 Problem Statement

Msteels are essentially inferior to conventional low-alloy martensitic steels in term of ductility, impact toughness, and elongation under the same strength level. The susceptibility of the steel to temper embrittlement [3] is also a problem. This is because in the case of stainless steels, increase of surface hardness and wear resistance accompany by a drop in corrosion resistance due to the precipitation of CrN [4].

As been state before, since not much information about the sensitization of nitrided martensitic stainless steel, so this project need to investigate or to study more about the sensitization of nitrided martensitic stainless during cooling down process.

1.3 Objectives

The main objectives for this project are:

- To determine the effect of the gas nitriding process on the hardness of the Martensitic Stainless Steel.
- To determine the effect of the sensitization of the gas nitriding process on Martensitic Stainless Steel during cooling down process.
- To observe and compare any microstructure changes of the samples of Martensitic Stainless Steel before and after being gas nitrided.
- To determine the microstructure and the sensitization of nitride martensitic stainless steel with different flow rate of nitrogen diffusion and different holding time.

1.4 Scope of Study/Project/Research

The project will cover on the conducting the gas nitriding during cooling process on Martensitic Stainless Steel. Since this project have time frame just about 2 semesters, a reduction of the research scope is necessary. For that, the following applies

- Study the sensitization during gas nitriding process at different temperature (high and low), nitriding duration (4 hours and 10 hours), hardness test (Vickers hardness test) will be carry out.
- Study the microstructure of the nitrided Martensitic Stainless Steel by LOM.
- Since quenching is not allowed, a type of cooling down the temperature is only slowly to room temperature.
- Sample or specimen of Martensitic Stainless Steel will go through under preparation like cutting, sectioning, mounting, polishing and grounding and etching.

After the experiment and analysis of the project, the mechanical properties like hardness are provably improved. Besides, the microstructure changes of before and after nitriding also were recorded. In this experiment, some analysis tools were used such as light optical microscopy, Vickers hardness testing, Scanning Electron Microscopy and Energy Dispersion X-Ray (EDX).

After the required data is acquired, the project is considered as complete. The result obtained can be used for future work.

CHAPTER 2: LITERATURE REVIEW

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

.

2.1 An Overview of Stainless Steel

2.1.1 Stainless Steel

Stainless steels are iron-base alloys with a minimum of 11.5% chromium content by weight [7]. Chromium content increases the oxidation and corrosion resistance of steel in aggressive environments and prevents the formation of rust. The corrosion resistance is provided by a thin surface film, known as ‘passive film’, which protects the underlying material. The chromium content of 11.5% by weight is the minimum quantity necessary for a continuous layer [8]. Upon increasing the chromium content, the passive layer becomes more stable. The best protections are reached with 25 to 30% chromium content in the non-nickel alloys, and 18-30% in the nickel austenitic alloys [7].

Today a large number of different alloys belonging to the stainless steel group are present on the market. They differ in the amount of chromium, that is some alloys reaches 30% and in the content of the other alloying elements, added to provide specific properties. For example, nickel and molybdenum are typically added to increase the corrosion resistance of the alloy, expanding the passivity ranges and reducing pitting (F.L LaQue and H.R.Copson 1963) [7], and (A.J. Sedriks 1979) [8]. Carbon, molybdenum, nitrogen, titanium, aluminium and copper are used to increase the strength while sulfur and selenium to facilitate the machinability [8]. Nickel is also added in order to improve the formability and toughness of the material [8].

2.1.2 Families of Stainless Steel

The most common stainless steels can be divided into five major families according to crystallography structure: ferritic, austenitic, martensitic, duplex and precipitation-hardening [9]. Each family has its typical mechanical properties and is characterized by a common nature in terms of resistance to particular forms of corrosion.

Austenitic stainless steels include the 200 and 300 series of which type 304 is the most common. The primary alloying additions are chromium and nickel. Ferritic stainless steels are non-hardenable Fe-Cr alloys. Type 405, 409, 430, 422 and 446 are representative of this group. Martensitic stainless steels are similar in composition to ferritic group but contain higher carbon and lower chromium to permit hardening by heat treatment. Types 403, 410, 416 and 420 are representative of this group. Duplex stainless steel is supplied with microstructure of approximately equal amounts of ferrite and austenite. They contain roughly 24% chromium and 5% nickel. Their numbering system is not included in 200,300 or 400 groups.

2.2 Martensitic Stainless Steel

The martensitic stainless steels are not as corrosion resistant as ferritic and austenite, but they are extremely strong and tough and can be hardened by heat treatment. The crystal structure is a body-centered tetragonal structure (BCT). They have lower chromium levels (11.5 to 17 by weight) [8] and relatively high carbon contents. The chromium content must be low because of its ferrite-stabilizing character. For this reason, the corrosion resistance of the martensitic grades turns out to be limited. Nitrogen, nickel and molybdenum can be added to improve the toughness and corrosion resistance [9].

Figure 1: Martensitic Stainless Steel in plate shape. (Ready to be cut)

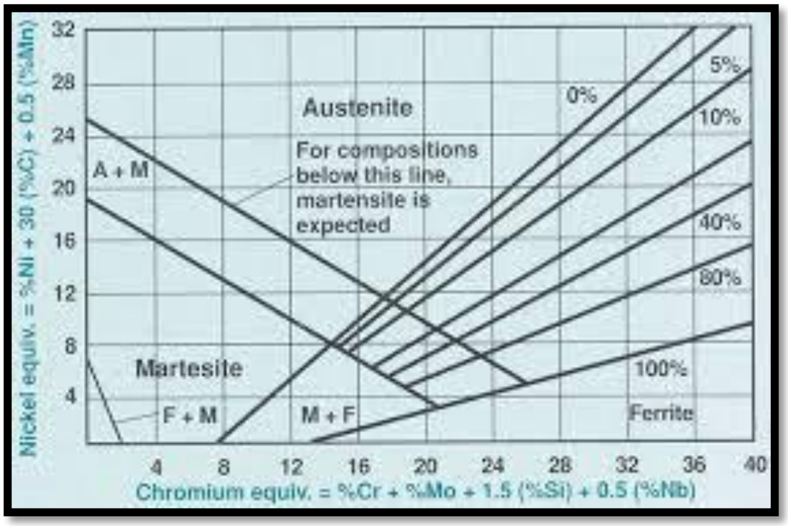
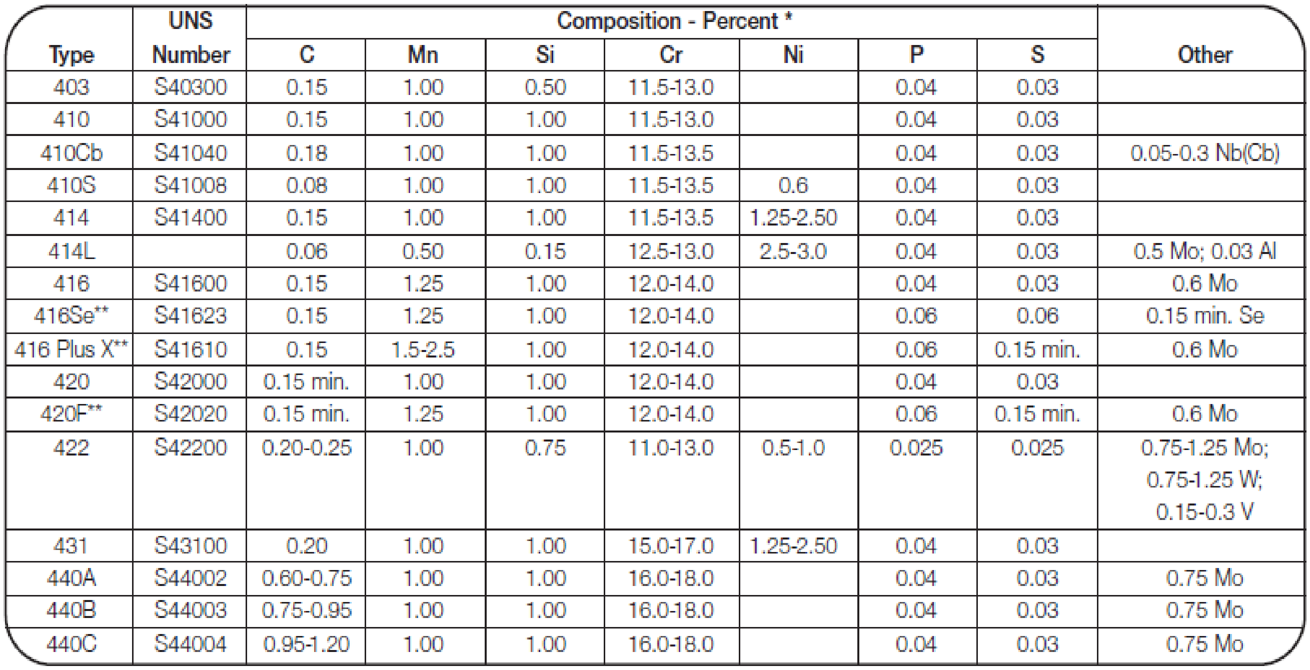


Figure 2: Schaeffler diagram

As we can see from Schaeffler diagram, martensitic stainless steel contain 11 to 18 % Cr, up to 1.20% C and small amounts of Mn and Ni and sometimes, Mo. These steels will transform to austenite on heating and therefore, can be hardened by formation of martensite on cooling. One of the disadvantage of martensitic stainless steel is they have a tendency towards weld cracking on cooling when hard brittle martensite is formed.

Table 1: Nominal composition in martensitic stainless steel



Type	UNS Number	Composition - Percent *							Other
		C	Mn	Si	Cr	Ni	P	S	
403	S40300	0.15	1.00	0.50	11.5-13.0		0.04	0.03	
410	S41000	0.15	1.00	1.00	11.5-13.0		0.04	0.03	
410Cb	S41040	0.18	1.00	1.00	11.5-13.5		0.04	0.03	0.05-0.3 Nb(Cb)
410S	S41008	0.08	1.00	1.00	11.5-13.5	0.6	0.04	0.03	
414	S41400	0.15	1.00	1.00	11.5-13.5	1.25-2.50	0.04	0.03	
414L		0.06	0.50	0.15	12.5-13.0	2.5-3.0	0.04	0.03	0.5 Mo; 0.03 Al
416	S41600	0.15	1.25	1.00	12.0-14.0		0.04	0.03	0.6 Mo
416Se**	S41623	0.15	1.25	1.00	12.0-14.0		0.06	0.06	0.15 min. Se
416 Plus X**	S41610	0.15	1.5-2.5	1.00	12.0-14.0		0.06	0.15 min.	0.6 Mo
420	S42000	0.15 min.	1.00	1.00	12.0-14.0		0.04	0.03	
420F**	S42020	0.15 min.	1.25	1.00	12.0-14.0		0.06	0.15 min.	0.6 Mo
422	S42200	0.20-0.25	1.00	0.75	11.0-13.0	0.5-1.0	0.025	0.025	0.75-1.25 Mo; 0.75-1.25 W; 0.15-0.3 V
431	S43100	0.20	1.00	1.00	15.0-17.0	1.25-2.50	0.04	0.03	
440A	S44002	0.60-0.75	1.00	1.00	16.0-18.0		0.04	0.03	0.75 Mo
440B	S44003	0.75-0.95	1.00	1.00	16.0-18.0		0.04	0.03	0.75 Mo
440C	S44004	0.95-1.20	1.00	1.00	16.0-18.0		0.04	0.03	0.75 Mo

*Single values are maximum values.

**These grades are generally considered to be unweldable.

(From *ASM Metals Handbook*, Ninth Edition, Volume 3)

2.3 Sensitization of Stainless Steel

Sensitization of stainless steel is the process that leads to the precipitation of carbides of nitrides at grain boundaries. This phenomenon occurs in austenite stainless steel when they are heated for some time in the sensitization temperature range of about 425 to 870°C [8] [9]. The precipitation of carbides and nitrides at the grain boundaries causes the depletion of chromium in the areas immediately adjacent and renders the stainless steel susceptible in particular to intergranular corrosion, but also pitting, crevice corrosion and stress corrosion cracking [9]. Therefore, the key to sensitization measurement is the convenient detection and quantitation of the chromium-depleted zone at the grain boundary or phenomena directly related to it, such as the loss of corrosion resistance [10].

Sensitization leads to intergranular corrosion in the heat affected zone as shown in the figure below. It is caused chromium carbide formation and precipitation at grain boundaries in the heat affected zone when heated in the 425° to 870°C temperature range. Since most carbon is found near grain boundaries, chromium carbide formation removes some chromium from solution near the grain boundaries, thereby reducing the corrosion resistance of these local areas. This problem can be remedied by using low carbon base material and filter material to reduce the amount of carbon available to combine with chromium.

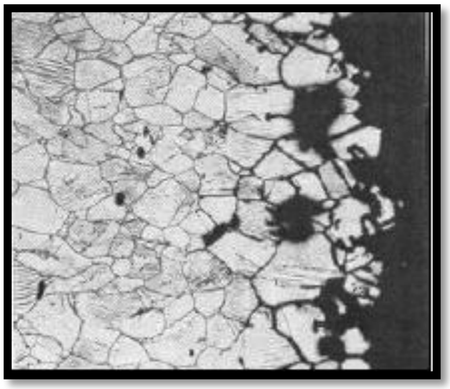


Figure 3: Parent plate of Intergranular Corrosion[23]

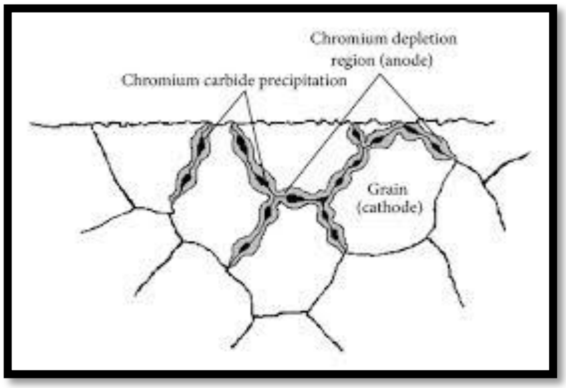


Figure 4: Chromium Depleted Zone[23]

2.4 Nitriding of the Stainless Steel

Nitridation if found when the material is exposed to high temperature gases containing nitrogen. Nitridation can result in the formation of internal precipitates such as carbides and nitrides, causing the alloy to suffer embrittlement as well as the degradation of other mechanical properties. The increase in nickel content improves further the resistance of the alloy. Regarding nitridation, high nickel contents is beneficial for the alloy, while molybdenum may be detrimental under particular conditions. Nickel-based alloys are more resistant to nitridation than iron-based alloys.

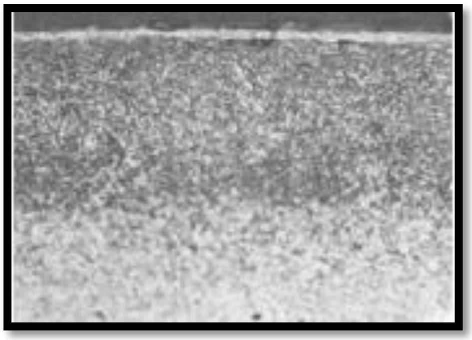


Figure 5: Structure of nitride layer

Stainless steel can be nitrided to some degree thanks to their high chromium content. The nitriding increases the surface hardness of the stainless steels, which improves wear resistance. At the same time, the conventional nitriding temperatures (500-650°C) of the gas nitriding affect the corrosion performance of the stainless steels, because of the formation of Cr-nitrides [11]. To avoid Cr-nitrides formation, traditional nitriding for stainless steels is performed at low temperatures, below 450°C, using mainly plasma nitriding (D.Q, Peng et al. 2010). The formation of expanded phases due to the large amount of nitrogen that can be entrapped into the lattice has been observed. Most studies regarding the nitriding of stainless steels have been carried out with austenitic stainless steels. Only a few have focused on ferritic and martensitic stainless steel.

Liang et al. [12] studied the surface modification of AISI 304 stainless steel by plasma nitriding. For nitriding temperatures between 430-450°C for 24 hour, the nitride layer without precipitation of nitrides was about 7-12 micrometer, while it was only 2-3 micrometer after nitriding at 350°C for 4 hour. Precipitates of Cr-nitrides were observed after nitriding at 465°C for 24 hour. The XRD showed the formation of expanded austenite at all the temperature, with the highest saturation of nitrogen reached at 420°C. At 460°C, Cr-nitrides started to precipitate in the expanded austenite layer, whereas at 500°C some iron nitrides appeared in the nitride layer. At this temperature, CrN, Fe_4N and Fe_4N phases were found in the nitride layer. The formation of expanded austenite improved the wet corrosion resistance of AISI 304 stainless steel, which was instead deteriorated by the precipitation of Cr-nitrides at treated temperature above 460°C.

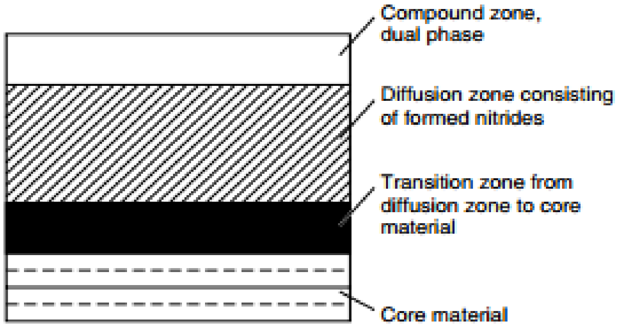


Figure 6: Schematic of a typical nitride case structure.

Semandi et al. [13] investigated the microstructure and corrosion behavior of AISI 316 stainless steel by plasma immersionion implantation treatment at temperature between 150°C and 520°C. The results showed that for nitriding temperature between 250 and 450°C, both the wet corrosion and wear resistance were improved by the formation of a nitrogen-expanded austenite. At 520°C, the extensive Cr-nitrides precipitation was accompanied by the transformation of the highly expanded austenite to martensite. This improved wear resistance of the material but deteriorated the wet corrosion resistance. The biggest depth of nitrogen penetration, above 14 micrometer, was obtained after nitriding at 520°C for 40 minutes. Also *Gil et al.* [14] studied that wet corrosion performance of the AISI 316L stainless steel after nitriding at 420°C for 8 hours. The XRD patterns showed formation of expanded austenite and precipitation of CrN. The formation of CrNin the compound layer depletes the adjacent matrix in chromium and lead to the sensitization of the material when the chromium content decreases below 11-12%.

Gontijo et al. [15] studied the S-phases formed on plasma nitride AISI 304L and AISI 316L austenitic stainless steels, and AISI 409L ferritic stainless steel. The alloys were plasma nitride between 350°C to 500°C. The presence of similar S phases layers were observed in both the austenite (BCC) and ferritic (FCC) stainless steels. The 409L series showed the formation of a layer with high amount of nitrogen, designed in the study as expanded ferrite or ferrite S^{α}-phase. The strain state was higher for the expanded ferritic phase in comparison with the expanded austenitic phases.

Sung et al. studied the phase changes of the AISI 430 ferritic stainless steel after high-temperature gas nitriding. The gas nitriding was performed at 1050°C and 1100°C. the relatively high chromium content of the ferritic 430 stainless steel, enables the nitrogen to permeate into interior. This effect is due to the strong affinity between nitrogen and chromium. The surface layer was changed into martensite plus ferrite and Cr_2N at 1050°C, while martensite plus a rectangular type retained austenite appeared at 1100°C by high-temperature gas nitriding. The high-temperature gas nitriding improved the wet corrosion resistance, while the precipitation of Cr_2N at the outmost surface area deteriorated the corrosion resistance.

Corengia et al. [16] investigated the mircrostructure and corrosion behavior of DC-pulsed plasma nitride AISI 410 nartensitic stainless steel. The DC-pulsed plasma nitriding was carried out at 350°C and 500°C. At the lower nitriding temperatures α-Fe and small amount γ'-Fe_4N are detected on the surface. CrN nitrides were not detected, since the CrN precipitation takes place at higher temperature. The shift and broadening of α-Fe peaks observed on the XRD patterns were associated with the formation of a nitrogen oversaturated phase, called expanded martensite. The presence of this expanded phase, in addition to the small Fe_4N nitrides precipitates, produces the high surface hardness observed. At higher Dc-pulsed plasma nitriding temperatures, the nitrogen solid solution decomposed into α and CrN. the precipitation of CrN depletes chromium of the expanded phase and deteriorates the corrosion resistance of the alloy. The plasma nitride AISI 410 was also investigated by *Li et al* [19]. After plasma nitriding at 450°C for 20 hours, the surface consisted of mainly γ'-Fe_4N and ϵ–$Fe_{2\text{-}3}N$ iron nitrides. CrN precipitation was observed on the XRD spectrum. The formation of expanded martensite, nitrogen solid solution into the surface, was suggested also in this study. However, it could not be confirmed since the outmost nitride layer was so thick to allow the penetration of the X-ray through to the substrate. The cross section microstructure of the plasma treated 410 showed the formation of two distinct layers. The outer layer was considered to be a "nitride" case rich in nitrogen, and the inner a 'carburized" layer rich in carbon.

Nevertheless, there have been fewer works on the nitriding of martensitic grades than on austenitic grades of stainless steel. In particular, the possibility of lowering the process temperature has not been systematically explored. During the last half decade or so, much work on the austenite grades has highlighted the desirability of treatment temperature of 400°C and lowers [17]. Aside from the obvious benefits of lower coast, faster turn-around and reduced distortion of the work piece, it is now clear that process temperatures over ~ 480°C permit Cr in the alloy to become mobile; the chromium preferentially forms CrN, the deposition of which certainly increases the hardness, but also results in a reduction in corrosion resistance through the depletion of Cr from solid solution in the alloy (Z.L. Zhang et al. 1985).

According to (Karadas, Celik et al. 2011) [4], low temperature gas nitriding in a fluidized bed reactor produced a surface layer consisted of iron nitride (ε-Fe3N, γ'-Fe4N) and expanded martensite (αN) on the surface of the AISI 420 grade martensitic stainless steel. After the low temperature gas nitriding, the surface hardness of the AISI 420 martensitic stainless steel increased about 6 times, when compared to the original state. The tribological performance of the AISI 420 grade martensitic stainless steel was remarkable enhanced upon formation of nitrogen enriched surface layer. The nitride martensitic stainless steel exhibited 21 times higher wears resistance than the original steel. The applied nitriding process also caused reduction in friction coefficient. The applied low temperature gas nitriding process also enhanced the corrosion resistance of AISI 420 grade martensitic stainless steel.

In the case of martensitic stainless steels, more research has to be done to avoid chromium depletion even before plasma nitriding, in the heat treatment condition. In the case of the precipitation hardening steel Corrax, a good corrosion behavior could be achieved with a better control of other nitriding process parameters than temperature, for example diminishing the nitrogen content in the gaseous mixture for nitriding or the nitrogen activity by current density control [14].

CHAPTER 3 : METHODOLOGY

The project work is divided into two sessions, which are research for the first semester and work for second semester. In the first semester, the project work focuses more on literature reviews and the material preparation. The experiment will be conducted during FYP 2 session due to time consuming. After some research, the flow or the work can be clearly understands by flow chart below.

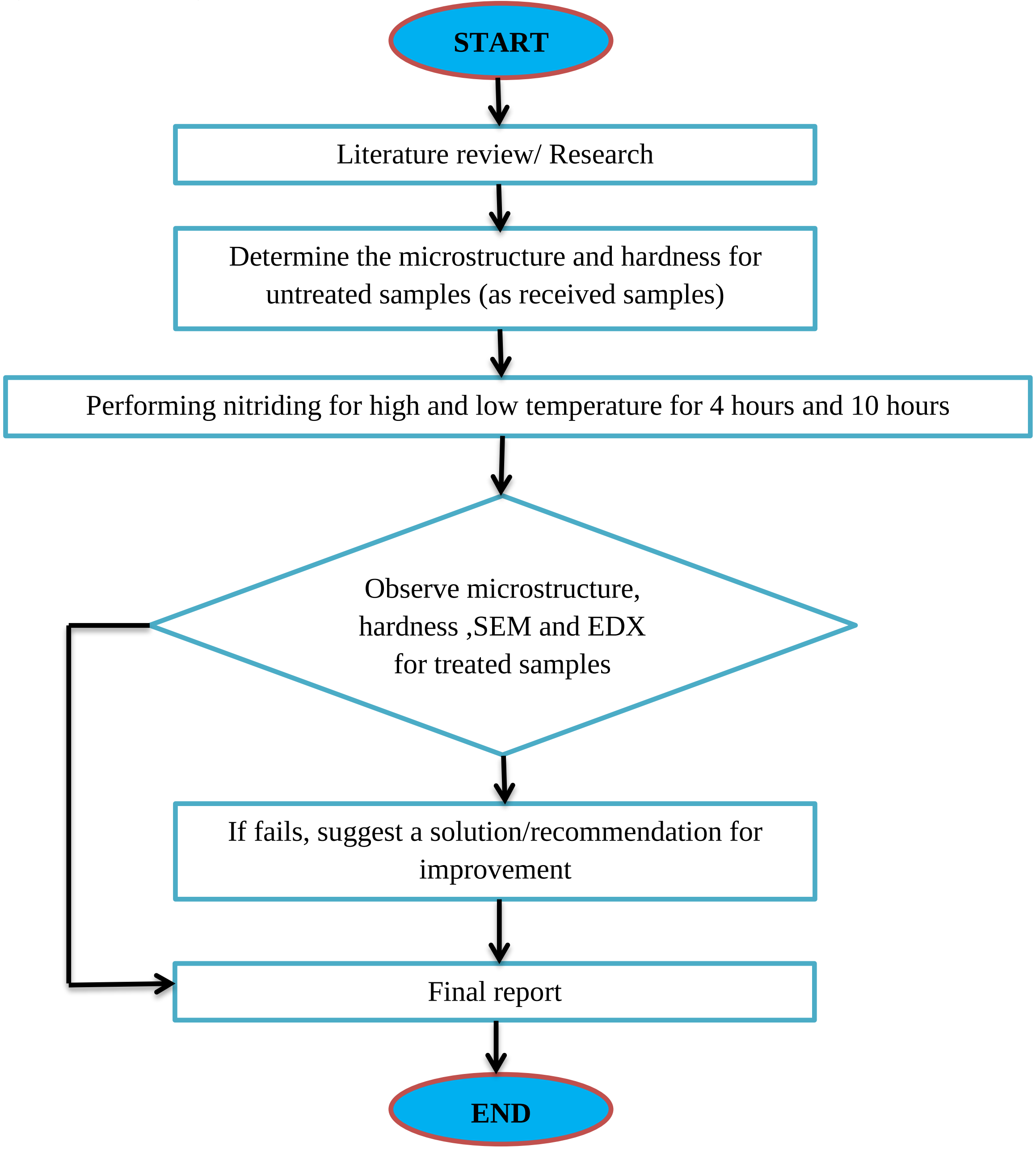


Figure 7: Project's flow chart

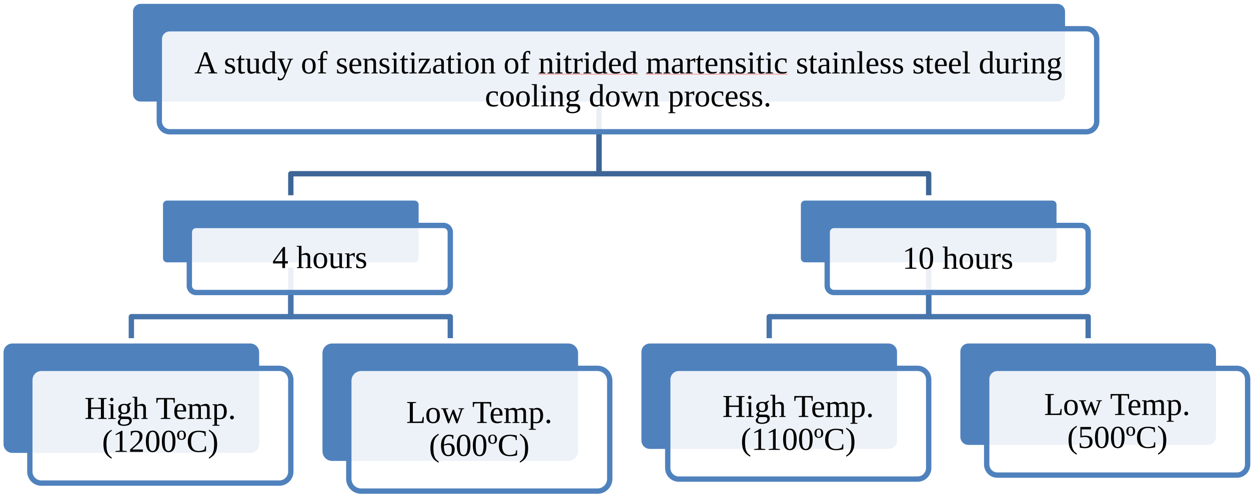


Figure 8: Experiment's planning

3.1 Procedures

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

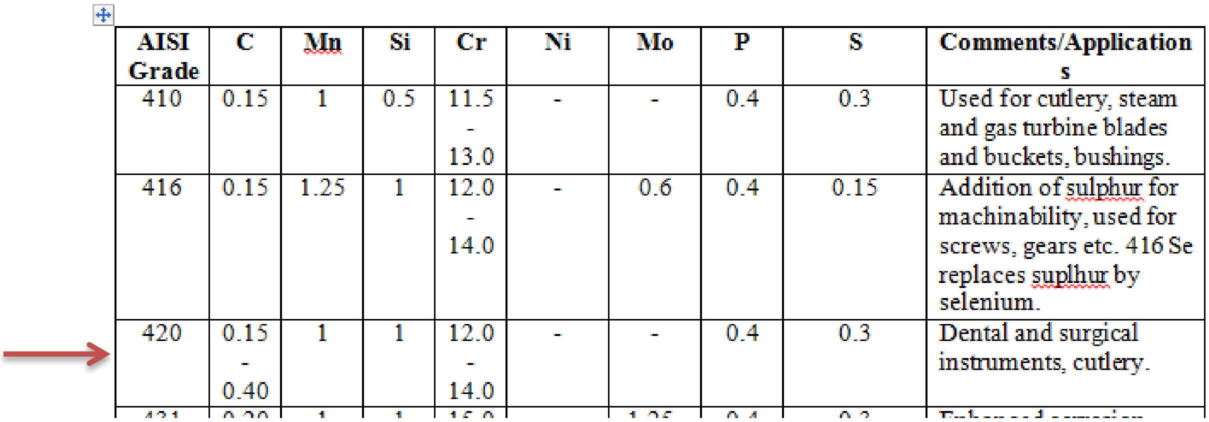
3.1.1 Research Methodology

This project began with the study on discovering the project objective and study on the phases of martensitic stainless steel and the nitriding process. There are several techniques used in performing the nitriding process which are gas nitriding, plasma nitriding and ion nitriding. For this project, high and low temperatures were chose to perform 4 hours and 10 hours of nitriding. After confirming the technique to be used, further study on its effect on the sensitization, microstructure and hardness were done from previous papers. The study provides information on the microstructure changes, hardness and the phase of the nitride martensitic stainless steel. Literature review will be done continuously by referring to books, reference and journals.

3.1.2 Metal Acquisition

In this work, AISI420 Martensitic Stainless Steel is chosen. They have fair resistance to fresh water, steam, oil gasoline, blood, perspiration, and alcohol and food environment.

Table 2: Composition in AISI 420 Martensitic Stainless Steel.



AISI Grade	C	Mn	Si	Cr	Ni	Mo	P	S	Comments/Applications
410	0.15	1	0.5	11.5 - 13.0	-	-	0.4	0.3	Used for cutlery, steam and gas turbine blades and buckets, bushings.
416	0.15	1.25	1	12.0 - 14.0	-	0.6	0.4	0.15	Addition of sulphur for machinability, used for screws, gears etc. 416 Se replaces suplhur by selenium.
420	0.15 - 0.40	1	1	12.0 - 14.0	-	-	0.4	0.3	Dental and surgical instruments, cutlery.

3.1.3 Sample preparation/Metallography Method

This project is a laboratory-based experiment. Lots of steps will be conducted to complete this work. The equipment, apparatus and materials are ensured to be available in the UTP laboratory and can perform well.

Metallography is the process of preparing a metal surface to reveal microstructural information. A properly prepared metallographic sample can be aesthetically pleasing as well as scientifically informative. Sample can provide information about chemical composition, heat treatment, processing, phase diagram and etc. Ceramic and polymeric materials can be prepared using metallography techniques, ceramography, plastography or simply materialography.

The basic steps for proper metallography specimen preparation include; sectioning and cutting, mounting and grinding, polishing, etching, microscopic analysis and hardness testing.

a) Sectioning and cutting

The AISI420 Martensitic Stainless steel is still in plate form as received. It needs to be sectioned to the area of interest and for easier handling. Dimesnsion of 5mm x 15mm x 15mm is choosed.. The items were cut into specimen by abrasive cutting. Proper sectioning is required to minimize damage, which may alter the microstructure and produce false metallography characterization. During cutting process, correct selection of abrasive type, bonding and size as well as proper cutting speed, load and coolant are very important [24].

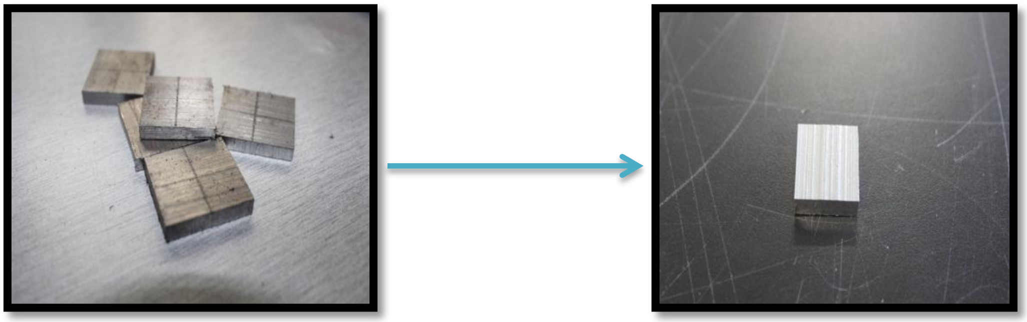


Figure 9: Large size of metal has been cut into desired dimension

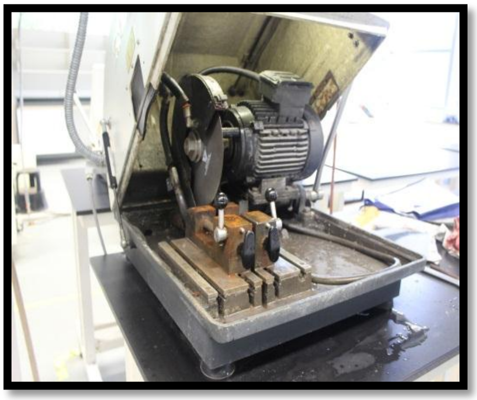


Figure 10: An abrasive cutter

b) Mounting

Mounting is done in order for ease handling of difficult shapes and size. Based on this project, the samples not go to be mounting before the nitriding process because bakelite or epoxy cannot stand with very high temperature. The specimen however will be mounting after nitriding process for ease handling for hardness testing and for microstructure analysis.

Figure 11: Mounting machine

Figure 12: Mounting specimen

c) Grinding

Grinding step is used in order minimize thickness of damaged layer from to the sectioning process. Grinding typically done using rotating disc covered with SiC paper and using water as lubricant. Initial abrasive size establishes a flat sample surface and remove damaged layer due to sectioning. Flatness of sample surface is ensured is maintained throughout the grinding steps. Before proceeding to the next grinding steps, the scratches from the entire current step is ensured are in single orientation.

Figure 13: Grinder

Figure 14 : Grinding process

d) Polishing

Since very small depth of field obtained from an optical microscope it is essential that the surface is flat, in fact it needs to be opticall flat, acting as z perfect mirror. Therefore, the specimen has to be polished. Polishing consist of rotating discs covered with soft cloth impregnated with micro-particles of diamond and lubricant. Polishing is done and have a scratch-free mirror like finish on the sample. The grade for the alumina powder is about 0.3 micron. During the process, light pressure is applied until the surface is free from scratches. Then, the specimen is examined by using microscope with 50 to 100 magnification to ensure it is free from scratches. This examined step must be done after the specimen is cleaned and dried [24].

e) Etching

Before nitriding process, the specimen did not go etching. Etching is carrying out basically to reveal the microstructure. Thus, it is carried out before analyze by using optical microscope. After polishing, the specimens were etching by nital solution. Since, the specimen is stainless steel, Nital solution is recommended. Nital is mixed of nitric acid and alcohol. The samples washed free from any adhering polishing compound and plunged into the etching solution and agitated vigorously for 1 minutes. Then, it is quickly transferred to running water on order to wash away the etchant as fast as possible. Then, it is examined by naked eye to check what extent etching has taken place. After that, the specimen is observed under the optical microscope and photomicrographs taken [24].

Figure 15: Etching solution

Figure 16 : Apply etching solution

3.1.4 Nitriding process

After cut, grind and polish, the samples were putted in alumina boat. The alumina boat will be placed at the center of the furnace. Steel wires were used to push the alumina boat to the center of the furnace. The furnace needs to be purged using nitrogen gas for 30 minutes to remove any gas inside the furnace from previous experiment. The heating rate was 5°C/min. The nitriding time for first phase is 4 hours and 10 hours was proceeding after that.

Furnace setting:

I. Cycle I, Segment I, ramp rate, target 1200°C,
II. Segmen II dwell, duration 4 hours
III. Segmen III Cooling target, 27°C room temperature
IV. Segmen IV, anti-dwell

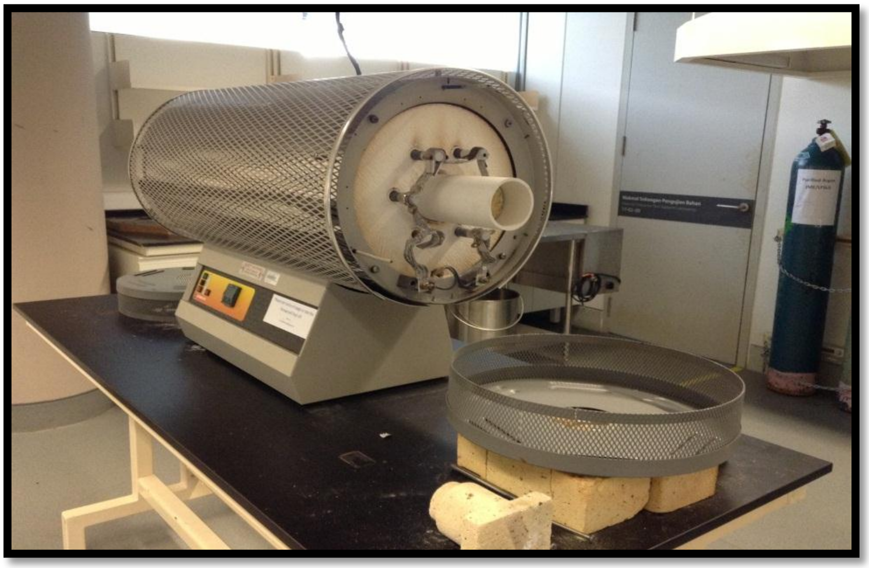


Figure 17 : Nitriding furnace

3.1.5 Cooling down process

After nitriding process, which means after the dwell time, the samples were let to cool down process. There two types of cooling down process that plan to carry out, which is slowly down to room temperature and the other one is by quenching. However, quenching is not suggested for the time being as it has some technical issues involved, so only cooling down to room temperature is proceeding.

3.2 Microstructure Examination

The purpose of microstructure examination is to examine the microstructure changes subsequent to nitriding process. This test was conducted using optical microscope and scanning electron microscope.

Figure 18: Microstructure examination by optical microscope

The chemical composition of the samples can be determined using energy dispersive X-ray spectroscopy that attached together with the scanning electron microscope. However, before conducting the microstructure examination, the samples need to be mounted, grinded, polished and etched. Mounting of specimen is required so that it is easier to handle during grinding and polishing.

For martensitic stainless steel, the etchant used is Nital solution. As further information, properly etchant will reveal better picture of grain boundary. Thus, sensitization can easily detect by formation of precipitate along the grain boundary. After swap the solution for about 1 minute, the specimen was washed using distilled water and alcohol. The specimen was dried and ready for microstructure examination.

3. 3 Vickers Hardness Testing

Hardness represents the resistance of material surface from abrasion, scratching and cutting, hardness after gives clear indication of strength. In all hardness tests, a define force is mechanically applied on the piece, varies in size and shape for different tests. Common indenter's are made of hardened steel or diamond.

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

For this project, hardness test will be carried out in order to measures the changes hardness before nitriding and after nitriding process. Then, these two will be compared to each other. In addition, the hardness for martensitic stainless steel with different nitriding temperature also will compare too. The load used is 300gf and the dwell time is 15 seconds.

Figure 19: Vickers Hardness Equipment

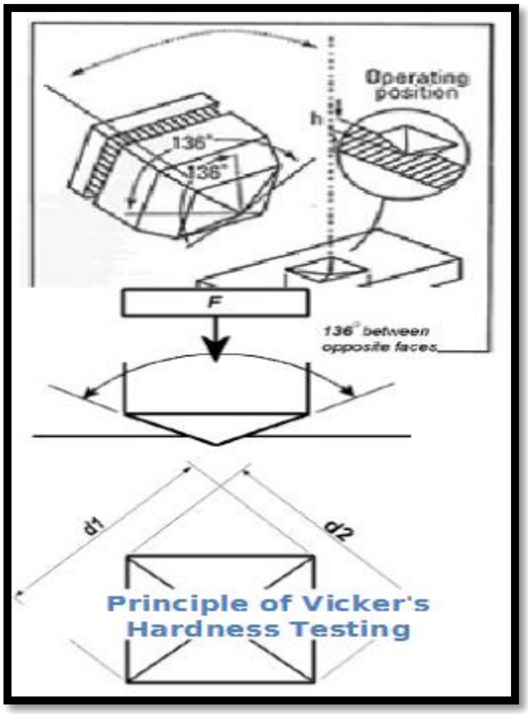


Figure 20: Principal of Vicker's Hardness Testing

3.4 FESEM with EDX

Field Emission Scanning Electron Microscopy is one of the most versatile and well known analytical techniques. Compare to conventional optical microscope, an electron microscope offers advantages including high magnification, large depth of focus, great resolution and ease of sample preparation and observation

Meanwhile, Energy Dispersion X-Ray or EDX are very useful tools widely used for chemical analysis. The intensity of backscattered electrons generated by electron bombardment can be correlated to the atomic number of the element within the sampling volume. Hence, qualitative elemental information can be revealed.

Thus, FESEM with X-Ray analysis is efficient, inexpensive, and non-destructive to surface analysis. It has wide ranges of application both in industry and research.

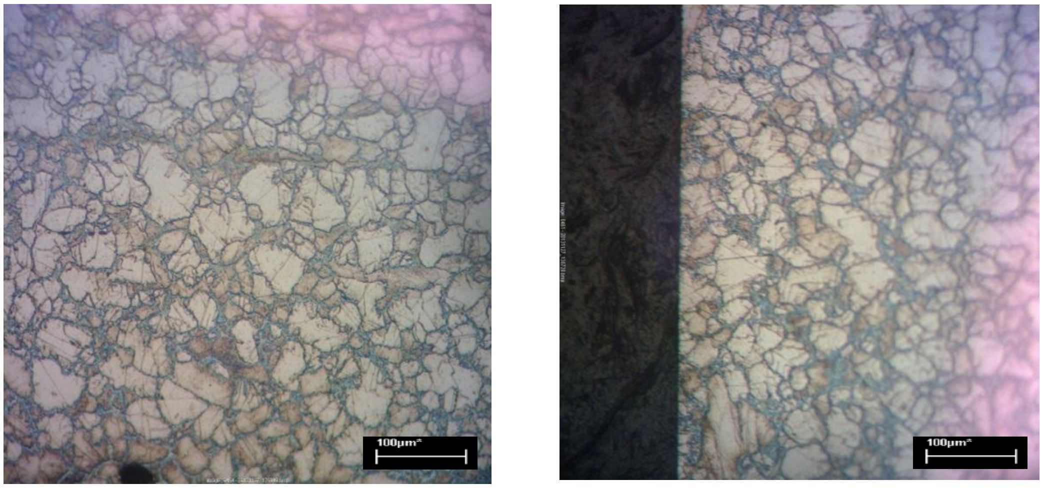
Figure 21 : SEM Machine

CHAPTER 4: RESULTS AND DISCUSSION

4.1. Analysis on untreated martensitic stainless steel

4.1.1 Microstructure

By using light optical microscope, we can see clearly the grain boundaries of the unnitrided sample the grains look small and compact each other. We also can see no precipitate along the grain boundaries. That's mean no carbide nitrides form yet.



(a) (b)

Figure 22: LOM images of unnitrided sample (a) center (b) edge

4.1.2 Hardness testing results

The hardness testing is by using Vickers. From the results, we can see that the hardness is higher near to the surface.

Table 3: HV values for unnitrided sample

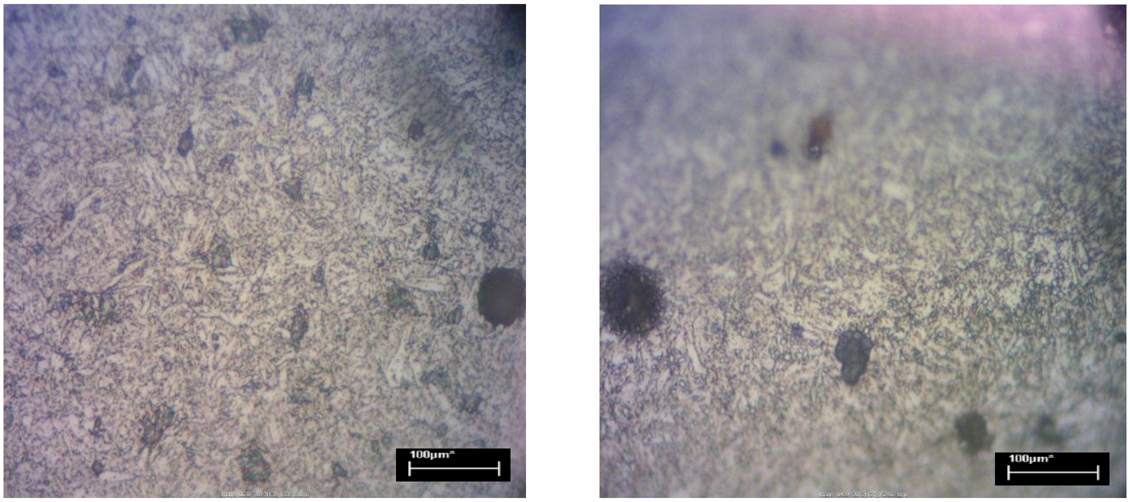
Distance from surface (mm)	**0.5**	**1**	**2**	**3**	**4.5**
Microhardness (HV)	294.5	289.9	266.5	291.3	295.4

4.2 Analysis on 4 hours nitriding duration

4.2.1 Microstructure

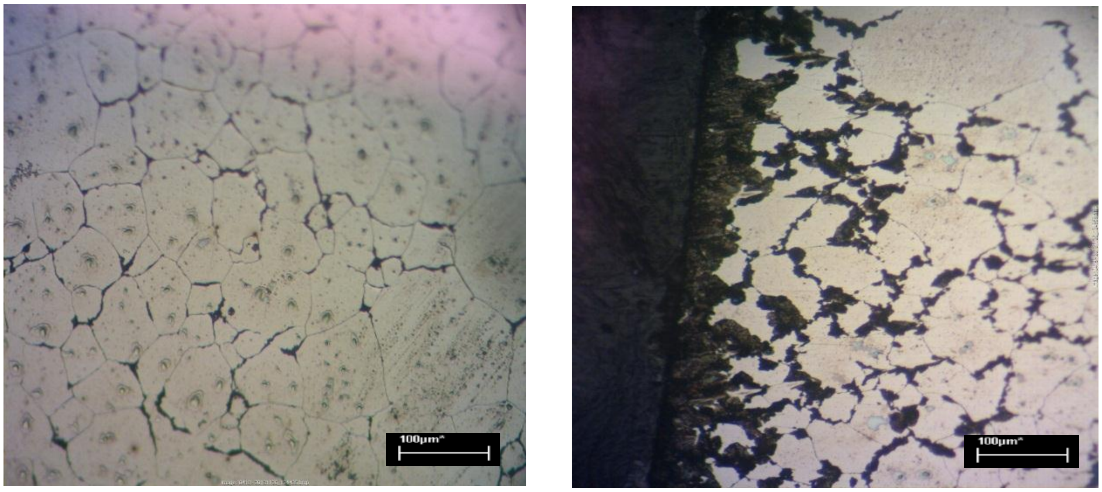
Image in Figure 23 are 600°C for 4 hours nitriding, meanwhile, in Figure 24, are the images for 1200°C. If we compare these both temperature, grain boundaries for 600°C look darker, small and compact to each other. However, for 1200°C, the grain boundaries are bigger and we can see clearly where the precipitation occur (intergranular corrosion).

Based on these image comparisons, higher temperature this is 1200°C having more sensitization occur. This is because, higher temperature such as 1200°C, during cooling down process, it will still have precipitation produced as they experienced in maximum sensitization range which is 500°C-800°C. Meanwhile, low temperature as 600°C will experience at the minimum and short.



(a) (b)

Figure 23: LOM images for 600°C (a) 100xmagnification, (b) 500xmagnification



(a) (b)

Figure 24: LOM images for 1200°C (a) center, (b) edge

4.2.2 Hardness testing results

From the table below, we can clearly conclude that surface of nitriding will having more sensitization, that's mean, where the most precipitate of chromium carbide depleted. More sensitization mean precipitate of chromium carbide occur, thus decrease corrosion resistance but hardness will increase. Generally, high temperature of nitriding will lead the bainite to form. The bainite that has been formed occupies more space than the original lattice.

Table 4: HV values for nitride sample (4 hours)

Distance from surface (mm)	**0.5**	**1**	**2**	**3**	**4.5**
Microhardness (HV) for 600° C	335.3	330.5	328.4	331.9	333
Microhardness (HV) for 1200° C	424	411	407.2	409.6	431

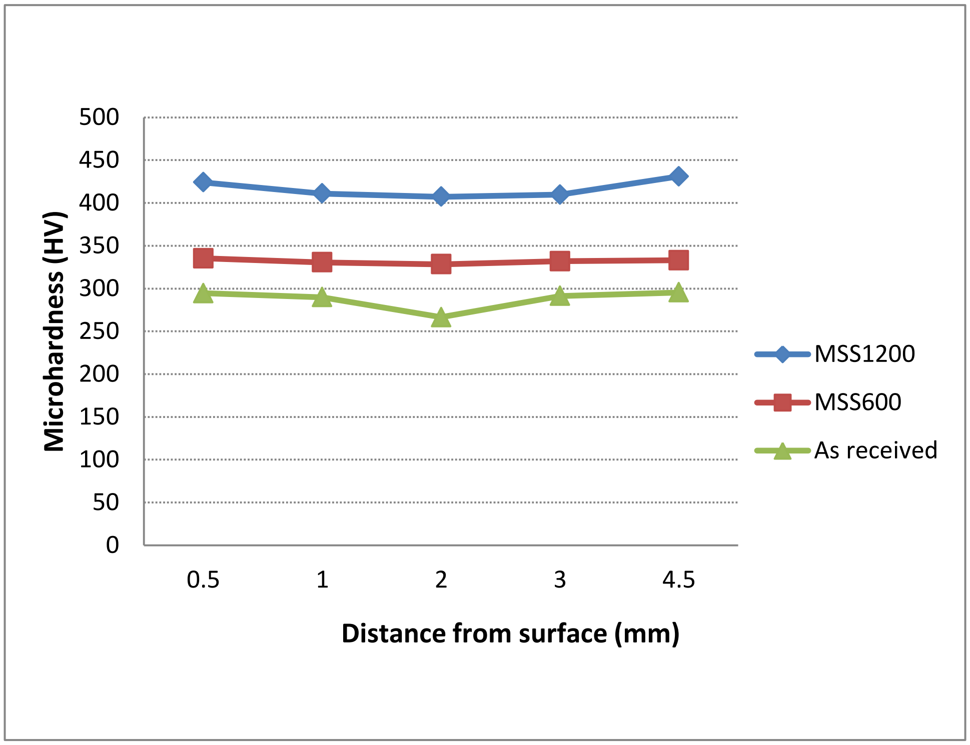


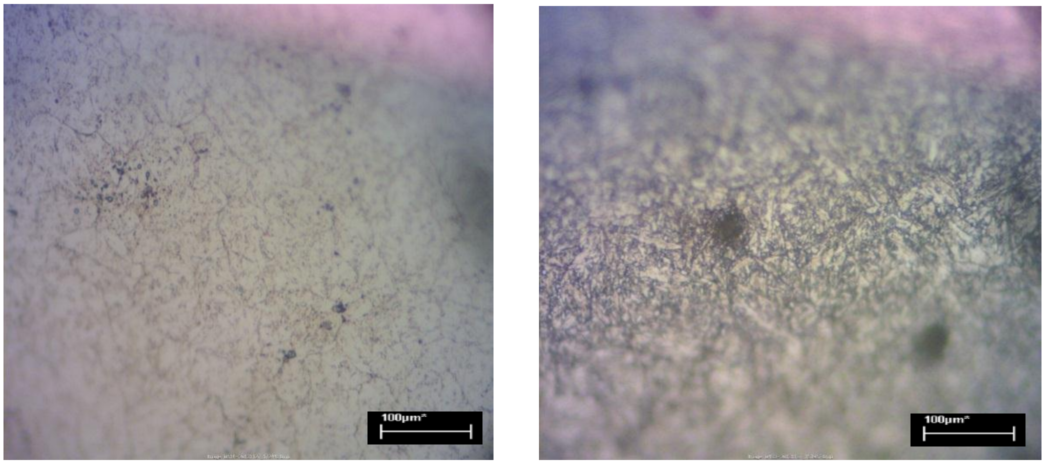
Figure 25: Graph of hardness for 4 hours nitriding

4.3 Analysis on 10 hours nitriding duration

4.3.1 Microstructure

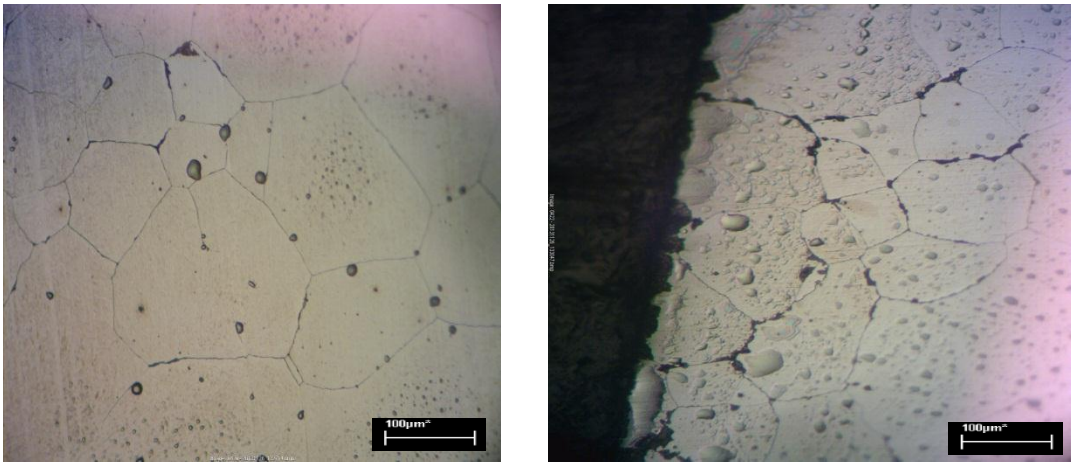
Same as 4 hours nitriding, image in Figure 26 are 500°C for 10 hours nitriding, meanwhile, in Figure 27, are the images for 1100°C. If we compare these both temperature, grain boundaries for 500°C look darker, small and compact to each other. However, for 1100°C, the grain boundaries are bigger and we can see clearly where the precipitation occur (intergranular corrosion).

Based on these image comparisons, higher temperature this is 1100°C having more sensitization occur. This is because, higher temperature such as 1100°C, during cooling down process, it will still have precipitation produced as they experienced in maximum sensitization range which is 500°C-800°C. Meanwhile, low temperature as 500°C will not.



(a) (b)

Figure 26: LOM images for 500°C (a) 100xmagnification, (b) 500xmagnification



(a) (b)

Figure 27: LOM images for 1100°C (a) center, (b) edge

4.3.2 Hardness testing results

Same goes with 4 hours, from the table below, we can clearly conclude that surface of nitriding will having more sensitization, that's mean, where the most precipitate of chromium carbide depleted. More sensitization mean precipitate of chromium carbide occur, thus decrease corrosion resistance but hardness will increase. Generally, high temperature of nitriding will lead the bainite to form. The bainite that has been formed occupies more space than the original lattice.

Table 5: HV values for nitrided sample (10 hours)

Distance from surface (mm)	**0.5**	**1**	**2**	**3**	**4.5**
Microhardness (HV) for 500° C	341	339.8	334.9	337.8	343.5
Microhardness (HV) for 1100° C	422.3	360.9	359.6	364	389.5

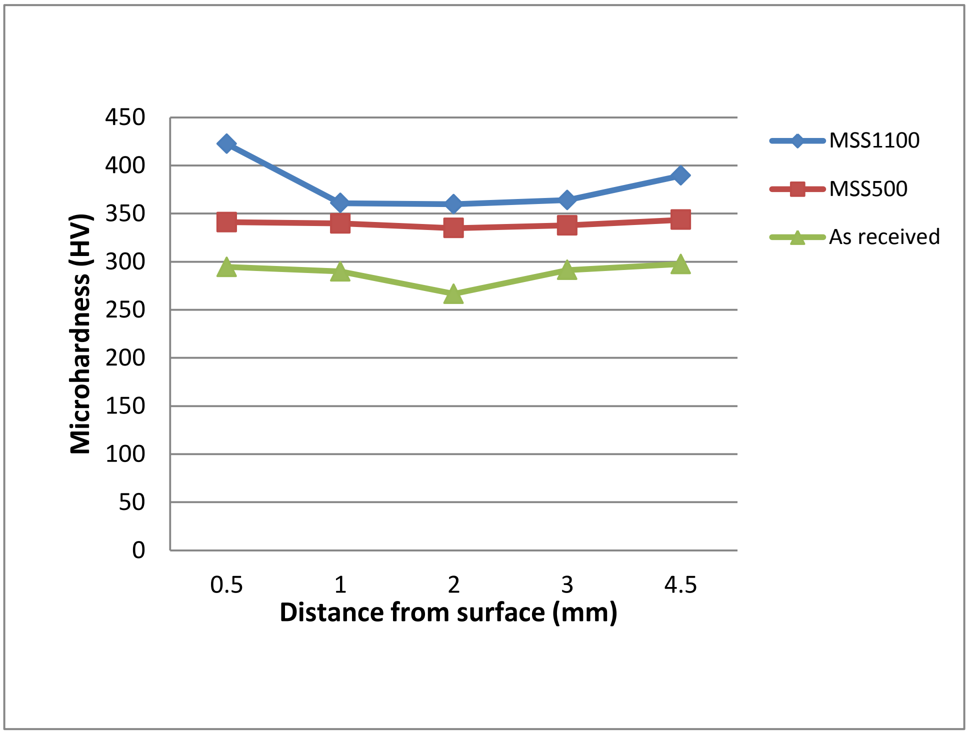


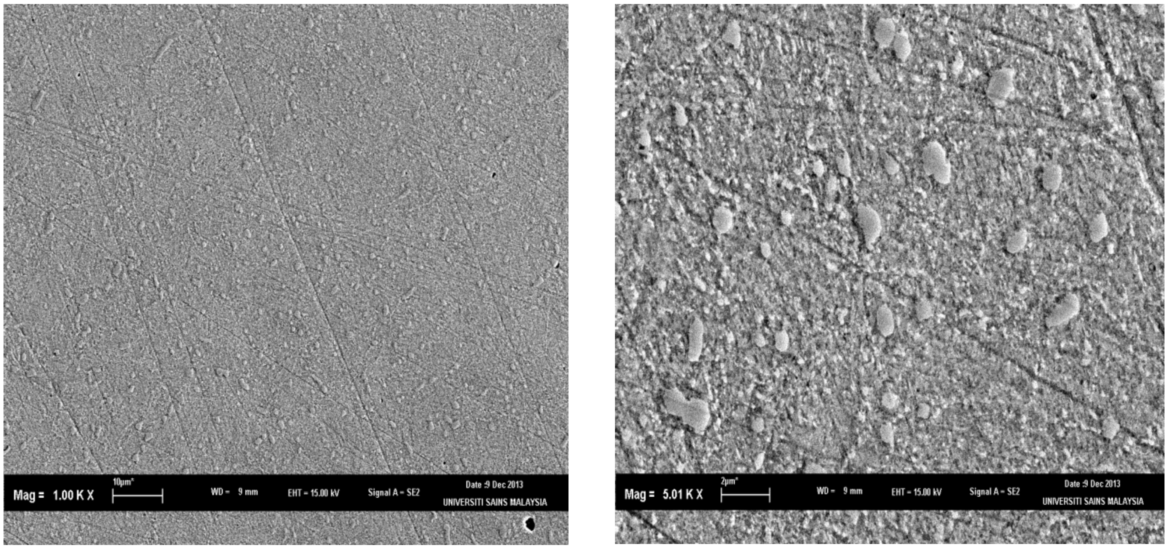
Figure 28: Graph of hardness for 10 hours nitriding

4.4 Analysis of SEM with EDX

The microstructure of all the samples were also analyzed using Scanning Electron Microscopy (SEM).

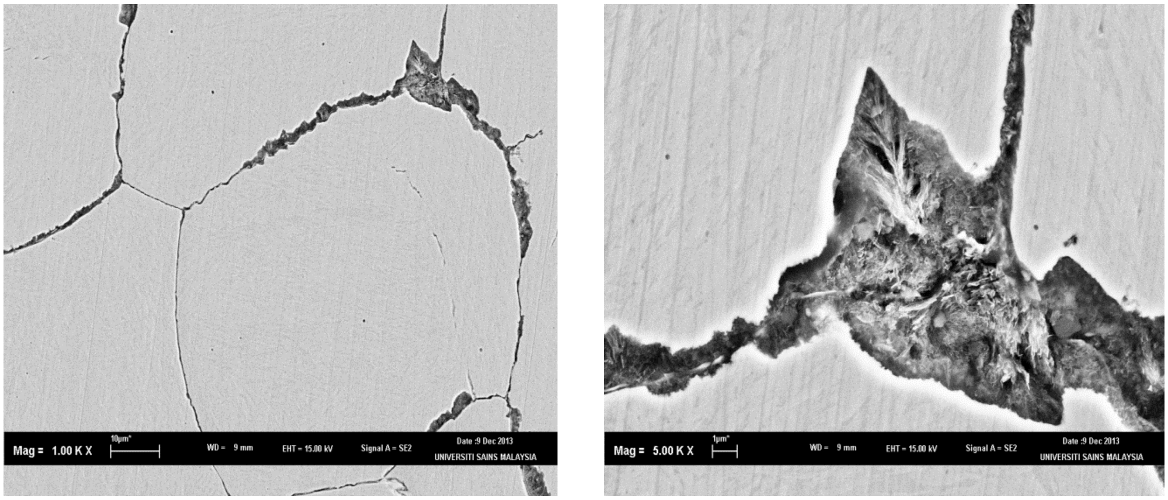
a. 4 Hours Nitriding

As per state before, temperature involve for this duration of nitriding is 600°C and 1200°C.



(a) (b)

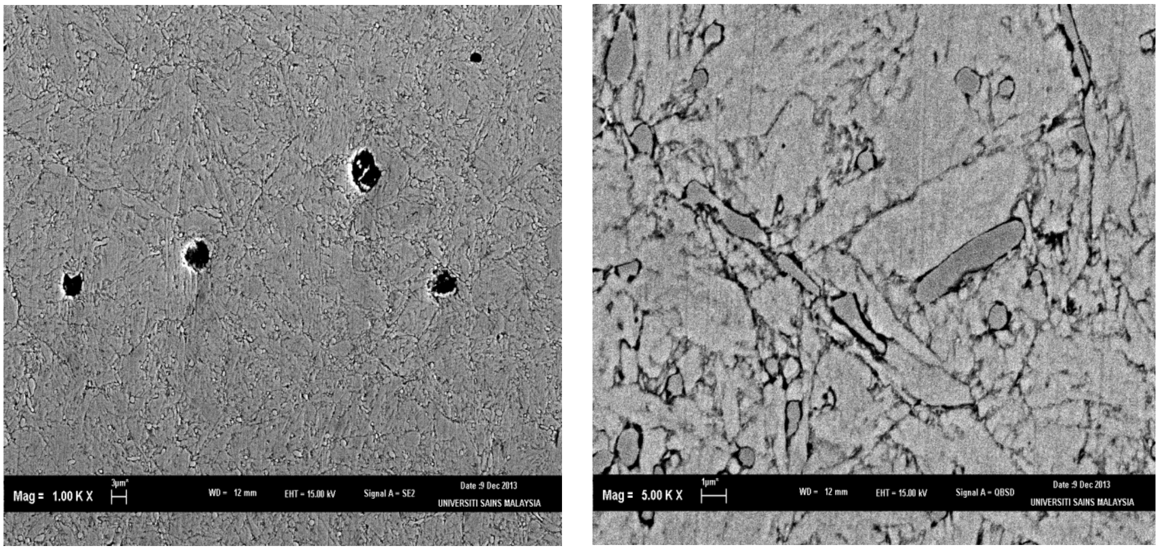
Figure 29: SEM images for 600°C (a) 1000xmagnification (b) 5000x magnification



(a) (b)

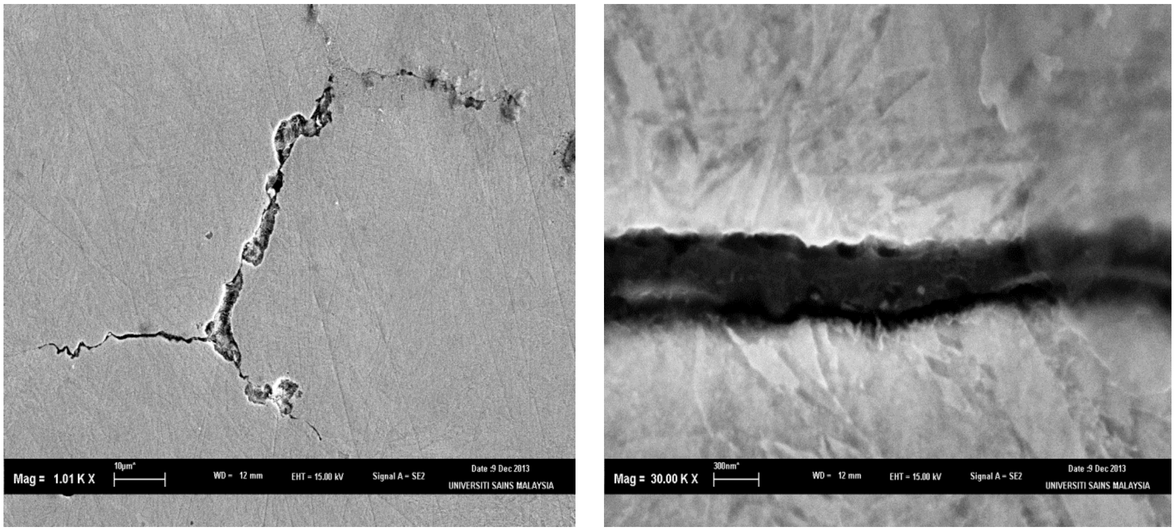
Figure 30: SEM images for 1200°C (a) 1000xmagnification (b) 5000x magnification

b. 10 Hours Nitriding



(a) (b)

Figure 31: SEM images for 500°C (a) 1000xmagnification (b) 5000x magnification



(a) (b)

Figure 32: SEM images for 1100°C (a) 1000xmagnification (b) 30000x magnification

EDX

Energy Dispersive X-Ray Analysis (EDX) is an x-ray technique used to identify the elemental composition of a specimen. The data generated by EDX analysis consist of spectra showing peaks corresponding to the elements making up the true composition of the sample being analyzed.

a. 4 Hours Nitriding

600°C

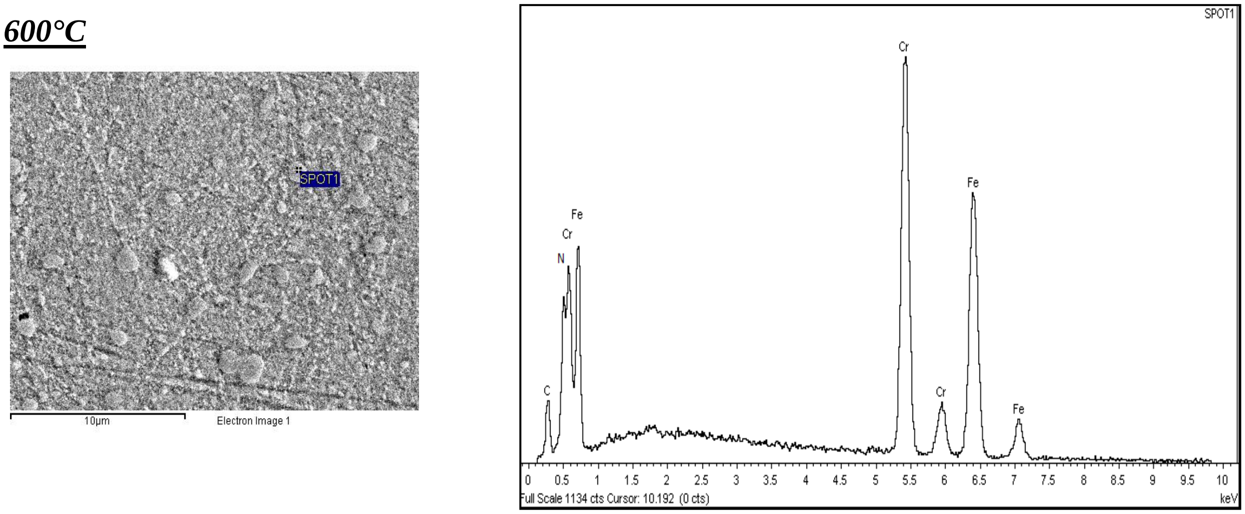


Figure 33: Image and qualitative results of nitride samples at 600°C.

1200°C

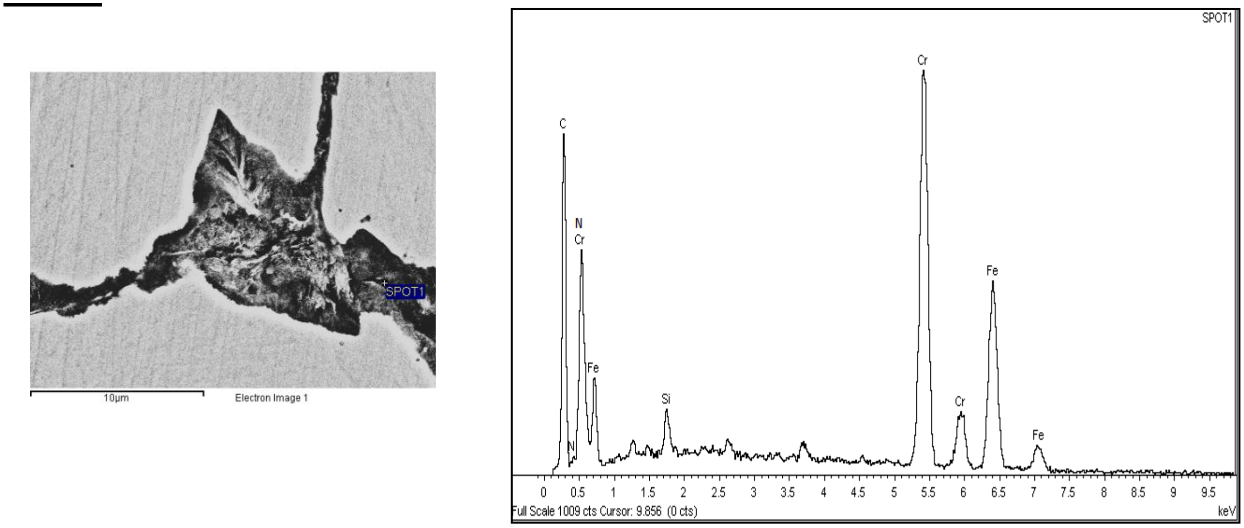


Figure 34: Image and qualitative results of nitride samples at 1200°C.

b. 10 Hours Nitriding

500°C

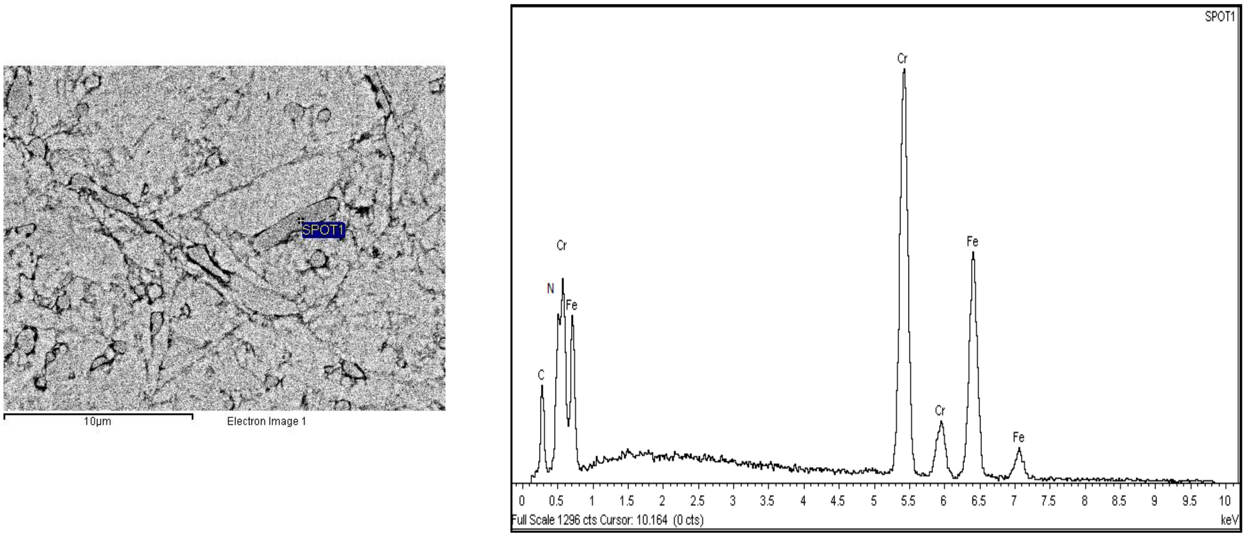


Figure 35: Image and qualitative results of nitride samples at 500°C.

1100°C

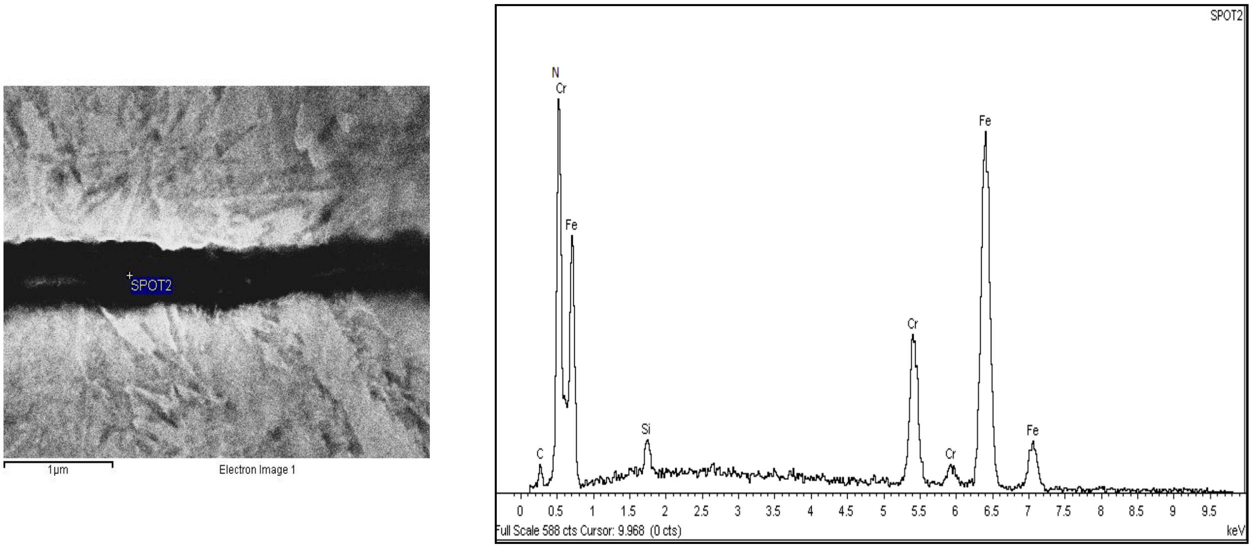


Figure 36: Image and qualitative results of nitride samples at 1100°C.

CHAPTER 5: CONCLUSION AND RECOMMENDATION

5.1 Conclusion

As for conclusion, we can conclude that, at 4 hours nitriding, the high temperature is having more sensitization compare to low temperature. This is because, during cooling down process for high temperature of nitriding, they will go through all the temperature until they reach at room temperature. Thus, they will experience the maximum sensitization temperature for martensitic stainless steel which is 500°C to 800°C. Compare to low temperature, they will have experienced the sensitization temperature range very little, thus, the sensitization mostly didn’t occur. So basically, low temperature of nitriding will have better corrosion resistance compare to high temperature. However, it will have less hardness compare to high temperature as proved in the hardness test result.

Next, for 10 hours nitriding, the same conclusion occur, where low temperature is less sensitization compare to high temperature of nitriding. This is because, during cooling down process for high temperature of nitriding, they will go through all the temperature until they reach at room temperature. Thus, they will experience the maximum sensitization temperature for martensitic stainless steel which is 500°C to 800°C. Compare to low temperature, they will have experienced the sensitization temperature range very little, thus, the sensitization mostly didn’t occur. So basically, high temperature of nitriding will have less corrosion resistance compare to low temperature. However, it will have excellence hardness compare to low temperature as proved in hardness test result.

5.2 Recommendation

There are some research regarding nitriding that state the sensitization of high temperature of martensitic stainless steel can be avoid by rapid cooling. This is because; rapid cooling or quenching will avoid them to face the sensitization temperature range. Thus, they will have better corrosion resistance and have a good hardness. The cooling rate used in quenching depends on the method of cooling and the size of the metal. Uniform cooling is important to prevent distortion. Typically, steel components are quenched in oil or water. During manufacturing, by varying the rate of cooling (quenching) of the metal, grain size and grain patterns are controlled. Grain characteristics are controlled to produce different levels of hardness and tensile strength. Generally, the faster a metal is cooled, the smaller the grain sizes will be. This will make the metal harder. Besides that, some manufacturer agreed that, another remedy is to use stabilized stainless steel based metal and filter materials which contain element that react with carbon, leaving all the chromium in solution to provide corrosion resistance. All these method can be used to maintain the corrosion resistance and increase the hardness.

5.3 Gantt Chart

Table 1: Process plan for FYP 2

WEEK (FYP 2)	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1. Preparation of samples (specimen) i.e buying, sectioning, cutting, polishing, grounding.	■	■	*											
2. Progress Report					■	■								
3. Examination of nitriding chamber.				■										
4. Optical Microscopy of unnitrided martensitic stainless steel		■	■	*										
5. Hardness testing for unnitrided martensitic stainless steel		■	■	*										
6. Nitriding process (Temp. 1200°C, 1100°C, 600°C, 500°C)					■	■	■	*						
7. SEM (with EDX) in total is 5 samples including unnitrided.								■	■	■	■	*		
8. Hardness testing for nitride martensitic stainless steel (4 samples)									■	*				
9. Optical Microstructure for nitride martensitic stainless steel (4 samples)									■	*				
10. Documentation process, viva, poster, presentation, dissertation													■	*

(*) key milestone

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