Study of the Physical and Mechanical Properties of Sintered Nitrided Austenitic Stainless Steel Powder

by

Noor Shahilia Binti Ishak

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

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CERTIFICATION OF APPROVAL

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Approved by,

_____

(AP. DR. PATTHI HUSSAIN)

UNIVERSITI TEKNOLOGI PETRONAS

TRONOH, PERAK

DECEMBER 2010

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.

_____

(NOOR SHAHILIA BINTI ISHAK)

ABSTRACT

This project presents the work on high temperature gas nitriding of austenitic stainless steel powder. Nitriding is one of the methods used in surface engineering to increase the hardness and wear resistance of austenitic stainless steel. Normally nitriding is done at bulk of steel but for this project different technique is chosen where nitriding is done on the powder of the austenitic stainless steel. The problem is when nitriding bulk austenitic stainless steel; the solid state diffusion will take place only at low case depth. However by nitriding the powder of austenitic stainless steel, the nitrogen content will be extended to the core of the steel. In the present work, the austenitic stainless steel powders were nitrided in Carbolite horizontal tube furnace in nitrogen atmosphere. Then the nitrided powders were compacted by using Auto Pelletizer machine and sintered in the furnace. Green and sintered densities, metallographic study and assessment of the samples hardness were performed to examine the result of the treatment. Green and sintered densities were reduced while the hardness of the samples increased with rises of nitriding time as well as nitriding temperature. Highest value of hardness: 675HV is achieved from sample nitrided at 1200 °C for 3 hours. Diffusion of nitrogen content leads to higher hardness. However, the microstructures of the nitrided samples show that pores were present which results in reduction of sintered densities.

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CHAPTER 1

INTRODUCTION

1.1 Background

Austenitic stainless steels are largely used in many industrial and biomedical applications where the need of resistance corrosion is required. However these types of steels are poor in hardness characteristic. Thus, many variety of processing techniques have been attempted to improve the surface hardness through method of surface treatment, which include nitriding process.

Nitriding is one of the techniques used in surface engineering to increase surface hardness and wear resistance of austenitic stainless steel [1]. The objective of any nitriding process is to create a hard layer on the surface and to retain corrosion resistance [5]. For this project, the process will be carried out by exposing the powder in pure nitrogen gas at high temperature for certain hours. The nitrogen then will be extended to the core of the steel and improve the hardness and wear resistance of the steel.

In this project, an experiment is designed to investigate the influence of nitriding process on the physical and mechanical properties of austenitic stainless steel. The influence on those properties can be investigated through optical microscopy, micro hardness measurements, scanning electron microscope (SEM) and X-ray diffraction analysis.

1.2 Problem Statement

In practical applications, normally nitriding process is employed for austenitic stainless steel bulk. Due to the limited speed of diffusion, especially in the iron nitride phases, a massive bulk piece of iron cannot be transformed into the pure nitride in practicable periods of time. The solid state diffusion will take place only at low case depth. However by nitriding the powder of austenitic stainless steel, the nitrogen content will be extended to the core of the steel. Thus the properties of the austenitic stainless steel can be further improved.

Diffusion takes place
at certain depth

(a) Steel bulk

Nitrogen extended to
the core of steel

(b) Steel bulk: nitriding powder
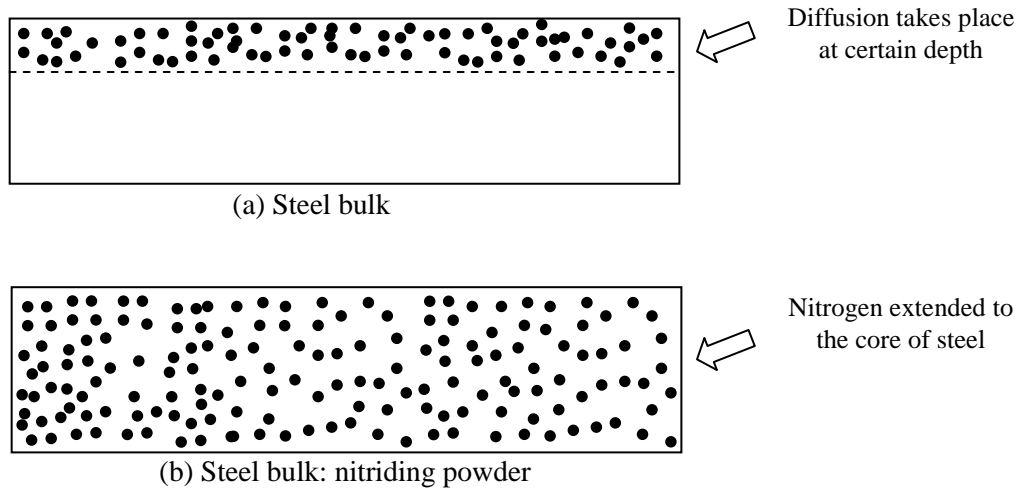
Figure 1.1: The basic illustration of nitriding process (a) performs on steel bulk (b) performs on the powder and then compacted

1.3 Objective

- To fabricate nitrided austenitic stainless steel samples by using powder metallurgy process.
- To investigate the influence of nitriding process towards physical and mechanical properties of austenitic stainless steel

1.4 Scope of Study

This project is mainly in the form of laboratory experiments. The experiment will be conducted by performing nitriding process on the austenitic stainless steel powder. Nitriding is one of the techniques used to improve the surface hardness of metals.

After nitriding process is done, analysis process will be carried out to investigate the physical and mechanical properties of the specimens throughout optical microscopy, micro hardness measurements, scanning electron microscope (SEM) and X-ray diffraction analysis.

The scope of this project will cover mechanical and physical properties describe as follows:

1) Density of the sample
2) Effect of nitriding on the microhardness
3) Microstructure of the nitrided layer

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 / THEORY

2.1 Powder Metallurgy

2.1.1 Principle of powder metallurgy

According to Lamar [16], powder technology is the science for the manufacture of parts from metal powders by compaction and heating that creates a homogeneous mass. Heating is executed in a furnace and is called sintering. The temperature at which sintering is performed is lower than the melting point of the powdered material. Sintering consists of diffusion in solid state by which particles of compacted powder are bonded together. This is the basic principle of powder technology.

2.1.2 Processes of powder metallurgy

The processes involved in powder metallurgy are the following:

Blending and Mixing: This is carried out to achieve uniformity of the product manufactured. Distribution of properly sized particles is attained by mixing elementary powder with alloy powders to obtain a homogeneous mixture. Lubricants are also mixed with powders to minimize the wear of dies and reduce friction between the surfaces of dies and particles of powder during compaction. Mixing time will depend upon the results desired, and overmixing should be prevented, or otherwise the size of particles will be decreased, and they will be hardened.

Pressing: The cavity of the die is filled with a specified quantity of blended powder, necessary pressure is applied, and then the compacted part is ejected. Pressing is performed at room temperature, while the pressure is dependent upon the material, properties of the powder used, and the density required of the compaction. Friction between the powder and the wall of the die opposes application of a proper pressure that decreases with depth and thus causes uneven density in the compact. Thus the ratio of length and diameter is kept low to prevent substantial variations in density.

Sintering: Changes occur during sintering, including changes in size, configuration, and the nature of pores. Commonly used atmospheres for sintering are hydrogen, carbon monoxide, and ammonia. Sintering operation ensures that powder particles are bonded strongly and that better alloying is achieved.
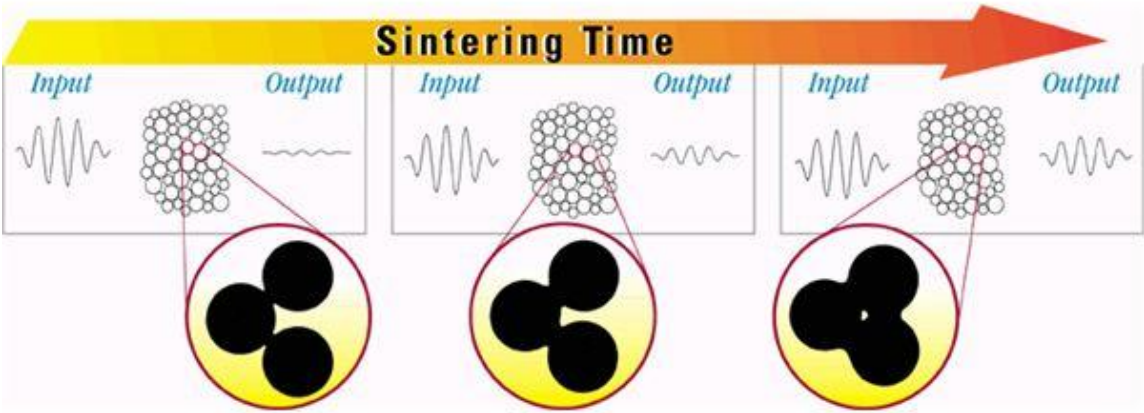
Figure 2.1: Illustration of sintering process [16]

2.2 Powder Production Techniques

According to Metal Powder Industries Federation website, the first step in the overall PM process is making metal powders. There are three main processes used to manufacture metal powders: atomization, mechanical comminution, and chemical.

2.2.1 Atomization

Atomization is the process used commercially to produce the largest tonnage of metal powders. In water and gas atomization (Figures 2.2 and 2.3, respectively) the raw material is melted then the liquid metal is broken into individual particles. To accomplish this, the melt stock, in the form of elemental, multi-element metallic alloys, and/or high quality scrap, is melted in an induction, arc, or other type of furnace. After the bath is molten and homogenous, it is transferred to a tundish which is a reservoir used to supply a constant, controlled flow of metal into the atomizing chamber. As the metal stream exits the tundish, it is struck by a high velocity stream of the atomizing medium (water, air, or an inert gas). The molten metal stream is disintegrated into fine droplets which solidify during their fall through the atomizing tank. Particles are collected at the bottom of the tank. Alternatively, centrifugal force can be used to break up the liquid as it is removed from the periphery of a rotating electrode or spinning disk/cup (Figure 2.4) [15].
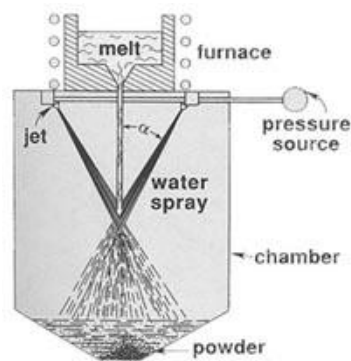
Figure 2.2: Water atomization process [15]
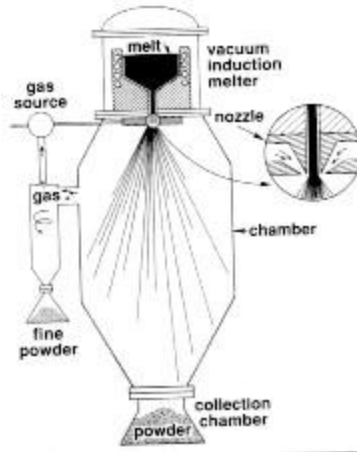
Figure 2.3: Vertical gas atomizer [15]
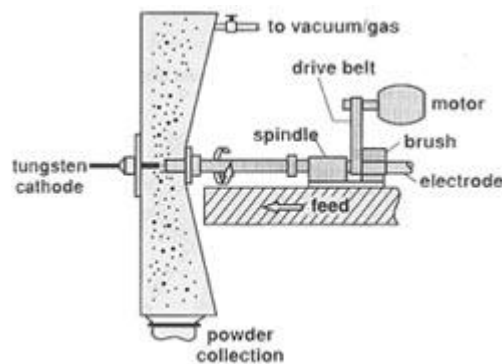
Figure 2.4: Centrifugal atomization by the rotating electrode process [15]

Additional alloying can be performed in the liquid metal bath after the original charge has become molten. Also, the bath can be protected from oxidation by maintaining an inert gas atmosphere as a cover over the liquid metal. Alternatively, the top of the furnace can be enclosed in a vacuum chamber. The furnace type and degree of protection are determined by the chemical composition of the bath and the tendency of the metal to oxidize [15].

2.2.2 Mechanical Comminution

Mechanical comminution methods, such as milling, lathe turning, and chipping, comprise the second powder manufacturing group. Milling (Figure 2.5) is the primary method for reducing the size of large particles and particle agglomerates. Ball, hammer, vibratory, attrition, and tumbler mills are some of the commercially available comminuting devices. During milling, forces act on the feed metal to modify the resultant particles. Impact, attrition, shear, and compression all influence powder particle size and shape. Lathe turning is a technique used for materials such as magnesium for creating coarse particles from billets. These particles are reduced in size subsequently by milling or grinding [15].
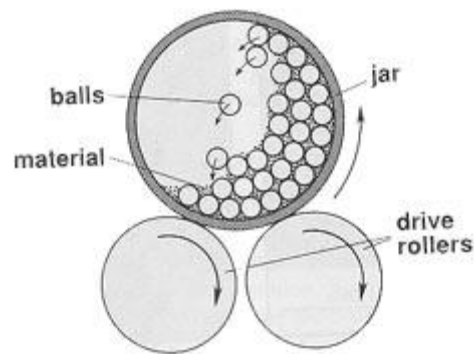
Figure 2.5: Particle size reduction by jar milling-schematic [15]

2.2.3 Chemical Method

Chemical methods constitute the final manufacturing group. Included are the production of metal powders by the reduction of metallic oxides, precipitation from solution (hydrometallurgy), and thermal decomposition (carbonyl).

Materials used for subsequent oxide reduction are iron ore (magnetite), mill scale, and metallic materials oxidized for oxide reduction. In the case of iron ore, a refractory tube is filled with a combination of iron ore and a mix consisting of coal, coke, and limestone. The tube is then passed through a kiln at ~1200°C. The mix decomposes,

producing a reducing atmosphere inside the tube and the magnetite ore is converted to metallic Fe.

Mill scale and oxidized metallic products are annealed to reduce both the oxygen and carbon contents. FeO, Fe_2O_3, or Fe_3O_4, are reduced in the presence of a reducing atmosphere. In addition, the carbon within the particles is removed via the formation of CO and CO_2.

Hydrometallurgical manufacturing and thermal decomposition comprise alternative chemical methods. Precipitation of a metal from a solution can be accomplished by using electrolysis, cementation, or chemical reduction. This is done either from a solution containing an ore, or by means of precipitation of a metal hydroxide followed by heating which results in decomposition and reduction.

Electolytic deposition is often categorized as a fourth mode of powder fabrication; here we include it as a chemical method. It involves the precipitation of a metallic element at the cathode of an electrolytic cell (Figure 2.6). The most common application is in the production of copper powder.
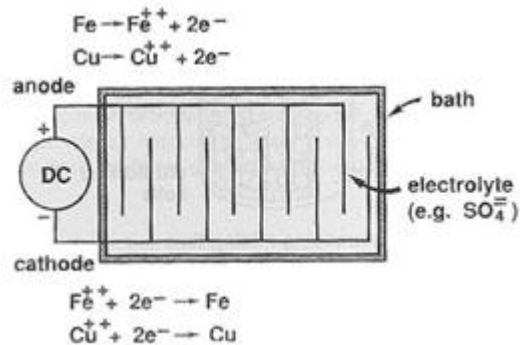
Figure 2.6: Electrolytic cell operation for deposition of powder-schematic [15]

These manufacturing techniques result in powders with different characteristics and appearance, for use in specific applications (Figure 2.7). Water atomization usually produces irregularly shaped particles free of internal porosity, whereas the shape of gas atomized particles is spherical, also without internal porosity. Metal powders produced

by oxide reduction are irregular in shape, have a large surface area, and usually contain a substantial amount of internal porosity. Particles fabricated by milling or other mechanical methods exhibit a spectrum of shapes, depending on the relative ductility or brittleness of the feed material. Ductile powders are generally flat with a high aspect ratio whereas brittle particles can be angular and regularly shaped. The milling of agglomerated particles can cause the agglomerates to break up, sometimes with little effect on the shape of the individual particles. Powder particles produced chemically can have shapes ranging from spherical to angular. Electrolytic powders are of high purity with a dendritic morphology [15].
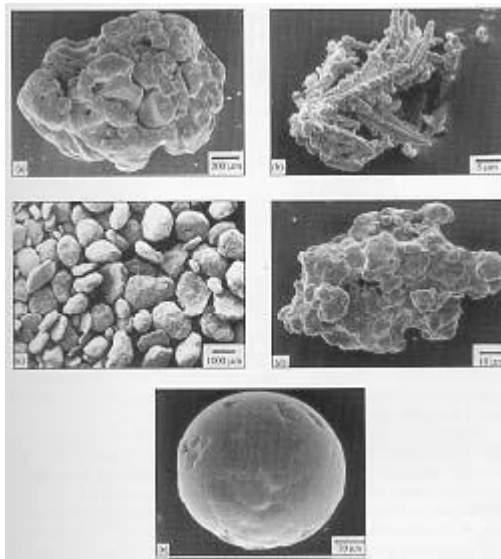
Figure 2.7: Representative metal powders: (a) chemical; sponge iron-reduced ore; (b) electolytic: copper; (c) mechanical: milled aluminum powder containing disperoids (17); (d) water atomization : iron; (e) gas atomization: nickel-base hardfacing Alloy [15]

Production of prealloyed powders is possible with the atomization process. The chemical composition of the feed material and alloy additions to the molten bath allow for the formulation of an almost unlimited combination of alloy compositions [15].

2.3 Austenitic Stainless Steel

This project is focusing on austenitic stainless steel rather than other types of steel such as ferritic stainless steel. The reason for choosing this type of steel is because it is widely uses in many industrial fields. Thus the physical and mechanical improvement will give advantages to those industries which really use this type of steel as material of their product.

 Austenitic stainless steels have a widespread use in many industrial fields owing to their excellent resistance due to the formation of passive surface film, but the low hardness and poor tribological properties of these materials can shorten the life of materials if subjected also to wear. Wear resistance of steel components is usually improved by using surface engineering techniques, which modify the characteristics of the surface layers by means either coating processes, like physical vapour deposition, chemical vapour deposition or plasma spray, or diffusion processes, like carburizing or nitriding [7].

Austenitic stainless steels of the AISI 304 or AISI 316 type are often used as construction materials in the chemical- and food-processing industries. Whereas the corrosion resistance of these materials is excellent, their hardness and wear resistance are relatively low [2].

Austenitic stainless steels such as AISI 304 are preferred choice for many industrial and biomedical applications where high corrosion resistance is required. However, these types of steels lack sufficient hardness to provide acceptable wear resistance [6].

According to T. Sourmail, specialist austenitic stainless steels are made with up to 0.4 wt% nitrogen when prepared at ambient pressure, and up to 1 wt% nitrogen using high-pressure melting techniques. The prime reason for adding nitrogen is that it is a very effective solid-solution strengthener. Not only do the misfitting nitrogen atoms interfere statically with moving dislocations, but there is also a drag due to nitrogen atoms being

carried along with the dislocations as they move through the lattice. The strength of such alloys makes them suitable for niche applications such as power generator retaining rings, high-strength bolts and superconducting magnet housings [11]. Figure 2.8 below shows the example of product produced by austenitic stainless steel.

Figure 2.8: Austenitic stainless steel cups [11]

2.4 High Temperature Gas Nitriding

According to Nakanishi, we attempted to improve the mechanical properties and corrosion resistance of commercial 316L austenitic stainless steel plates by means of "solution nitriding" (nitrogen absorption treatment or high temperature gas nitriding (HTGN) [9]), which is one of chemical heat treatments to add nitrogen into stainless steel. It is well known that the nitrogen addition to austenitic stainless steel has many advantages including:

1. the tensile strength of the steels drastically increase without reducing the ductility too much
2. the transformation to martensitic structure (generation of magnetism) can be reduced
3. corrosion resistance, especially pitting corrosion resistance is improved
4. nitrogen is considered to be harmless to the human body

Solution nitriding is a simple and powerful technique to obtain high nitrogen stainless steel without requiring any special equipment [4].
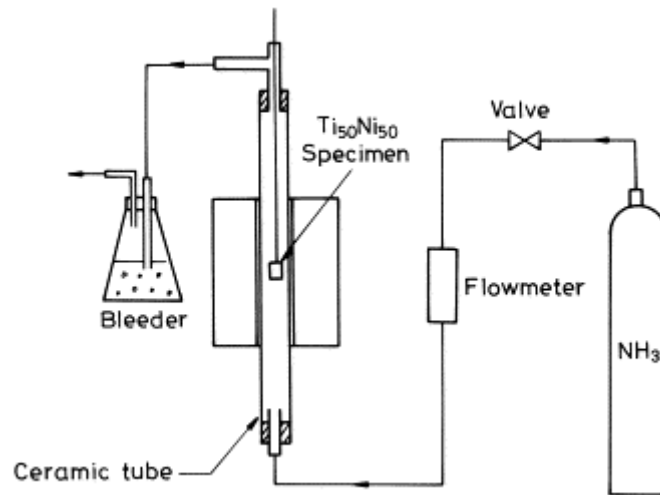
Figure 2.9: Schematic illustration of the gas nitriding equipment [4]

A new high temperature gas nitriding (HTGN) treatment that allows obtaining high nitrogen cases, about 1 mm in depth, on stainless steels was developed. In this treatment, high nitrogen contents, $\sim$0.5–1.0 wt.%, are dissolved in austenite, in the 1273–1473 K temperature range. Berns et al. showed that when HTGN is applied to austenitic–ferritic, martensitic and austenitic stainless steels, their cavitation erosion (CE) resistance is considerably increased. This new HTGN treatment is different from conventional nitriding, usually performed between $\sim$750 and 850 K, in which intense chromium nitride precipitation occurs, greatly increasing the hardness, but impairing the corrosion resistance of stainless steels. Additionally, quite different from conventional gas nitriding, where ammonia–hydrogen (NH_3–H_2) gas mixtures are used, the HTGN treatment is performed in still (N_2) gas atmosphere which is neither explosive nor toxic. As gas flux and gas control equipments are not necessary, energy losses and costs are diminished [12].

The growth rate of the nitrided layer can be increased by increasing the nitriding temperature, which is the basis for development of the solution nitriding or high temperature gas nitriding process for stainless steel. The process is carried out at

temperatures above 1050°C in pure nitrogen normally only for few hours and a hardened case layer over 300µm can be provided with a gradual nitrogen concentration, and hence hardness, profile form surface to inner parts of the substrate. Because the nitrogen solubility in the γ-phase decreases at higher nitriding temperatures, nitrogen pressure higher than normal atmospheric pressure is often used in the nitriding process to compensate for the decreased nitrogen solubility [6].

2.5 Powder Nitriding

Instead of nitriding austenitic stainless steel bulk, this project will go in other ways around by nitriding powder of austenitic stainless steel. When nitriding powder of austenitic stainless steel, the nitrogen will extend to the core of the steel as compare if we nitriding its bulk, the diffusion only happen at the low case depth.

According to Nobuyuki Nakamura et. al, the results obtained from his research as follows:

1) Grain boundaries within powder particles play a role of free path for nitrogen diffusion. So the process will proceeds not only from the particle surface but also from grain boundaries within each powder particle.

2) Nitriding rate greatly depends on the grain size within powder particles, although it is dependent on particle size itself when particles are of single crystal. As the grain size within powder particles become smaller, nitriding rate is increased [10].

CHAPTER 3

METHODOLOGY

3.1 Project Planning

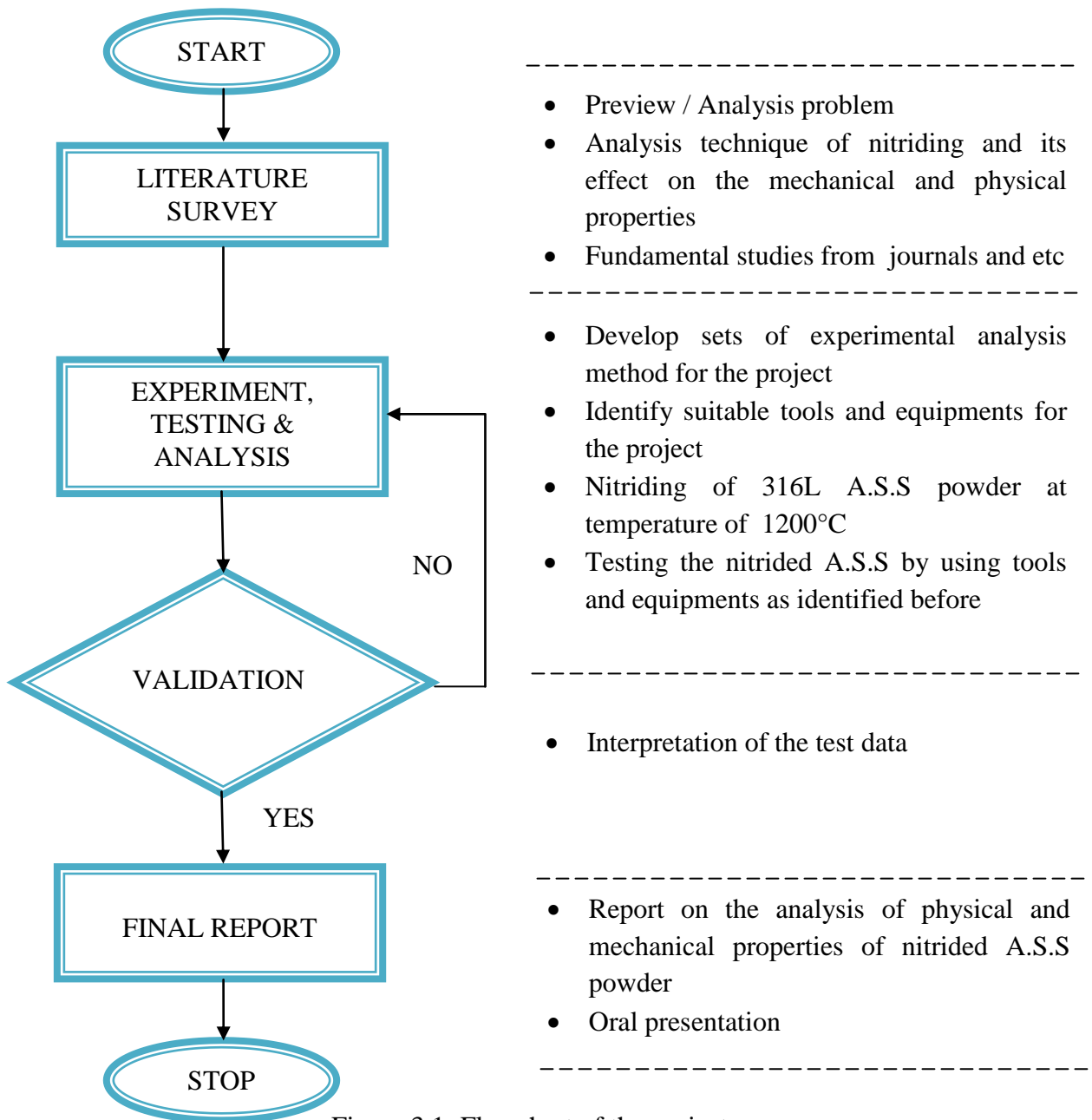In order to conduct the research project, the flow of methodology is designed as follow:

Figure 3.1: Flowchart of the project

Throughout the stages of research, the listed steps shown in the flowchart as in Figure 3.1 were followed accordingly. Details of the flow are described in Gantt chart shown in next section of Figures 3.2 (a) and 3.2 (b).
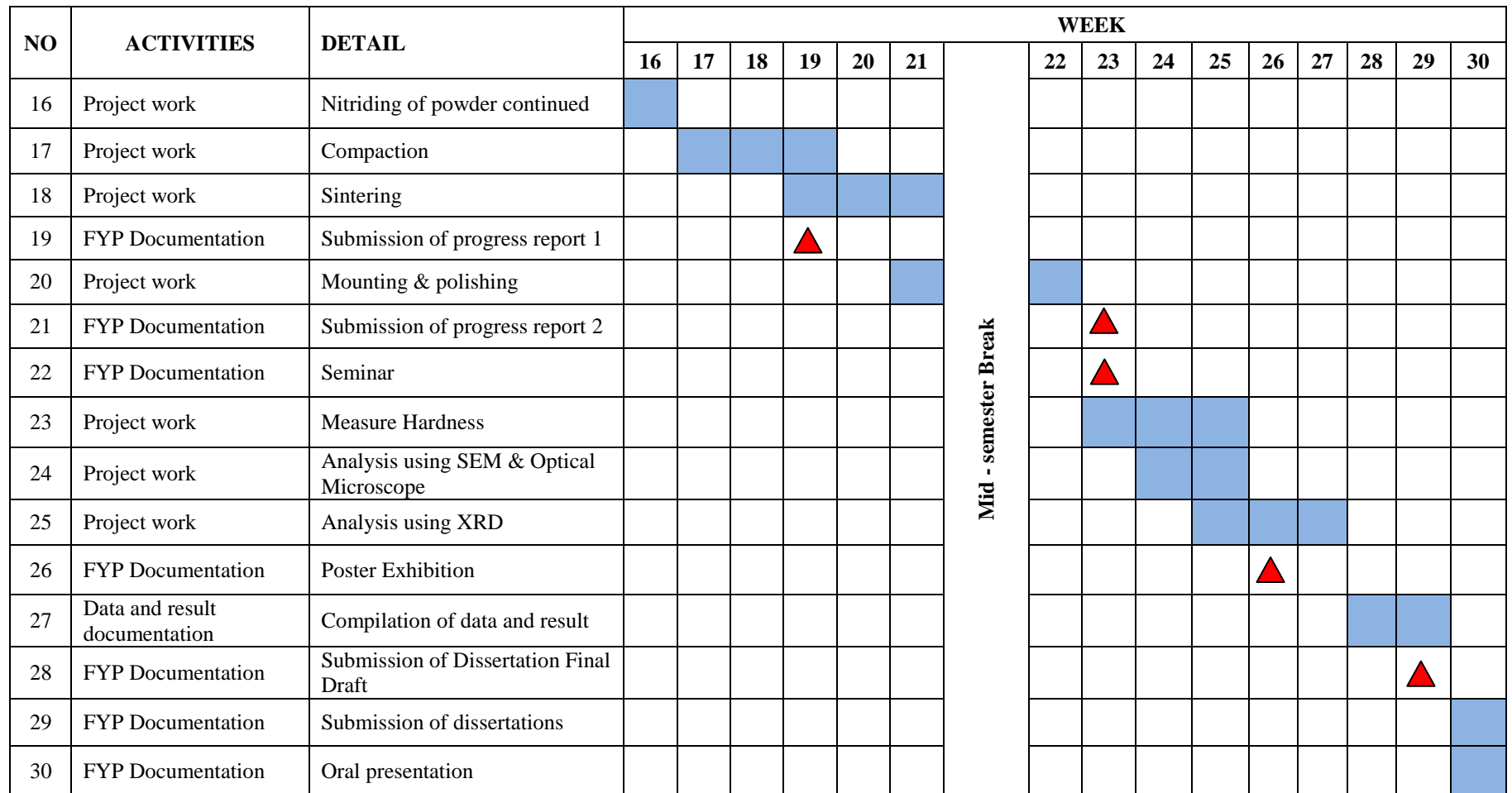
3.2 Gantt Chart of the Project

NO	ACTIVITIES	DETAIL	WEEK															
			1	2	3	4	5	6		7	8	9	10	11	12	13	14	15
1	FYP documentation	Submission of title proposal	▲															
2	Literature review	Concept of gas nitriding	■	■	■	■												
3	FYP documentation	Preliminary report					▲											
4	Literature review	Types of SS: Austenitic Stainless Steel (316L)					■	■										
5	Literature review	Power nitriding					■	■		■								
6	Literature review	Powder production technique					■	■		■								
7	Literature review	Powder metallurgy					■	■		■								
8	FYP documentation	Progress report I									▲							
9	FYP documentation	Seminar I									▲							
10	Methodology development	Develop procedure of nitriding based on literature review									■	■	■	■	■			
11	Literature review	Continue on literature review										■	■	■	■			
12	Project work	Powder characterization: XRD, XRF and SEM										■	■	■	■			
13	Data and result documentation	Compilation of initial data and results														■	■	■
14	FYP Documentation	Oral presentation																▲
15	FYP Documentation	Submission of interim report																▲

Note: column between week 6 and week 7 is labelled "Mid - semester Break"

Figure 3.2 (a): Gantt chart of project research

▲ Key milestones

■ Process

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3.2 Gantt Chart (continue)

NO	ACTIVITIES	DETAIL	16	17	18	19	20	21	Mid - semester Break	22	23	24	25	26	27	28	29	30
16	Project work	Nitriding of powder continued	█															
17	Project work	Compaction		█	█	█												
18	Project work	Sintering				█	█	█										
19	FYP Documentation	Submission of progress report 1				▲												
20	Project work	Mounting & polishing						█		█								
21	FYP Documentation	Submission of progress report 2									▲							
22	FYP Documentation	Seminar									▲							
23	Project work	Measure Hardness									█	█	█					
24	Project work	Analysis using SEM & Optical Microscope										█	█					
25	Project work	Analysis using XRD											█	█	█			
26	FYP Documentation	Poster Exhibition												▲				
27	Data and result documentation	Compilation of data and result														█	█	
28	FYP Documentation	Submission of Dissertation Final Draft															▲	
29	FYP Documentation	Submission of dissertations																█
30	FYP Documentation	Oral presentation																█

Figure 3.2 (b): Gantt chart of project research

▲ Key milestones

█ Process
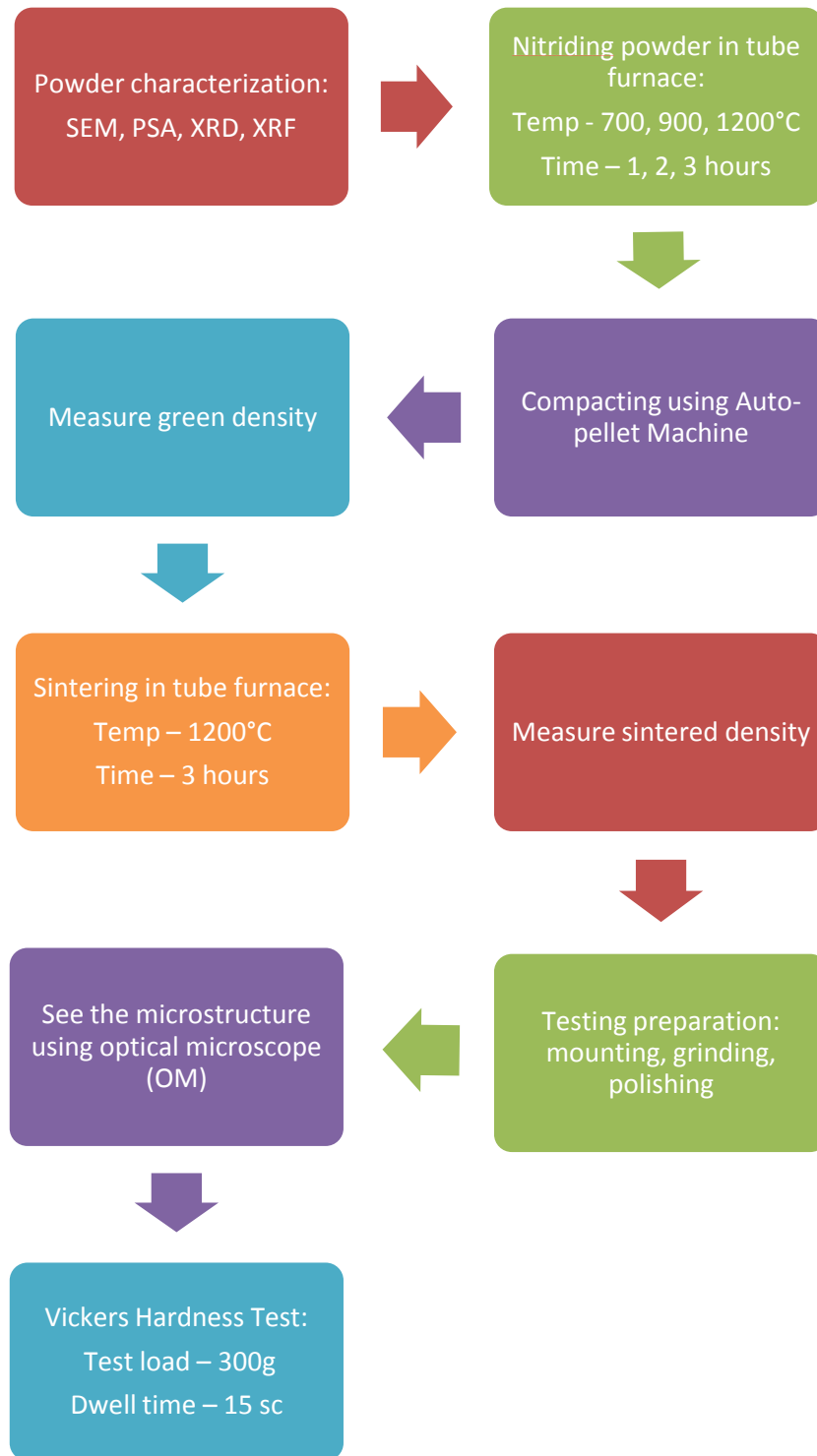
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3.3 Project Methodology

Figure 3.3: Flow chart of methodology used for research project

Throughout the stages of experimental methodology as in Figure 3.3, the listed steps shown in the flowchart were followed accordingly. Details of the flow are described in next section.

3.4 Laboratory Works

3.4.1 Materials

A number of 9 samples of austenitic stainless steel nitrided at 700°C, 900°C, and 1200°C for 1, 2 and 3 hours are required for the experiment. Raw materials needed to produce the samples are austenitic stainless steel powder and nitrogen gas used as the nitriding atmosphere.

3.4.2 Tools and Equipments

Major tools and equipments that are used in the laboratory experiment for the research are as following:

i. Carbolite horizontal tube furnace
ii. Scanning Electron Microscope (SEM)
iii. XRD analyzer
iv. Weighing scale
v. Marble mortar and pestle
vi. Auto Pelletizer
vii. Archimedes density measuring equipment
viii. Sintering furnace
ix. Hot mounting machine
x. Grinder and polisher
xi. Sand papers
xii. Optical microscope
xiii. Hardness Tester (Vickers)

3.4.3 Experimental procedure

i.   Austenitic stainless steel powders were prepared.

ii.   The characteristics of the powders including the particle sizes, composition and XRD analysis were recorded.

iii. The powders were nitrided in the Carbolite horizontal tube furnace. For each treatment parameter, powder was placed in the ceramic boat and inserted into the heating zone

iv.   Before the powder was heated, the air in the furnace was purged with nitrogen for 15 minutes to prevent oxidation of the powder. Heating at 5°C/minute was started immediately after the purging was completed. Nitrogen was introduced into the furnace with the flow rate of 1000 cm^3/min when the temperature reached the treatment temperature. (Plots of the nitriding conditions are attached in Appendix A)

v.   The treatment parameters are as following

Table 3.1: Treatment parameter for nitriding process

Temperature (°C)	Time (hour)
700°C	1
	2
	3
900°C	1
	2
	3
1200°C	1
	2
	3

vi.   The nitrided powders were slow cooled in the air atmosphere.

vii. After that, the nitrided powders were mixed with binder (wax) by using marble mortar and pestle to form a homogeneous mixture.

viii. The mixtures were compacted at approximately 17000lbs with dwell time of 5 minutes.

ix. The compact was removed from die.

x. The compact was weighted, its dimension was recorded and the green density was determined.

xi. The steps were repeated to produce the rest of the samples.

xii. By using a sintering furnace, all compacts of each treatment parameter were sintered at temperature of 1200°C for 3 hourss. The heating and cooling rates of the sintering process are 5°C/minute and 10°C/minute respectively.

xiii. The sintered compacts were weighted, their final dimensions were recorded, and their sintered densities were determined using Archimedes density measuring equipment.

3.4.4 Polished specimen preparation

Before the samples were tested, some preparation was done including mounting, grinding and polishing. The nitrided austenitic stainless steel compacts were mounted by using hot mounting machine. Phenolic powder is used as the mounting media which was poured into the mounting press according to desirable mounting height. The process involved heating Phenolic powder above 150°C at a constant pressure about 30Mpa for a cycle time of 15 minutes. The mounted compacts were then cleaved off using the Polisher and Grinder machine. Three grades of sand papers (120, 240, 320, 400, 600, 800 and 1200 grit) were used to polish the compacts at 200 rpm speed of grinder plate.

3.4.5 Analysis procedure

Vickers microhardness apparatus with 300g load was used to measure the hardness across the section of the nitride samples. Optical microscope was employed to observe the microstructure of the treated samples after etching with Fry's reagent.

CHAPTER 4

RESULT AND DISCUSSION

4.1 Powder Characterization

4.1.1   Particle Size of Austenitic Stainless Steel Powder

Particle size of austenitic stainless steel powder was analyzed by using scanning electron microscopy (SEM). Figure 4.1 shows that the diameter of the powder is about 3.517 μm. This diameter was taken from the smallest particle. While another particle shows that diameter is higher which 10.94 μm is.

From the image, the size of particle is varied. Some are bigger and some are smaller. This is due to the clogging of the particle. The particles are very lust and they tend to stick to each other. If not because of the clogging the size of the particle will be much smaller and it is believed that the actual particle size is nanometers.

Thus the particle size of the powder should be checking again. The use of magnetic tape is needed in order to get a better result. This is to ensure that the powder is not sticking on each other or to form agglomerate.
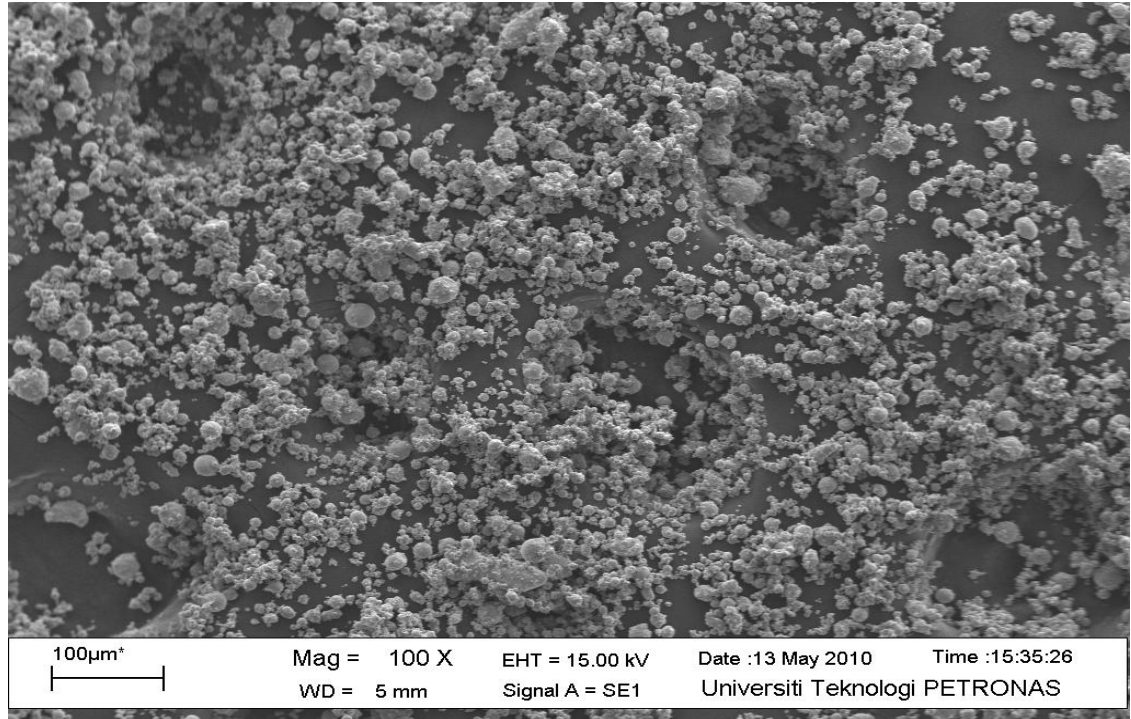
Figure 4.1: SEM image of unnitrided austenitic stainless steel powder particle (100X)
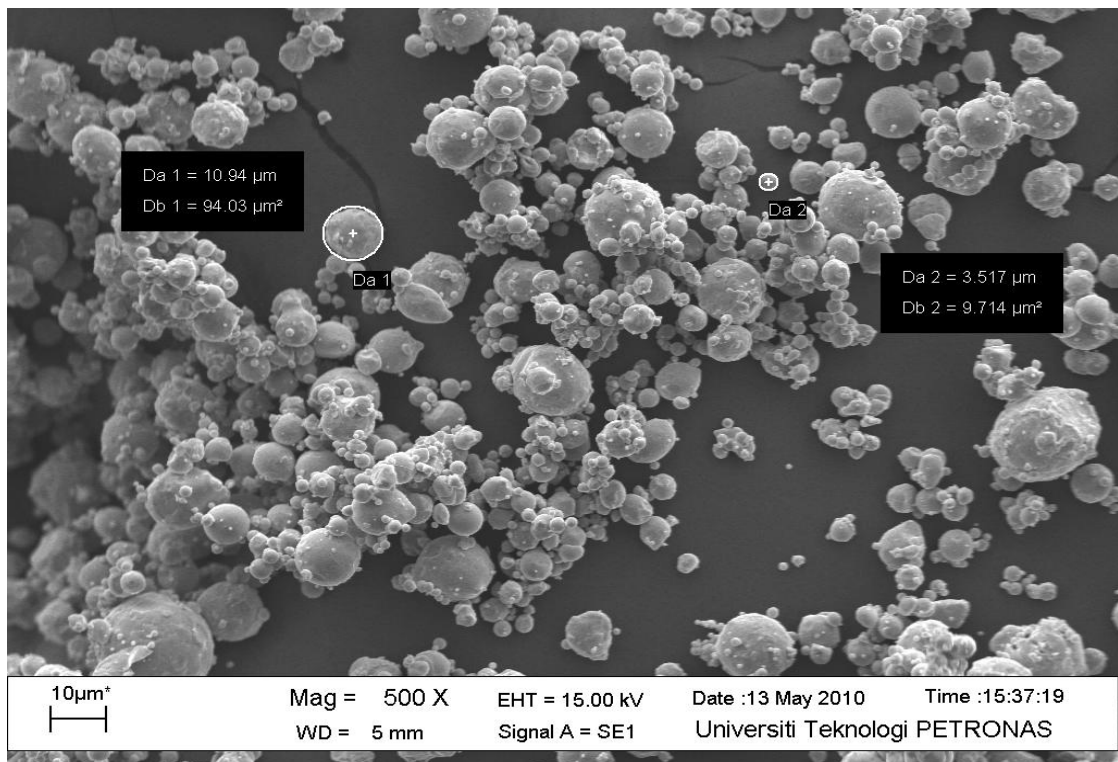
Figure 4.2: SEM image of unnitrided austenitic stainless steel powder particle (500X)
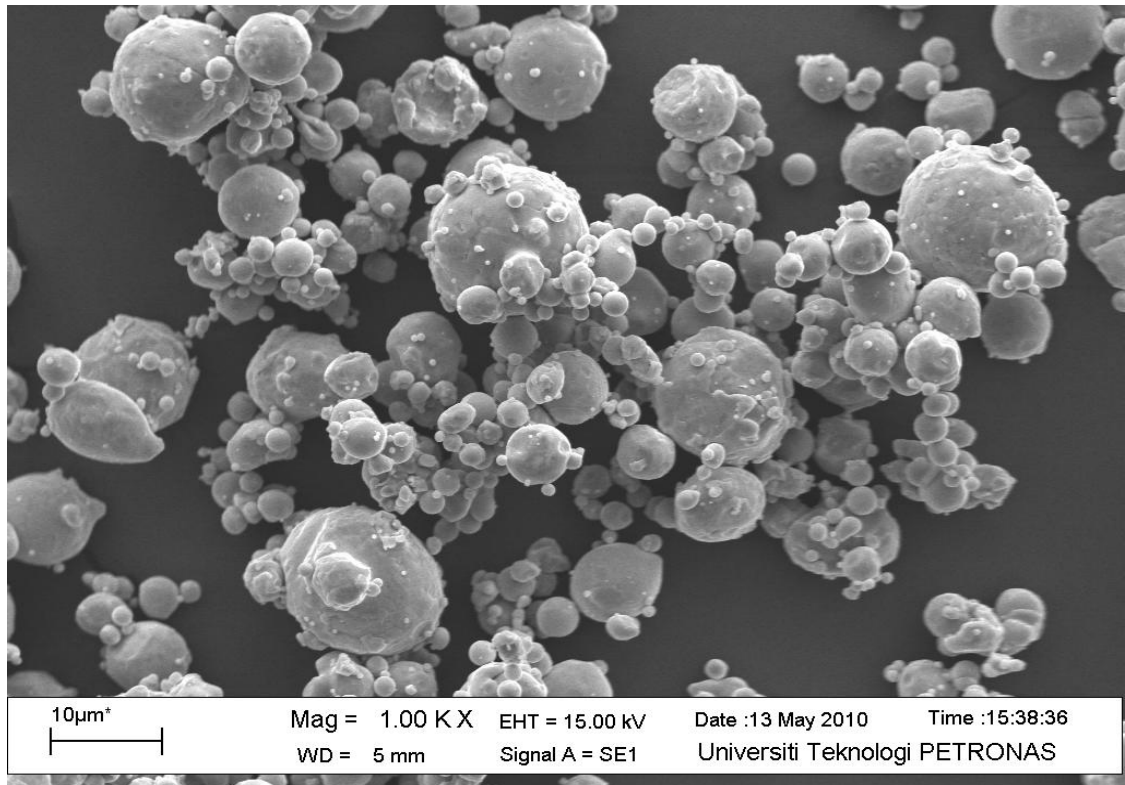
Figure 4.3: SEM image of unnitrided austenitic stainless steel powder particle (1000X)
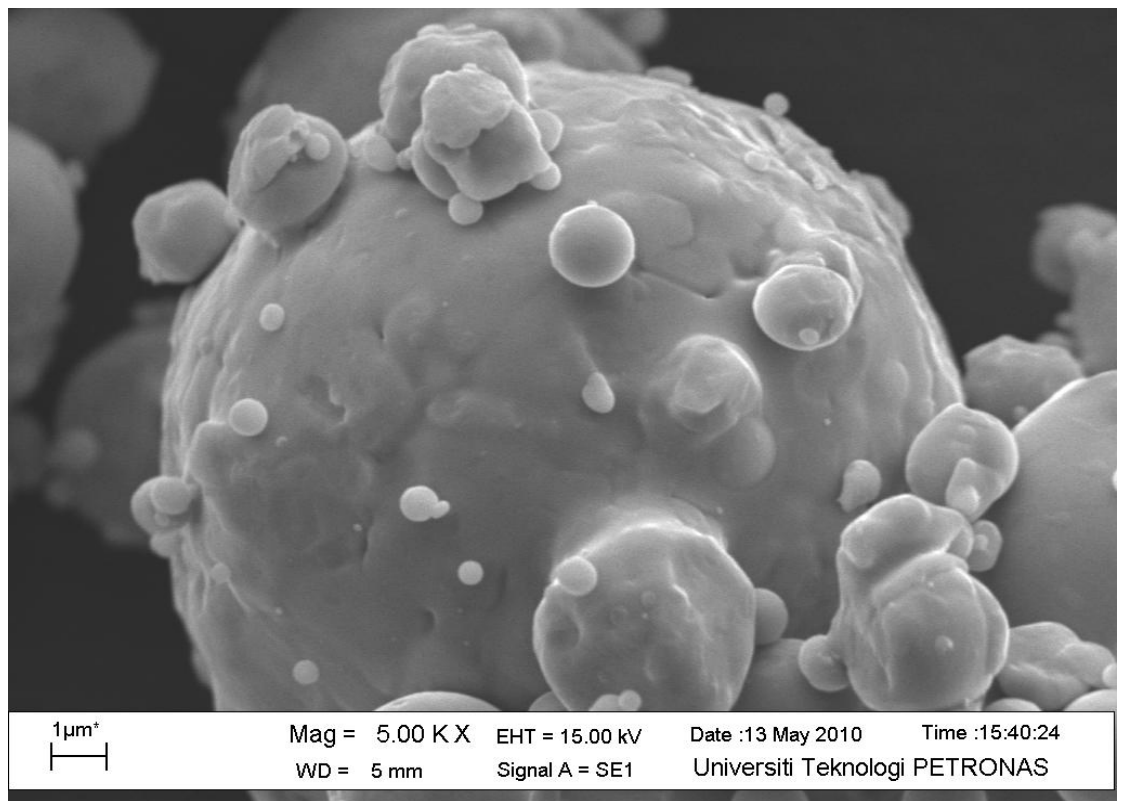
Figure 4.4: SEM image of unnitrided austenitic stainless steel powder particle (5000X)

4.1.2 XRD Analysis
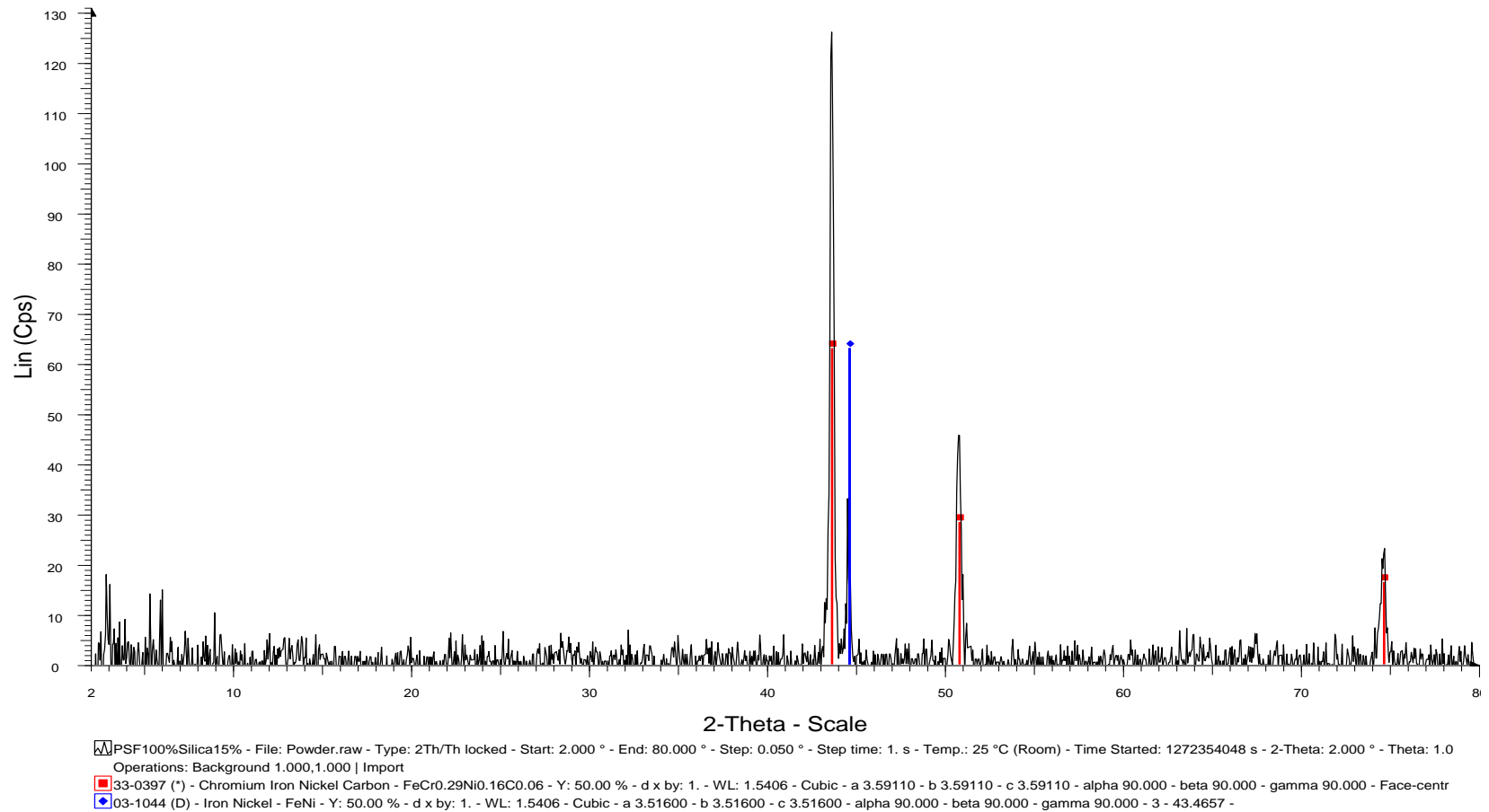
4.1.2.1 Unnitrided austenitic stainless steel powder

PSF100%Silica15% - File: Powder.raw - Type: 2Th/Th locked - Start: 2.000 ° - End: 80.000 ° - Step: 0.050 ° - Step time: 1. s - Temp.: 25 °C (Room) - Time Started: 1272354048 s - 2-Theta: 2.000 ° - Theta: 1.0
Operations: Background 1.000,1.000 | Import
33-0397 (*) - Chromium Iron Nickel Carbon - FeCr0.29Ni0.16C0.06 - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.59110 - b 3.59110 - c 3.59110 - alpha 90.000 - beta 90.000 - gamma 90.000 - Face-centr
03-1044 (D) - Iron Nickel - FeNi - Y: 50.00 % - d x by: 1. - WL: 1.5406 - Cubic - a 3.51600 - b 3.51600 - c 3.51600 - alpha 90.000 - beta 90.000 - gamma 90.000 - 3 - 43.4657 -

Figure 4.5: XRD pattern for unnitrided powder of austenitic stainless steel

26

4.1.2.2 Nitrided austenitic stainless steel powder
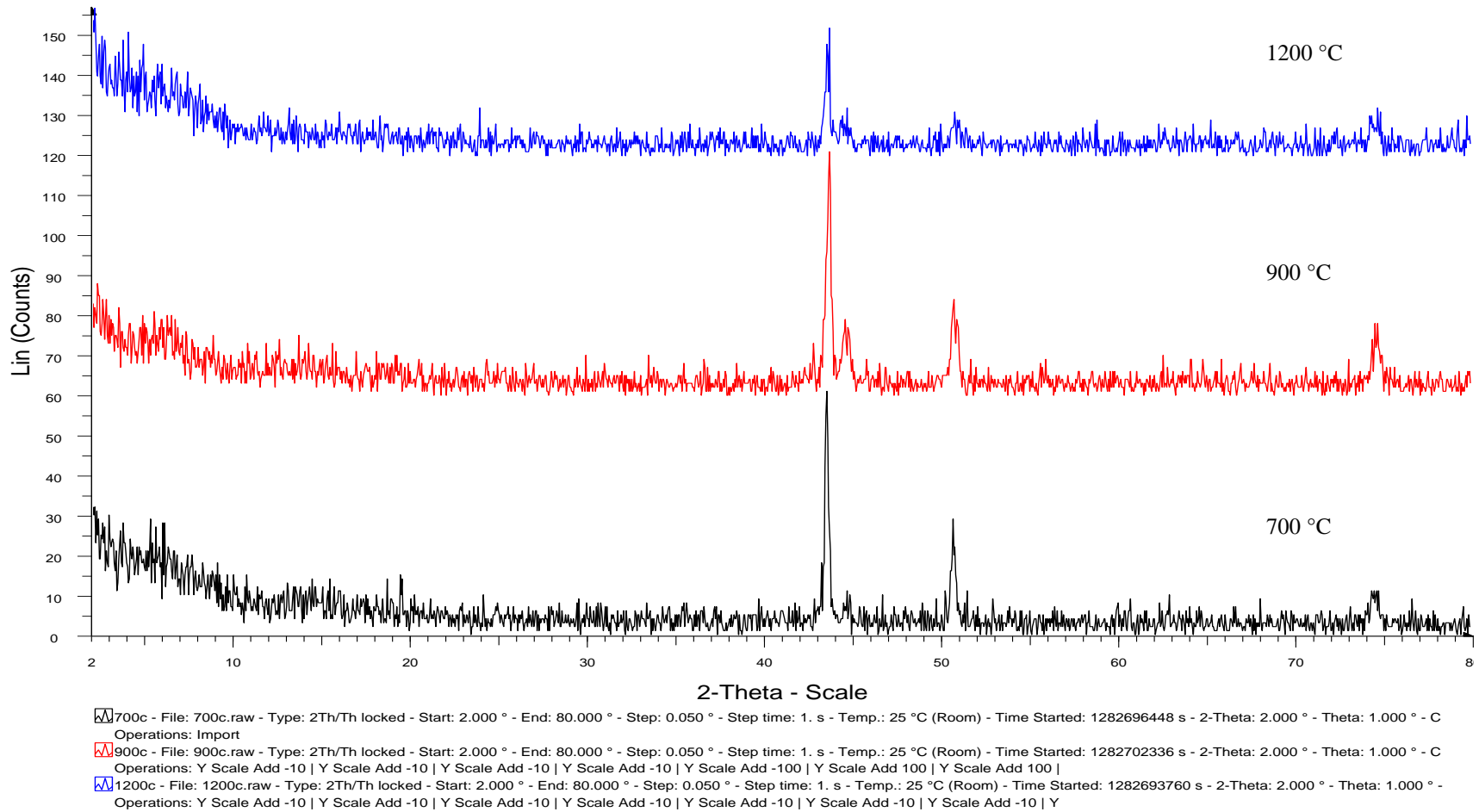
Figure 4.6: XRD pattern of austenitic stainless steel powder nitrided at 700°C, 900°C and 1200°C
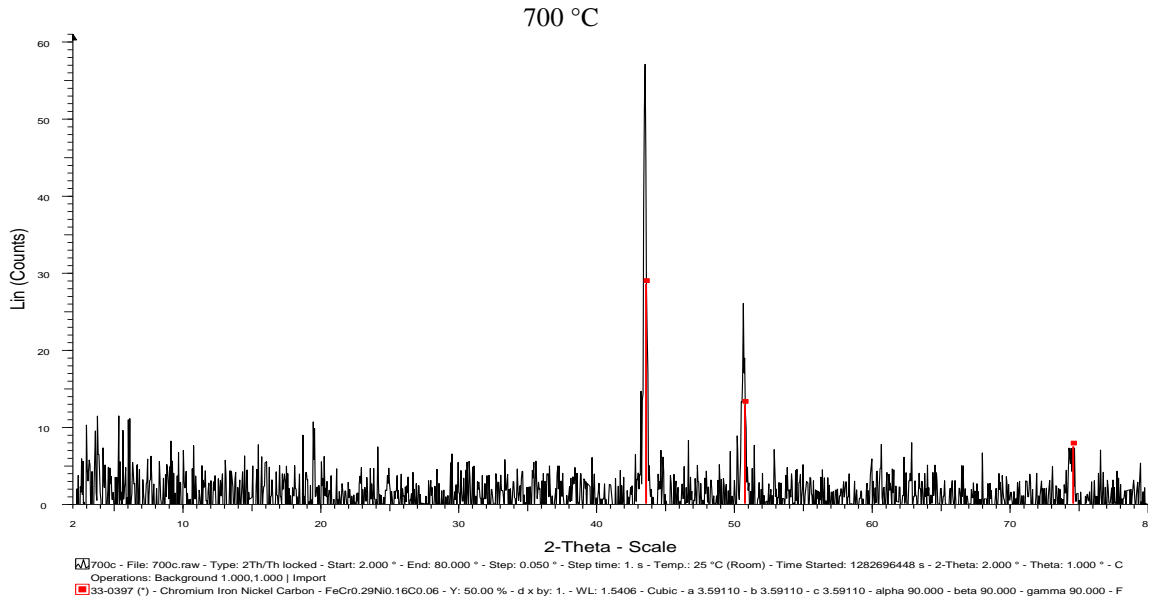
700 °C

Figure 4.7: XRD pattern for nitrided powder of austenitic stainless steel at 700°C
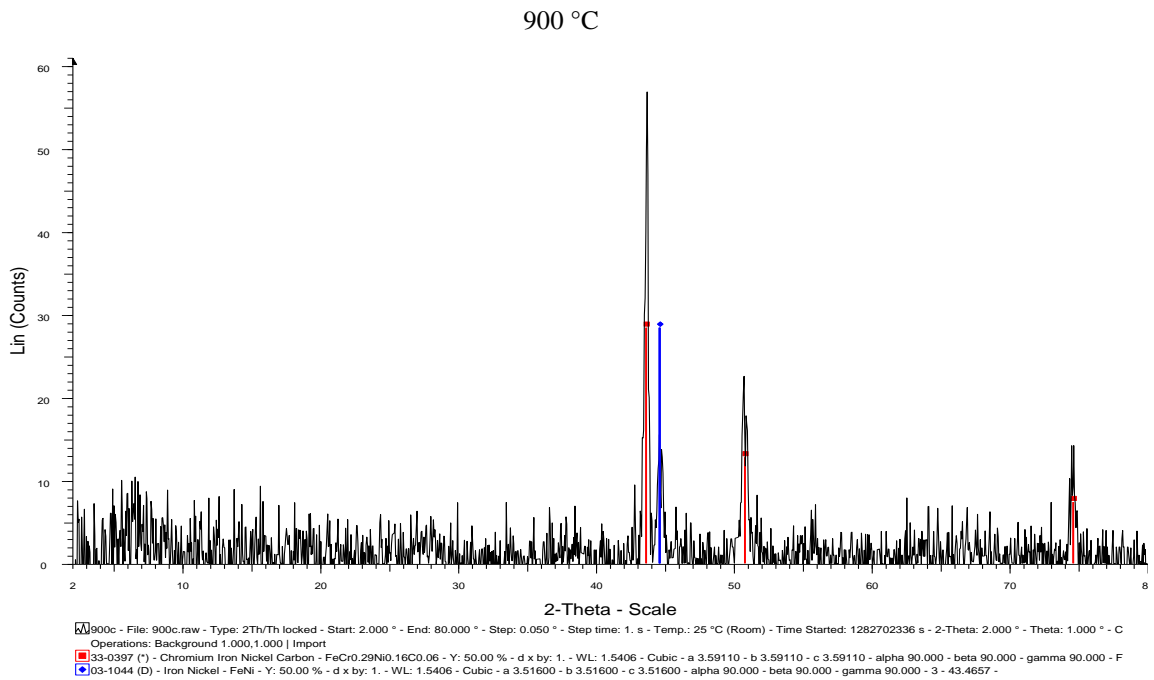
900 °C

Figure 4.8: XRD pattern for nitrided powder of austenitic stainless steel at 900°C
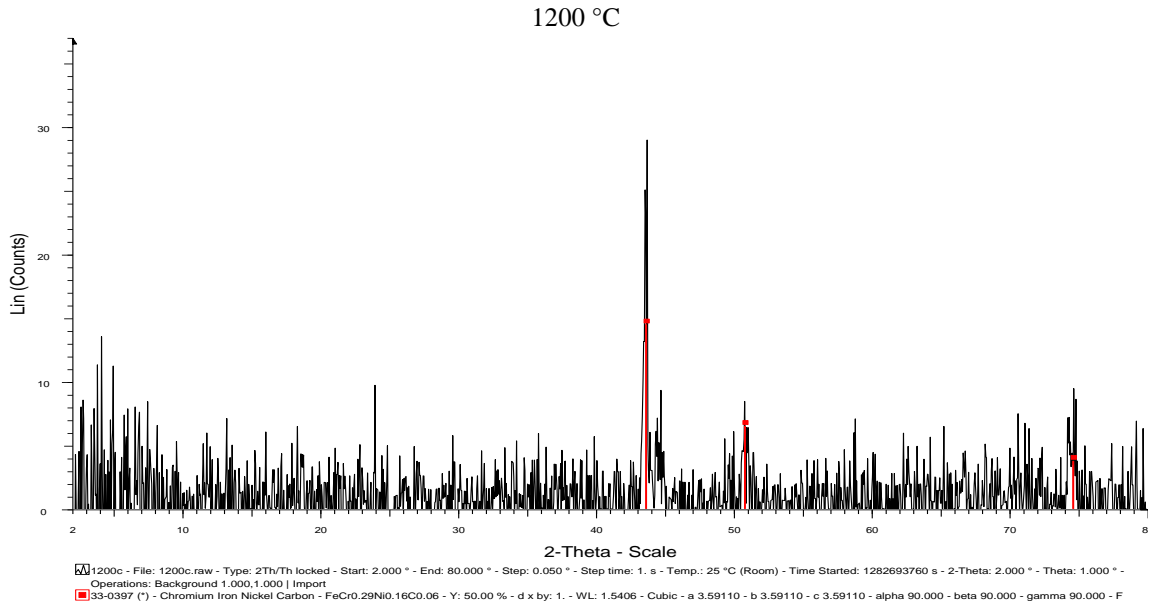
1200 °C

Figure 4.9: XRD pattern for nitrided powder of austenitic stainless steel at 1200°C

One of the primary uses of x-ray diffraction is for determination of crystal structure. For that purpose, a sample of austenitic stainless steel powder underwent this testing process to determine its crystal structure. Figure 4.5 show the X-ray diffraction patterns of unnitrided austenitic stainless steel powder sample. It can be confirmed that the powder is austenitic stainless steel. This is due to crystalline structure of face-centered cubic.

Austenitic stainless steel have a F.C.C atomic structure which provides more planes for the flow of dislocations, combined with the low level of interstitial elements (elements that lock the dislocation chain), gives this material its good ductility. This also explains why this material has no clearly defined yield point, which is why its yield stress is always expressed as a proof stress [14].

After nitriding process, no new phase has formed because the diffusion of nitrogen through interstitial diffusion is not enough to change the crystalline structure. This shows that the XRD patterns are similar for both nitrided and unnitrided powders. However, XRD pattern for nitrided sample (Figure 4.6) shows a shifted in the lattice strain due to the stress result from the addition of nitrogen.
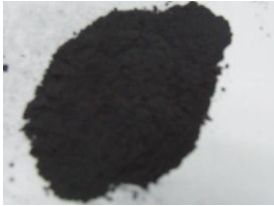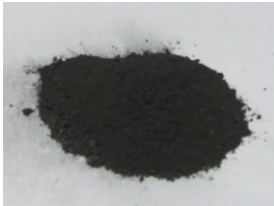
4.2 Sample Preparation

4.2.1   Nitriding

Nitriding was performed in Carbolite horizontal tube furnace. For each treatment powder was placed in the ceramic boat and inserted into the heating zone. Before the samples were heated, the air in the furnace was purged with nitrogen for 15 minutes at a flow rate of 1000cm^3/min to prevent oxidation of the sample. Heating at 5ºC/minute was started immediately after the purging was completed. Nitrogen was introduced into the furnace with the flow rate of 1000 cm^3/min when the temperature reached 1200ºC. At the end of the process, the powder were removed from the furnace and cooled in the environment.

Figure 4.10: Unnitrided austenitic stainless steel powder

Table 4.1: Austenitic stainless steel powder after nitriding process

Time Temperature	1hour	2 hours	3 hours
700 °C			
900 °C			
1200 °C			

From Table 4.1, it shows that the colour of nitrided powder became darker than the unnitrided one (Figure 4.10). Besides that, the powders with nitriding temperature of 1200°C tend to form agglomerate and stick together. This is due to semi liquid phase between the particles shifting from the solid state to the liquid state. The high temperatures (near melting temperature) melt the powder and bond the particles together. Then after cooling it tends to stick together.

4.2.2   Mixing

In order to bind the particle together, wax was used as the binder. Mixing process was done manually by using marble mortar and pestle due to small volume of mixtures. This is the best way to achieve homogeneity in the mixture as compared by using the actual mixer or blender since the powder tend to stick to the wall of the mixer, thus reducing the volume of the mixtures.

4.2.3   Compacting

The nitrided powders for each parameter were compacted by using cold press machine, Auto Palletizer. The mold available in the laboratory produced sample with ±13 mm in diameter. For each sample, the pressure used to compact it was 17000 lbs with dwell time of 5 minutes. The selection of compression pressure and dwell time was done after several tests were conducted. During compaction process, there was a problem where the powders were not easily bind together. This is due to sphere shape of the powder. For powder metallurgy process, irregular shape is most preferred compared to sphere shape.

4.2.4   Sintering

To improve the hardness of the samples, we proceed with the sintering process. Sintering is a process where the samples were heated nearly its melting temperature. When were heated, the outer layer of the samples become liquid while the inner stay solid. The outer layer diffuses with each other and enhances its hardness.

Sintering was conducted in the Carbolite horizontal tube furnace for 3 hours at temperature of 1200°C. During sintering stage some changes were occurred, including changes in size, configuration, and the nature of pores. The densities of the samples

before and after sintering called green and sintered density respectively were measured, as it is included in the scope of this research.

The thickness and diameter of the green samples were measured and its density was calculated as in the table attached in Appendix C. (Sample calculation for green density are attached in Appendix D). While for the sintered samples, the density was measured by using Archimedes's density measurement instrument. The green and sintered densities are tabulated in Table 4.2 below:

Table 4.2: Green and sintered densities of the nitrided and unnitrided samples

Nitrided Sample		Green Density (g/cm³)	Sintered Density (g/cm³)
Temperature (°C)	Time (hour)		
700°C	1	6.951	5.693
	2	6.512	5.792
	3	6.375	5.467
900°C	1	6.006	4.629
	2	5.994	5.287
	3	5.950	4.940
1200°C	1	5.946	5.549
	2	5.761	5.212
	3	5.730	4.820
Unnitrided		6.011	6.240

From the table, it shows that the sintered density for unnitrided sample increased as compared to green density. It is due to the improvement of densification after sintering. Besides that, reduction of inherent porosity in the powder mass as the sintering process continues at higher temperatures results in elimination of pores by bulk diffusion to grain boundaries. This reduction in the amount of porosity, hence results in an increase in the density of the powder compact.

Plot of experimental data, comparing the green and sintered densities can be seen in figures shown in the next page. Figures 4.11, 4.12 and 4.13 show that sintered density

reduces as compared to green density. For all temperature of nitriding, their sintered density is lower than green density. This situation is contradicted with the common theory where usually the sintered density is expected to be higher than the green density. Practically, sintered products will have improved densities. Thus it is assumed that during sintering, decomposition of nitrides occurred.

During nitriding, nitrogen dissolves into the austenite to form nitrides which are CrN and Cr_2N. Then the powder is sintered at high temperature. During sintering process, the nitrides which are formed during slow cooling process of nitriding will decompose into Cr and Nitrogen molecules. Possible reactions are as below:

$$CrN \rightarrow Cr + 1/2\ N_2 \qquad\qquad\qquad\qquad\qquad\qquad (Eq.\ 1)$$
$$Cr_2N \rightarrow 2Cr + N_2 \qquad\qquad\qquad\qquad\qquad\qquad (Eq.\ 2)$$

The decomposition of nitrides basically occurred at temperature below 1200°C. Thus, we can say that at sintering temperature of 1200°C, the nitrides decomposed. Based on Equation 1, chromium nitrides decomposed into chromium and nitrogen molecules. However, N_2, a decomposition product will diffuse out through open pores and trapped at the surface of the compacts. As a result, it will leave porous parts in the compacts and hence influence the densification behavior. Consequently, this will cause the density to be reduced due to the existence of more pores.

Besides that, it is assumed that the sintered density decreased as wax burn out during sintering process. As the wax burn out, it is expected that the porosity is doubled comparing to the green one. The large porosities reduced the sintering densities due to a wide polymer burn off range leaving residual porosity. As a result material is expanded, volume increased and density decreased. This is comparable to A. Gökçe et al. [18] which found that Acrawax lubricant provides a reasonable green density, however it had a deleterious effect on sintered density mainly owing to its wide burn off range.

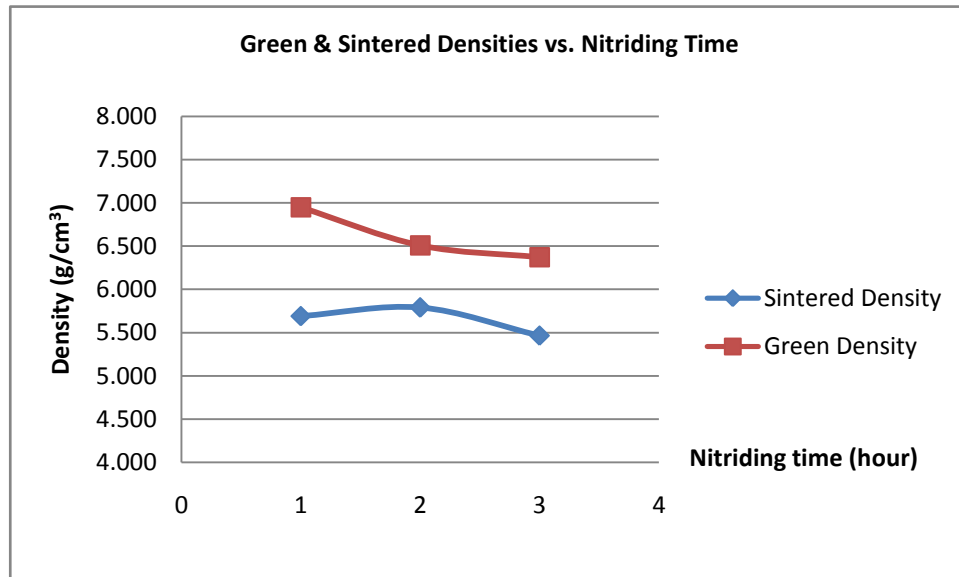Green and sintered densities vs. nitriding time of samples nitrided at 700°C

Figure 4.11: Green and sintered densities of samples nitrided at 700 °C

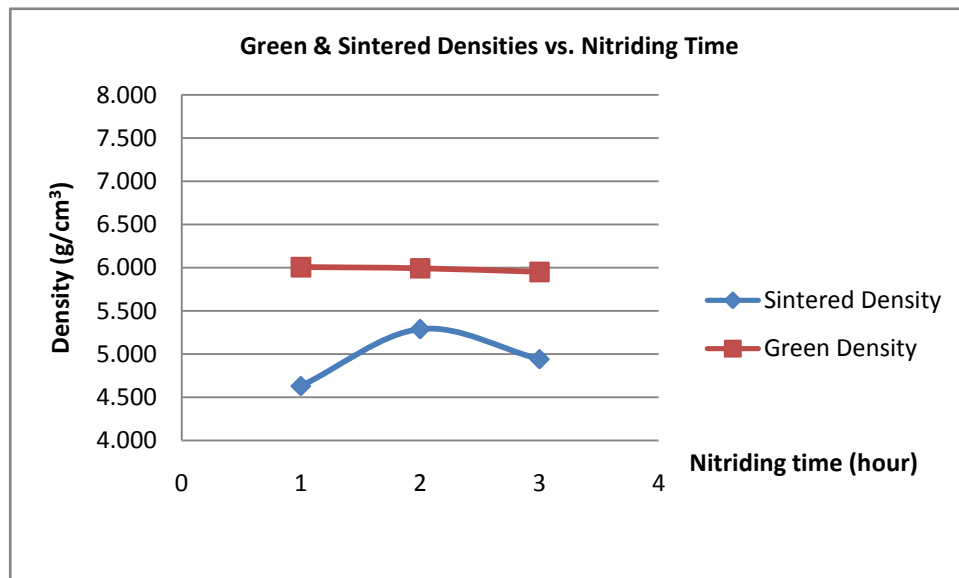Green and sintered densities vs. nitriding time of samples nitrided at 900°C

Figure 4.12: Green and sintered densities of samples nitrided at 900 °C

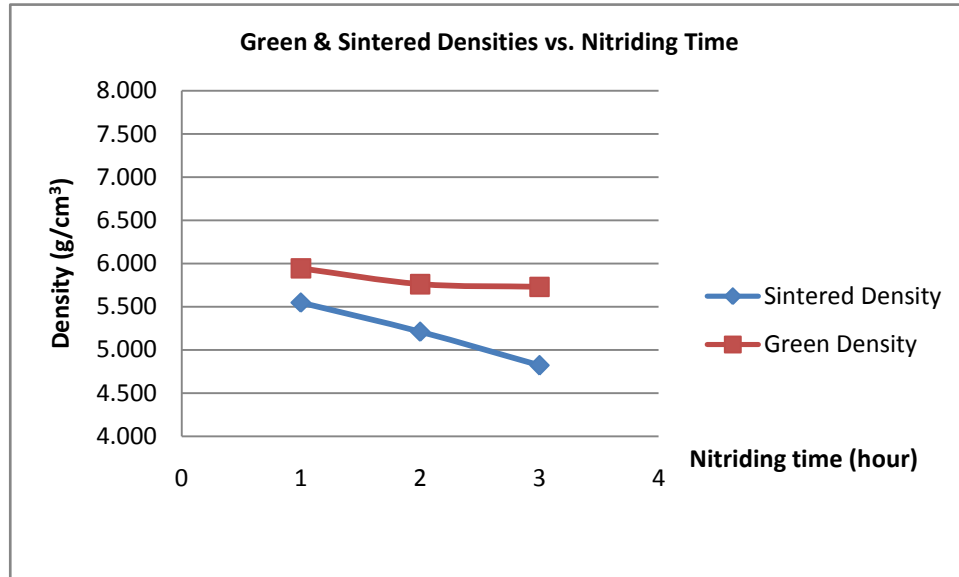Green and sintered densities vs. nitriding time of samples nitrided at 1200°C

Green & Sintered Densities vs. Nitriding Time

Figure 4.13: Green and sintered densities of samples nitrided at 1200 °C

In addition, by referring to the mechanism of plastic deformation, the obtained results can be further analyzed. As indicated by Bingham plastic model, plastic flow accelerates at higher temperature, which enhances the densification process. As result, parts of atomic group in powders fill into neighboring pores by plastic flow. At higher temperature, an expansion of pores called Ostweld ripening occurred. In this case, a certain small pores, formed at grain boundaries through vacancy diffusion will deform and even gather together to form big pores because of effect of plastic deformation. When size of these big pores is greater than a critical size, they will grow and merge each other which will consequently reduce the density of the samples sintered at higher temperature.

Green density vs. nitriding time of samples nitrided at 700°C, 900°C and 1200°C
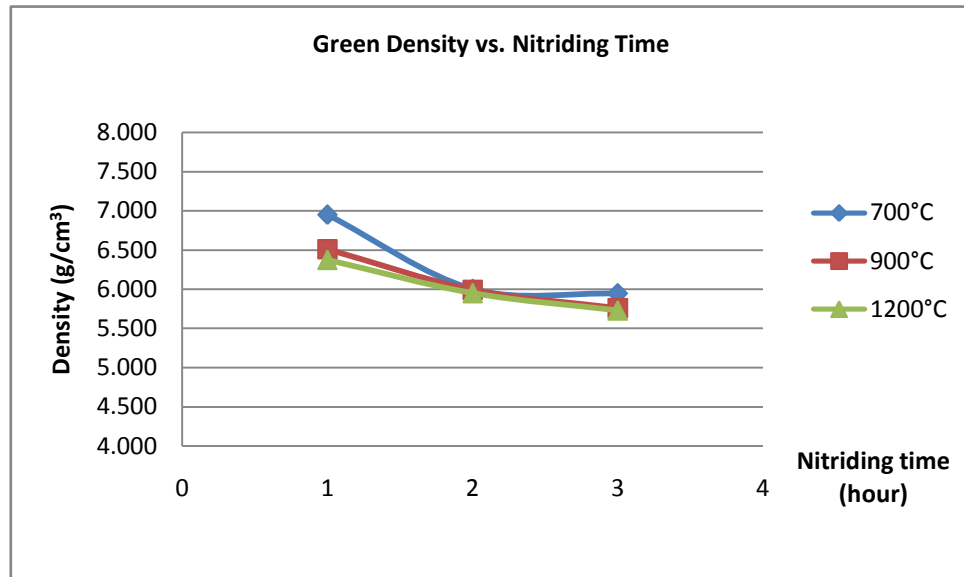

Figure 4.14: Green density of samples nitrided at 700 °C, 900 °C and 1200 °C

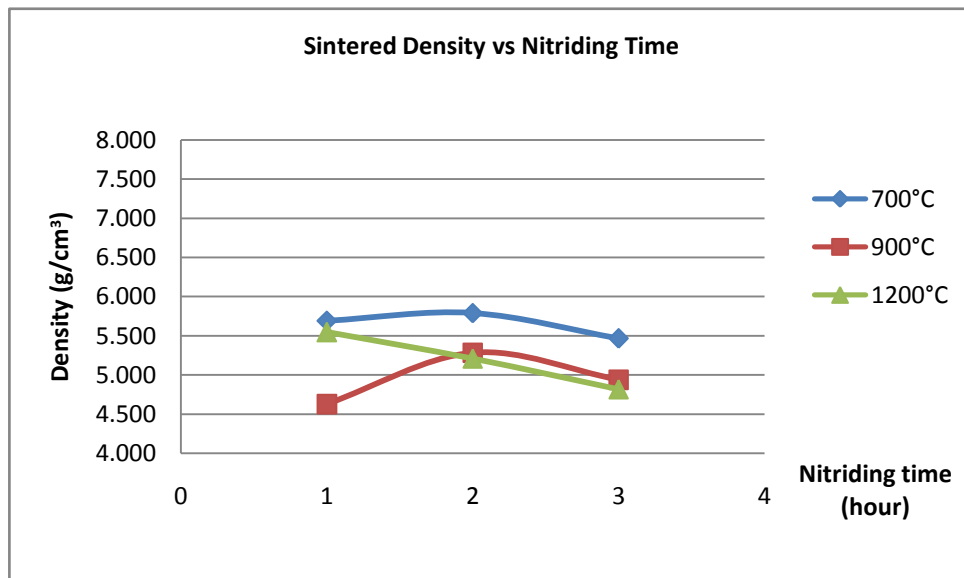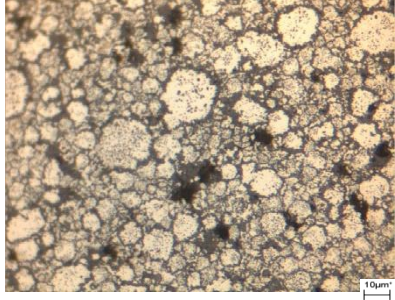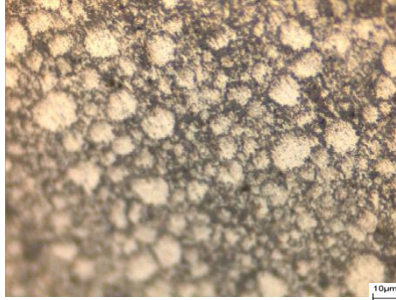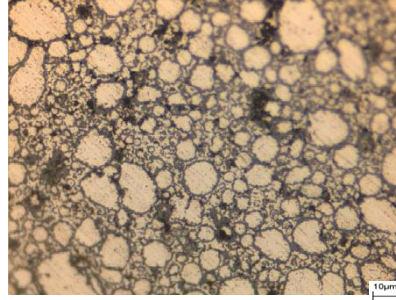Sintered density vs. nitriding time of samples nitrided at 700°C, 900°C and 1200°C
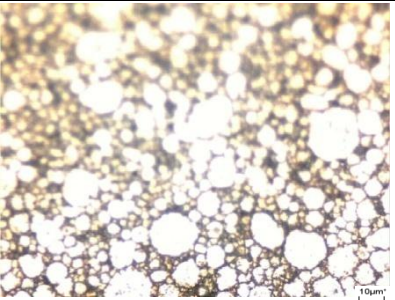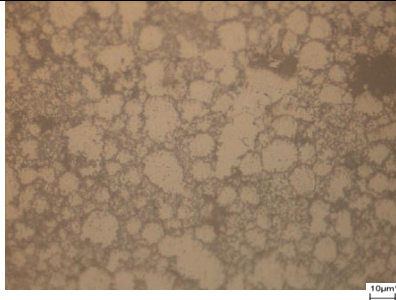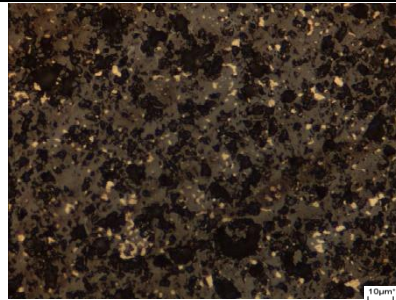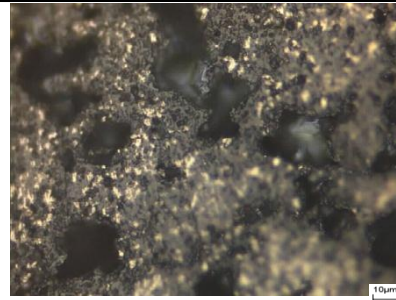
Figure 4.15: Sintered density of sample nitrided at 700 °C, 900 °C and 1200 °C

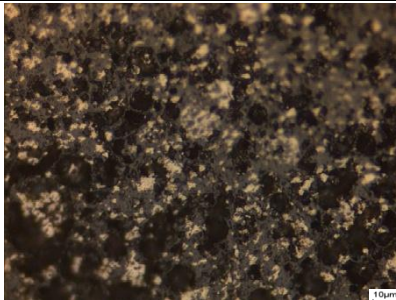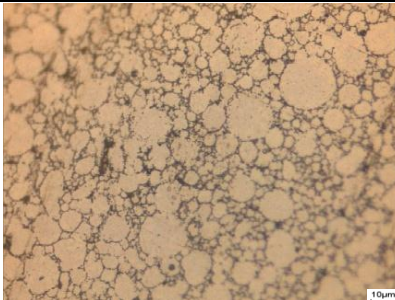In the other way, the results given in Figure 4.14 shows that longer nitriding time reduces the green density of the samples. Longer nitriding time is expected to diffuse more nitrogen into the steel. Hence it can be assumed that higher nitrogen content leads to lower green density as more nitrogen content make the sample become lighter, thus less density.

4.3 Microstructure

Table 4.3: Optical micrograph image of samples nitrided at 700°C, 900°C and 1200°C for1 hour, 2 hours and 3 hours

T_{nitriding} / Time (hour)	1	2	3
700°C			
900°C			
1200°C			

A sample without undergone nitriding process is prepared before nitriding treatments were performed. This would be used later as a comparison with the nitriding result. The microstructure of unnitrided sample is as in Figure 4.16. It shows a fine uniform distribution over the whole surface and some black spot which is assumed as nitrides and pores.
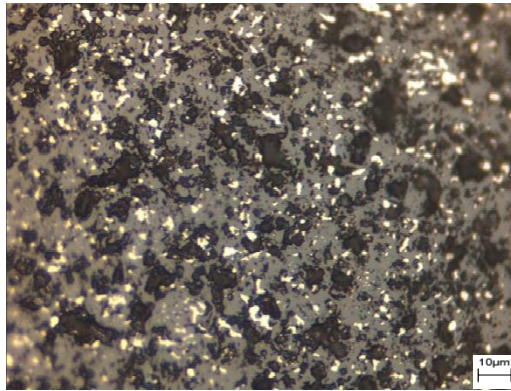

Figure 4.16: Optical micrograph image of unnitrided sample

From the figure in Table 4.3, it shows that some black spots were presence on the surface of all samples. Again, it is assumed that the additions of wax had deleterious effect on sintered density and microstructures as well. This can be related to the reduction of sintered density owing to its wide burn off range and hence incomplete removal during sintering leaving some black residue.

Besides that, pores were present in all sintered samples under every nitriding condition. Pores and small interconnected pores at grain boundaries were optically visible which reduced the sintered densities due to a wide burn off range leaving residual porosity.

At higher temperature, the size of voids increased. As discuss in the previous topic, this is due to expansion behavior of pores where larger pore growing at the expense of smaller pores. Plastic flow accelerates at higher temperatures and thus results in deformation of the small pores which formed at grain boundaries through vacancy

diffusion. Then all these small pores gather to form big pores because of the effect of plastic deformation

4.4 Microhardness

To measure the hardness of the samples, Vickers mirohardness apparatus with load of 300g and dwell time of 15 seconds was used. . Five readings were randomly taken on the samples and the average value was calculated. The results of the measurement are tabulated in Table 4.4 as below:

Table 4.4: Microhardness measurement across the samples of the nitrided austenitic stainless steel

Nitrided Sample		Vickers Microhardness (HV)					Average HV
Temperature (°C)	Time (hour)	1	2	3	4	5	
700°C	1	246.4	264.1	258.8	252.6	242.2	**252.82**
	2	390.8	383.9	387.3	393.9	387.9	**388.76**
	3	404.8	402.4	399.8	400.7	393.5	**400.24**
900°C	1	451.4	430.6	456.5	441.8	438.3	**443.72**
	2	487.2	474.7	470.9	483.5	477.9	**478.84**
	3	532.6	516.2	539.9	526.5	530.4	**529.12**
1200°C	1	606.4	599.0	599.4	609.4	586.6	**600.16**
	2	605.4	629.2	612.8	615.7	628.8	**618.38**
	3	646.7	647.6	639.0	660.1	674.9	**653.66**
Unnitrided		225.9	232.1	240.5	236.9	235.8	**234.24**

The hardness of the surface of the samples is given in Table 4.4. All samples undergone nitriding process show that their hardness are increased. Apparently nitriding as short as 1 hour has increased the hardness of the steel. As compared with the unnitrided sample, all nitriding applied to the samples show that a very high hardness was achieved.

The results given in Figures 4.17, 4.18 and 4.19 also illustrate that higher hardness is achieved by samples nitrided at longer time. Longer nitriding time is expected to diffuse more nitrogen into the steel. Thus it can be assumed that higher nitrogen content in the austenite leads to higher hardness. However more examination on the nitrogen content at the treated samples by using suitable equipment is required.

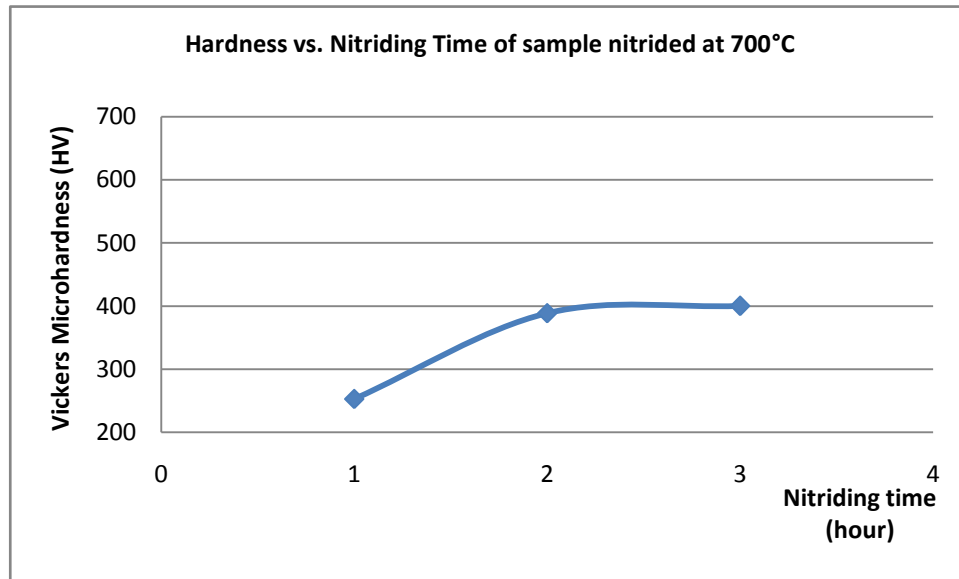Hardness of sample nitrided at 700 °C

Figure 4.17: Microhardness measurement of samples nitrided at 700°C
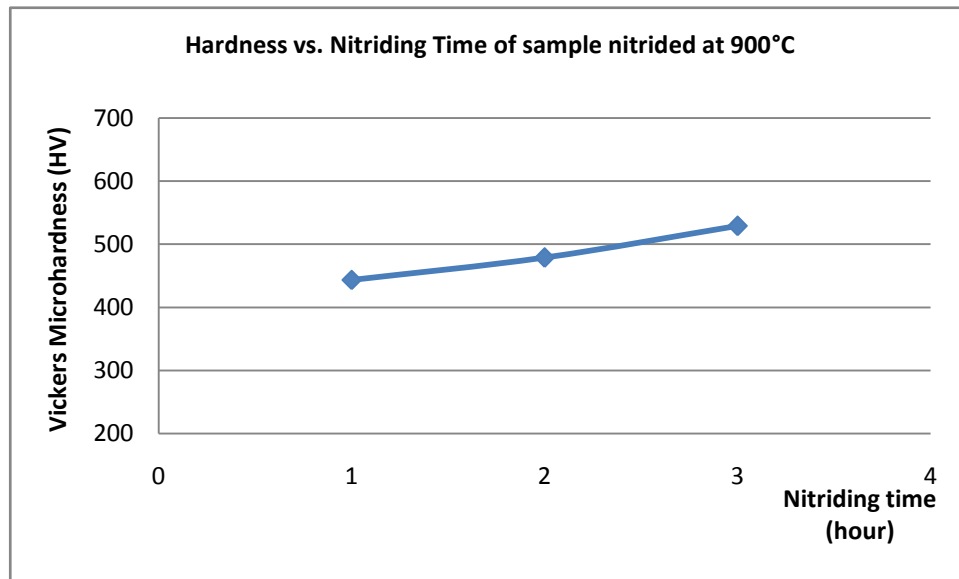
Hardness of sample nitrided at 900 °C

Figure 4.18: Microhardness measurement of samples nitrided at 900°C

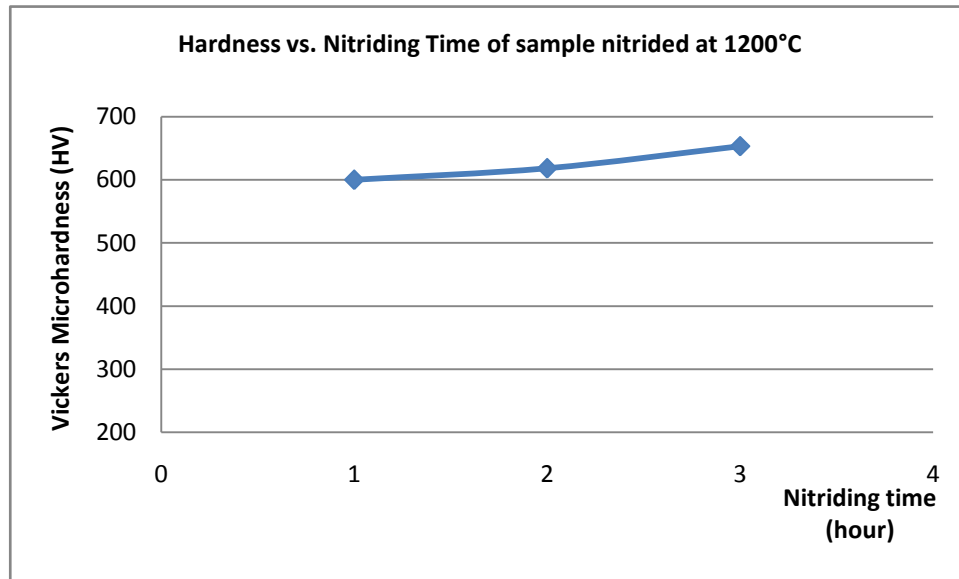Hardness of sample nitrided at 1200 °C

Figure 4.19: Microhardness measurement of samples nitrided at 1200°C

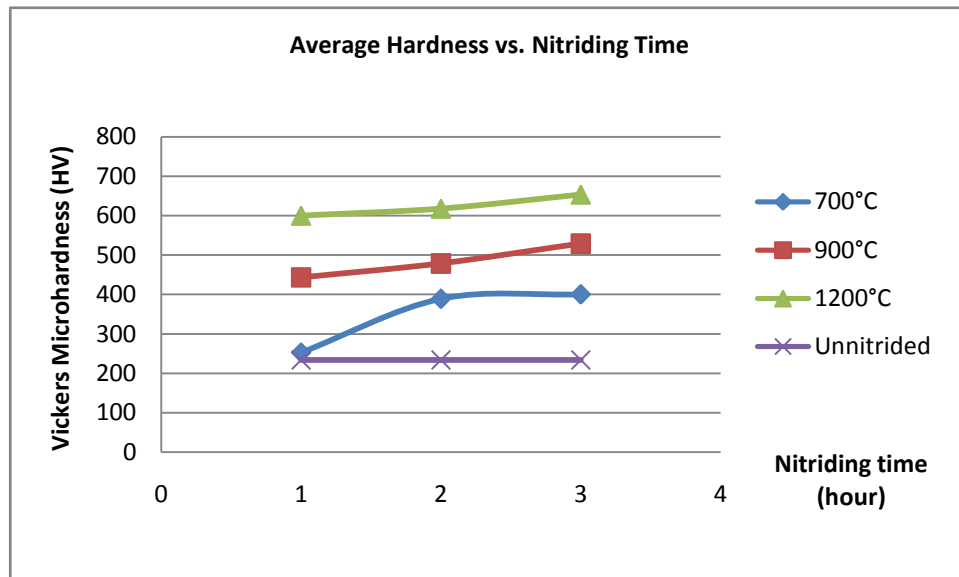Average hardness of sample nitrided at 700 °C, 900 °C and 1200 °C

Figure 4.20: Average microhardness vs. nitriding time of samples nitrided at 700°C, 900°C and 1200°C

Besides that, nitriding at higher temperature also increased the hardness of the steel. Nitriding for 1 hour at 1200°C, the hardness profile is observed to have the highest hardness as compared to nitriding at 700°C and 900°C for the same period of time. This pattern is also the same for nitriding time of 2 hours and 3 hours. This finding is in accordance with Oliveira et.al (2003), where their findings showed that the thickness and hardness of the nitrided layer increases with increasing nitriding temperature.

From Figure 4.20, it is verified that the nitriding temperature affects the surface hardness significantly, in all of the samples. The nitrided sample obtained at $1200^{o}C$ presented higher microhardness values (~650HV) in relation to the samples nitrided at $900^{o}C$ (~529HV) and $700^{o}C$ (~400HV), probably due to higher concentration of nitrogen.

In addition, the highest hardness can be observed from the hardness profile of the sample nitrided for 3 hours at 1200°C. This sample exhibits hardness profile which is higher than the others. Again it could indicate that the diffused nitrogen increases the hardness of the steel.

CHAPTER 5

CONCLUSION AND RECOMENDATION

5.1 Conclusion

As a conclusion, the objectives set up for this research has been accomplished which are basically to produce nitrided austenitic stainless steel samples and to investigate the effect of nitriding process towards the physical and mechanical properties of the austenitic stainless steel.

The high temperature gas nitriding has successfully improved the surface of austenitic stainless steel. Longer nitriding time improves hardness of the steel due to the diffusion of nitrogen into the steel. Similarly, the hardness rises as the nitriding temperature increased. Highest hardness; 650HV is achieved by sample nitride at 1200 °C for 3 hours.

Analysis on the physical properties shows that the sintered density reduced in comparison to green density. It is expected that decomposition of nitrides occurred and the wax burn out during sintering process. The burning of wax affected the densities as the porosity is doubled comparing to the green one. The large porosities then reduced the sintered densities due to a wide burn off range leaving residual porosity. As a result material is expanded, volume increased and density decreased.

In general, the microstructural studies by using optical microscope illustrates that pores were present in all sintered samples under every nitriding condition. This is due to wide burn off range leaving residual porosity in which reduced the sintered densities.

5.2 Recommendation

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

i. Examine the elements and phases exist in nitrided samples thoroughly to provide further details on the microstructural behavior and strengthening effects.

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

iii. Identify the optimum parameters such as the compaction pressure and most suitable nitriding temperature and time to improve the properties of the steel.

iv. Try to use other types of binder as it might affect the compacted sample and densities.

REFERENCES

[1]   A.M De Oliveira, 2003, *"Effect of the Temperature of the Plasma Nitriding in AISI 316L Austenitic Stainless Steel",* v.22, n.2, 63-66

[2]   E. Menthe and K.-T Rie, 1999, *"Further Investigation Of The Structure And Properties Of Austenitic Stainless Steel After Plasma Nitriding",* Surface and Coatings Technology: 116-119 (1999) 199-204

[3]   E. Menthe and A. Bulak, 2000, *"Improvement Of Mechanical Properties Of Austenitic Stainless Steel After Plasma Nitriding",* Surface and Coatings Technology: 133-1134 (2000) 259-263

[4]   Tomonori Nakanishi, Toshihiro Tsuchiyama, 2007, *"Effect Of Partial Solution Nitriding On Mechanical Properties And Corrosion Resistance In A Type 316L Austenitic Stainless Steel",* Material Science and Engineering A: 460-461 (2007) 186-194

[5]   Liang Wang and Shijun Ji , 2006, *"Effect Of Nitriding Time On The Nitrided Layer Of AISI 304 Austenitic Stainless Steel",* Surface and Coatings Technology: 200 (2006) 5067-5070

[6]   K.Y. Li and Z.D. Xiang, 2010, *"Increasing Surface Hardness Of Austenitic Stainless Steel By Pack Nitriding Process",* Surface and Coatings Technology: xxx (2010) (paper in press)

[7]   F. Borgioli and A. Fossati , 2005, *"Glow-Discharge Nitriding Of AISI 316L Austenitic Stainless Steel: Influence of Treatment Temperature",* Surface and Coatings Technology: 200 (2005) 2475-2480

[8]   S. Lampman, in: ASM Handbook, vol. 4, ASM International, Materials Park, OH, USA, 1997, p.259

[9]   C.M Garzon, A.P Tschiptschin, Processing of The International Conference on High Nitrogen Steels 2004, GRIPS media GmbH, Bad Harzburg, 2004, pp. 205-213

[10]   Nobuyuki Nakamura and Setsuo Takaki, 1999, *Nitriding and Sintering Mechanisms of 12%Cr Ferritic Stainless Steel Powder Compacts in Nitrogen Atmosphere*, Tetsu-to-Hagane, vol.79(10), pp. 1204-1209

[11]   T. Sourmail and H. K. D. H. Bhadeshia, *Stainless Steels,* from http://www.msm.cam.ac.uk/phase-trans/2005/Stainless_steels/stainless.html

[12]   José Francisco, Carlos Mario and André Paulo, *Improvement of the cavitation erosion resistance of an AISI 304L austenitic stainless steel by high temperature gas nitriding,* Material Science and Engineering A,Volume 382, 25 September 2004, Pages 378-386

[13]   Mars G. Fontana*, Corrosion Engineering*, McGraw-Hill Internatinal Edition, Material Science and Engineering Series, 3th Edition, 2009

[14]   John Dyson, *Austenitic Stainless Steels*, retrieved on from http://www.gowelding.com/met/austenitic.html

[15]   Retrieved August 10 2010, from http://www.mpif.org/apmi/doc4.htm

[16]   Lamar Stonecypher, 2010, *What is Powder Metallurgy?,* Bright Hub Website, retrieved February 22 2010, from http://www.brighthub.com/engineering/mechanical/articles/38034.aspx#ixzz13c yHA7Iv

[17]   Serope Kalpakjian and Steven R. Schmid, *Manufacturing Processes for Engineering Materials,* 5th Edition, Pearson Education, 2002

[18]   A. Gökçe, 2008 "*Mechanical and physical properties of sintered aluminum powders",* Journal of Achievements in Materials and Manufacturing Engineering, Vol.30, Issue 2, 157-164

APPENDIX A – Details of Nitriding Process
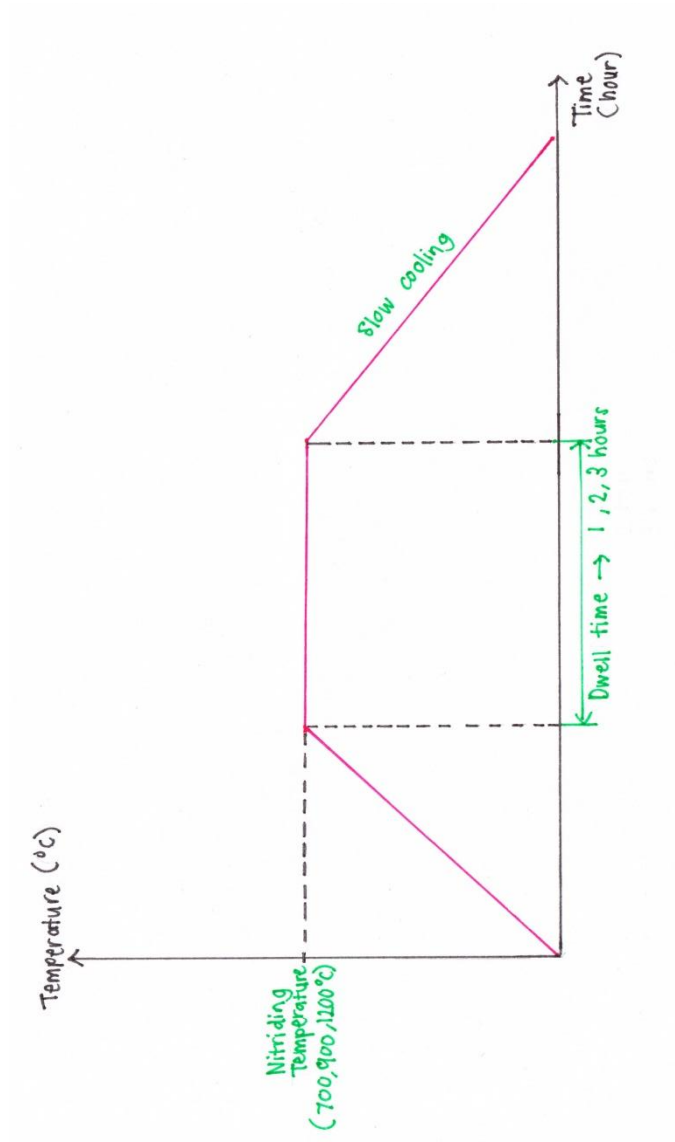
APPENDIX C – Table of Dimension and Density of Green Samples

Nitriding		Green Sample					
Time	Temperature	Mass (g)	Diameter (mm)	Thickness (mm)	Volume (mm^3)	Density (g/mm^3)	Density (g/m^3)
1	700°C	2.017	13.10	2.16	291.167	0.0069	6.927
1	900°C	2.024	13.10	2.50	336.999	0.0060	6.006
1	1200°C	2.219	13.12	2.76	373.184	0.0059	5.946
2	700°C	3.653	13.04	4.20	560.984	0.0065	6.512
2	900°C	2.020	13.10	2.50	336.999	0.0060	5.994
2	1200°C	2.266	13.14	2.90	393.310	0.0058	5.761
3	700°C	2.019	13.24	2.30	316.701	0.0064	6.375
3	900°C	2.022	13.00	2.56	339.839	0.0059	5.950
3	1200°C	2.384	13.20	3.04	416.071	0.0057	5.730
Unnitrided		2.042	13.10	2.52	339.695	0.0060	6.011

APPENDIX D – Density Calculation for Green Samples

Equation and sample calculation:

<u>Sample nitrided at 700°C for 1 hour</u>

$$Volume = \pi r^2 h$$
$$= \pi \frac{13.10}{2} (2.16)$$
$$= 291.167 \frac{g}{mm^3}$$

$$Density = \frac{Mass}{Volume}$$
$$= \frac{2.017\ g}{291.167\ mm^3}$$
$$= 0.006927 \frac{g}{mm^3}$$
$$= 6.927 \frac{g}{m^3}$$