Jimma University, Institute of Technology

Faculty of Materials Science and Engineering

A Novel Method of Pack Nitriding of AISI 1018 and 1045 Steels Using Melamine Derived from Urea

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Declaration

I, Elias Tadessse, declared that this research project is the result of my own research work and all sources and materials used for the research work were appropriately acknowledged. This research project is submitted for the partial fulfillment of the requirements for award of master of degree in Materials Science and Engineering in the specialization of Metallurgical Engineering.

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Abstract

Steels are one of the most broadly used ferrous metallic engineering materials used in many application. Example medium carbon steels are used in gears, railway wheels and tracks, crankshafts, axles, and other structural components. Having all these applications medium carbon steels often face the problem of corrosion and fatigue resulting less strength, less hardness, wear, and other mechanical failures. Surface Engineering is used as a method to overcome all of these problems. Surface engineering is applied for purpose of: increasing wear resistance, strength, hardness, corrosion resistance and impact resistance.

Nitriding is a thermochemical surface treatments process in which nitrogen diffuses to the surface of the metal. The surface of the metal changes chemical composition and mechanical properties but the inner core of the metal remains unaffected.

In this research pack nitriding was used for surface treatment of AISI 1018 mild carbon steel (low carbon steel) and AISI 1045 medium carbon steels. The effect of temperature, time, concentration of nitrogen, furnace cooling and air cooling was studied. Samples with a dimension of 0.1cm×1cm×1cm were taken and heated at 500°C, 530°C, 550°C, 580°C at the rate of 10°C/min for 2, 3,4,5 and 6 hours.

The prepared samples were buried in a dry melamine-urea powder as a source of nitrogen. This was done in a silica crucible kept in a container made of stainless steel sealed tightly using fire clay to prevent leaking of gases.

The nitrided surface of the metal formed two layers. These are compound layer and diffusion zone. The microstructural, mechanical and corrosion properties of the samples before and after nitriding were investigated. Thickness of the samples before and after nitriding were measured using micrometer screw gauge. Phases present in the surface of samples were investigated using XRD. γ' and ε phases were identified in the compound zone of the metal and metal nitride precipitates in the diffusion zone.

All nitrided samples were characterized using powder XRD, hardness testing and further characterized for corrosion resistance using cyclic voltammetry.

Key Words: Nitrding, melamine, compound layer, heat treatment, case hardening, diffusion zone

Acknowledgement

List of Acronyms and Abbreviations

XRD	X-ray diffraction
SEM	scanning electron microscope
μm	micrometer
mm	millimeter
TGA	thermogravimetric analysis
EDS	energy dispersive spectroscopy
CR	corrosion rate
mpy	miles per year
WL	weight loss
mmpy	millimeter per year

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Chapter 1

Introduction

1.1. Background of the Study

Case Hardening it is also called surface hardening is a thermochemical heat treatment process of surface hardening of metal objects through diffusion of carbon, nitrogen, boron or combination of each atoms. The beginning of case hardening goes to 1400 BC when the ancient people began to harden their weapons' edge by plunging in oil or cold water. Today case hardening has a remarkable industrial benefits to increase the durability of materials by attain new properties on the surface of the material [1, 2].

During the case hardening, the surface of the metal object becoming harder and forms thin hard skin layer from 5-20 μm thickness and diffusion zone next to thin skin layer with 100s of μm thickness. The most widely used types of case hardening thermochemical heat treatments are: nitriding, carburizing, boriding, nitrocarburizing and carbonitriding[3-5].

Nitrding is the diffusion of nitrogen to the surface of metals at the temperature between 500°C-590°C. In this research pack nitriding was done by packing of samples in dry powder grains of nitrogen bearing sources. At the time of nitriding the diffusion of nitrogen forms hardened surface. The hardened surface create two divisions, which are compound and diffusion zone layers. The compound layer include [ε –Fe_{2-3}N), γ' -Fe_4N or mixture of (ε+γ'). The compound layer has a good wear, friction and corrosion resistance characteristics. In the diffusion zone, nitrogen diffuses interstitially and forms metallic precipitates with high fatigue resistance property [3, 4, 6-10].

Urea is a nitrogenous fertilizer having 40-45% of nitrogen and decomposes to ammonia and isocyanic acid at 350°C and subsequently to melamine at 400°C in a method[11] describe afterwards. The decomposed ammonia reacts with the surface of the metal and release nitrogen. Isocyanic acid decompose to ammonia and carbon dioxide at 600°C. Carbon dioxide reacts with hydrogen that was released from ammonia and yields carbon monoxide. Melamine on heating liberates only nitrogen. Finally active nitrogen adsorbed to the surface of the metal [6, 12-15].

Pack nitriding is the cheapest and safest method. It does not use the expensive equipment like plasma/ion and gas nitriding and does not use poisonous cyanides like salt baths[12, 16]. Since nitriding uses low temperature, parts are getting less distorted[3, 17].

1.2. Statement of the problem

Nitriding is a promising and common thermochemical heat treatment. The most usual nitriding types are ion or plasma nitriding, gas nitriding and salt bath nitriding. But those types of nitriding types need expensive equipment, not available for local production, required very skillful personnel and some of them like cyanide nitriding are very poisonous. They are also performed at high temperature and cause material distortion. This research aims to search for an inexpensive, easily available method of hardening for local manufacturing companies, performed at lower temperature with no distortion of material and less toxic source source using melamine obtained by the decomposition of urea at 400ºC and develop a simple nitriding procedure. This research finds a suitable pack nitriding case hardening and creates a clean environment by using melamine. This research also aims to enhance the mechanical properties of steel such as hardness and fatigue life, to improve wear and corrosion resistance.

1.3. General Objective

Investigation of the hardness, wear resistance and corrosion resistance of AISI 1018 mild and AISI 1045 medium carbon steels by packing in melamine-urea powder.

1.4. Specific Objectives

- ✓ Finds an alternative way of nitriding of low and medium carbon steels using melamine-urea source of nitrogen.
- ✓ Investigation of corrosion rate of low and medium carbon steels using melamine-urea as a source of nitrogen.
- ✓ Investigation of wear rate and wear resistance of steels using melamine-urea.
- ✓ Investigate case depth and surface layer by varying the soaking time and soaking temperature.
- ✓ Provide a cheap nitriding process for small and large metal manufacturing companies.

1.5. Scope

In this research varieties of properties such as morphological microstructure, case depth, hardness, fatigue limit, toughness, wear-resistance, and corrosion resistance were studied.

Chapter Two

Literature Review

1.1. Surface Engineering

Surface engineering also called surface treatment is one of the discipline of science and engineering deals with the treatment and modification of the surface of materials to permit the surface to perform functions that are different from the bulk of the material. It is an attractive and economical method to improve the functional properties of case or surface of materials such as chemical, electrical, mechanical, physical and magnetic properties that are different from the inter core of the material. The surface engineering used in area of applications includes chemistry, electrical and electronics, mechanical and material engineering [18-22].

D.T.Gawne[23] outlined the principle of surface engineering and the reasons for the development of surface engineering as pervasive manufacturing technology. His study justified as surface engineering has tangible industrial benefits. Surface engineering provides corrosion protection and wear protection in the areas of transportation, automotive and aerospace. The study shows United Kingdom expend 2.5 billion US$ per year for coatings.

Materials are surface engineered for many reasons:

    i.   To control corrosion

    ii.   To control wear

    iii.   To increase hardness

    iv.   To control fatigue

    v.   Decorative and aesthetic appearance

    vi.   To use as a catalyst

Wear, corrosion and fatigue causes to the failure of materials. They are the main enemies of the countries' economy. In developed economies it is estimated that 4 % of the GDP losses because of the surface degradation[24, 25].

1.2. Techniques of thermochemical Surface Treatments

Thermochemical diffusion techniques

Carburize				Cabontride			Ferritic nitrocarburize			Boronize		Nitride			
Pack	Gas	Salt	Ion	Gas	Salt	Ion	Gas	Salt	Ion	Pack	Gas	Pack	Gas	Salt	Ion

Diffuses carbon into the steel surface Process temperatures 1600-1950°F (870-1065°C) Case depth: medium	Diffuses carbon and nitrogen into the steel surface Process temperature 1550-1650°F (845-900°C) Case depth: shallow	Diffuses carbon nitrogen, sulfur, oxygen (individually or combined) into the steel surface Process temperatures 1050-1300°F (565-705°C) Case depth: shallow	Diffuses boron into the steel surface Process temperatures 1400-2000°F (760-1095°C) Case depth: shallow	Diffuses nitrogen into the steel surface Process temperatures 600-1020°F (315-550°C) Case depth: shallow

Figure 1. Techniques of diffusion surface hardening[17]

1.3. Nitriding Surface Treatment

Nitriding is a ferritic thermochemical treatment in which a nascent nitrogen diffuses to the surface of ferrous alloys with the help of heat. It is based on the solubility of nitrogen in metals. In the present case it is steel. The nascent nitrogen transported and adsorbed on to the surface of the metal from the atmosphere contains nitrogen source. To obtain the nascent nitrogen, the nitrogen source substance decomposed to ammonia and then ammonia decomposed to nascent nitrogen atoms and hydrogen gas with the help of the metal surface as a catalyst. The ferrous metal is heated in the presence of nitrogen bearing material at a temperature of 495-565°C[17, 26, 27]. The nascent nitrogen diffuses interstitially to the surface of the metal and forms iron nitrides[4, 28, 29].
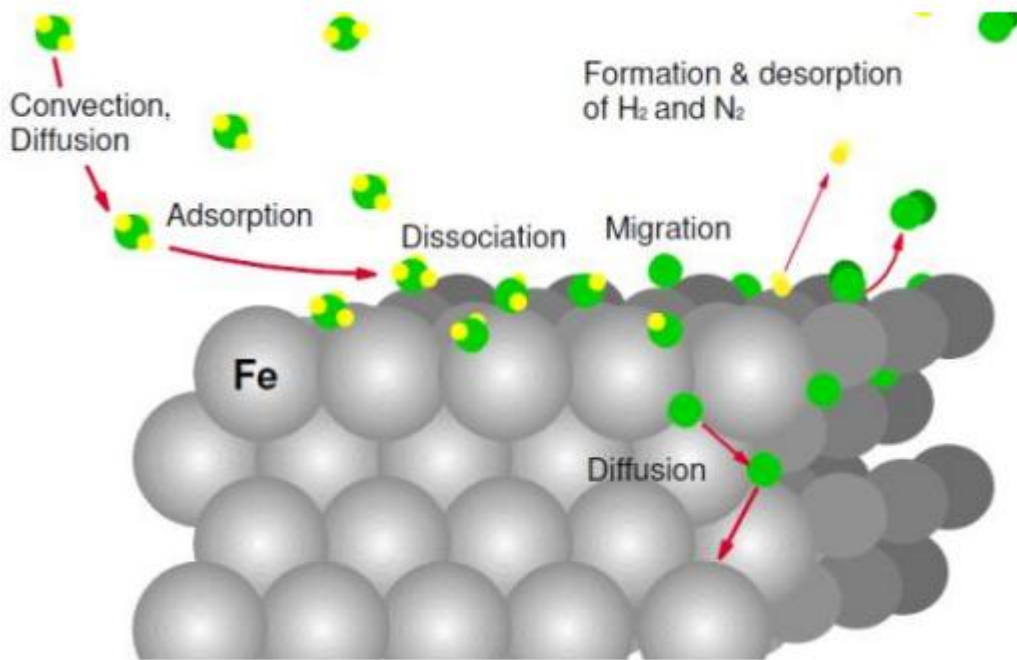
Figure 2. Schematic diagram of nitriding[4]

Nitriding was firstly developed in 1900s when Adolph Machlet discovered the solubility of nitrogen in iron[4, 17]. Nitrogen solubility (nitriding potential, K_N) at the surface of the metal is determined by the following equilibrium:

$$NH_3 \rightleftharpoons \frac{3}{2}H_2 + [N] \qquad\qquad 2.1$$
$$K_N = (_pNH_3)/(pH_2^{3/2}) \qquad\qquad 2.2$$
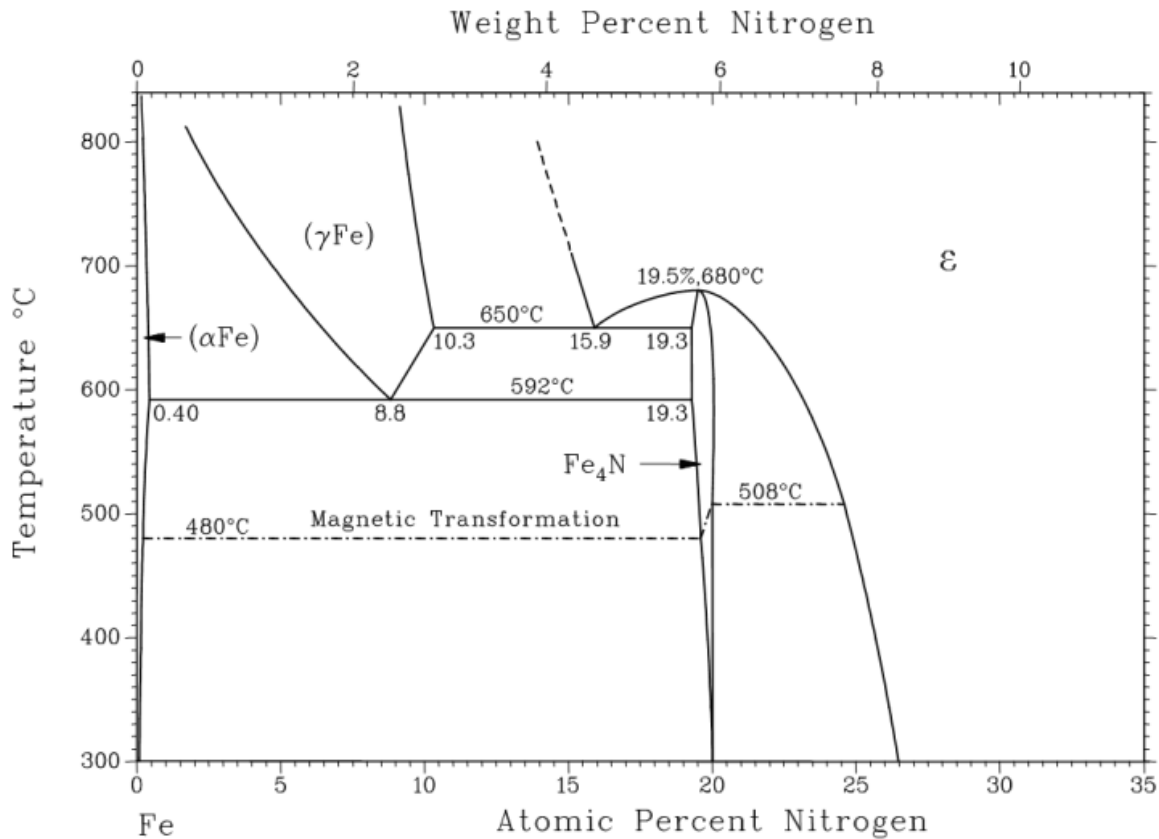
Figure 3. Part of the (metastable) binary Fe-N phase diagram. [30]

The solubility limit of nitrogen depends in the temperature. In the case of nitriding the temperature goes up to 580°C. In this case the solubility of nitrogen in gamma prime (Fe_4N) 6.1%. Beyond this weight percentage the phase changes to epsilon (ε) phase. The phase change from gamma prime to epsilon phase influenced by the carbon content of the steels. There is a more potential for the formation of epsilon phase for higher carbon content. As the temperature is further raised to the gamma prime phase temperature at 490°C, the limit of solubility begins to decrease at a temperature of 650°C[4, 17, 28, 31-33].

There is no phase chance in nitriding process from ferrite to austenite and the steel remains in the ferritic phase during the whole procedure. That means there is no change in the molecular structure of bcc to fcc that happened in carburizing. Since free cooling is take place in nitriding, no transformation from austenitic to martensite.

At different time, different researchers reported about the nitriding techniques. Hirotaka Kato[34] studied the wear resistance of steels using gas nitriding. He got a thick compound layer with high hardness and high wear rate. To reduce the thick compound layer and to reduce the wear rate a pack nitriding method of surface treatment which is dominated by epsilon iron nitride was used.

Sule Yildiz Sirin, Kahraman Sirin and Erdinc Kaluc [35] studied the effect of ion nitriding in the AISI 4340 steel and improve the fatigue strength, wear, corrosion and surface hardness of the steel. The study was limited in studying the diffusivity of nitrogen throughout the case depth. It was also faced for fatigue crack.

Elisangela Aparecida dos Santos de Almeida, Júlio César Giubilei Milan and César Edil da Costa [36] studied the hardness and wear properties of the tool steels (AISI H13, AISI P20 and N-8550) using solid nitriding, plasma nitriding and gas nitriding. They studied the properties of the tool steels by comparing of the three types of nitriding. They presented that solid nitriding shows good hardness and best wear resistant due to the formation of nitriding layer. The source of nitrogen for the solid nitriding was Fe_4KCN. They used expensive equipments which are unavailable for local manufacturers. The source of nitrogen is also difficult to obtain for the plasma and gas nitriding. They used a poisonous Fe_4KCN for solid nitriding that cause environmental and health problems.
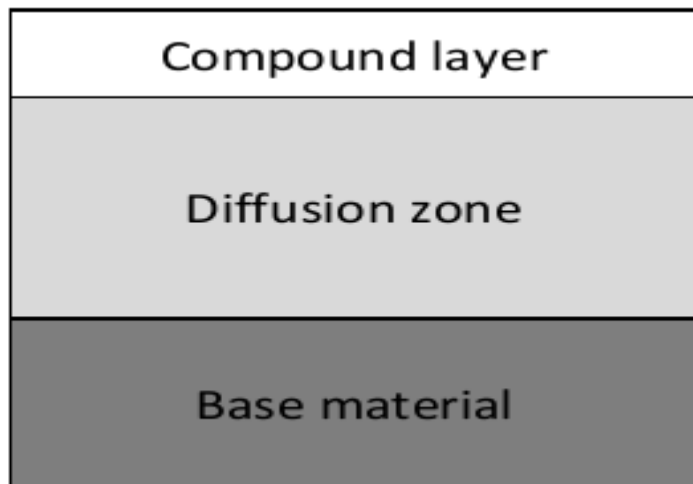
Figure 4. Schematic diagram of compound zone and diffusion zone[37]

As shown in the schematic diagram, the compound layer and diffusion zone changes their chemical composition and mechanical properties, but the base metal (inner core of the metal) remains unchanged[17].

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1.4. Case Depth

After the metal hardened their surface, the thickness of the hardened layer of the metal is called case depth. There are two types of case depth[28, 38, 39].

Effective case depth is the distance from the surface of a hardened case to the point for which a specified hardness is maintained. It is 2/3 or 3/4 of the total case depth.

Total case depth is the distance from the hardened surface to the point where there is no difference in the chemical or physical properties of the specimen. The distance is measured perpendicular from the hardened surface to the desired point in both effective and total case depth.

F.E Harris[38] defined a formula to describe the effect of temperature and time on nitriding case depth. Effective case depth changes linearly with the square root of time.

$$\text{Case depth} = K\sqrt{(t)} \qquad\qquad 2.3$$

Where K is temperature factor, t is time in hours and the unit of case depth expressed in inches.

The temperature factor for F.E Harris equation are listed in the below table.

Temperature (^{o}C)	Temperature factor, K	Temperature (^{o}C)	Temperature factor, K
460	0.0015	510	0.00217
470	0.00155	515	0.0023
475	0.00172	525	0.00243
480	0.00195	540	0.00262
500	0.0021		

Table 1. Temperature factors for Harris equation[38]

Hardness of the case depth decreases from the upper surface to the inner core of the specimen.
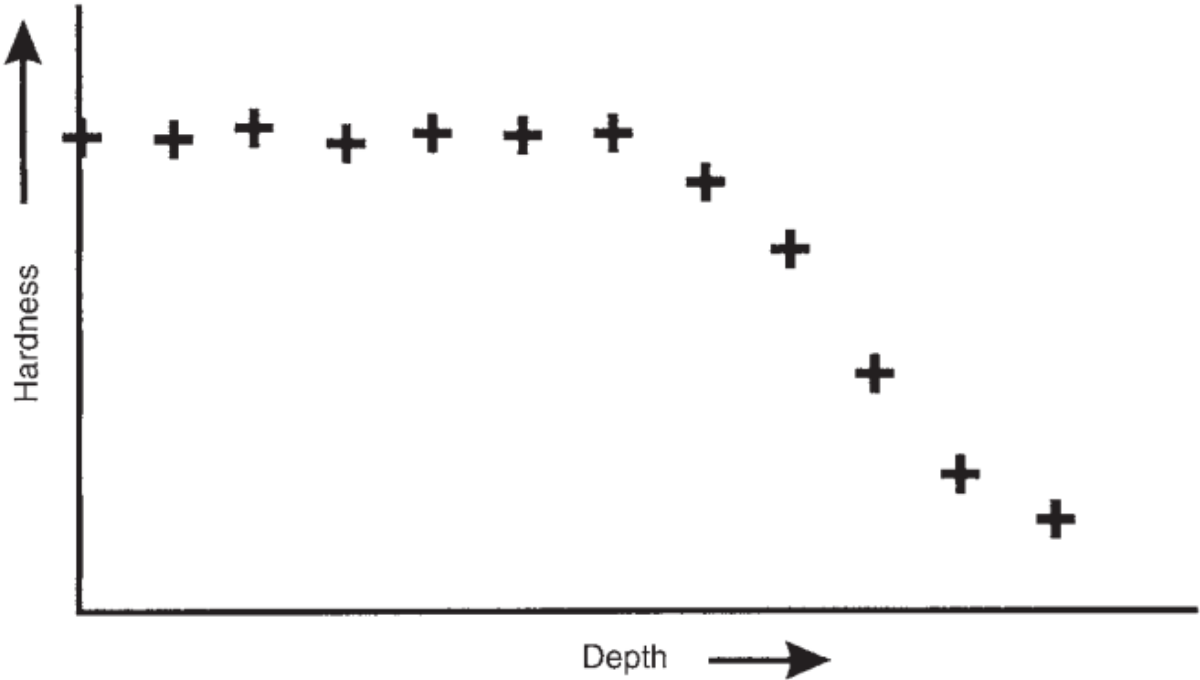
Figure 5. Hardness values versus case depth[17]

1.5. Ferritic Nitrogen Diffusivity

Nitrogen diffusivity is a kinetic parameter which defines nitrogen diffusion in the substrate and growth of the nitrides. The diffusivity of nitrogen and carbon in iron ferrite was studied by Silva and McLellan[40]. According to their experimental data, the diffusivity of nitrogen and carbon at high temperature does not obey the classical formula.

$$LnD = LnD_o - Q/KT \qquad 2.4$$

Instead

$$LnD_C = -2.087 - \frac{1.197 \times 10^4}{T} + \frac{3.7 \times 10^5}{T^2} \qquad 2.5$$

And

$$LnD_N = -4.485 - \frac{0.9979 \times 10^4}{T} + \frac{1.4 \times 10^5}{T^2} \qquad 2.6$$

are more suitable.

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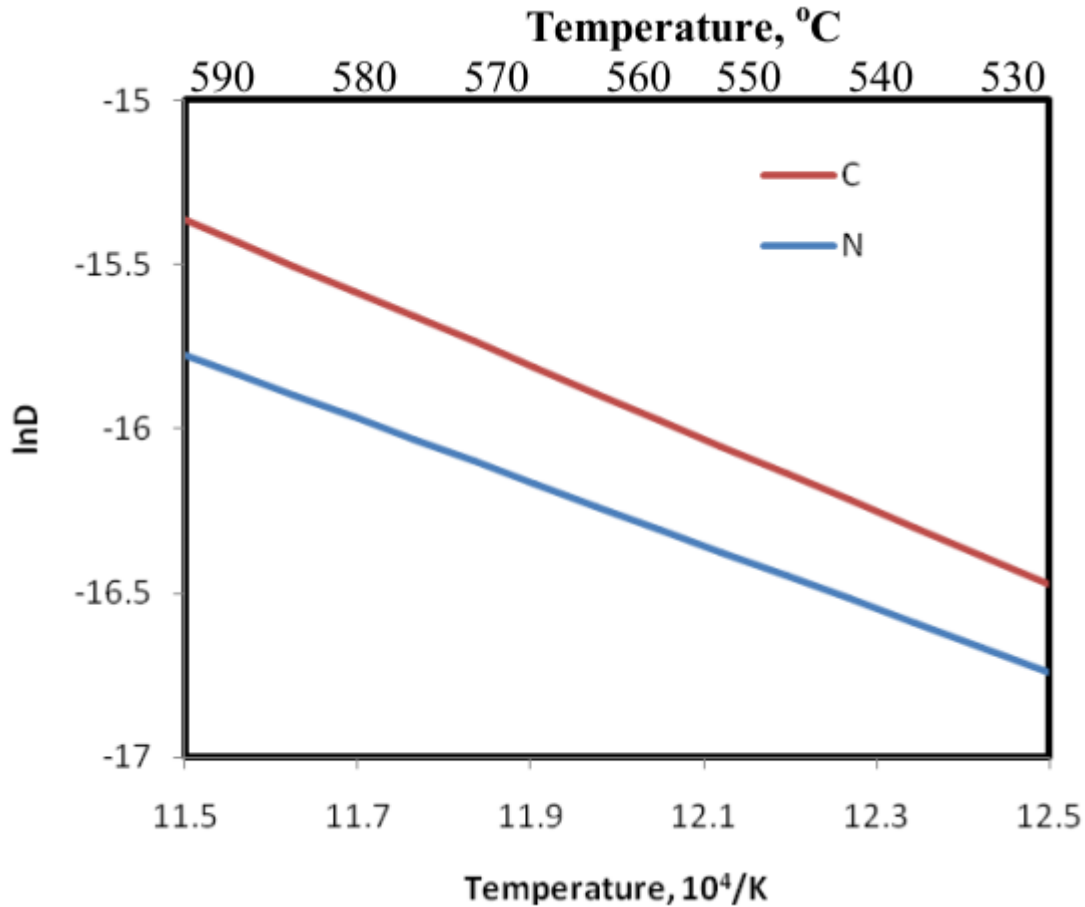
Figure 6. Diffusivity of nitrogen and carbon in iron ferrite[17, 28]

1.6. Parameters of Nitriding

There are a number of parameters need to be control in order to obtain a successful nitriding process. Most of these parameters can be controlled with simple instrumentation and methods. The parameters include[17]:

- Time
- Furnace temperature
- Process control factors
  - ✓ Total surface area to be nitride
  - ✓ Process pressure inside the sealed process chamber
  - ✓ Gas delivery pressure system into the sealed process chamber
  - ✓ Preheat treatment prior to nitriding
  - ✓ Quality and integrity of the steel surface
  - ✓ Steel chemistry (alloying elements)
- Gas activity control
- Gas flow
- Process chamber maintenance

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These parameters assist to minimize distortion during nitriding process. Controlling of these parameters insure the formation of acceptable metallurgical surface. Repeatability of metallurgical requirements cannot be guaranteed without controlling of these parameters[17].

1.7. Nitriding Techniques

Nitriding is classified as ion/plasma nitriding, gas nitriding, salt bath nitriding and pack nitriding according to the source of the nitrogen used.

a. Ion/plasma Nitriding

Ion nitriding uses plasma discharge reaction at lower temperature to absorb active nitrogen to the surface of the metal. Nitrogen is absorbed by the metal surface (working piece) after high voltage electrical energy is applied in a vacuum to form nitrogen ions. The nitrogen ions heat to the metal and gives active nitrogen to diffuse in to the metal[28].

b. Gas Nitriding

Gas nitriding is carried out by holding the metal at a temperature between $500^{\circ}C$-$600^{\circ}C$ in nitrogenous gas source. The mostly used nitrogenous gas source is ammonia which dissociates to nitrogen and hydrogen. Nitrogen diffuses to the metal surface and forms iron nitride and chromium, aluminum, vanadium and manganese nitrides if the metal is alloyed with these elements. Gas nitriding is advantageous for nitriding of complicated shapes[41].

c. Salt Bath Nitriding

Salt bath nitriding uses molten salt bath of cyanides as nitrogen source. Cyanides are decomposed to cyanates. And nitrogen is liberated and diffuses to the surface of the metal[17].

1.8. Application of Nitriding

Nitriding process play a vital role in many applications. It is used in automobile components, textile machinery, gears, crankshafts, camshafts, die casting tools, forging dies, extrusion dies, firearm components, injectors, plastic mold tools, cam followers, valve parts, turbine engine systems, extruder screws and bearings. In all these applications ferrous metals nitride to increase their corrosion resistance, wear resistance, for aesthetic appearance, to decrease friction and to increase hardness [17, 42, 43].

1.9. Other Thermochemical Surface Treatments

1.9.1. Carburizing

Carburizing is the introduction of carbon to the mild steels by the diffusion of carbon. Carburizing is carried out at high temperature which is higher than the ferritic temperature. The carbon diffuses to the steel surface from the carbon bearing source of materials[17, 44].

The iron-carbon phase diagram for carburizing shown in the figure 3. From the diagram, the phase up to maximum solubility of 0.01% is pure iron (α-ferrite). α-ferrite exists in solid solution of BCC Fe at low temperature. It transform to austenite at 912ºC and it is magnetic below the temperature of 768ºC. Austenite has a maximum solubility of 2.14%. It is solid solution of carbon in FCC Fe. At higher temperature δ-ferrite exists. During heating austenite transform to BCC δ-ferrite at a temperature of 1395ºC. δ-ferrite has a melting point of 1538ºC. The phase with a maximum percentage of carbon (6.7%) is cementite, Fe₃C.
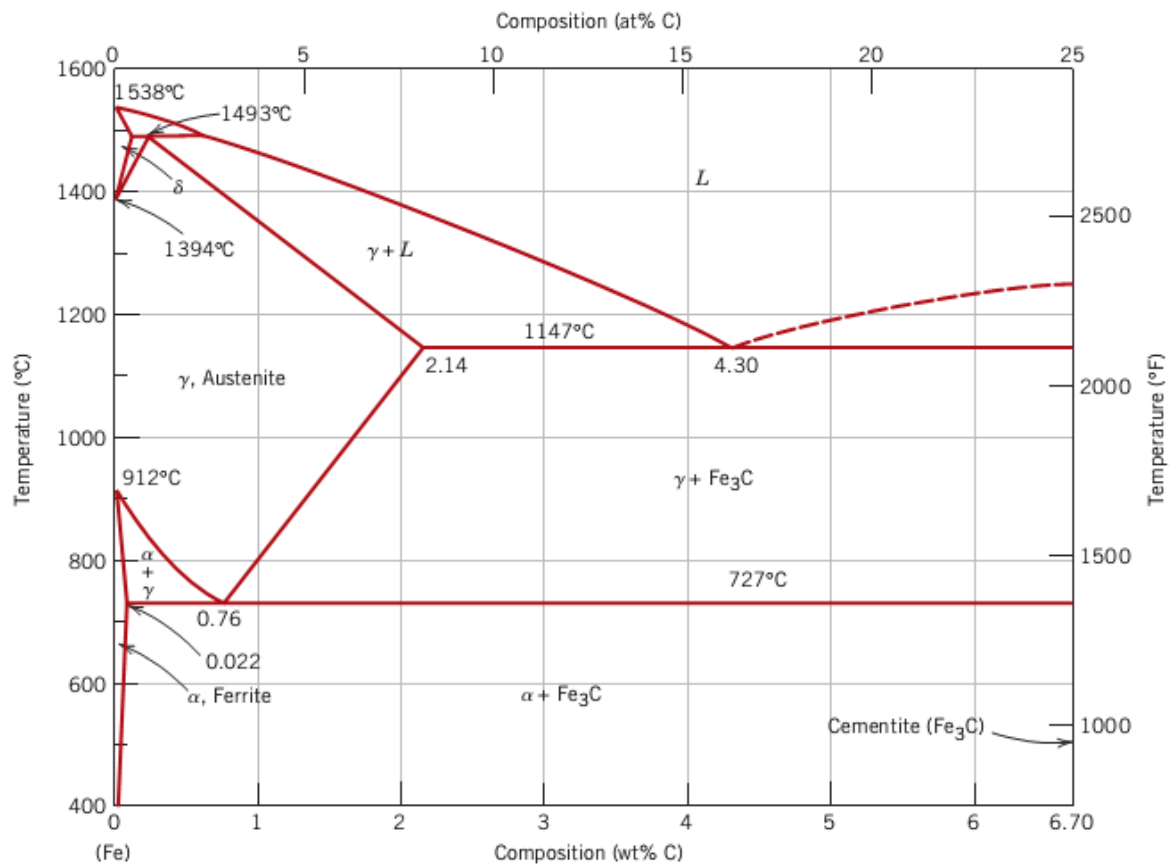
Figure 7. Iron-carbon phase diagram[45]

1.9.2.   Carburizing Techniques

Carburizing is classified in varieties of process based on the source of carbon used.

a. Pack carburizing

It uses a solid carbon bearing sources such as charcoal and coke and heated the packed samples in sealed container[17, 46].

b. Liquid/salt Bath Carburizing

The surface treatment and case hardening is carried out in molten cyanide baths. Salt bath cyaniding gives low distortion and easy control process, but environmental problems due to the poisonousness of the cyanides[17, 47].

c. Gas Carburizing

Gas carburizing is carried out in a furnace consists of a carrier gas to avoid soot formation by ensuring a positive furnace pressure and enriching gas (hydrocarbon gases like methane, propane) gives a source of carbon[17, 48].

d. Vacuum Carburizing

In vacuum carburizing the diffusion of carbon is takes place in a vacuum. The treated samples quench in oil or gas. It is helpful to obtain excellent uniformity and reproducibility of samples, short cycle time and good mechanical properties due to lack of oxidations[17, 49].

e. Ion/plasma Carburizing

It is a vacuum process uses glow discharge method to carbon containing ions to the metal surface for diffusion[17, 50].

1.10. Nitrocarburizing

Nitrocarburizing is the diffusion of nitrogen and carbon (small amount of carbon) to the surface of metals mainly ferrous metal at the temperature between $500^{o}C$-$590^{o}C$ in a ferritic state. By diffusing the nitrogen and carbon it forms a thin compound layer containing ε $-Fe_{2-3}(C, N), \gamma'$ - $Fe_{4}(N,C)$ or combination of ε and γ' and diffusion zone[3, 6].
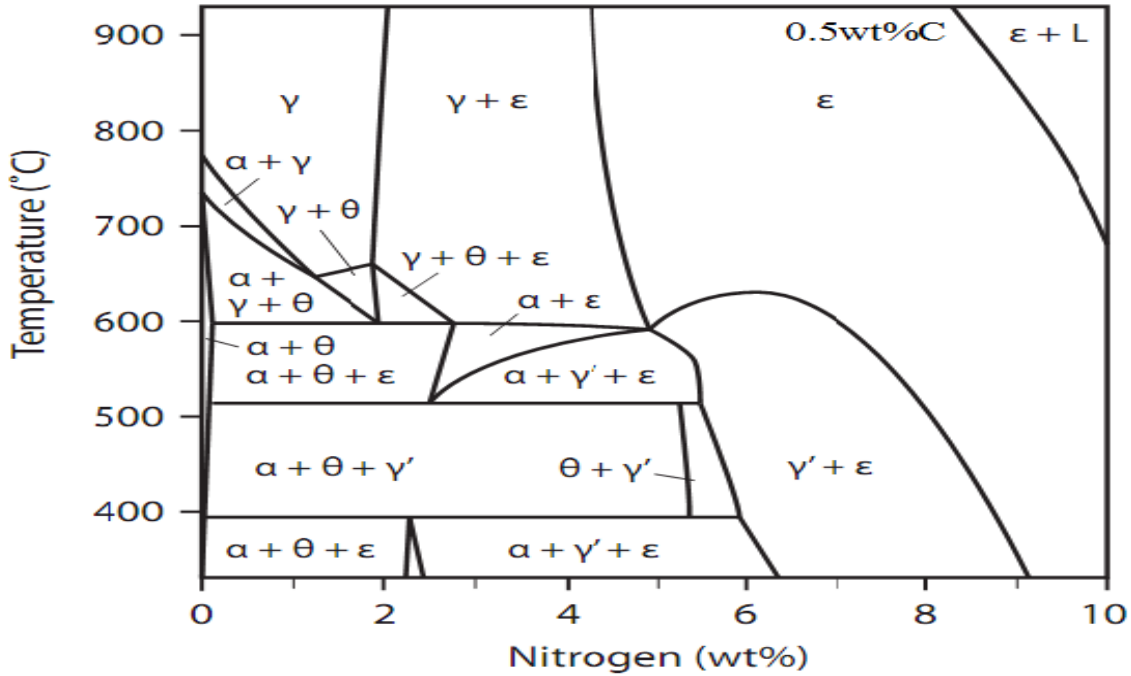
Figure 8. phase diagram of Fe-N-C[3]

1.11. Nitrocarburizing Techniques

a. Fluidized Nitrocarburizing

Fluidized Nitrocarburizing is done by blown of methane, ammonia and pressurized air to fluidized catalyst like Al-Ni-Mg or aluminum oxide. The heating media for fluidized nitrocarburizing is either electric or gas. The heat is transferred from the heating medium to the sample by the finely divided catalysts[51].

b. Plasma/Ion Nitrocarburizing

Ion nitrocarburizing produce a compound layer and diffusion zone on the surface of the steel by using nitrogen, hydrogen and carbon bearing gases at a low pressure using a glow discharge with high ionization[52].

c. Salt Bath Nitrocarburizing

The salt bath nitrocarburizing uses a cyanide or non-cyanide molten salts containing nitrogen and carbon to the surface treatment of the steel metals. The surface of the steel forms a compound layer and diffusion zone when the nitrogen and carbon from the salt bath reacts with the metal surface[53].

d. Gas Nitrocarburizing

To produce compound layer and diffusion zone on the steel surface, the gas nitrocarburizing thermochemical process uses hydrocarbon and ammonia as a source of nitrogen and carbon. It is also possible to use carbon bearing gases such CO and CO_2 instead of hydrocarbon. The active atomic nitrogen and carbon diffuse to the steel [54].

e. Vacuum Nitrocarburizing

In vacuum nitrocarburizing, ammonia and carbon producing gases are transferred into vacuum furnace holds a sample. Then the sample is heated in the vacuum furnace at the temperature between $500^{o}C$ and $590^{o}C$ by varies the temperature and time to find different thickness of the compound layer and diffusion zone[55].

1.12. Carbonitriding

Carbonitriding is the modified gas carburizing. In carbonitriding ammonia is introduced into gas carburizing atmosphere to add small amount of nitrogen to the carburized surface. Carbonitriding is carried out at a lower temperature ($700^{o}C$- $870^{o}C$) and shorter time than the carburizing (gas carburizing)[56].

1.13. Boronizing/Boriding

Boronizing is the surface treatment method by which boron diffuses to the metal surface at the temperature of 760-$1095^{o}C$. After heating to the boronizing temperature the surface forms a metal borides such as FeB (more concentrated on the surface), Fe_2B (concentrated in the inner surface) and other metal nitrides formed due the metal alloying elements of the steel, such as borides of nickel and cobalt. They have very high hardness, high corrosion and wear resistance[57, 58].

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1.14. Diffusion of Nitrogen in Nitriding

Diffusion is the material or atomic transport form high concentration region to lower concentration of the region. When metals are heat treated there is diffusion of atoms. Diffusion in solid materials is either atoms of one solid material diffuse in to another solid material, called interdiffusion/impurity diffusion or the diffusion in pure solid materials (metals) by exchanging the position of the same atoms called self-diffusion[45].

1.14.1. Diffusion Mechanisms

Diffusion is migration of atoms from one lattice site to another lattice site[45].

For the movement of the atoms:

i.   There must be an empty adjacent site

ii.   The diffusing atom must have enough energy to break bonds and cause to lattice distortion at the time of displacement.

There are two types of mechanism of metallic diffusion[45].

i.   Vacancy Diffusion

In vacancy diffusion atoms are interchange from normal lattice position to the neighboring vacant lattice site. There is an exchange of the diffusing atoms and vacancies. To move atoms from one lattice to another lattice they need an energy comes from the thermal energy of atomic vibrations (K_BT). This energy break the adjacent bonds.
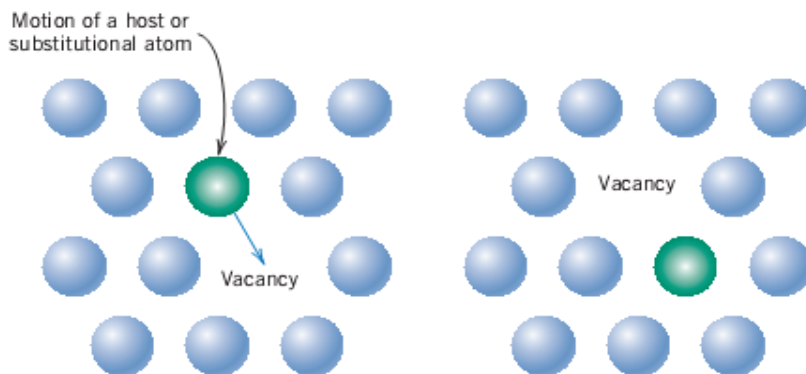
Figure 9. Schematic diagram of vacancy diffusion[45]

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ii.   Interstitial Diffusion

It is the interdiffusion of small atomic radii elements such as hydrogen, carbon, oxygen and nitrogen which are small enough to fit into the interstitial positions. Interstitial diffusion happens faster than vacancy diffusion due to smaller and more mobility of atoms depending on the lattice type of base metal to which diffusion is allowed to perform[45].
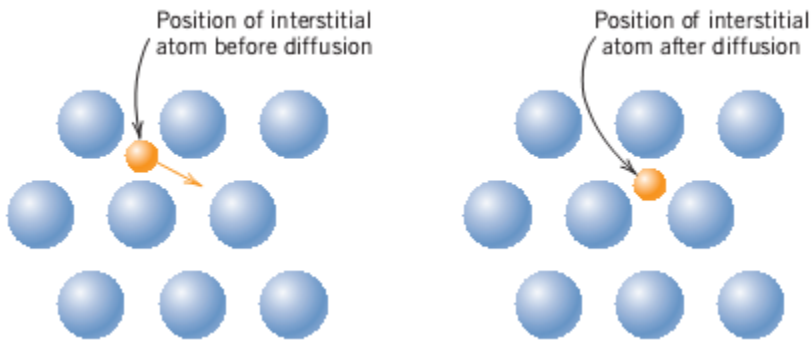
Figure 10. Schematic diagram of interstitial diffusion[45]

1.15. Diffusion Modelling
1.15.1. Steady State Diffusion

Steady State diffusion is a diffusion in which the numbers of moles of particles cross for a given interface is constant with time. The rate change of concentration with distance, dC/dX is constant and change of concentration with time, dC/dt is zero through the system.

In steady State diffusion, the diffusion flux does not change with a time. Diffusion flux is expressed as: the number of atoms (M) diffusing through a material perpendicular to the cross sectional area (A) of solid material per unit time (t)[45].

$$J = \frac{M}{At}$$

2.7

Concentration profile (plot of concentration, C versus distance, x within a solid) at a particular point gives concentration gradient (slope).

$$\text{Concentration gradient} = dC/dx$$

2.8

In steady state diffusion, the concentration profile is assumed linear, so

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Concentration gradient=$\Delta C/\Delta x$=$(C_A-C_B)/(x_A-x_B)$ and the flux is proportional to the concentration gradient:

$$J=-D\frac{dC}{dx}$$ 2.9

Where D is diffusion coefficient in meters square per second for a given pair of system.

This equation is called Fick's first law[45].
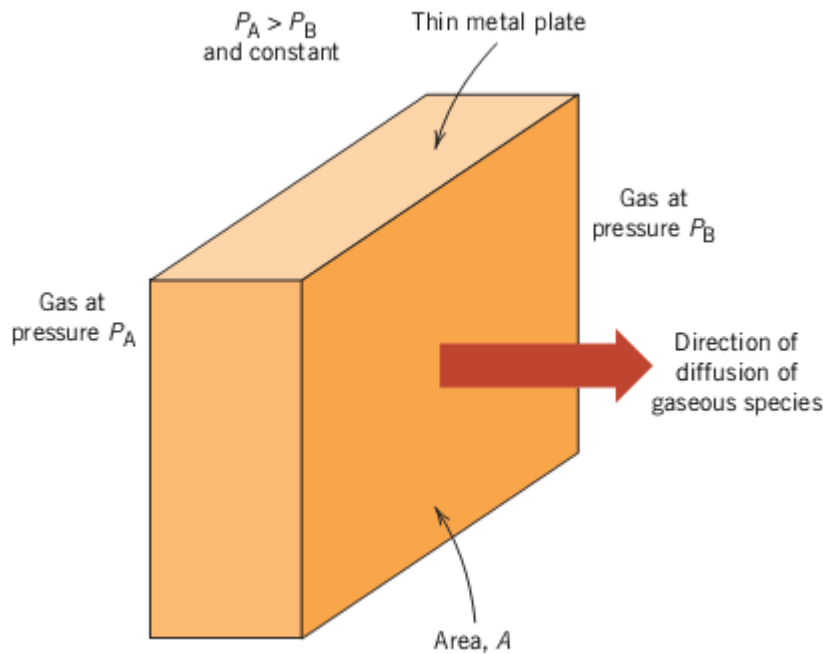
Figure 11. Steady state diffusion across thin plate[45]

1.15.2. Unsteady/Non-steady State Diffusion

In non-steady state diffusion, the rate of diffusion is as a function of time. So the rate of concentration with distance, dC/dx is different from constant and change of concentration with time, dC/dt is not zero[45].

$$\partial C/\partial t=\partial/x(D\partial C/\partial x)$$ 2.91a

This equation is called Fick's second law. This simplified to

$$\partial C/\partial t=D\partial^2 C/\partial x^2$$ 2.91b
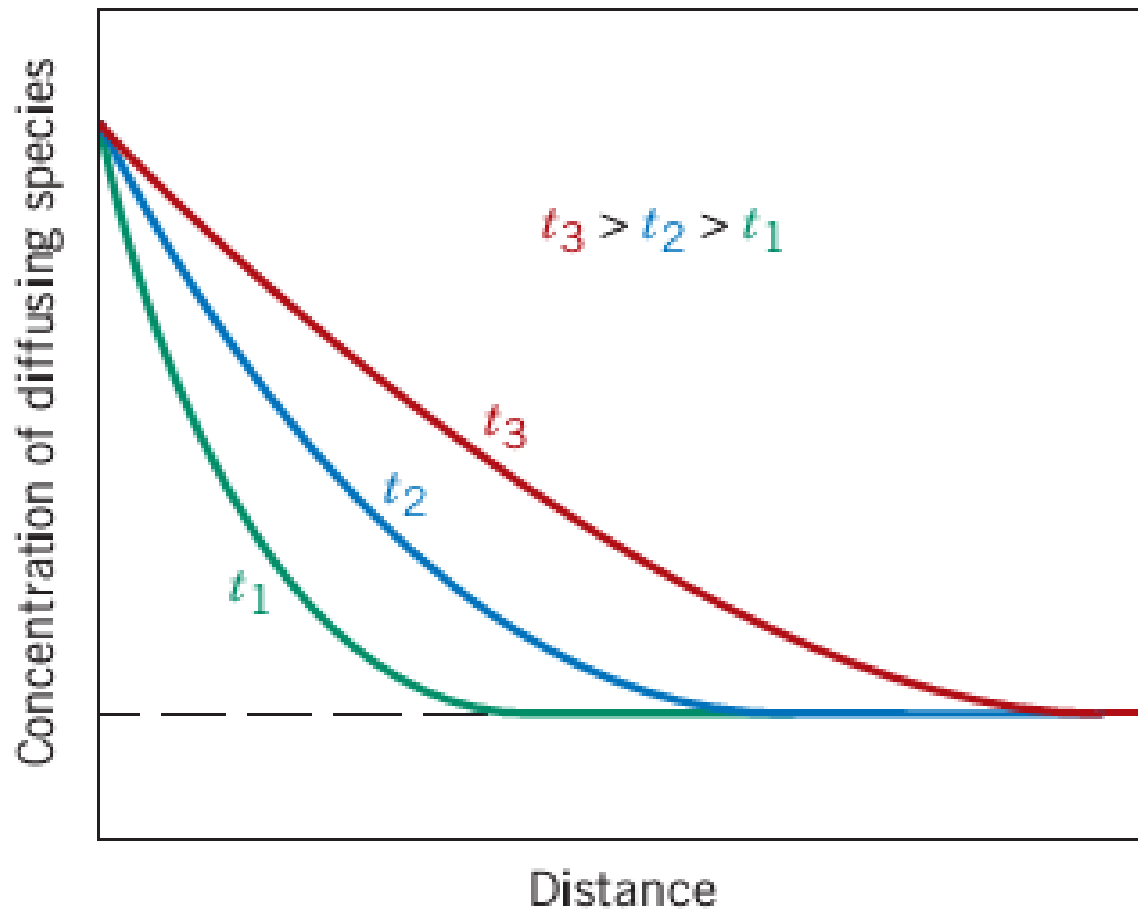
Figure 12. Concentration profiles for non-steady state diffusion at three different times t1, t2 and t3[45]
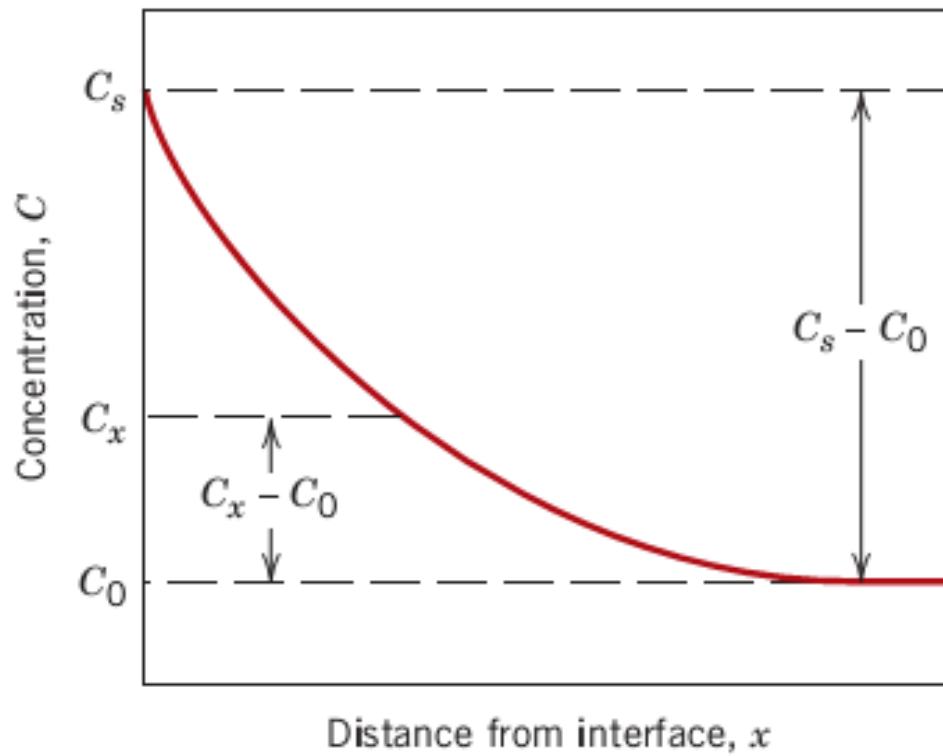
Figure 13. Concentration profile for non-steady state diffusion with respect distance from the interface[45]

$$\text{For t=0, C=C}_o \text{ at } 0 \leq x \leq \infty \qquad\qquad 2.92$$

$$\text{For t>0, C=C}_s \text{ at x=0} \qquad\qquad 2.92b$$

$$\text{C=C}_o \text{ at x=}\infty \qquad\qquad 2.92c$$

Equation 2.91b yields the solution for the boundary conditions[45].

$$\frac{Cx-Co}{Cs-Co}=1\text{-erf}(\frac{x}{2\sqrt{Dt}}) \qquad\qquad 2.93$$

1.16. Metallic Corrosion and Protection

Corrosion is a destructive results by chemical or electrochemical reaction of a metal with the environment. It is irreversible deterioration of a metal. In nature metal atoms are present in the form of chemical compounds such as oxides, hydroxide, and sulfides. Thus the refined metal tends to convert to more chemically stable form of its compound. Corrosion returns the metal to its chemical compound. Corrosion is the omnipresent and omnipotent universal phenomena [22, 25, 59-62].

Corrosion is the most serious problem in the modern time results losses every year hundreds of billion dollars. Studies shows that each nation invests approximately 1 to 5% of its GDP for corrosion costs. The global cost of corrosion estimates US$2.5 trillion. This is direct economic cost of corrosion. The indirect costs causing from actual corrosion are more challenging to estimate, but they are possibly even greater. The indirect sources of corrosion costs include: plant downtime cost, loss of product, loss of efficiency, contamination and overdesign[59-61].

Corrosion results failure in transportation, electric power generating plants, chemical process and manufacturing plants, constructions and household materials. Airline accidents, bridge collapse, failure of welded liquid gasoline pipeline, ship sinking and structure collapse are the usual failures due to corrosion[60, 61].

Corrosion penetration of metals calculates using the following formula.

$$\text{CPR} = \frac{KW}{\rho A t} \qquad\qquad 2.94$$

Where K is a CPR constant having a value 87.6, W is the loss of weight after time exposure (g), ρ is the density in g/cm^3, A is an area in cm^2 and t is time in hours.

1.17. Corrosion Protection

All the forms of corrosion have different techniques to prevent corrosion. The most widely general techniques to prevent corrosion are: cathodic protection, environmental alteration, material selection, proper design and coatings. The method of prevention may also differ from one type of metal to other.

In this research the type of the corrosion prevention method studied is thermochemical surface treatment, which is thin surface layer formed by pack nitriding of steels[22, 60, 72].

Chapter Three

Methodology

3.1. Material Collection

The materials needed for this research were collected from different sites. The steels needed for pack nitriding thermochemical heat treatment were collected from Burka Gibe Metal Shop. AISI 1018 mild steels and AISI 1045 rod steels were collected and cut to the desired size. The urea was collected from chemical seller shops. It is standard and manufactured for the purpose of experiment.

3.2. Materials Used in the Experiment

The raw materials and instruments used to achieve this research are the following: mild and medium carbon steel samples, urea, cutter machine, grinder, electronic balance, furnace, glove, stainless steel box and oven. Other instruments such as SEM, atomic absorption spectroscopy, XRD, metallurgical optical microscopy, TGA, micrometer screw gauge, cyclic voltammetry, Vickers' hardness tester and Brinell hardness tester machines were used for characterization.

3.3. Experimental Design

The experimental design investigated the effect of nitriding on the mechanical properties of steels (hardness, wear and strength) and the chemical properties such corrosion. It includes from the collecting of the steels until their characterization. It can be summarize as in the following schematic diagram.

```
                    ┌─────────────────────────┐
                    │   Material Collection   │
                    └─────────────────────────┘
                                 │
                    ┌─────────────────────────┐
                    │   Sample Preparation    │
                    └─────────────────────────┘
          ┌──────────────────┐
          │  Characterizati  │
          └──────────────────┘
                    ┌──────────────────────────────────────┐
                    │  Heating of the sample inside a furnace│
                    │  with urea to 400ºC at the rate of 10ºC/min│
                    │           and wait for 1 hour          │
                    └──────────────────────────────────────┘
                    ┌──────────────────────────────────────┐
                    │  Heating of the inside a furnace to 500, 530,│
                    │       550 and 580ºC for different hours│
                    └──────────────────────────────────────┘
                    ┌─────────────────────────┐
                    │   Cooling of Samples    │
                    └─────────────────────────┘
                    ┌─────────────────────────┐
                    │     Characterization    │
                    └─────────────────────────┘
```

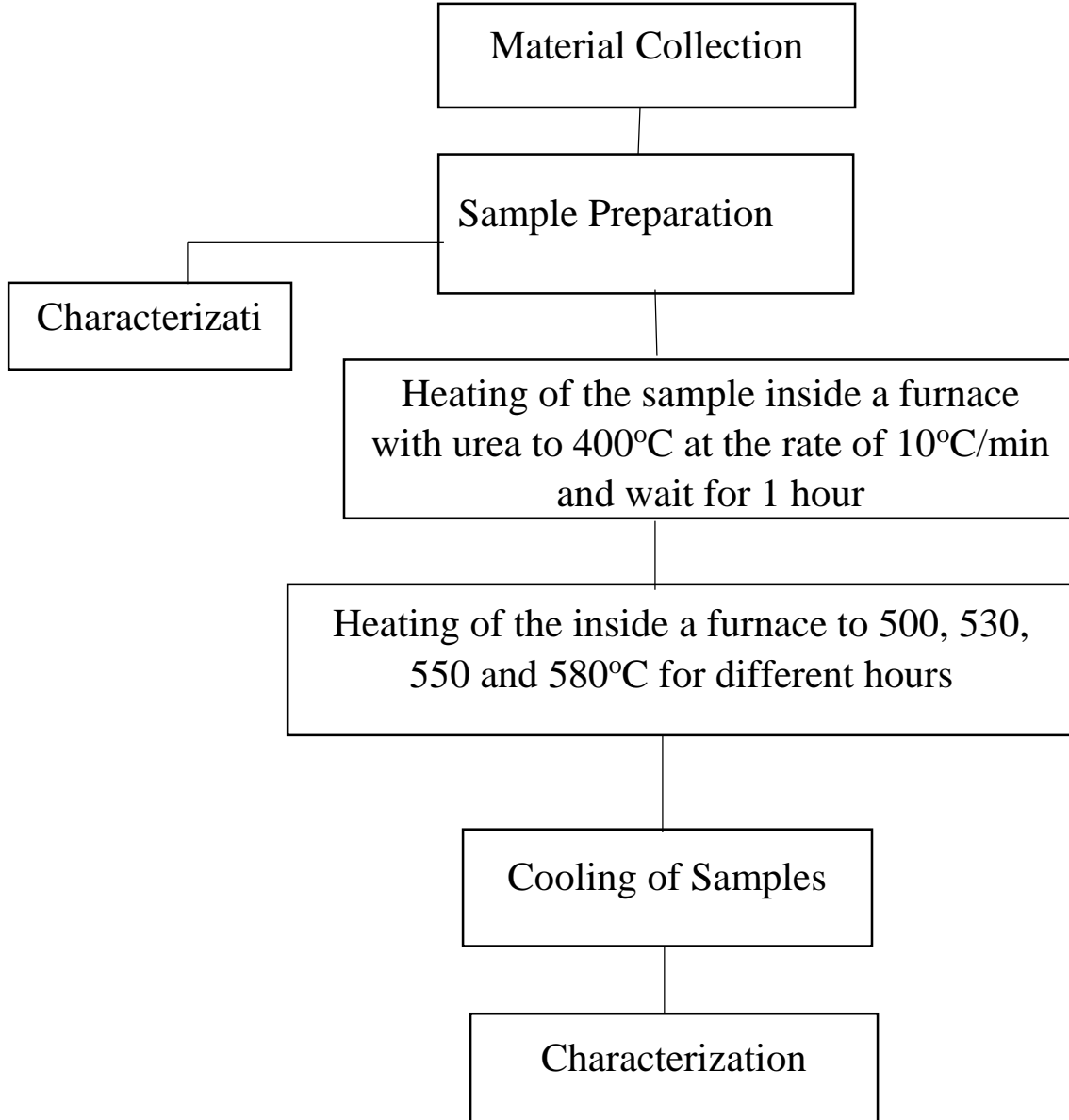Figure 14. Schematic diagram of experimental design

3.4. Sample Preparation

The samples prepared for pack nitriding were steels with different composition. To study the effect of the pack nitriding AISI 1018 mild (low) carbon steels and AISI 1045 medium carbon steels were prepared and studied the effect of the pack nitriding of each material. Their chemical composition is given the table 1 and 2[73-76].

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Element	C	Si	Mn	S	P	Fe
Percentage	0.15-0.20	0.15-0.35	0.60-0.90	0.05 (max)	0.04(max)	Balance

Table 2. Chemical Composition of AISI 1018 steel (wt. %)

Element	C	Mn	S	Cr	Al	Mo	V	P	Si	Ni	Fe
Percentage	0.45	0.75	0.008	0.017	0.048	0.002	0.02	0.011	0.257	0.13	Balance

Table 3. Chemical composition of AISI 1045 (wt. %)

The carbon steels (AISI 1018 and AISI 1045 steel) samples were collected from Burka Gibe Metal Shop. In the mechanical shop the medium carbon steels are used for making of crank shafts and gears. Samples are then cut to the desired size using cutter machine. The round metal bars (shafts) with a diameter of 26 mm are reduced to 10 mm using milling machine and then cut to height of 4 mm. After the samples are milled and grounded using SiC emery papers from the coarsest 120, 240, 320, 400, 600, 800, and 900 to the finest 2400.

During grinding the specimen is held in a fixed position on the emery paper to prevent scratches in the different directions. The scratches must be in one direction. Holding the specimen in fixed position is also helps to apply an even and moderate pressure during the grinding. When the emery paper changed, the direction of specimen must be change 90° to disappear the scratches from previous polishing. Then samples are polished using 1.0, 0.5 and 0.1 μm of alumina (Al_2O_3) paste. The scratches during grinding are polished and became smooth and mirror finish surfaces and free of any scratches. During each polishing the samples are rinsed to avoid carrying of particles and contaminants from one wheel to another wheel.

Low carbon steel sheet metal samples were also collected and prepared with 0.1cm×1cm×1cm. The procedure to prepared those samples are the same with the round bar preparations. The samples are polished until they became mirror finish. Microstructure analysis was made to compare the result after samples were pack nitrided. Experiments for hardness and XRD were also made before pack nitriding to see the effect of the treatment.

After samples are prepared, pack nitriding was made in a furnace, Nabertherm GmbH B180. Samples were buried with urea in silica crucibles inside a box made up of stainless steel and sealed by fire clay to prevent any entering of gases to the sample and to prevent escaping of

gases from the system. Sealed the box is also important for safety, because ammonia gas may escape and cause health problems.

The sample having urea heated to the temperature of 400ºC at the rate of 10ºC/min and waiting for 1 hour to obtain melamine. After waiting time of 1 hour, the temperature rises up to 580ºC at heating rate of 5ºC/min to decompose the melamine in to ammonia and ammonia to nascent nitrogen. At this temperature the sample also waited for specified period of time. The nascent nitrogen diffuses to the steel. The diffusion depth depends in time and the temperature used. Elevated temperature and long diffusion time allows the nitrogen to diffuse in more depth. At this research the effect at the temperature of 500ºC, 520ºC, 550ºC and 580ºC were studied. The effect of time was also studied. 2, 3, 4, 5, 6, 7 and 8 hours were taken to observe the effect.

Samples were cooled in the furnace. Samples were removed from the furnace and cooled in air and other samples cooled inside the furnace and their difference was studied.

The concentration of diffusing elements i.e nitrogen was also studied by changing the amount of urea used.
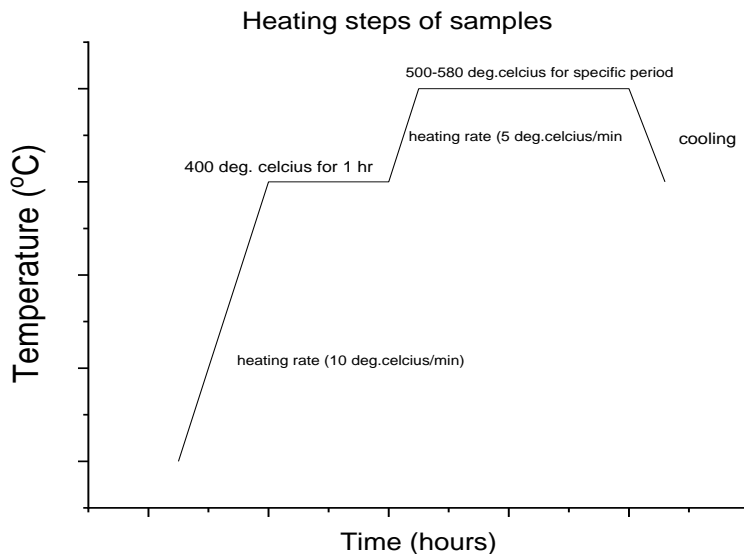

Figure 15. Schematic diagram of heating process during nitride

3.4.1. Metallographic Sample Preparation

Metallography is the study of microstructure of metals and alloys. Studying the microstructure of metals and metal alloys helps in controlling of the metals and alloys. The detail study of the microstructure of the materials has an important role in studying of materials developments, selection of materials and investigation of the failure of the metals. The microstructure of the metals were studied using optical microscope, electron microscope such scanning electron microscope, transmission electron microscope, atomic force microscope, field ion microscope, auger microscope, scanning tunneling microscope, ultrasonic microscope, acoustic microscope , atomic force microscope and others for specific studying and uses of the materials. The technique of the sample preparation for different microscopes may vary for the different types of microscopes.

To observe samples using optical microscope grinding, polishing and then they were etched with Nital. To observe using SEM the sample must be conductive. For the samples which are not conductive, samples were coated with gold.

3.4.2. Sample Preparation for Hardness Test

Standard test sample were prepared according ASTM. Round rods with a diameter of 12 mm were taken and cut in to a length of 4 mm for the shafts and rectangular plates with length of 10mm, 10mm width and 1mm of height for the mild steel sample. Samples were cleaned to remove any contaminant such as dust, lubricants or oil and other dirty materials.

To study the hardness of coatings of the case hardened materials, Vickers hardness is more preferable because it uses small load to indent the surface of the material. The Vickers's machine available in the laboratory used to study this research was with a minimum load of 1 kg. So all the samples were tested using 1 kg load.
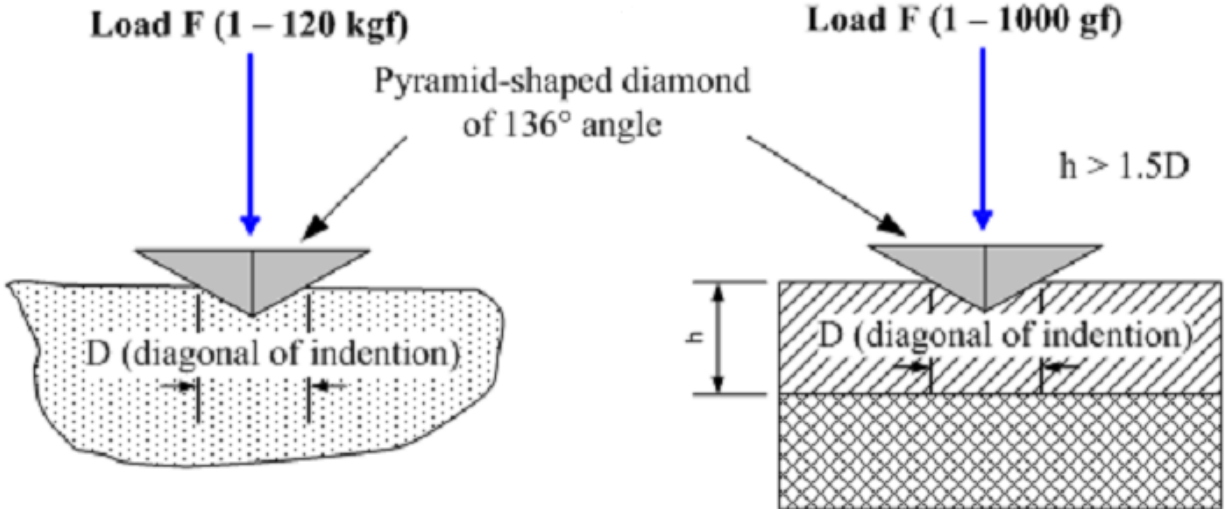
Figure 16. Schematic diagram for Vickers's hardness test

3.4.3. Sample Preparation for XRD

The samples for XRD experiments were cut with size of the sample holder of XRD diffractometer. Then the samples were cleaned and free of any contaminants and dusts. Solid objects can be fixed in the sample holder for non-standard sample sizes and shapes using modeling wax or plasticine. Samples must be put in the center of goniometer. The diameter of the cavity is 44 mm, the maximum sample height is 6.5 mm.

3.5. Characterization Techniques

3.5.1. Thermogravimetric Analysis (TGA)

Thermogarvimetric analysis (TGA) is a technique used to measure mass change of a sample as a function of time or temperature in controlled atmosphere. The temperature changes with time and temperature constantly. Time or temperature showed in x-axis and the mass change or weight percentage in the y-axis. The data was recorded in the form of graph called TGA curve or thermogram and displayed from left to right. The mass change data recorded in thermobalance and displayed in computer. TGA measures the mass change during heating or cooling.

The mass decrease or may increase. Thermal reactions of TGA happened in different environments such in vacuum, carburizing gases, inert gas, and nitrogen atmosphere. This atmosphere controls the environment of the sample. Thermogaravimetric analyzers have a furnace made of quartz and the temperature goes until 1000ºC.

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TGA gives information of the sample such as thermal decomposition, phase transition, adsorption, absorption, moisture content, desorption and reaction of solid-gas. The change in the mass is due to thermal decomposition, absorption or desorption, adsorption and reaction. The heating rate is usually in the range of 10-20°C/min and sample weight up 100mg.

In this research TGA-4000 installed with a software called Pyris thermal analysis was used to study the thermal decomposition of urea and phase changes occurred in urea. The urea sample weight was taken 15mg at heating rate of 20°C/min in N_2 gas atmosphere.
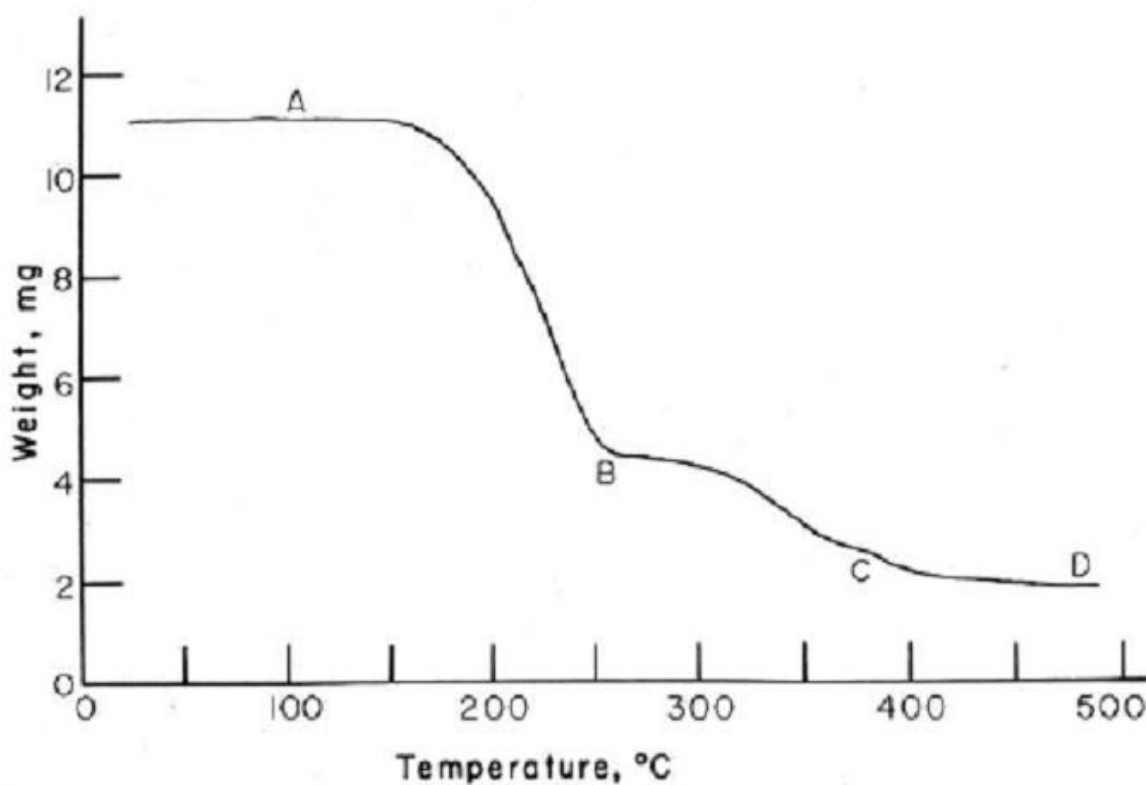
Figure 17. Decomposition of urea on heating

3.5.2. Brinell hardness testing

In Brinell hardness test a 2.5, 5.0 or 10.0 mm steel ball indenter used to indent the sample, A Brinnel hardness tester, HB-3000HB was used to study the hardness.

The loading force for indentation varies from 30 kg to 3000 kg for a specified time in the range of 10-30 sec. Materials with small hardness use small load and materials with high hardness use

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large load. Brinell hardness obtained by measuring the impression/indentation of the sample using an optical lens. The lens was not connected to the machine.

Brinell hardness, HB number is calculated using the following formula:

$$\text{HB} = 2F/(\pi D(D - \sqrt{(D^2 - d^2)})) \qquad 3.1$$

Where F is applied load in kg, D is steel indenter diameter and d is indentation diameter in mm.
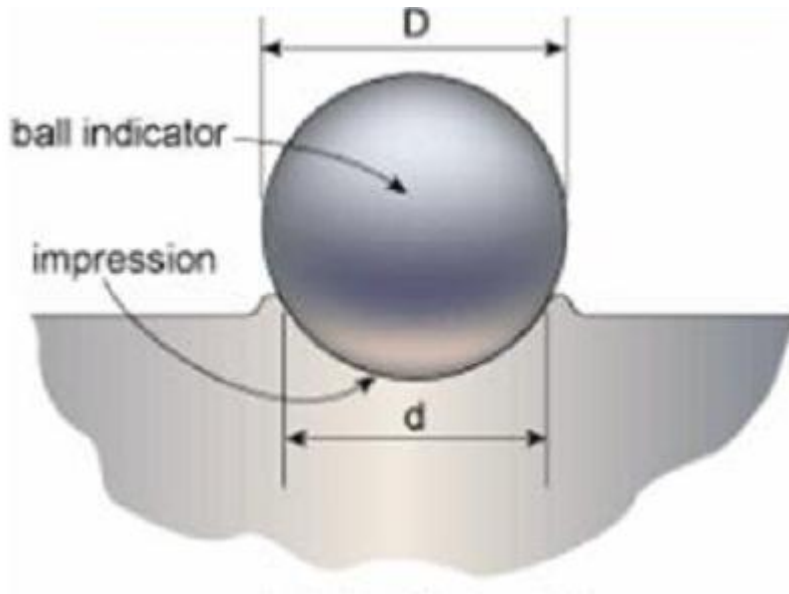
Figure 18. Brinell Indentation

3.5.3. Vickers Hardness Testing

Vickers hardness tester machine, HVs-50 connected with optical lens was used to investigate the surface hardness of the samples. Vickers hardness has similar principle with Brinell hardness and it is an alternative hardness test with diamond indenter of 136° square based. The indentation measured using optical microscope connected to the machine. Comparing with Brinell hardness, the indentation formed by Vickers are clearer and more accurate than in the Brinell. The loads varies ranging from a few grams to several kilograms. Vickers micro hardness varies from 1 gram to 1kg and other ranged up to 120 kg which measure large indentation areas.

The formula used to calculate the Vickers hardness is:

$$\text{HV} = (1.854F)/D^2 \qquad 3.2$$

Where F is applied load, D is the diagonal of the indentation.

The load used to test samples in this research was 1kg and loading time of 15 seconds.

3.5.4. Metallurgical Optical Microscopy

Metallurgical optical microscope also called light metallurgical microscope uses light and lenses to create images of small materials. The object put in stage and the image shows in the display screen or directly through the eyepieces of the microscope. Optical microscopes can magnify up to 2000 times (2000X) and their resolution is up to 0.20μm (200nm). LH100-1 type optical microscope having ScopeImage software was used to investigate the microstructure.

3.5.5. Scanning Electron Microscopy (SEM)

SEM uses beam of electrons to give an image by scanning the surface of the sample. The beam of the electrons from the electron gun source interact with the atoms of the sample to produce variety of signals having an information about the surface topography, chemical composition of the sample, crystalline structure and orientation of the materials. The signals contain low energy secondary electrons (50 eV), back scattered electrons and diffracted back scattered electrons produce image of the sample.

The magnification of SEM is up to 3,000,000X and resolution between 1 nm to 20nm. In SEM data were collected and imaged in specific area of the sample approximately ranging from 1 cm to 5μm in width.

The sample for SEM analysis need good conductivity and low magnetic. Nonconductive samples are coated with conductive materials.

Figure 19. Scanning electron microscope

3.5.6. X-Ray Diffraction (XRD)

XRD is a rapid nondestructive analytical method to characterize crystalline materials. It helps to identify the phase of the materials, structure, and crystal orientation, strain of materials, atomic spacing, average grain size, crystal defects and crystallinity. Peaks of the XRD are produced by constructive interference of monochromatic beam of x-rays. These x-ray beams are scattered from lattice planes of the sample at specific angles. X-rays are produced from cathode ray tube and directed to the sample. Before directed and hit the sample, x-rays were filtered to monochromatic radiation and collimate to concentrate.

A constructive interference produced by the interaction of the incident rays with the sample when the condition for Bragg's law satisfy.

$$n\lambda = 2d\sin\theta \qquad\qquad 3.3$$

Where n is an integer, λ is wavelength of the X-rays, d is the interplanar spacing of the diffraction and θ is the angle of diffraction.
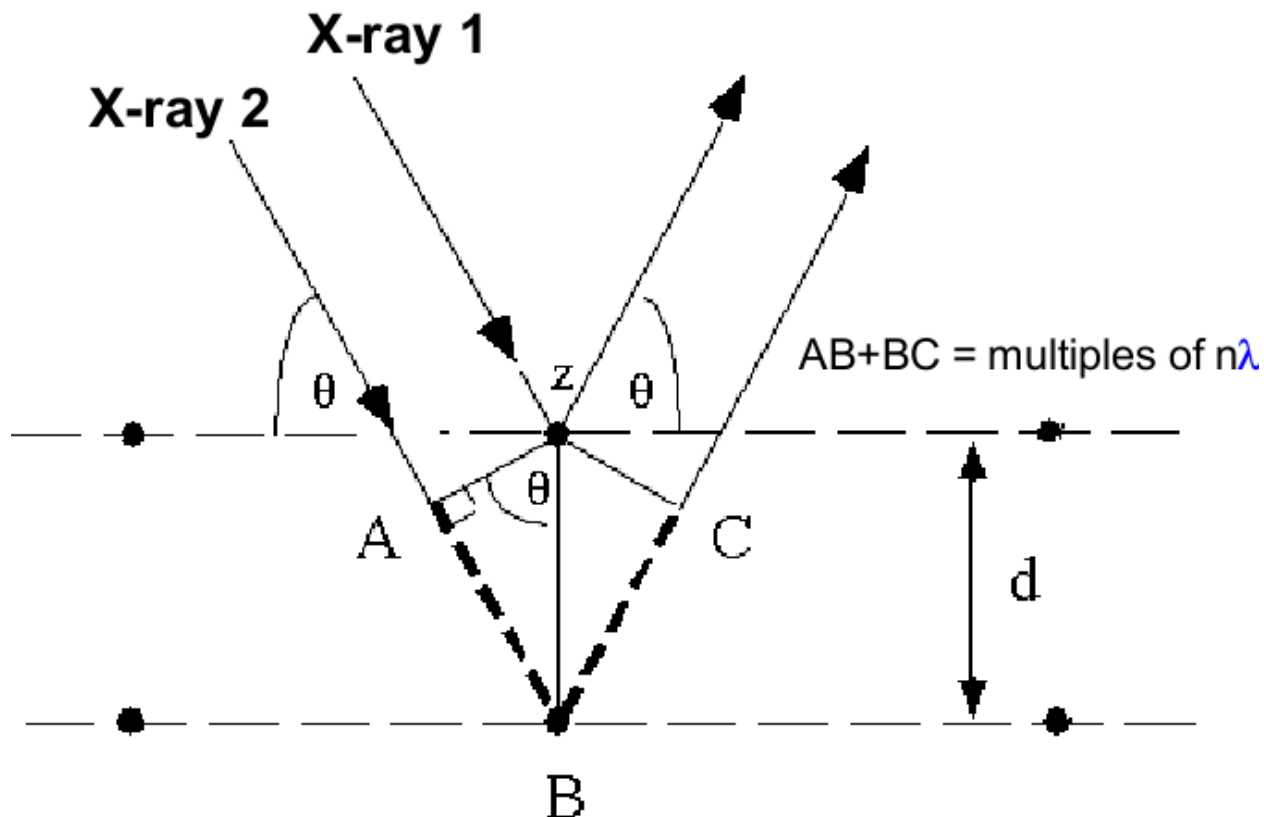
The x-rays scanned the sample through the angle of 2θ. Each compounds have unique d-spacing.

3.5.7. Cyclic voltammetry

Cyclic voltammetry is the most commonly used electroanalytical technique to study electrochemical reactions. It provides information about the location of oxidation and reduction potentials of chemical species. Cyclic voltammetry works in the principle of potentiostatic.

Cyclic voltammetry is the simple and give high information than all the other voltammetry. Cyclic voltammetry has three electrode system. It contains working electrode, reference electrode and counter or auxiliary electrode.

3.5.8. Micrometer screw gauge

Micrometer is a device for object measurements with U-shaped frame. It is highly precise and accurate device operates by measuring objects by placed between an anvil (hard stop) and spindle (movable surface). The spindle is move closer or farther away from the anvil by turning the thimble (lock nut).

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To measure the thickness or length of objects using micrometer, the thimble is spinning by applying a force in the ratchet until the object to be measure pinched between the anvil and spindle. Then a scale was read from the main scale (sleeve scale also called barrel) and thimble scale.
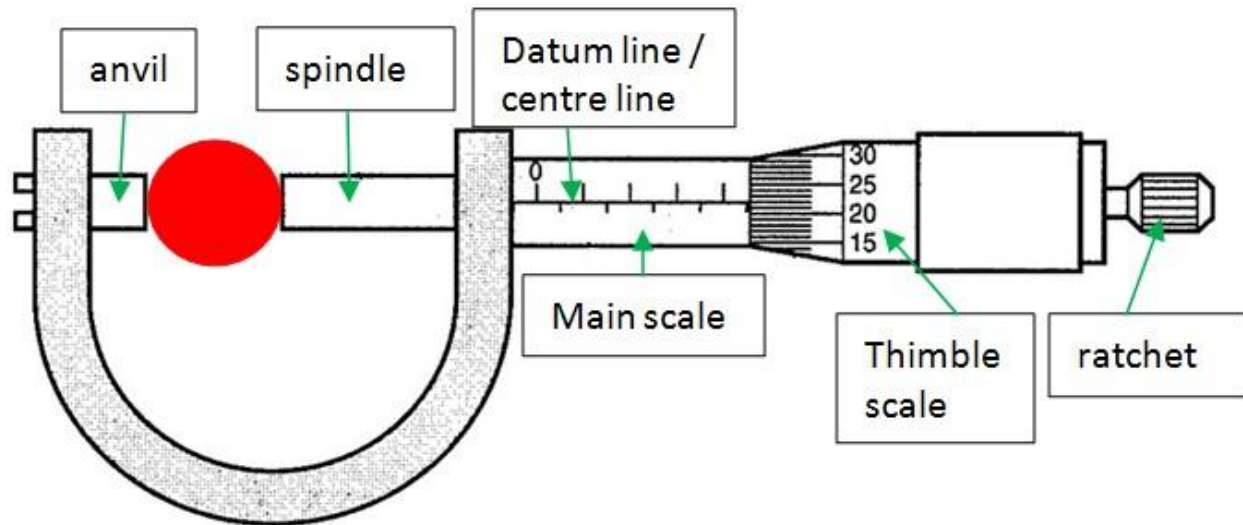

Figure 20. Schematic diagram of Screw gauge micrometer

3.5.8.1. Reading Value of Micrometer Screw Gauge

The value of the micrometer read from the main scale and the thimble scale (circular scale) after the object pinched between the faces of anvil and spindle. The thimble scale divided in 50 equal parts. There is also micrometer screw gauges their spindle scale divided in to 100 equal parts.

The least count in screw gauge micrometer differs from one type of screw gauge to other. It depends on the pitch (distance between the corresponding points in the main scale) and the number of divisions in the thimble scale.

 Least count=pitch of the screw gauge/number of divisions of the circular scale   3.4

The type of the micrometer screw gauge used to measure the thickness of the compound layer and the area of coupons was with a pitch of 0.5 mm and circular scale with 50 equal divisions. So, the least count (L.C) is:

L.C=0.5mm/50=0.01mm, i.e 10μm.

The value of the main scale is in mm and the value of the thimble scale multiplies by a least count (0.01) to change in to mm. Both the values added to get the reading/measurement.

The micrometer screw gauge was used to measure the thickness of the compound layer by comparing the measurement before and after nitriding. It was also used to measure the surface area of the coupons for the measurement of the weight loss calculations of corrosion rate.

3.6. Corrosion Rate Measurement Using Weight loss of Coupons

For Accurate Results and to work with coupons, the reliability and reproducibility depends in the proper preparation of the sample. Good results depends good sample preparation, in the immersion of the sample to the solution and removal & cleaning of the corrosion products.

Coupon samples for weight loss measurement of corrosion prepare in different forms. They may prepare in plate form, disc form and round shape. The surface must be smooth.

3.6.1. Solution Preparation for the Immersion of Coupons

From 10 to 15% of HCl solution prepared for corrosion product removal. After immersed in this solution the samples were washed in other glass that contains water and dry then weight.

During the insertion of coupons to the solution and removal of corrosion products, it is advisable wearing of gloves to prevent contact of the skin moisture and oil.

During the soaking of the coupon samples to the NaCl solution, samples must be put in separate containers in order to prevent any electron flow between the different samples.

3.6.2. Cleaning Methods

  - ➢ Mechanical wire bristle brushing. In this research manual wire bristle brushing was used.
  - ➢ Sand blasting
  - ➢ Chemical cleaning

The accuracy of the corrosion removal depends in the type of the cleaning method.

3.6.3. Cleaning corrosion product cycles

There are three mainly used corrosion removal. Sand blasting is preferable corrosion removal due to high accuracy. Mechanical wire bristle brushing is difficult to remove corrosion from irregular shapes and surfaces with pins. The chemical immersion cleaning is fast but it damages the samples and can cause additional removal of particles from the sample coupon and results an error. The corrosion cleaning method used in this work was manual wire bristle cleaning.

Then washing coupons in running water and dry in an oven of 70°C for 15 minutes and then washing with acetone to dry. After the cleaned and dried, it weighted in an electronic balance to see the weight difference before and after corrosion. The weight difference is the weight loss due to corrosion. Weight loss increases with time and corrosion rate decreases with time.

$$\text{Corrosion rate} = KW/\left(\rho At\right) \qquad\qquad 3.5$$

The constant K value varies according to the unit of area, A and the unit of the corrosion rate measured.

For area in inch^2 CR in mpy, k=5.34×10^5,

For area in cm^2 CR in mpy, k=3.45×10^6,

For area in cm^2 CR in mmpy, k=8.75×10^4

Chapter Four

Result and Discussion

4.1. Experimentally Observed Hardness

To test samples using Brinell hardness test machine smooth and clean surface was indented with an indenter with a diameter of 2.5mm, loading force 187.5 kg and loading time 30 sec.

The hardness of the samples were measured using the Brinell hardness tester machine and Vickers tester machine. Vickers hardness test was appropriate to measure the layer hardness of the samples. The hardness difference of sample from the surface to the depth of bulk material was studied using Vickers hardness tester machine. The hardness of the nitrided and untreated samples are shown below. There is a great increase in the hardness of steels contains alloying elements such as Al, Mo, V and Cr. These elements form hard precipitates. The surface hardness increases from 325HV1 to 724HV1. The nitrided surface hardness shows 123% increment than the untreated sample.
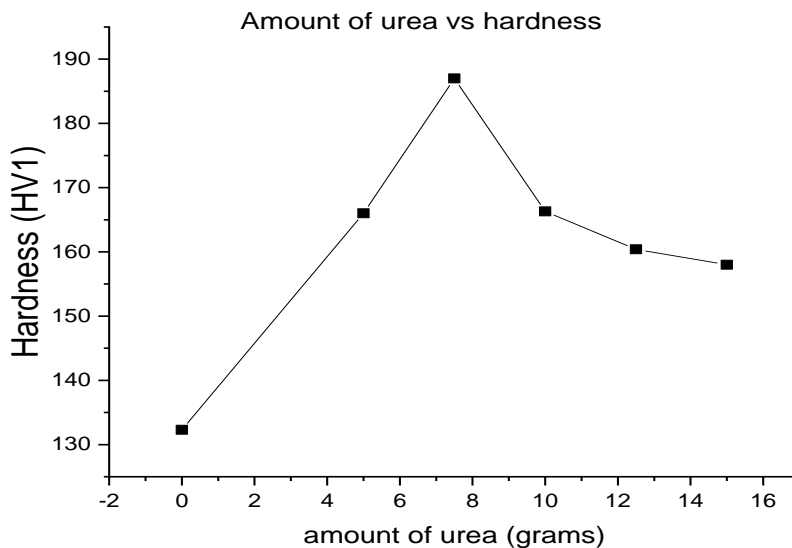
Figure 21. Hardness versus amount of urea of AISI 1018 mild steel

The hardness of the low carbon steels increase with the increase of the amount of urea. An optimized hardness got at 7.5g of urea. The hardness before nitriding was 132HV1, then its hardness raised to 166HV1 after nitriding with 5g of urea, 187HV1 with 7.5g of urea. But it decreases as the amount of urea increases after 7.5g of urea. 10g of urea drops the hardness to 164HV1, 12.5g of urea to 160HV1 and 15g to 158HV1. This is due to the formation of high concentration potential of nitrogen causes to the formation of gamma prime iron nitrides with low hardness. The only varying parameter in this experiment was the amount of urea and the other parameters temperature and time were the same for all the amount of urea. The nitrding temperature was 500°C and time of 2 hours.

To study the effect of the temperature 7.5g of urea (the amount urea where optimal hardness was recorded) was taken and temperature varies.
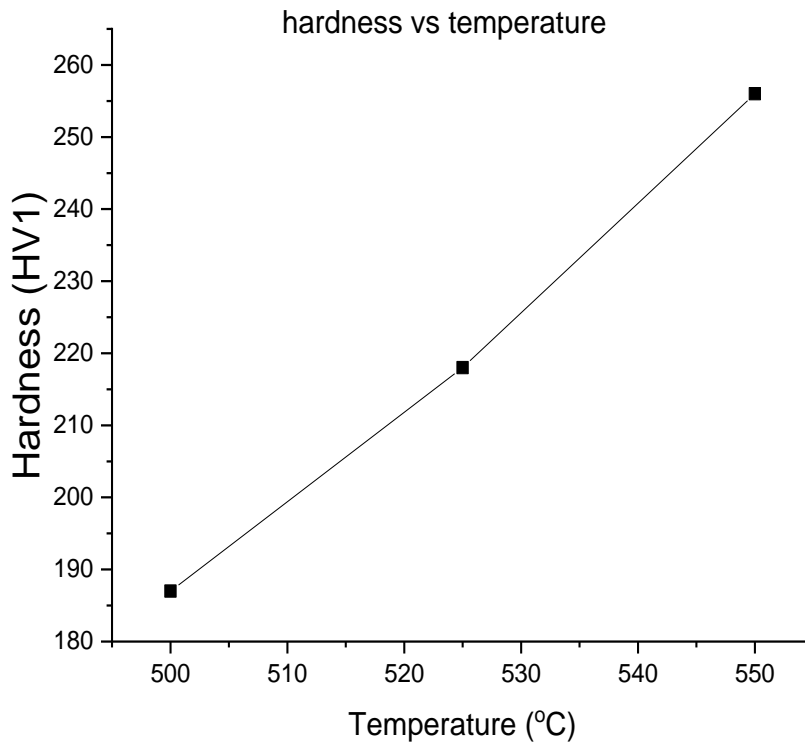

Figure 22. Hardness versus temperature of AISI 1018 mild steel

With the increasing of the temperature, the hardness increases. Hardness increases from 187HV1 at 500ºC to 218HV1 at 525ºC and then raises to 258HV1 at 550ºC. This is due to the formation of very thin compound layer dominated with epsilon iron nitrides. With increasing of the temperature, the formation of gamma iron nitride decreases. The precipitation also increases with increasing of temperature. Precipitates were hard with the presence of alloying elements. But the temperature was at ferritic. Above that temperature it cause phase change and material distortion happened.

Time also has a great effect in nitriding. Hardness increases with increasing of time. The material has the opportunity to diffuse nitrogen interstitially and forms precipitates and the formation of gamma prime phase decreases.
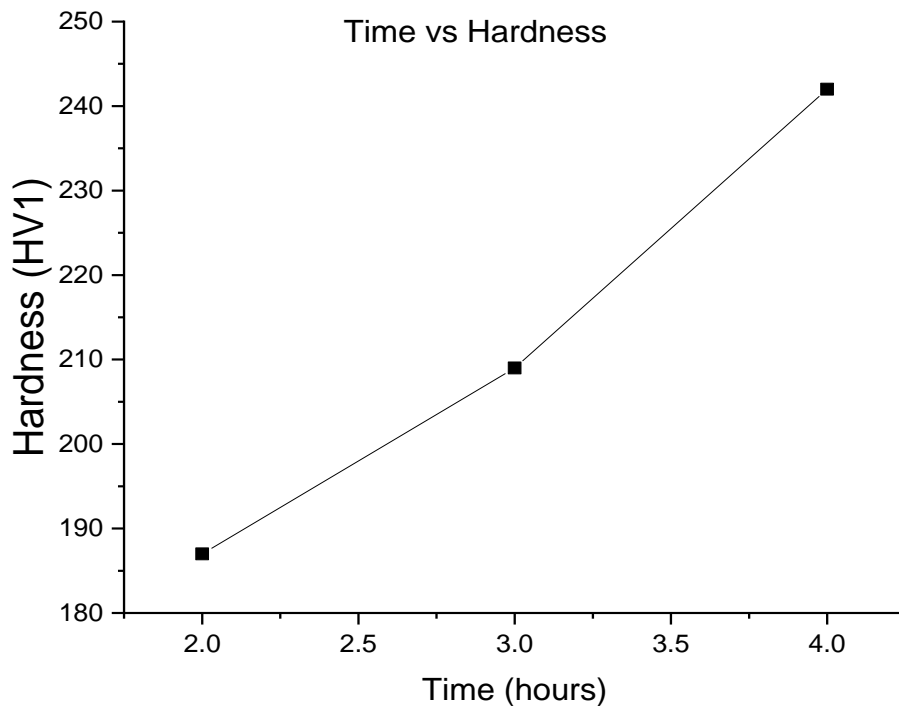

Figure 23. Hardness versus time of AISI 1018 mild steel

The hardness of the nitrided low carbon steels is lower than the hardness of the nitrided medium carbon steels. This is due to the medium carbon steels contain more alloying elements such as manganese, chromium, molybdenum and vanadium. Those alloying elements form hard metal carbides and metal nitrides.

To study the hardness of medium carbon steels, 4mm height and 10mm diameter of cylindrical medium carbon steels were taken. Like in the low carbon steels the hardness increases with time and temperature. But it is dramatically increase its hardness in medium carbon steels due to the presence of alloying elements. For medium carbon steels, 20g of urea was taken and the hardness with varying time and temperature was studied.

The hardness of medium carbon steels increases with increasing of the temperature from 500°C to 580°C at 3 hours for all the temperatures.
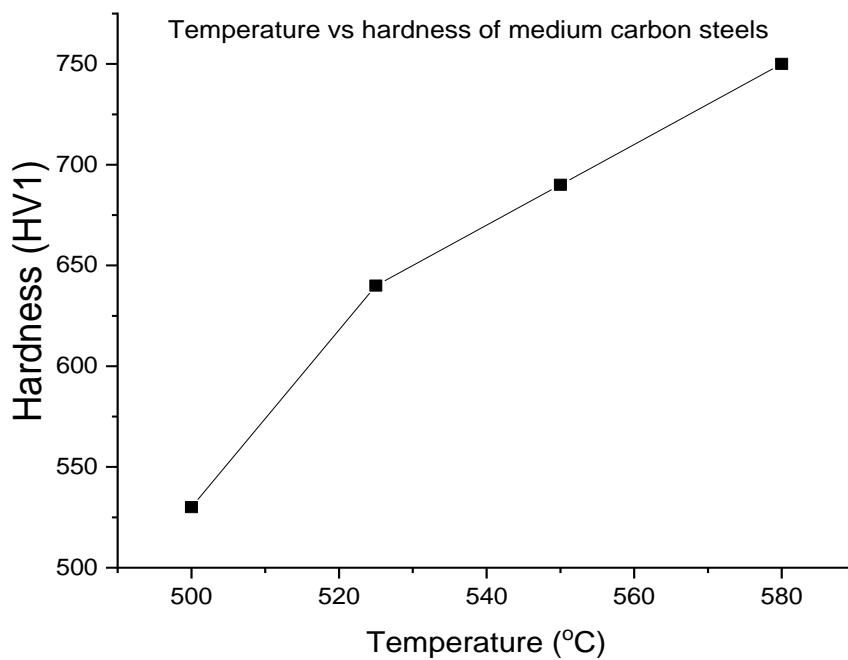

Figure 24. Hardness versus temperature of AISI 1045 medium carbon steel

The 4mm height with 10mm diameter of cylindrical shaft was nitrided at 580°C with varying time from 1 hour to 4 hours. The hardness of the medium carbon steel before any treatment was

325HV1. Nitrided of the medium carbon steel at 580ºC in 1 hour raises the hardness to 522HV1, to 620HV1 at 2 hours, to 680HV1 at 3 hours and to 724HV1 at 4 hours. The hardness increases with increasing of temperature.
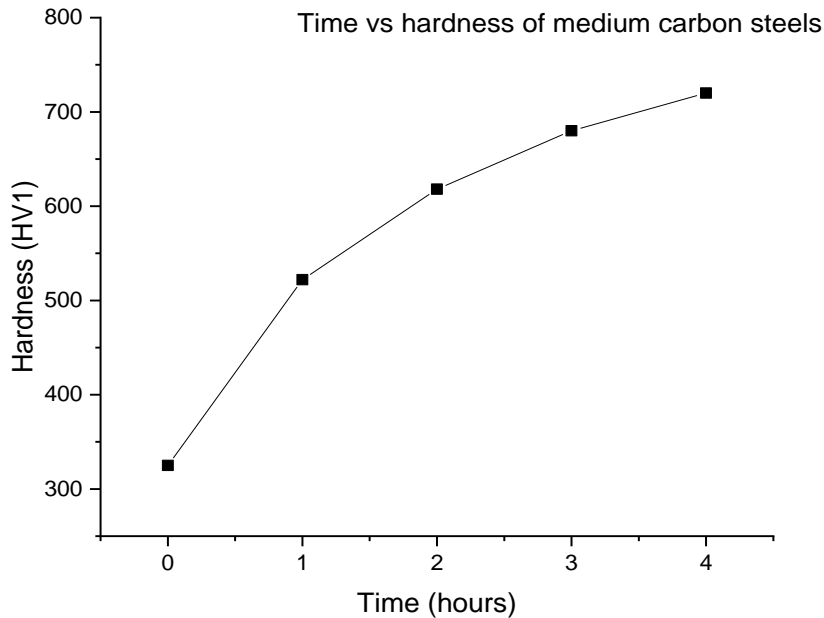

Figure 25. Hardness versus time of AISI 1045 medium carbon steel
The hardness decreases from the surface of materials as it goes to the inner core of the material.

The sample which nitrided at 580ºC 3 hours was studied its hardness by changing the depth from the surface. The hardness at the surface of the nitrided medium carbon was measured 750HV1. After measurement of the surface hardness to observe the hardness difference due to the depth of sample from the surface, 0.5mm surface thickness was ground and removed using SiC emery papers (that is at the depth of 0.5mm from the surface). At this depth the measured hardness was 640HV1. Next at the depth of 1mm from the surface of the sample was ground to obtain hardness of 530HV1. Then at the depth of 1.75mm, the obtained hardness was 480HV1, at the depth of 2.5mm with hardness of 425HV1 and at the depth 3mm from the surface with the hardness of 360HV1.
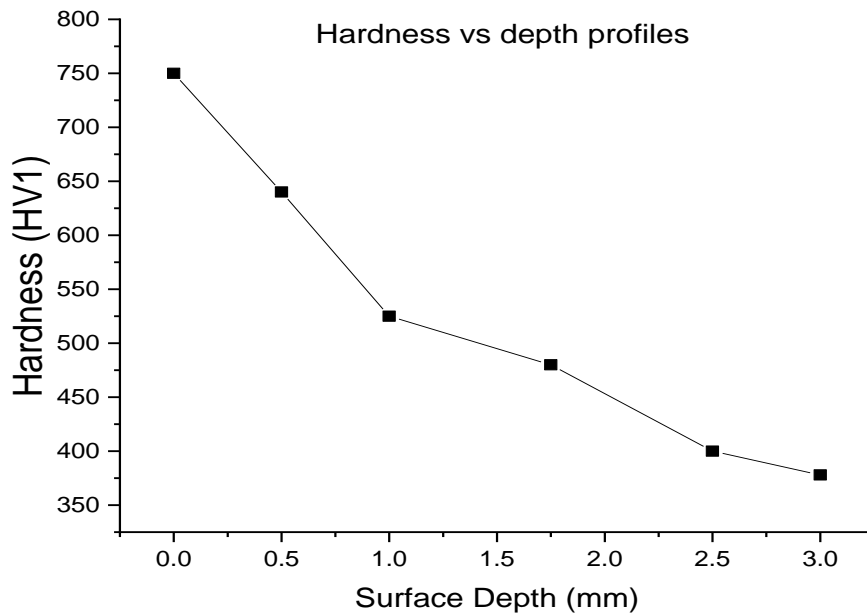
Figure 26. Hardness of AISI 1045 medium carbon steel with increasing of case depth

The hardness of the nitrided steels decreases as it goes from the surface to the inner core of the material. It is harder at the surface and softer at the inner core.

4.2. Cooling Effect

The cooling medium of the steels has a great effect in the properties of the steels. Cooling inside the furnace was better in terms of hardness, corrosion resistance and fatigue resistance because it helps to form precipitates of nitrogen to the depth of the sample by forming diffusion zone. These precipitates help the steel to increase its hardness, to increase its corrosion resistance property and to increase the fatigue resistance of the steel. It also helps to prevent residual stress of the samples. Cooling in air is more rapid that than cooling inside the furnace and results residual stress.

4.3. Microstructure

The microstructure of the specimens was studied using metallurgical optical microscope and scanning electron microscope.

The prepared sample etched with 2% Nital was put in the stage and observed through the objective lenses has a magnification of 50X, 100X, 200X, 500X and 1000X. The samples were cross sectioned and the image of the compound layer, diffusion zone and base metal were displayed in the computer screen. The best image with good magnification and resolution was displayed on the screen using scope image software.

The microstructural structure of compound layer and diffusion zone shown in figure 35. The upper layer is called the compound layer contains gamma prime and epsilon iron nitrides. The next layer is called the diffusion layer. Diffusion zone thicker than the compound layer. It contains precipitates of iron nitrides.
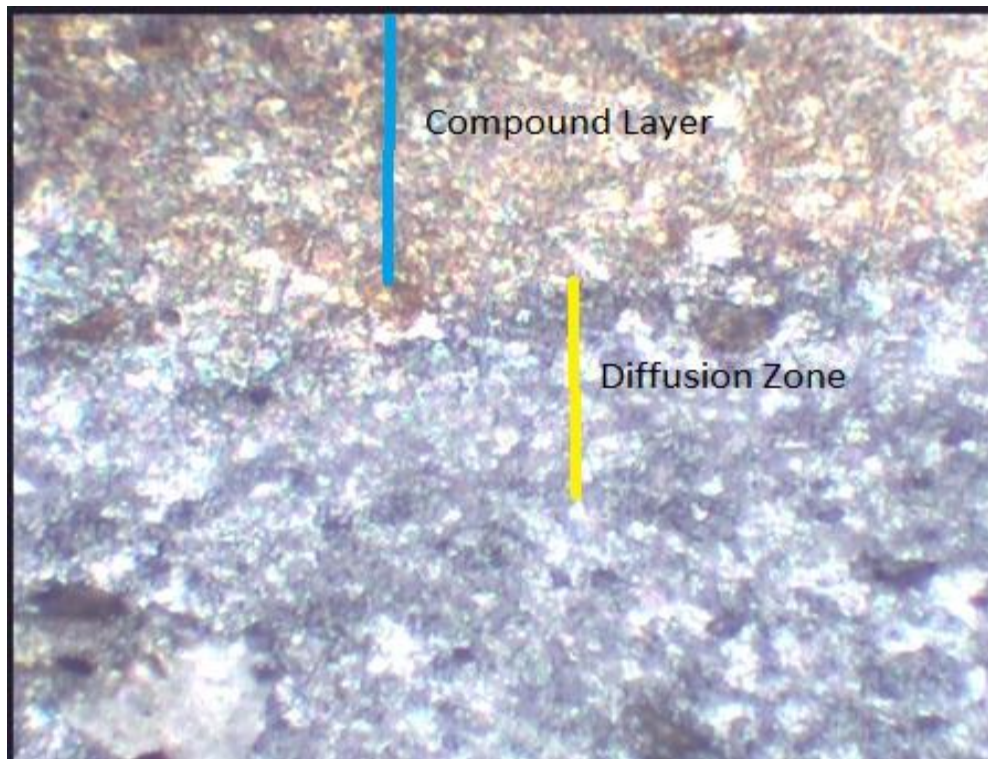
Figure 27. Optical microstructure of untreated AISI 1018 mild steel at 200X
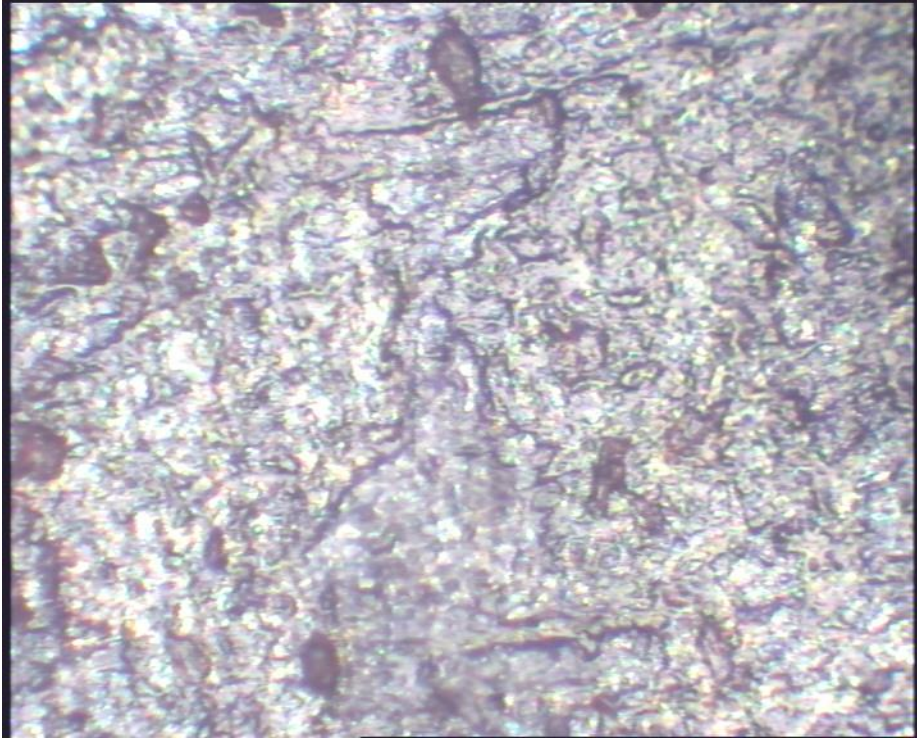
Figure 28. Optical microstructure of nitrided AISI 1018 mild steel at 200X
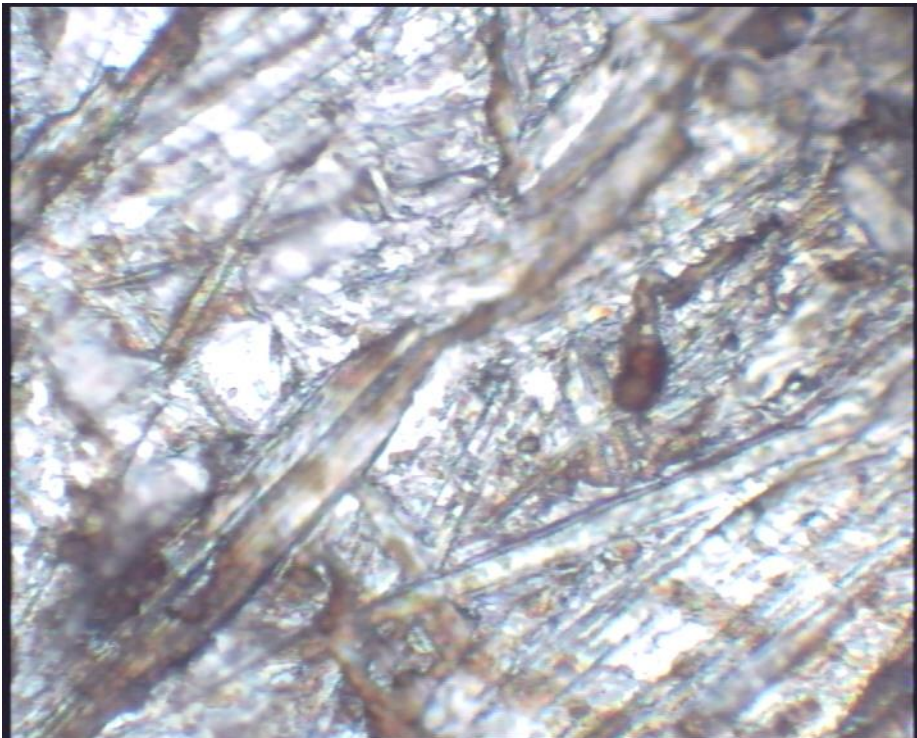
Figure 29. Optical microstructure of untreated AISI 1045 medium carbon steel at 500X
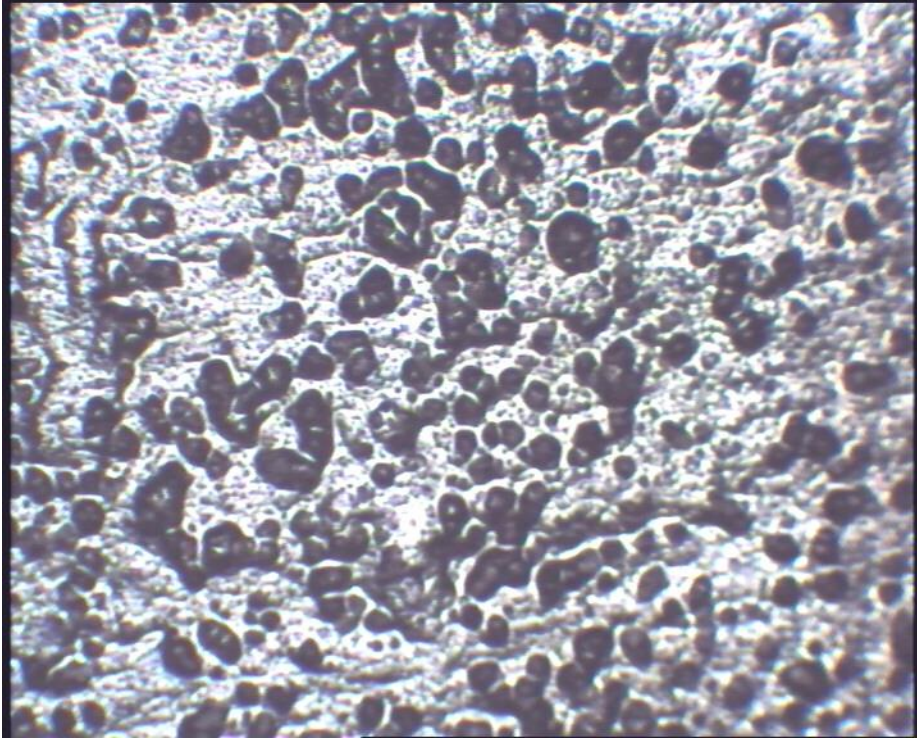
Figure 30. Optical microstructure of nitrided AISI 1045 medium carbon steel at 500X

The surface composition and microstructure of the specimens were investigated using the electron microscope.

The microstructural result of electron microscope is shown below. Elemental analysis at the surface of the medium carbon steels studied using SEM. In the figure 44 elemental carbon shows as black, the clustered red color is nitrogen and the dotted white color is iron. Due to scarcity of funds, we could record only one SEM micrograph of the samples.
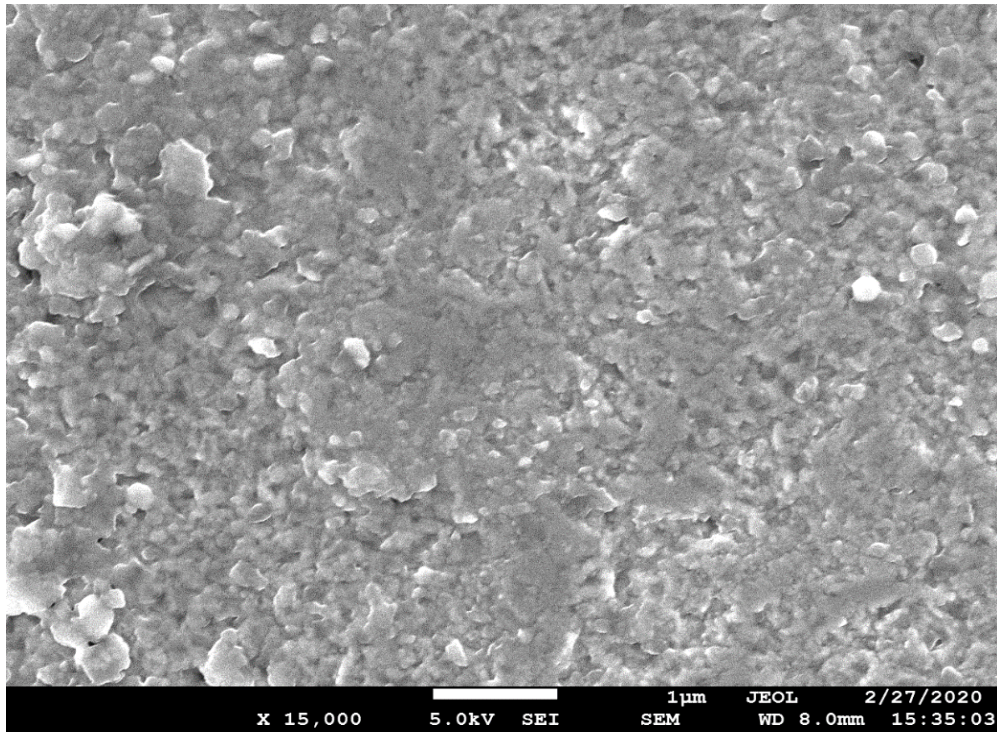
Figure 31. Microstructure of AISI 1045 medium carbon steel using scanning electron microscope
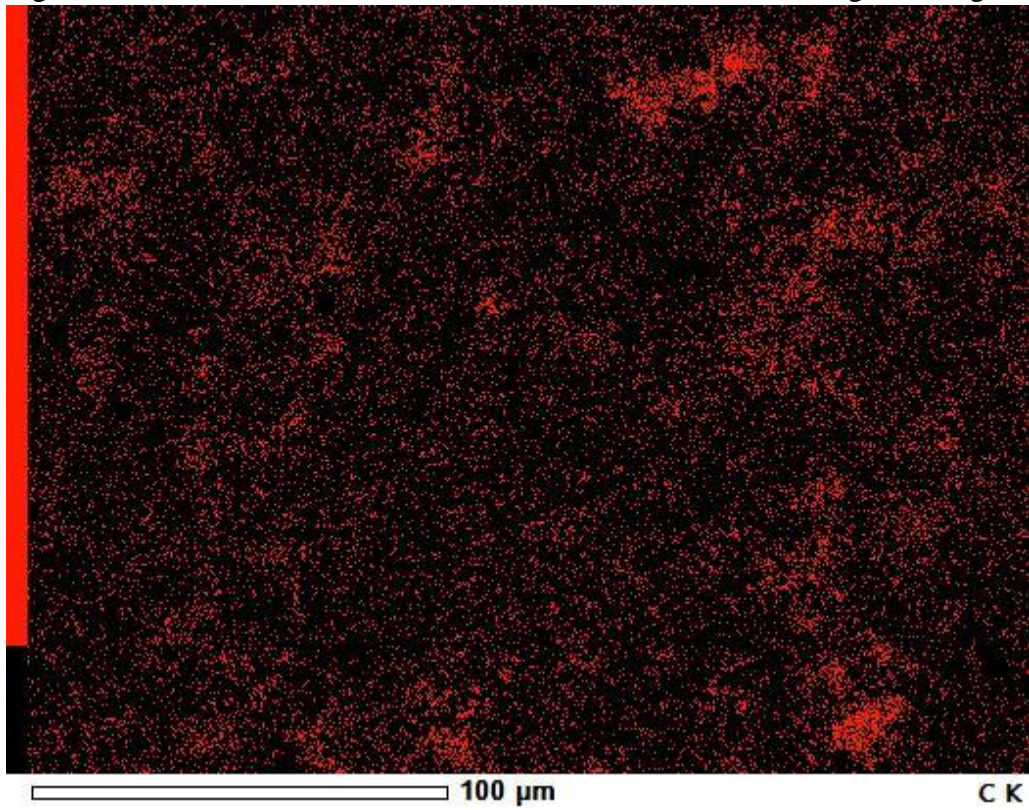
Figure 32. Atomic elements at the surface of AISI 1045 medium carbon steels after nitriding using SEM

4.4. Phase Identification

The phase of the specimens were studied using X-ray diffractometer (XRD 7000) using CuKa operating at 25KV and 25 mA at the step size of 0.01 installed with JADE5 software. The recorded 2θ (degrees) angle was from 20°-90°.

Sharp and high intensity additional peaks were observed in the nitrided steels. These are iron nitride and iron nitride ($Fe_{2-3}N$, Fe_8N and Fe_4N) peaks.

The most undesirable among iron nitrides is γ'-Fe_4N. Its most intense peak is observed at 2θ=48.47 degree. It is nearly absent (very weak) in the case of nitrided mild steel and medium carbon steel suggesting that our quality of surface engineering is good present but its intensity is not high enough. Other noticeable peak due to γ'-Fe_4N at around 2θ= 40 degree is not discernable in our case.

Peaks due to ε-Fe_3N considered to be benign, appears at 2θ=46.54 merges with that of 110 peak of iron.

Figure 33. XRD graph untreated AISI 1018 mild steel

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Figure 34. XRD of nitrided AISI 1018 mild steel

Figure 35. XRD of nitrided AISI 1045 medium carbon steel

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4.5. Electrochemical Reactions

To study the electrochemical reaction (oxidation and reduction) of the specimens, cyclic voltammetry was used.

To measure the corrosion susceptibility and corrosion behavior of the treated and untreated steels, first 3 cylindrical samples with a diameter of 3 mm and height of 4 cm were prepared. Before any heat treatment was 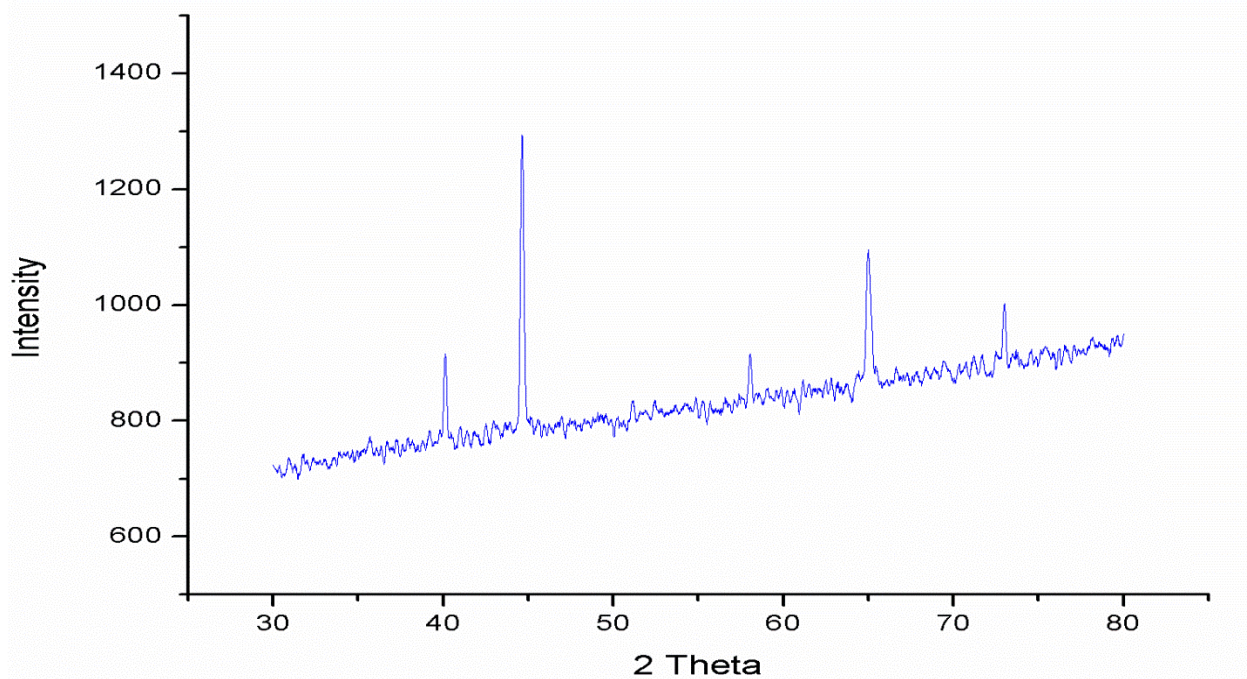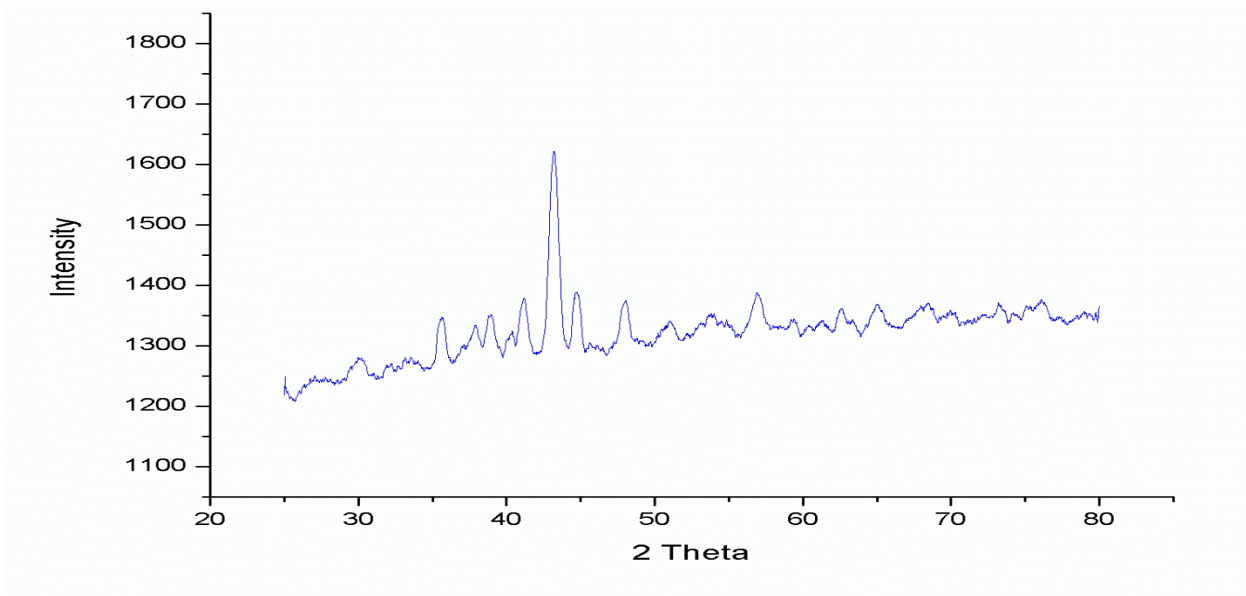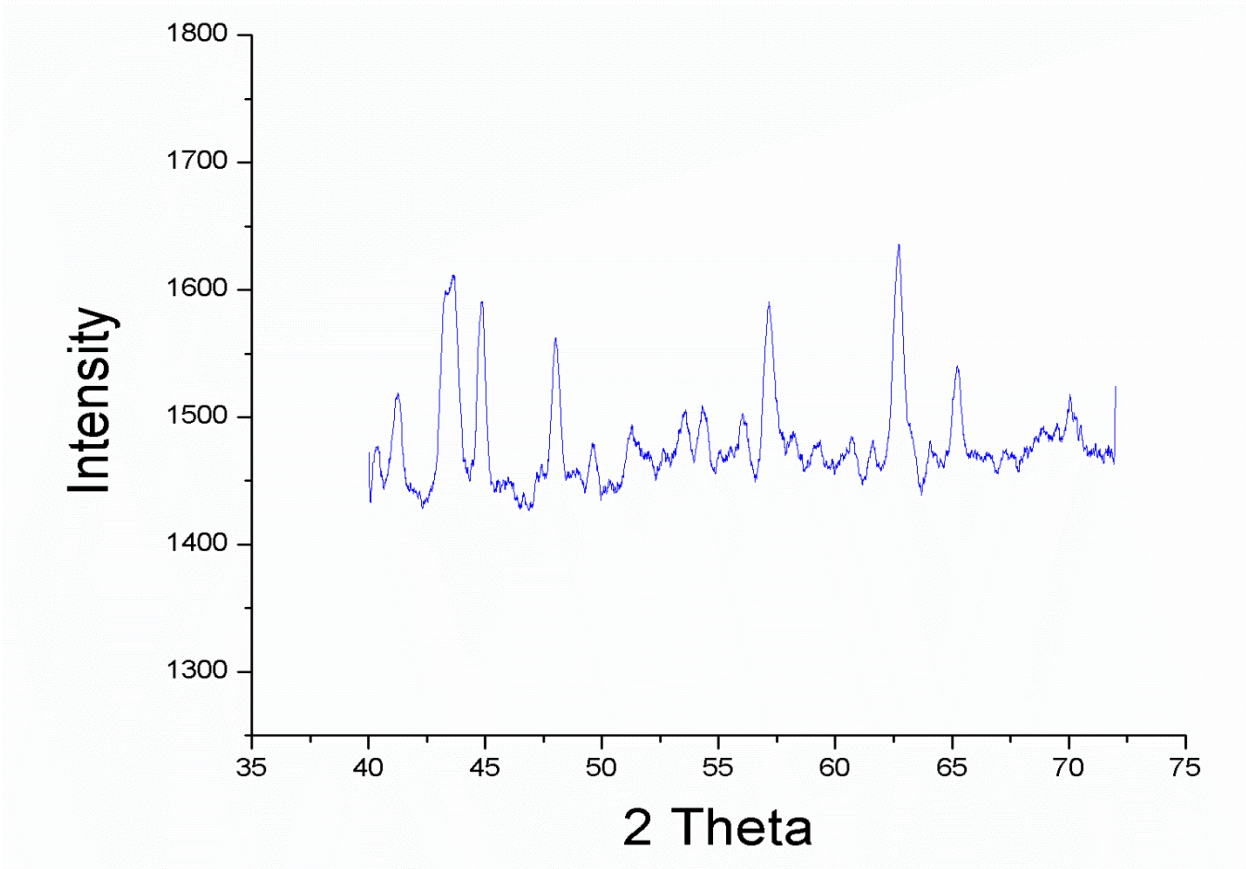took place samples were ground, polish with emery papers starting from the coarser emery paper P600 to the finest emery paper P2400. Then samples were cleaned and washed with water and acetone to remove contaminants and grease from the surface of the steel. One sample was nitrided at 550^oC for 2 hours and the second sample was nitrided at 550^oC for three hours by buried the samples in melamine-urea powder inside of a stainless steel container sealed with fire clay. The third sample was untreated. The nitrided samples were cooled to room temperature inside the furnace.

Samples were covered with epoxy resin by leaving specified small area to expose the sample in NaCl solution. The only area exposed to solution was the bottom surface of the samples. The area is: $A=\pi r^2$, r=3 mm which is 0.30 cm, so $A=\pi \times 0.300^2 = 0.2826$ cm^2

Cyclic voltametery measurements were made using BASi EPSILON potentiostat. The machine was connected with a computer having Epsilon software to draw the voltagrams and record data from the Basi Epsilon machine. The initial and final potential set was -150mV and scan rate (rate change of potential with time) of 100 mV/s.

To characterize the samples using CV, 5% of NaCl solution was taken as a corrosive environment. The set up contains Ag/AgCl reference electrode, platinum wire as auxiliary electrode and the sample to characterize as a working electrode.

Cyclic voltammetry experiment was made for the 3 samples without using NaCl solution to understand the effect of the NaCl solution to the samples.

All the samples were soaked in the 5% of NaCl solution for 3 hours and CV experiments was made. All the three samples also soaked in 5% of NaCl solution for 48 hours.

In potentiostatic, the potential changes linearly as a function of time. As the potential changes, the current response was measured. The current response was obtained due to electron transfer

between the energy levels of the working electrode and molecular energy level of the system under investigation.
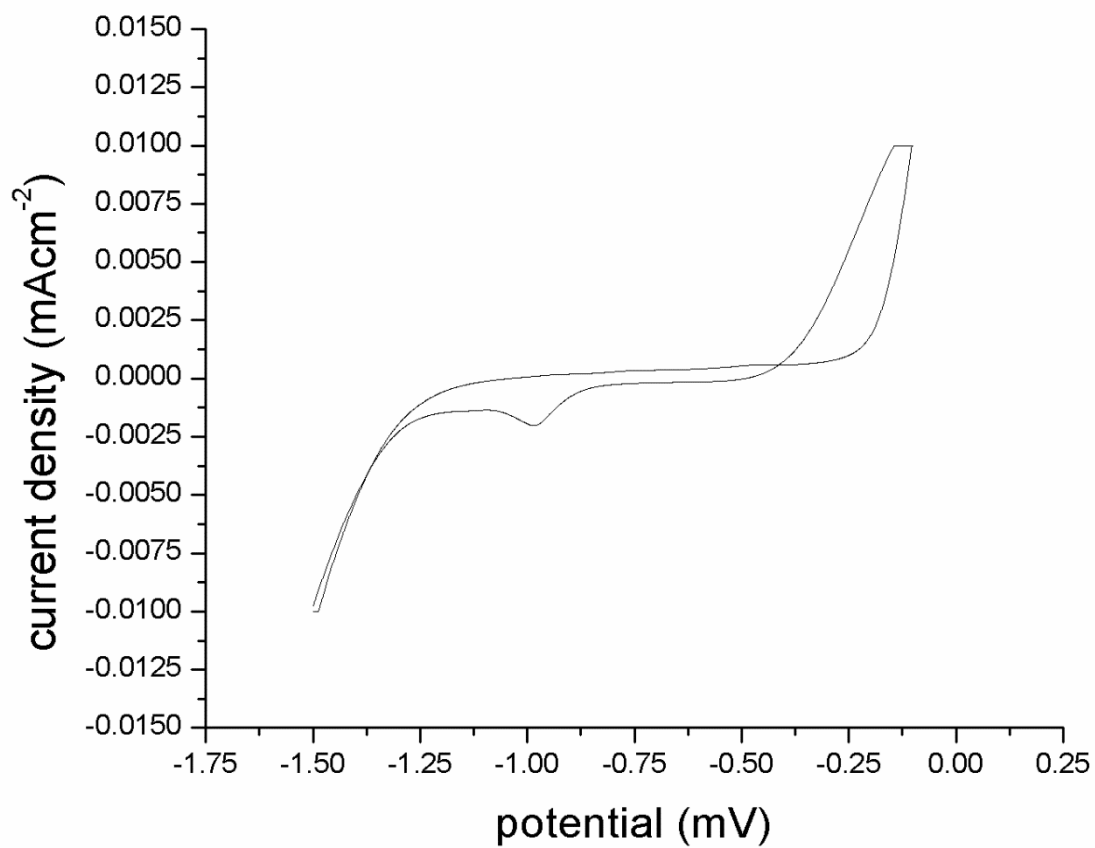
Figure 36. CV of untreated AISI 1045 medium carbon steel soaking for 48 hrs
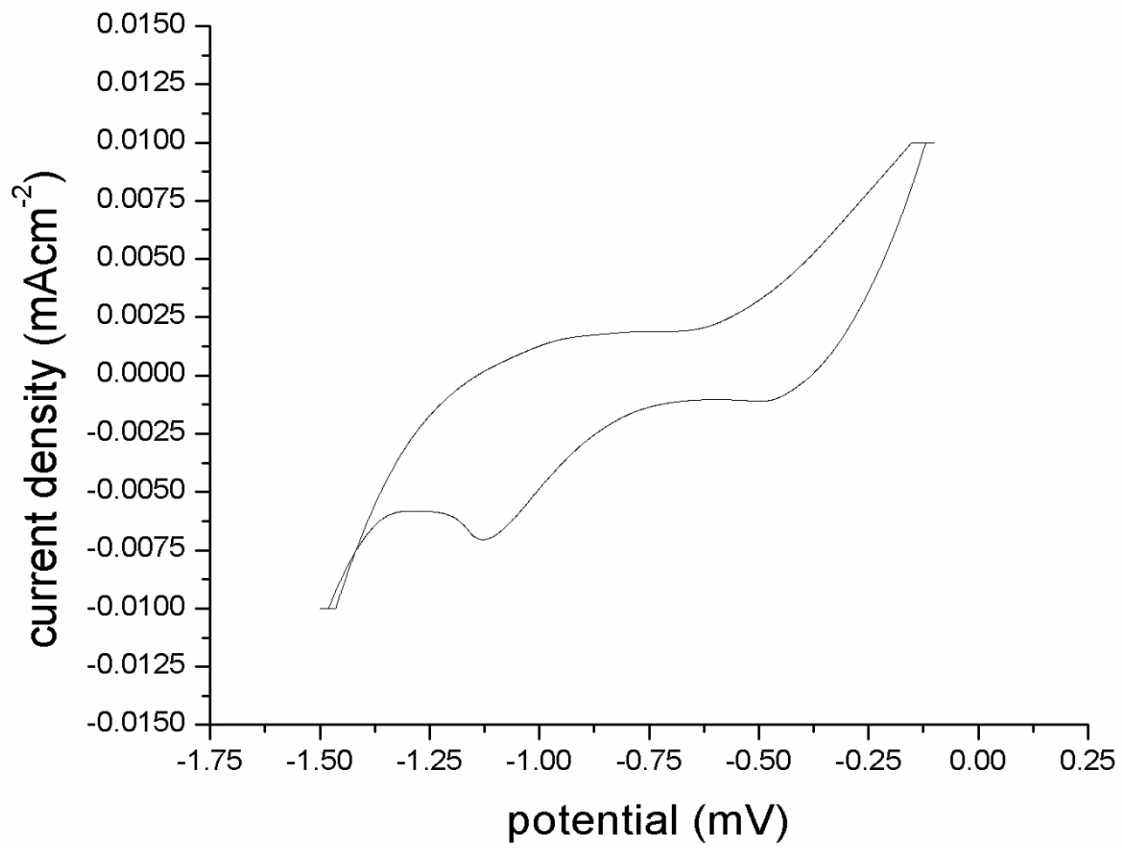
Figure 37. CV of nitrided AISI 1045 medium carbon steel at 550ºC for 2 hrs soaking for 48 hrs
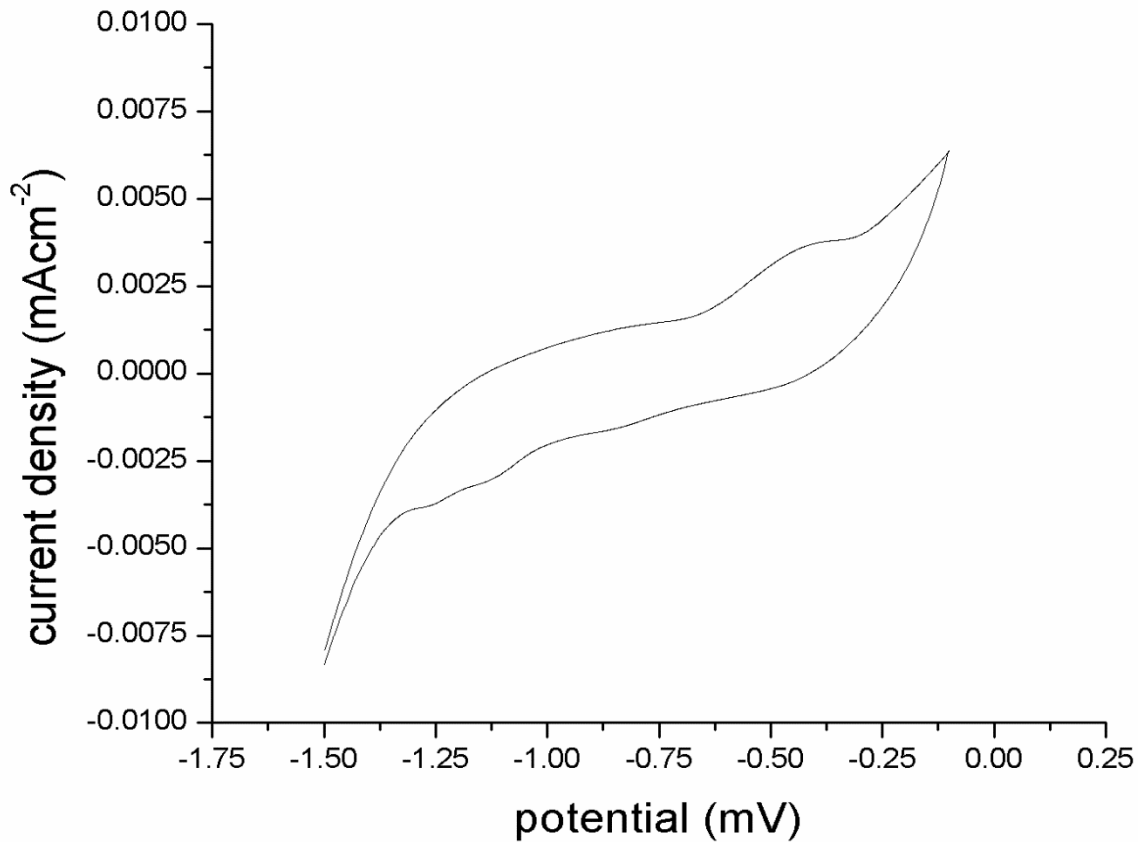
Figure 38. CV of nitrided AISI 1045 medium carbon steel at 550°C for 3 hrs soaking for 48 hrs

In case of untreated steel corrosion appears at -0.1V but in case of nitride steel oxidation/ reduction takes place at higher voltage i.e -1.20V according to figure 51 and 52. This proves that corrosion in nitride steel requires higher voltage or in other words more resistant to corrosion.

4.5.1. Weight Loss Measurement

12 AISI 1018 samples with the area of 2.40 cm^2 were prepared to measure the weight loss due to corrosion. Four samples were untreated samples, four samples treated (nitrided) for 2 hours at 550 and other four samples treated (nitrided) for 3 hours at 550. Each of the four samples were immersed in 5% of NaCl solution for 1 day, 3 days, 5 days and 7 days to see the effect of duration of time for corrosion rate and weight loss of the samples.

When samples were cleaned it must be properly done. Each sample was cleaned until 0.2% of the final result of weight loss and weighted at each step of cleaning.

All the samples follow the same procedure for weight loss and corrosion rate measurements. The table below shows the measurement of weight loss before immersion to 5% NaCl solution and after the immersion in 5% of NaCl solution for 24 hours. For the untreated sample the initial mass of the sample was 2.4965 gram and after cleaning it was recorded as: 2.4923, 2.4917, 2.4915 and 2.4914 grams. So mass loss=2.4965-2.4918=0.0047 grams.

Percent mass loss= (0.0047/2.4965) ×100=0.1884% per day.

Sample Type	Before immersion (g)	W1(g)	W2(g)	W3(g)	W4(g)	(W1+W2+W3+W4)/4 (g)	Weight loss(g)
Untreated samples	2.4965	2.4923	2.4917	2.4915	2.4914	2.4918	0.0047
Nitrided for 2 hours at a T of 550°C	2.6063	2.6059	2.6054	2.6052	2.6052	2.6054	0.0009
Nitrided for 3 hours at T of 550°C	2.7206	2.7201	2.7198	2.7197	2.7195	2.719775	0.000825

Table 4. Weight loss measurement

The weight loss was small in the nitrided samples. It is due to a low corrosion in the nitrided samples. It forms thin layer called compound zone. This layer prevents losing of materials due to corrosion and preserves from weight loss.

The weight loss, W and corrosion rate, CR of the samples summarize as follow:

	$W_o(g)$	1 day		3 days		5 days		7 days	
Sample Type		W(g)	CR(mmpy)	W(g)	CR(mmpy)	W(g)	CR(mmpy)	W(g)	CR(mmpy)
Untreated samples	2.4965	0.0047	7.96	0.0051	0.96	0.0058	0.40	0.0065	0.23
Samples nitrided for 2 hours at a T of 550ºC	2.6063	0.0009	1.53	0.0013	0.25	0.0017	0.12	0.0024	0.083
Samples nitrided for 3 hours at a T of 550ºC	2.7206	0.000825	1.40	0.0016	0.30	0.002	0.14	0.0029	0.10

Table 5. Corrosion penetration measurement

W_o is the initial weight of the sample before immersed to the solution. W_1, W_2, W_3 and W_4 are weight measurements after the sample removed from the NaCl solution.

CR (mmpy) of the above table is calculated using $CR=KW/(\rho At)$

K=87.6, W is weight loss in gram, ρ is the density in g/cm^3, A is area exposed to 5% of NaCl solution in cm^2, t is exposure time in hrs.

The area exposed to the solution was 2cm^2, ρ=7.87 g/cm^3. The time of exposure for the samples was 1, 3, 5 and 7 days.

Weight loss and corrosion rate was higher in the untreated samples and lower in the treated samples. And weight loss increases with the increasing of time of exposure, but the corrosion rate decreases with the increasing of the time of exposure.

4.6. PH meter Measurement

Due to the formation chloride ions in the solution of 5% of NaCl solution, the PH decreases from 6.9 to 6.3. This indicates the neutral NaCl solution changes to acidic. These chloride ions attack the surface of the metal especially the metals with pitting. Chloride ions also form uniform corrosion on the surface of the metal.

Since PH is in the acidic zone, there is no change of pitting, at least at experiment.

4.7. Thickness Measurement Using Micrometer Screw Gauge

The increment of surface thickness of the compound zone and the diffusion zone was measured using micrometer screw gauge. The difference between the thickness measurement after nitrided and thickness before nitrided was the increment of the layer thickness. The thickness increases with increasing of the amount of urea used. To measure the thickness, the sample was measured 4 to 5 times and the average measurement was taken.

The layer thickness measurement using screw gauge has summarized as following in the form of table.

Sample	Before nitriding	After nitriding	Thickness increment
Low carbon steel using 5g urea	0.82mm	0.835mm	0.015mm=15μm
Low carbon steel using 7.5g urea	0.82mm	0.84mm	0.02mm=20μm
Low carbon steel using 10g urea	0.82mm	0.842mm	0.022mm=22μm

Table 6. Comparison of specimens' thickness before and after treatment

The samples increase their thickness after nitriding. The thickness is higher for the samples with high amount of urea/melamine. In this case higher thickness (22μm) was observed at 10g of urea. This is the reason that, the higher amount of urea release high concentration of nitrogen. The higher concentration of nitrogen, the higher diffusion. This means that more nitrogen diffuses to the metal surface and thicker surface formed.

Chapter Five

Conclusions

Pack nitriding was carried out at the temperature of 500ºC, 530ºC, 550ºC and 580ºC at the rate of 10ºC/min at different hours and summarizes as following.

1. The thickness of compound zone increases with increasing the amount of urea used for pack nitriding.

2. The surface hardness increases with increasing of temperature and time.

3. The surface hardness is higher for alloyed steels but lower for unalloyed steels. This is due to the alloying elements forms very hard precipitates.

4. Furnace cooling results good hardness and strength due to the formation of thick diffusion zone contains metallic precipitates and thin compound zone with low gamma prime iron nitrides.

5. Corrosion resistance of nitrided samples is higher than the untreated due to the formation of thin surface layer.

Chapter Six

Recommendation

Based on this research and finding I can formulated the following recommendations

- ✓ Pack nitrided using melamine/urea is a cheap surface engineering needs to adapt in small, medium and large metal manufacturing companies to treat corrosion, wear and to improve hardness.

- ✓ There is a lack of equipment such as SEM, atomic absorption spectra, EDS, chemicals and other equipment to characterize the samples. So the government agency/university must fulfil these equipment to do better research. It was very challenging to do full research in the laboratory of Jimma University.

- ✓ Using of the laboratory was limited due to the pandemic situation. I challenged doing my research without problem. I did not able doing my research by moving to another laboratories inside the country and outside the country.

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