Corrosion Study of Nitrided X-52 Carbon Steel in CO_2 Environment

By

SHALINI A/P SUBRAMANIAM

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

May 2011

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

Corrosion Study of Nitrided X-52 Carbon Steel in CO_2 Environment

by

Shalini A/P Subramaniam

A project dissertation submitted to the

Mechanical Engineering Programme

Universiti Teknologi PETRONAS

in partial fulfillment of the requirement for the

BACHELOR OF ENGINEERING (Hons)

(MECHANICAL ENGINEERING)

Approved by,

(Ir.Dr.Mokhtar Che Ismail)

UNIVERSITI TEKNOLOGI PETRONAS, TRONOH, PERAK

May 2011

CERTIFICATION OF ORIGINALITY

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

SHALINI A/P SUBRAMANIAM

ABSTRACT

Carbon Dioxide (CO_2) corrosion is one the most studied form of corrosion in oil and gas industry. Carbon is preferred material of construction for offshore pipelines due to economy, availability and strength but this material are not corrosion resistant. As such the use of carbon steel is usually implemented with the corrosion control such as corrosion allowance, corrosion inhibitor and coating. Since corrosion involves interaction between metal surface and the environment, surface alteration by surface hardening method such as nitriding could protect the metal from corrosion. The objective of the project is to study the performance of different nitrided carbon steel based on 450°C, 480°C and 520°C in CO_2 environment. The corrosion rates of the nitrided samples were investigated at pH 3 and pH 4 by linear polarization resistance and electrochemical impedance spectroscopy. At ph 4, corrosion rate of sample nitrided at 450°C and 480°C decreases by 30%. However the corrosion rate increases by 50% for sample nitrided at 520°C. This may be due to the poor surface preparation of the sample and uneven nitride layer fails to protect the sample. At pH 3, the corrosion rates of nitrided samples at 480°C and 520°C were higher than untreated sample by 3% for sample nitrided at 480°C and by 70% for sample nitrided at 520°C. For the sample nitrided at 450°C, the corrosion rate was similar as the untreated sample. The slight decrease and increase in the corrosion rate at pH 3 indicate that the presence of nitriding layer was detrimental. This negative effect can be linked to porous nitriding layer that lead to galvanic coupling between the nitriding layer and bare metal. Further studies need to be conducted to confirm this possibility.

ACKNOWLEDGEMENT

First and foremost, I would like to thank my Final Year Project (FYP) Supervisor, Ir. Dr. Mokhtar Che Ismail for all the guidance and the assistance in completing my project. Dr. Mokhtar's professionalism in the corrosion's industry and his ever willingness to lend his helping hand were a great inspiration to me. He had always be there to guide me in whatever difficulties that I had experienced throughout this one year of project period. I truly appreciate his exceptional dedication.

Special thanks to UTP corrosion graduate assistants, Mr.Yuli, Mr. Martin, Miss Rafidah, and Pak Askar for all their generosity in helping and guide me to do all the laboratory simulation testing and nitriding treatment. And also, special thank to Mr.Faisal, senior technician, for helping me to solve all the problems in completing this project, especially the problems related to the equipments in the corrosion laboratory.

Last but not least, I would like to thank my family and friends for the support. FYP II project finally completed with the help of all the people mentioned above.

TABLE OF CONTENTS

CHAPTER 1: INTRODUCTION

CHAPTER 2: LITERATURE REVIEW

CHAPTER 3: METHODOLOGY

LIST OF FIGURES

LIST OF TABLES

NOMENCLATURES

E_{corr}	Corrosion potential
I_{corr}	Current density
R_p	Polarization Resistance
R_s	Solution Resistance
C_{dl}	Double layer capacitance
R_{ct}	Charge transfer resistance

ABBREVIATIONS

XRD	X-ray diffraction
SEM	Scanning electron microscope
ppm	Pounds per galloon
LPR	Linear polarization resistance
EIS	Electrochemical impedance spectroscopy
CPE	Constant phase element

CHAPTER 1

INTRODUCTION

1.1 Project Background

Carbon Dioxide (CO_2) corrosion of carbon steel material is one the most studied form of corrosion in oil and gas industry. This is due to the fact that the crude oil and natural gas from the oil reservoir and gas well usually contains some level of CO_2. The major concern with CO_2corrosion in oil and gas industry is that CO_2 corrosion can cause failure on the equipment especially the main down hole tubing and transmission pipelines and thus can disrupt the oil and gas production. This can result in great economic loss and catastrophic accidents. Leakage of the crude oil can cause fire accident, environmental pollution and water resource. CO_2 may be the only corrosive species present in the environment (sweet service) or a combination of CO_2 and H_2S may be present in the well stream.

In the design stage, the continuity of the service is evaluated and material selection is done based on the predicted corrosion rate. Carbon and low alloy steel are preferred material of construction due to economy, availability and strength but this material cause high corrosion rate. When corrosion is high, corrosion resistance alloy (CRA) must be used but the cost is prohibitive. In any case that carbon steel is selected, the corrosion control can be implemented by corrosion allowance, corrosion inhibitor and coating. Since corrosion reaction is an interaction between the steel surface and environment, surface alteration like nitriding can be used as corrosion mitigation method. Nitriding is a thermo chemical treatment that allows the diffusion of nitrogen to form nitride layer on the surface to improve the corrosion resistance of carbon steel

From open literature, there are limited studies done on the performance of nitrided carbon steel in CO_2 corrosion. This method is recommended because it is economically affordable and environmentally harmless.

1.2 Problem Statement

The altering of steel surface by nitriding could reduce corrosion by providing a barrier, isolating steel surface and CO_2 environment. However the performance of nitrided carbon steel in CO_2 environment in not known. In order to perform the nitriding treatment, certain parameters need to be considered to ensure successful nitriding. The parameters that need to be controlled during nitriding are temperature, gas composition and duration of experiment. These parameters will influence the properties of layers produced on the surface. Therefore in the present work, CO_2 corrosion properties of gas nitride layers are evaluated in the context of gas nitriding condition (temperature).

1.3 Objectives and Scope of Studies

The objective of this project is to study the effect of various nitriding layers in CO_2 environment.

- To determine the performance of different nitriding layers produced at three different temperatures which are 450°C, 480°C and 520°C. The other parameters, gas composition and duration of experiment are set constant.

- To study corrosion protection mechanism by nitriding. The nitriding treatment produce barrier which protects the steel surface from the CO_2 environment. Efficiency of this method will be proven by potentiodynamic test and ac impedance studies.

CHAPTER 2

LITERATURE REVIEW

2.1 Nitriding

David (2003) mentioned that nitriding is a heat treating process that alloys nitrogen onto the surface of a metal to create a case hardened surface. The unique advantages of the nitiding process were recognized by the Germans in 1920s. It was used in applications that required; high torque, high wear resistance, abrasive wear resistance, corrosion resistance and high compressive strength. According to Mouri (2001), corrosion resistance of such modified structures has not been studied to great extent. Jolanta (2006) said that nitriding treatment is an effective surface hardening treatment increasing the wear resistance and hardness of steels. According to him also, since it was found that low temperature nitriding (below 500˚C), produce corrosion resistance layer, a lot of research were done in this field. Whilst it is possible to nitride many steels grades but high hardness is only obtained when using special nitriding alloys containing aluminium, chromium, molybdenum or vanadium. Ashrafizadeh (2003) said these elements form hard and stable nitrides as soon as they come into contact with nitrogen atoms at surface of the workpiece.

Several factors helped nitriding gain acceptance:

- Compared to other case hardening methods, nitriding is a relatively low temperature process.
- Nitriding is relatively easy to control in terms of process parameters

- It produces enhanced corrosion resistance in low-alloy and low-carbon steels
- Core hardness is not significantly affected, due to preheating and tempering
- No quenching is required, thus reducing distortion.

There are three main methods for nitriding are:

- Gas Nitriding: The ammonia with contact of heated work piece disassociate into nitrogen and hydrogen where the nitrogen will diffuse into the surface of the material.
- Salt Bath Nitriding: A nitrogen containing salt like cyanide salt will be used to donate carbon to the workpiece surface making salt bath as a nitrocarburising process
- Plasma Nitriding: Intense electric fields are used to generate ionized molecules of the gas around the surface to be nitrided.

2.2 Gas Nitriding

David (2003) mentioned that gas nitriding is surface hardening heat treatment where nitrogen is introduced into the surface of a solid ferrous alloy at a temperature range in contact with nitrogenous gas, usually ammonia. He also mentioned that the nitriding temperature for all steels are 495-565°C ranging up to 90 hours, involved the diffusion of nitrogen into the surface to produce layer of hard alloy-nitrides. Unlike the high-temperature case-hardening treatments like carburizing, nitriding of steels with low temperature produce less distortion and deformation than either carburizing or conventional hardening. Due to the long process times, increased material and treatment cost, and lack of sufficient control of the process, gas nitriding has never been developed to its full potential.

The compound layer of plain carbon steel is always thicker compared with alloy steels containing nitride formed with alloying elements because nitride forming elements contain more nitrogen than those formed with iron. After gas nitriding, the result reveals that the compound layer contain both γ and ε phases with some iron oxide.

The following reaction will happen at the gas-solid interface during nitriding:

$$2NH_3 \rightarrow 2N + 3H_2$$

The rest if atomic nitrogen will form molecular nitrogen which is inert. The life of atomic nitrogen is very short so the supply of ammonia must be continuous. This is done to ensure atomic nitrogen produced through the dissociation available to the whole part to be nitride. It is important to maintain the predetermined rate of dissociation of ammonia as it influences the mechanical properties of the treated components.

2.3 Effects of different Parameters on Nitriding

Formation and thickness of the nitride layer is influence by:

a) Time
b) Temperature
c) Gas composition

2.3.1 Temperature

Jolanta (2003) mentioned that, sample that was treated above 500°C, chromium nitrides can be seen, and their quantity increases with the increase of temperature and ammonia content in the atmosphere. He also stated that nitrogen content in the layers depends much more on the atmosphere composition than the temperature. It corresponds to the shifts in diffraction peaks in the direction of the lower angles on the diffraction patterns.

But Basu (2008) in his paper stated that nitride volume fraction increases with nitriding temperature. Nitride volume fraction was also found to increase with increase in nitriding temperature. While in the as received sample shows only α-Fe peak, XRD patterns of plasma nitrided samples record number of peaks due to different nitrides. It can be noted that relative intensity of Fe_xN peaks increase with increase of temperature indicating an increase in volume fraction of the nitride phases. It can be observed that nitrides form very fine and uniformly distributed on the surface of the treated steel.

2.3.2 Time

Basu (2008) also stated that relative intensity of Fe_xN peaks increase with increase of nitriding time indicating an increase in volume fraction of the nitride phases. Nitride volume fraction was also found to increase with increase in nitriding time. Comparison between the sample treated for 5 hours and sample treated at 1 hour shows different nitride volume fraction. In another research, Bouanis (2008) found that the inhibiting power of plasma nitrided increases with time of plasma treatment and attains a maximum value after 24 hours.

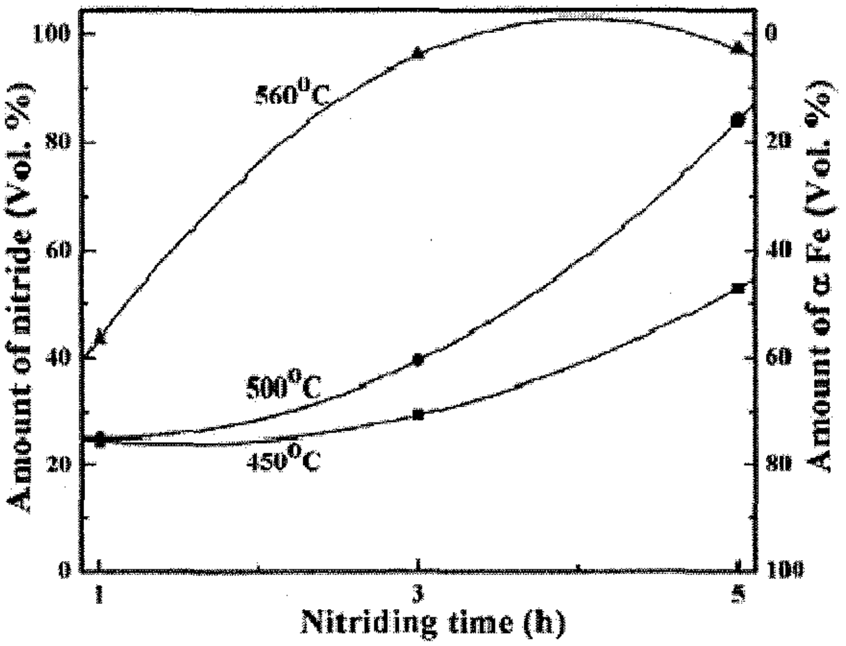

Figure 2.1: Variation of amount of nitrides with nitriding time for nitriding at different temperature by Basu (2008)

2.3.4 Gas composition

Jolanta (2006) mentioned that nitrogen content in the layers depend much more on the atmosphere composition. A very high nitrogen content level in the layers nitrided in pure ammonia is responsible for very high internal stresses in the layers, which produce characteristics relief and damage on the surface. After nitriding in an atmosphere with lower ammonia content the surface remains smooth and without defects. The internal stresses could produce cracks in the layer. This particularly visible in the treatment temperature higher than 500°C. Bouanis (2010) also stated in his paper that 75% N_2/ 25% H_2 nitrided C38 exhibits a more pronounced affect than those of 25% N_2/ 75% H_2 and pure N_2 nitrided C38 substrates.

2.4 Effects of nitriding parameters on corrosion rate

2.4.1 Temperature

Jolanta (2006) results reveal that for all the samples the potential decreased with the temperature of the treatment, but this decrease correspond to the quantity of nitrided in the layers. According to him, all the nitrided layers exhibit better corrosion resistance (except those nitrided at 575°C in 100% ammonia) than untreated sample. Also, the corrosion currents are much lower than those observed for non treated samples. Surface of the corroded sample at high treatment temperatures could be seen that corrosion attack was particularly strong in the damage. When the sample in contact with the solution, very rapid corrosion can take place. For the sample nitrided at 400 C, only little damage on the surfaces was found. The layer was not affected by corrosion test.

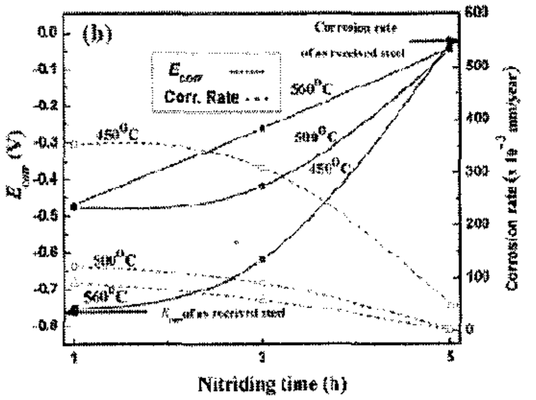

Figure 1.2: Variation of E_{corr} and corrosion rate with nitriding time at different temperatures by Jolanta (2006)

Basu's (2008) result shows that with increasing in nitriding temperature, the corrosion potential (E_{corr}) increases, whereas the corrosion current density (I_{corr}) and corrosion rate decreases and resistance to polarization (R_p) increases which means nitriding can increase the corrosion resistance. The corrosion phenomena can be attributed to the presence of a dense nitride layer on the surface. As nitride is a noble phase, formation of more nitride helps to cover the surface from corrosion attack and for this reason with increase in nitriding time or temperature corrosion resistance improve. Earlier Ensinger (1992) compared the microstructure and corrosion resistance of nitrided steels subjected to different surface engineering techniques and concludes that a dense nitrided layer irrespective of type of nitrides would always enhance corrosion resistance of steel.

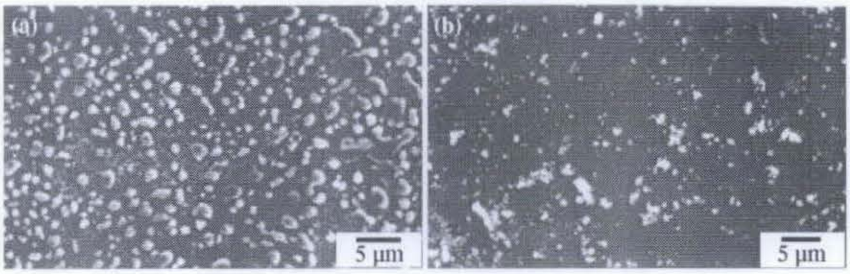

Figure 2.3: Post corrosion SEM pictures (a) as received (b) nitride by Basu (2008)

2.4.2. Gas composition

Jolanta (2006) investigation shows that internal compressive stresses generated in the layers are mainly the result of high ammonia content. As a result of very high stress may form cracks on the layer. For the sample nitrided at low ammonia atmosphere, only small inter granular changes were observed after the tests.

2.4.3. Time

Bouanis (2010) says that plasma nitriding increases impedance of nitrided steel with time of plasma treatment and the maximum of impedance recorded for the longest tested time of plasma nitriding. Inspection of the results shows that the R_{ct} values obtained for nitrided samples generally increase with the processing time. The efficiency (E %) increases for all nitriding and the highest efficiency is achieved for the longest time of treatment. The decrease of capacitance values also related to longer treatment time. This enhancement caused by the formation of nitrided phases on the steel surface.

In another paper, Bouanis (2009) proves that the nitriding treatment decreases I_{corr} significantly with the increase of treatment time. The decrease in I_{corr} indicates that the incorporation of nitrogen in the steel surface, which can be form after nitriding can significantly improve corrosion characteristics. In addition, the nitriding treatment modifies the value of b_c showing that the steel surface is modified after nitriding treatment.

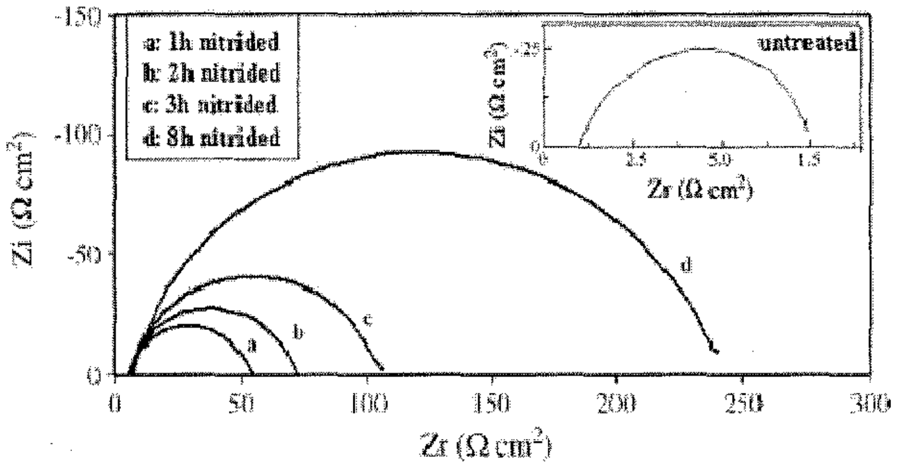

Figure 2.2: Nyquist Diagram of untreated and nitrided steel after various treatment time

2.5 CO_2 Mechanism

The problem of CO_2 corrosion has been long recognized and has prompted extensive studies. Kermani (1997) mentioned that dry CO_2 gas is not itself corrosive at the temperatures encountered within oil and gas system, but is so when dissolved in an aqueous phase through which it can promote an electrochemical reaction between steel and the contacting aqueous phase. Various mechanisms have been postulated for the corrosion process but all involve either carbonic acid or the bicarbonate ion formed on dissolution of CO_2 in water. The overall reaction is:

$$H_2CO_3 + H_2O + \text{Fe} \rightarrow FeCO_3 \text{ (iron carbonate)} + H_2$$

Das (2004) mentioned that aqueous CO_2 corrosion of carbon steel is an electrochemical process involving the anodic and cathodic evolution of hydrogen. The overall reaction is:

$$\mathrm{Fe} + CO_2 + H_2O = FeCO_3 + H_2$$

The electrochemical reactions are often accompanied by the formation of films of solid $FeCO_3$, which can be protective or non protective depending on the condition under which they are formed. One of the most important individual reactions is the anodic dissolution of iron:

$$\mathrm{Fe} = Fe^{2+} + 2e^{+}$$

It is believed that the presence of CO_2 increases the rate of corrosion of mild steel in aqueous solution by increasing the rate of the hydrogen reaction. The presence of H_2CO_3 enables hydrogen evolution at a higher rate even when pH increases. Thus at a given pH as the partial pressure of CO_2 increases, the solubility of CO_2 in the solution increases which lead to increase in the corrosion rate.

2.6 Linear Polarization Resistance

Electrical conductivity (the reciprocal of resistance) of a fluid can be related to its corrosiveness. A two or three electrode probe is inserted into the process system, with the electrodes being electrically isolated from each other and the process line. A small potential in the range of 20mV (which does not affect the natural corrosion process), is applied between the elements and the resulting current is measured. The polarization resistance is the ratio of the applied potential and the resulting current level. The measured resistance is inversely related to the corrosion rate. The electrical resistance of any conductor is given by:

V = IR

R = Effective instantaneous resistance

V = Applied voltage

I = Instantaneous current between electrodes

If the electrodes are corroding at a high rate with the metal ions passing easily into solution, a small potential applied between the electrodes will produce a high current, and therefore a low polarization resistance. This corresponds to a high corrosion rate.

In the Nace Resource Center (2011) mentioned that with this widely used technique in corrosion monitoring, the polarization resistance of a material is defined as the slope of the potential-current density (DE/Di) curve at the free corrosion potential, yielding the polarization resistance R_p that can be related (for reactions under activation control) to the corrosion current by the Stern-Geary equation: (reference)

$$R_p = \frac{B}{i_{corr}} = \frac{(\Delta E)}{(\Delta i)}_{\Delta E \to 0}$$

- R_p is the polarization resistance
- i_{corr} the corrosion current
- The proportionality constant , B,

2.7 Electrochemical Impedance Spectroscopy

Electrochemical impedance theory is a well-developed branch of alternation current theory that describes the response of a circuit to an alternating current or voltage as a function of frequency. In dc theory (a special case of ac theory where the frequency equals 0 Hz) resistance is defined by Ohm's Law:

$E = I R$ (1)

Using Ohm's law, you can apply a dc potential (E) to a circuit, measure the resulting current and compute the resistance (R).Potential values are measured in volts (V), current in amperes or amps (A), and resistance in ohms (Ω). A resistor is the only element that impedes the flow of electrons in a dc circuit. In ac theory, where the frequency is non-zero, the analogous equation is:

$$E = I\,Z \qquad (2)$$

As in Equation 1, E and I are here defined as potential and current, respectively. Z is defined as impedance, the ac equivalent of resistance. Impedance values are also measured in ohms (Ω). In addition to resistors, capacitors and inductors impede the flow of electrons in ac circuits. Figure 1 show a typical plot of a voltage sine wave (E) applied across a given circuit and the resultant ac current Waveform. Note that the two traces are different not only in amplitude, but are also shifted in time.

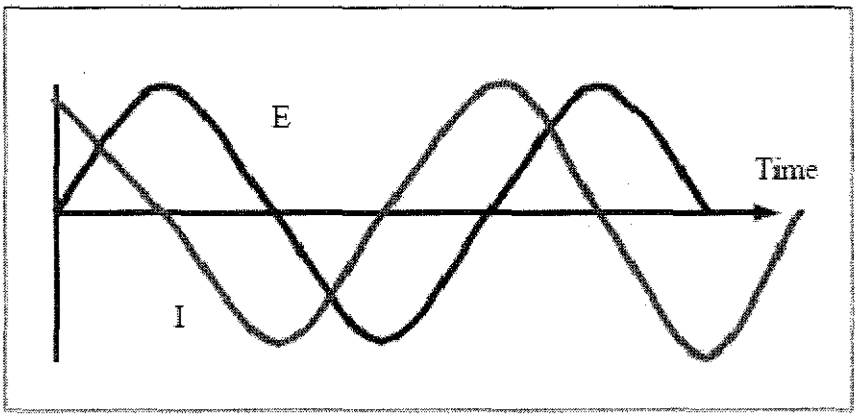

Figure 2.5: AC Waveforms for an Applied Potential and a Resulting Current.

What is Impedance? The terms resistance and impedance both denote an opposition to the flow of electrons or current. In direct current circuits, only resistors produce this effect. However, in alternation current (ac) circuits, two other circuit elements, capacitors and inductors, impede the flow of electrons.

2.7.1 Data Presenting:

The electrochemical impedance spectroscopy are presented as below:

1. The Nyquist plot

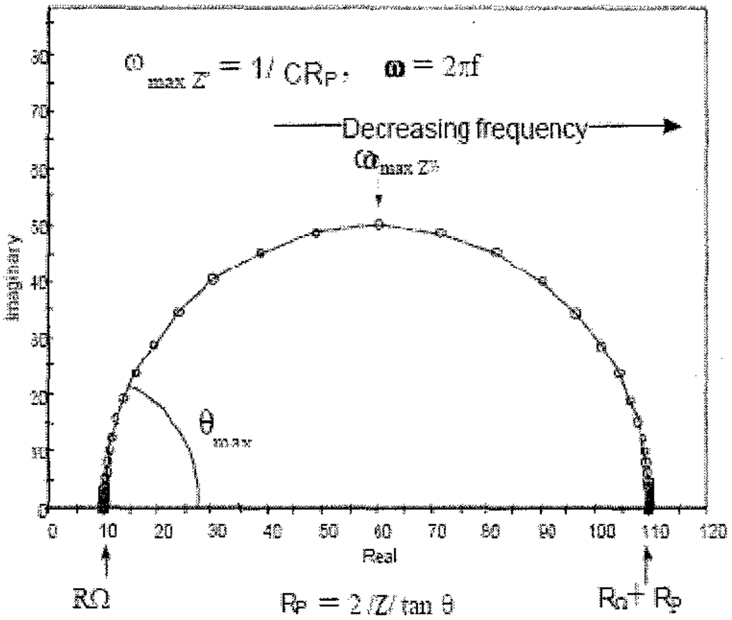

Figure 2.6: Format for evaluating electrochemical impedance data, the Nyquist plot.

2. The Bode Plot

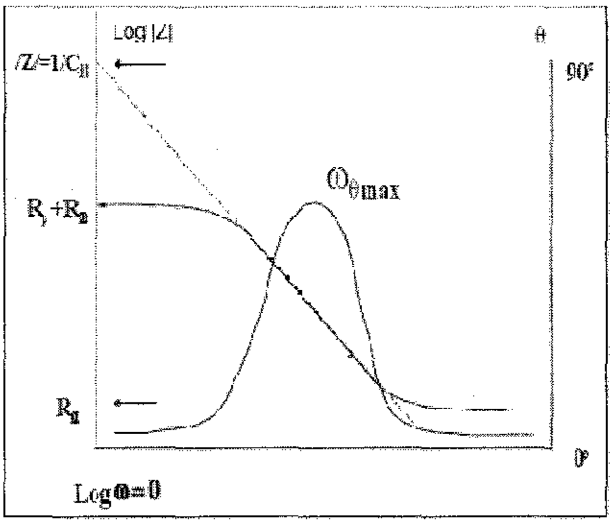

Figure 2.7: Bode Plot for a Simple Electrochemical System Evaluating Capacitance

2.8 Factors Affecting CO_2 Corrosion

Vengkatasubramaniyan (2009) mentioned that there are several environmental factors which affect the formation of corrosion product scales on the surface of the metal, which in turn affect the corrosion rate of the metal. The factors include pH, hydrodynamics, partial pressure of CO_2, temperature and concentration of Fe^{2+} ions. He described as below:

2.8.1 Effect of pH

In increase in pH of the bulk solution decreases the solubility of iron carbonate and increases the precipitation rate, thereby increasing the rate of formation of the protective iron carbonate layer. The increase in concentration of H_2CO_3 and HCO_3^- ions with increasing pH increases the overall rate of cathodic process until the iron carbonate layer formed as a result of anodic process reaches its critical thickness. Honarvar (2010) mentioned that raising the pH increased the compactness of the layer, while the most compactness was seen at pH 6.5 for both of any temperatures.

2.8.2 Effect of temperature

Increasing the temperature initially increases the rate of corrosion until a critical temperature is reached at 30°C. Beyond the critical temperature, the precipitation of an iron carbonates film starts which reduce the corrosion rate of the metal by acting as a diffusion barrier. At low pH when the protective film does not form, the corrosion rate increases with increasing temperature. Increasing the temperature will increase the rate of precipitation and enables the formation of protective iron carbonate films and decreases the corrosion rate. Honarvar (2010) results show that the thickness of $FeCO_3$ layer increased with increasing temperature. Therefore, it could be concluded that the optimum conditions for producing a compact and thick layer of $FeCO_3$ was obtained at temperature of 85 °C and pH 6.5.

CHAPTER 3

METHODOLOGY

3.1 Methodology chart

Figure 3.1 shows the flow of this project:

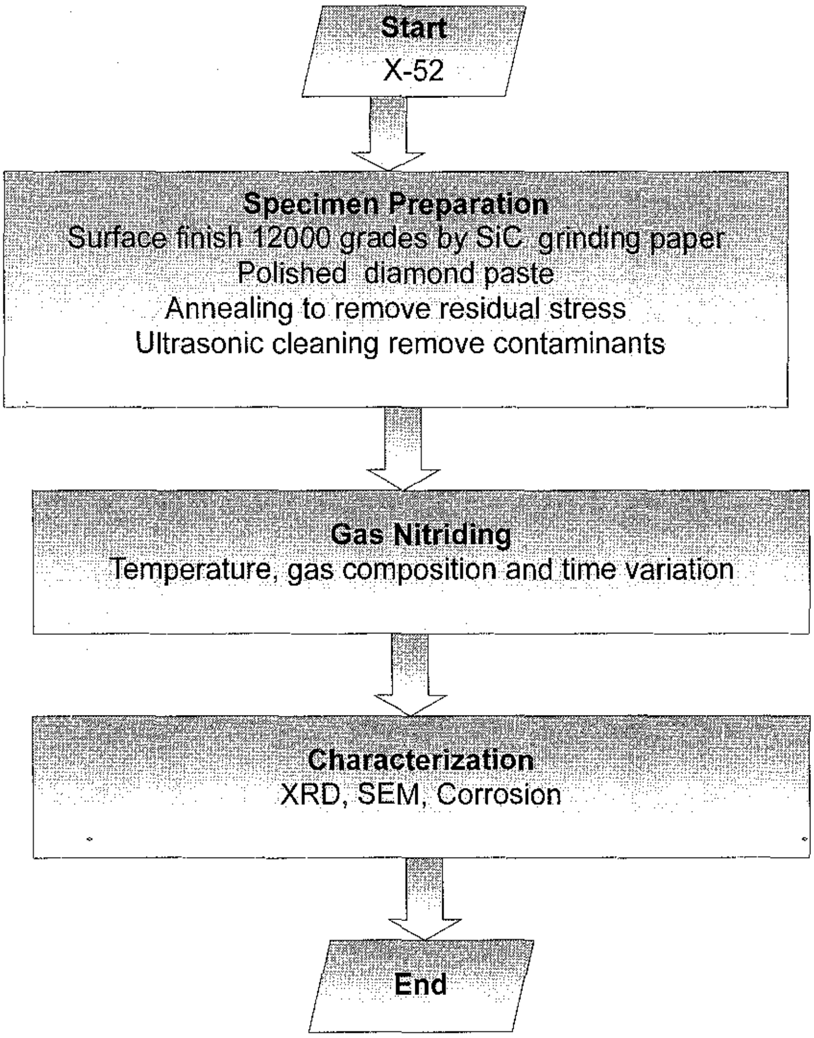

Figure 3.1: Flow of Project

3.2 Materials

The material used in this study was X-52 carbon steel with chemical composition listed as in table 3.1:

Table 3.1: X-52 Compositions

Steel	C	Mn	Si	S	P	Ni	Cr	Nb	Al
X-52	0.16	0.36	.0.31	0.006	0.017	0.01	0.01	0.02	0.03

i. *Grinding and Polishing*

The samples were machined using diamond saw into the form of blocks of 10 mm x 10 mm x 10 mm as shown in figure 3.2. Before nitriding, the X-52 carbon steel samples were pretreated prior to the experiment by grinding with emergy paper SiC (120, 600, 800, 1200) to produce a fine surface finishing and then manually polished by diamond paste (6 μm and 0.25 μm) to produce a fine surface finishing

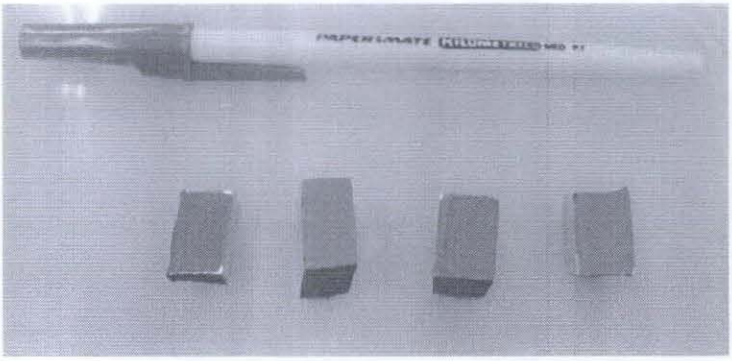

Figure 3.2: The prepared samples

ii. *Annealing*

Annealing is to remove residual stress after machining. The samples were annealed for one hour. The temperature rise is 5°C for every 1 minute. After 1 hour of annealing, the samples left for furnace cooling at about 180°C.

iii. *Ultrasonic Cleaning*

The samples were degreased in acetone in ultrasonic bath for about 10 minutes and dried at room temperature before use.

3.3 Nitriding process setup and method

The samples were gas nitrided using horizontal carbolite tube furnace. A schematic representation of the experimental set-up is shown in figure 3.3. The experiment producers for nitriding are described below.

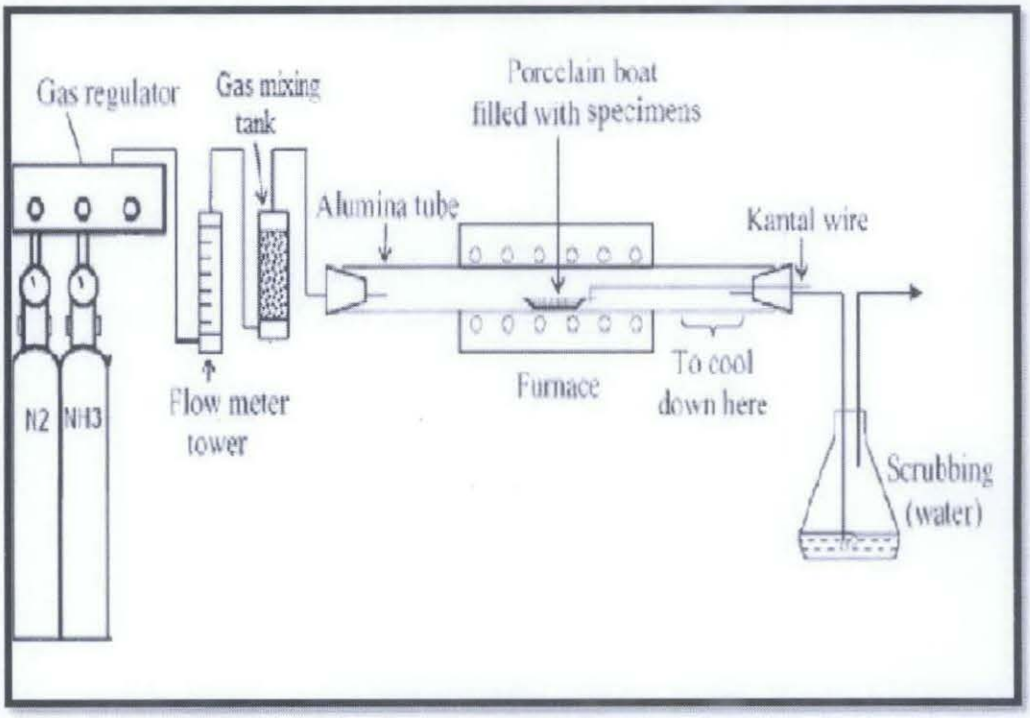

Figure 3.3: Schematic representation of the nitriding experiment by Basu (2008)

1. The experiment setup is shown in figure 3.4.

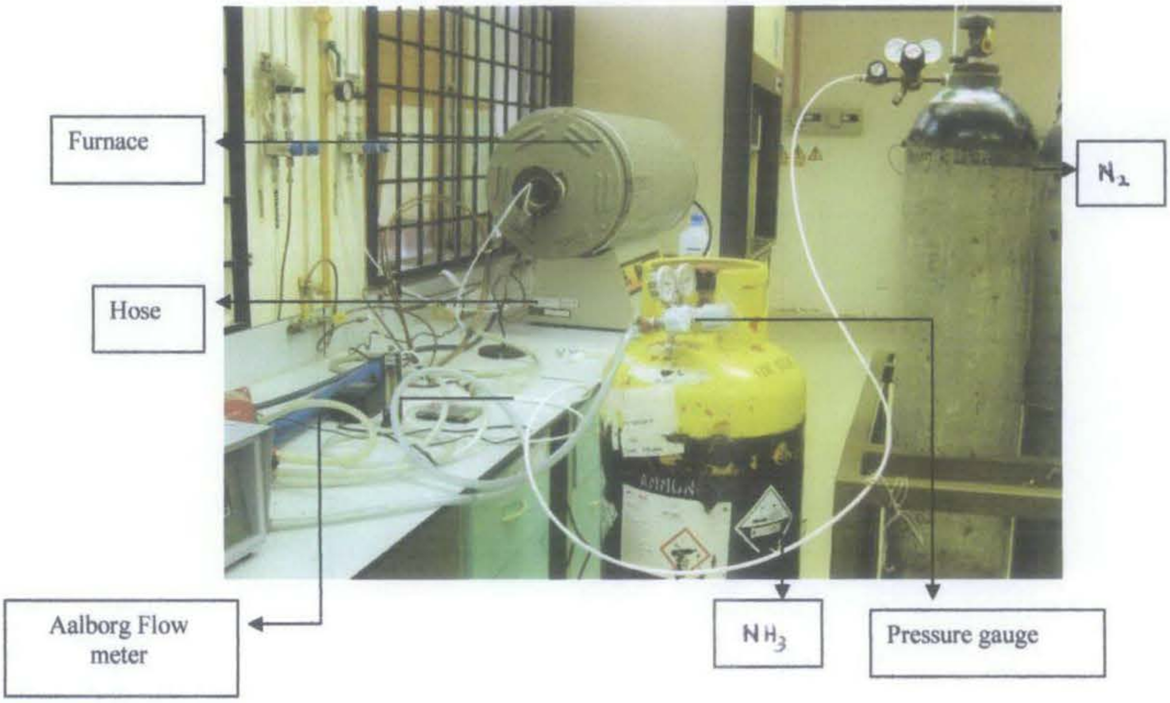

Figure 3.4: Gas nitriding setup in laboratory

2. The flow meters were calibrated according to the required amount of flow for each gas. The type of flow meter used was Aalborg Command Module for AFC 26. The total flow rate was 2000 ml/min. The amount of flow for each gas shown in table 3.2.

Table 3.2: Gas flow rate

Type of Gas	Percentage %	Flow Rate, ml/min
Ammonia,	50	1000
Nitrogen	50	1000

3. After ultrasonic cleaning, the samples were placed on an alumina block before putting inside the furnace.

4. For the first experiment, the samples were nitrided at 450°C.

5. Gas nitrogen purged into the furnace for 30 minutes to allow the furnace to become inert. The flow rate of the nitrogen was 2000 ml/min (free from any other gases). After that, gas nitrogen and ammonia purged simultaneously with the above flow rate.

6. The heating rate depends on the nitriding temperature. The heating period was 20 minutes. Example: For nitriding temperature of 450 °C, the heating rate is 22.5 °C/min.

7. After the required nitriding temperature attained, this temperature was set to be constant for 8 hours.

8. After 8 hours of nitriding, the samples were slow cooled in the furnace before removed.

9. The steps 1-8 were repeated for all the other nitriding temperatures as shown in table 3.3.

Table 3.3: Test Matrix for Gas Nitriding

Sample **Parameters**	**Sample 1**	**Sample 2**	**Sample 3**
Temperature, °C	450	480	520
Gas composition N_2/ NH_3 ,%	50/50	50/50	50/50
Time, hours	8	8	8

3.4 Characterization

1. X-ray diffraction (XRD)

After gas nitriding, samples were studied by X-ray diffraction analysis to confirm the micro structural evolution in terms of identification of phases of nitride layer and the composition of layer. The measurements were made using x-ray diffractometer. Measurement made in the scan range 2° to 80° with step size 0.05°.

2. Scanning Electron Microscope (SEM)

This testing will be able to find information about the sample surface topography and composition by the cross section of the sample.

3.5 Corrosion setup and methods

The electrochemical characterization was carried out by potentiodynamic polarization connected to a standard three electrode cell comprising the working electrode, reference electrode and counter electrode. The procedures were:

1. Solution medium of sodium chloride 3% prepared by mixing 30g of sodium chloride into 1 liter of distilled water.

2. The solution prepared saturated with CO_2 by purging for at least one hour prior to exposure of electrode. The pH value is checked by microcomputer pH-meter. The indication of the cell is saturated with carbon dioxide can be tested with the pH meter.

3. The electrochemical measurements are based on a three-electrode system, using a commercially available potentiostat with a computer control system. The potentiostat used was ACM Instruments. The reference electrode used was a silver chloride (AgCI) electrode and the auxiliary electrode was a platinum electrode. The working electrode consists of samples of different nitriding temperature. The area exposed to the solution was $0.1cm^2$.

4. The first experiment was conducted at $25^{o}C$ and acetic acid was not added to maintain the pH of 4. The working electrode used was untreated X-52 carbon steel. Prior to the immersion of the specimen, it is degreased with acetone and rinsed with distilled water.

5. Once the chemicals and electrodes added into the solution, the data acquisition system accessed from the computer connected to the ACM Instruments Version 5, run Gill 12 Weld Tester Serial No. 1350 –Sequencer and the Core Running software.

6. All the parameters set for the measurement of the experiment keyed into the the Sequencer software. The experiment duration was set 1 hour.

7. The ACM instruments run and data gathered automatically into the ACM Analysis Version 4.The experiment setup shown in figure 3.5:

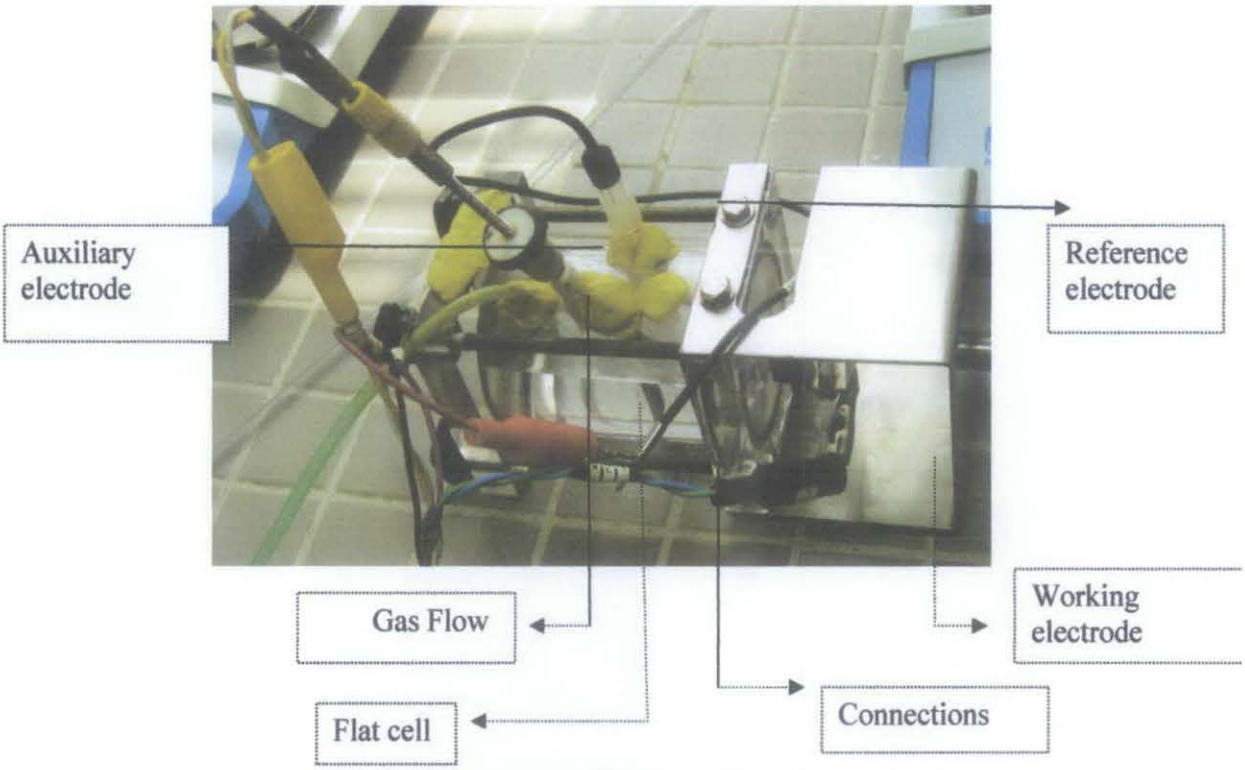

Figure 3.5: Laboratory setup of the flat cell used for polarization resistance

8. The test matrix is shown in table 3.4:

Table 3.4: Test Matrix for corrosion experiment

Parameters / Samples	Temperature, °C	Period, hours	Acetic acid ,ppm
Untreated	25	1	0
Nitrided 450°C	25	1	0
Nitrided 480°C	25	1	0
Nitrided 520°C	25	1	0
Untreated	25	1	100
Nitrided 450°C	25	1	100
Nitrided 480°C	25	1	100
Nitrided 520°C	25	1	100

9. The impedance data were analyzed and simulated using software NOVA.

10. The steps 1-9 repeated for all the other samples according to the test matrix in table 3.4.

CHAPTER 4

RESULTS AND DISCUSSIONS

4.1 Nitriding characterization

Phase evolutions for nitrided samples were characterized by X-ray diffraction (XRD) analysis. While as received sample showed only Fe peak, XRD patterns of gas nitrided samples recorded number of peaks due to different nitriding temperatures. Figure 4.1 show the XRD profile of as received and gas nitrided samples treated at different temperatures for 8 hours.

4.1.1 Effects of nitriding temperature on microstructure and phase

From the above graphs, iron nitride formed at 450°C, 480°C and 520°C. The comparison between the untreated sample and nitride samples shows some shifting of the peaks as a result of lattice distortion. According to previous investigation, the 'shifting' means there are formations of new phases as a result of nitrogen diffusion. It has been proven from the previous investigation that the nitride volume fraction increases with nitriding temperature.

Figure 4.1 shows the XRD pattern for untreated and gas nitrided X-52 carbon steel for 8 hours:

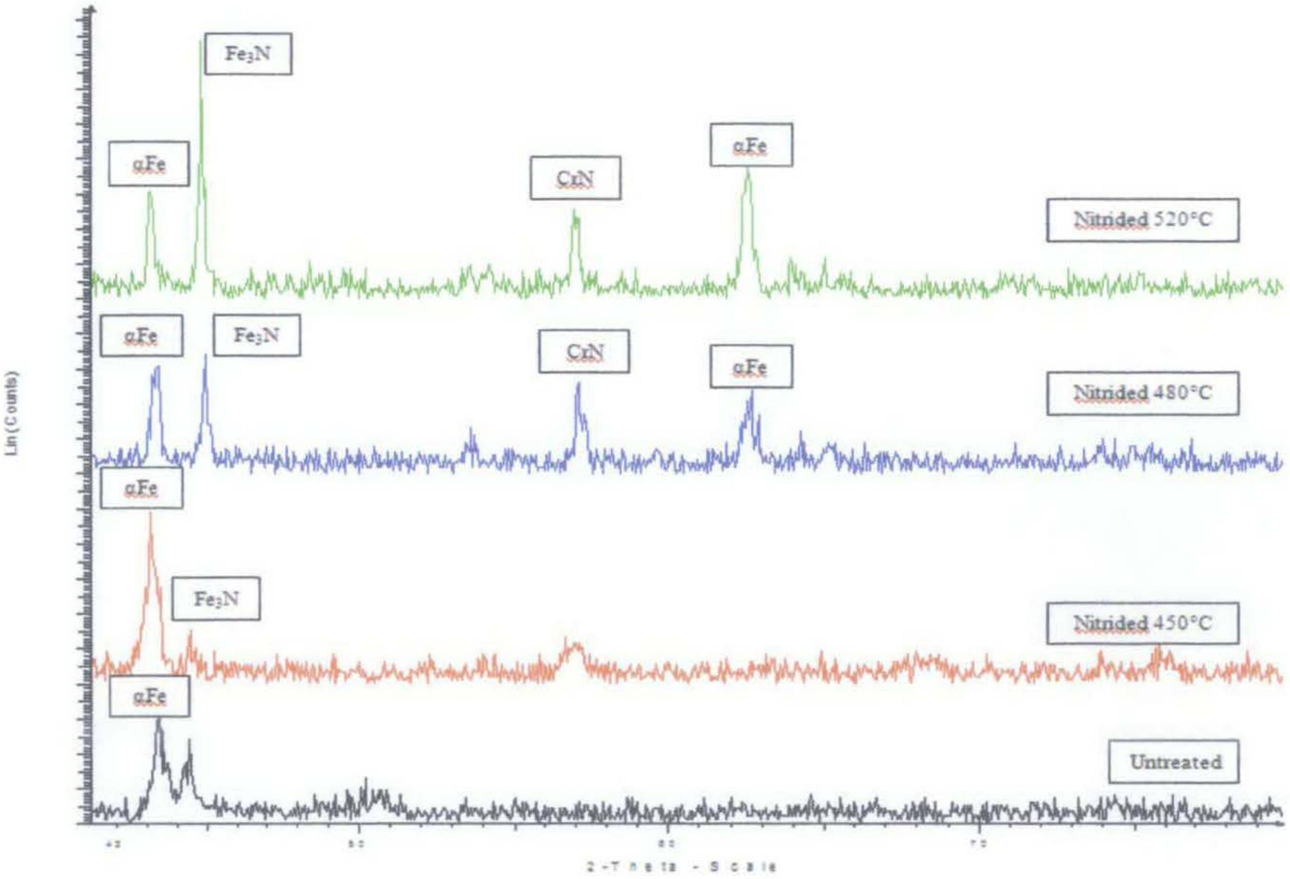

Figure 4.1: XRD profile for untreated and gas nitrided X-52 carbon steel for 8 hours at different temperatures.

4.2 Microscopic Observations in Diffusion zone

The microstructure of untreated and nitrided X-52 carbon steels sample surfaces observed under the scanning microscopes are shown in figure 4.2 to figure 4.4.Surface exposed to a nitriding medium will generally form two distinct layers. The outside layer is called a compound layer (or white layer) and its thickness generally falls between zero and 0.001" (25 μm). Underneath the white layer is the diffusion case or diffusion zone. Both together comprise what is generally referred to as the case. Below the compound layer, the diffusion zone is formed composing stable nitrides comprising alloying elements. These strong nitride forming elements are the major nitride forming elements.

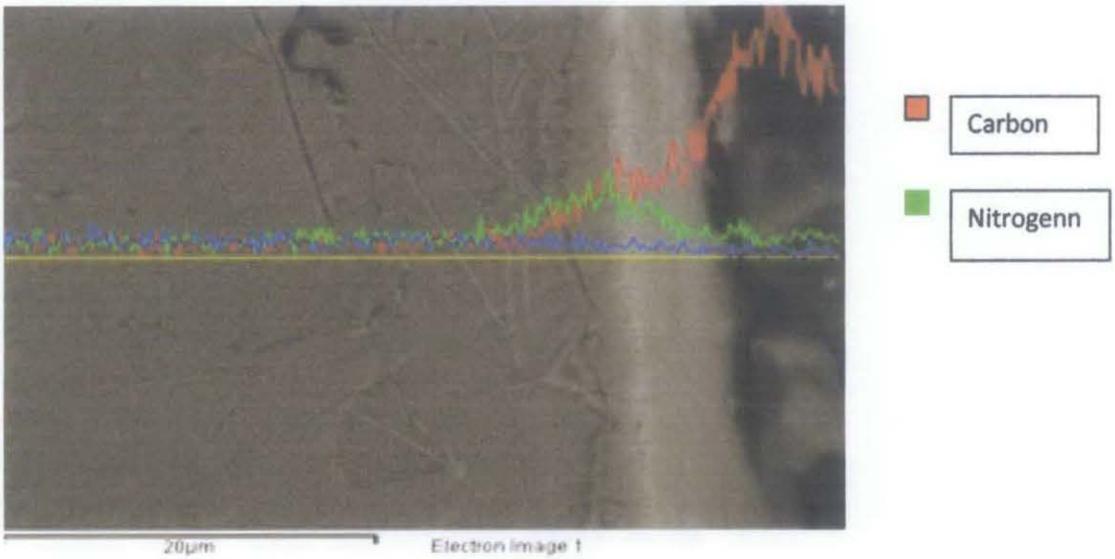

Figure 4.2: Scanning electron microscopes shows the cross section of nitrided layer formed by nitriding X-52 carbon steel at 450°C for 8 hours

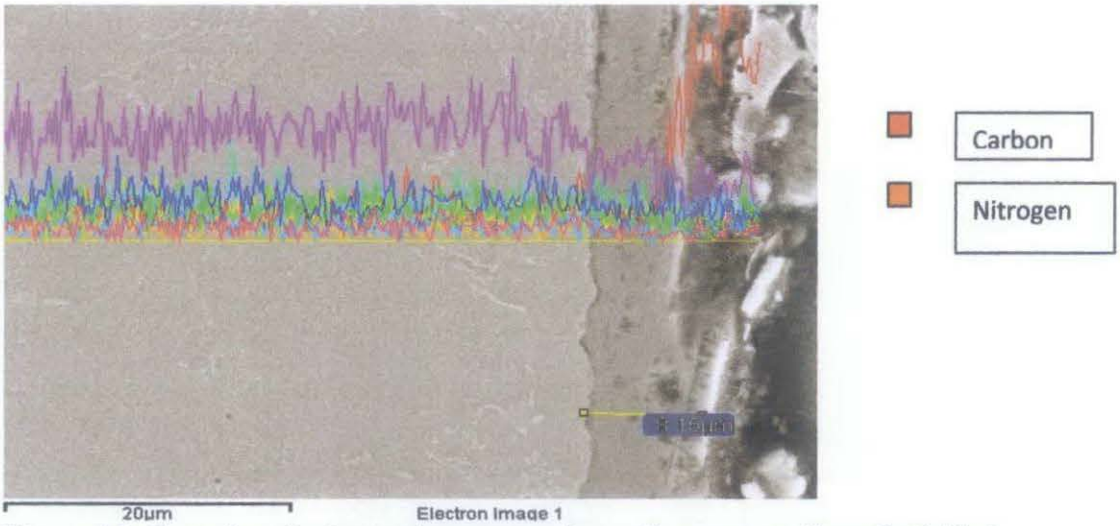

Figure 4.3: Scanning electron microscopes shows the cross section of nitrided layer formed by nitriding X-52 carbon steel at 480°C for 8 hours.

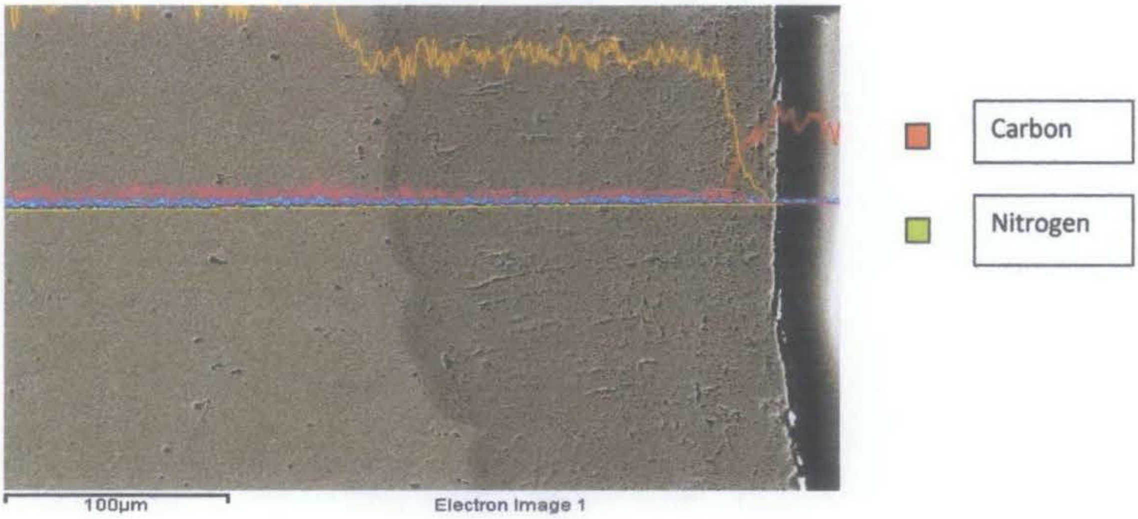

Figure 4.4: Scanning electron microscopes shows the cross section of nitrided layer formed by nitriding X-52 carbon steel at 520°C for 8 hours.

4.2.1 Effect of nitriding temperature on nitrogen diffusion

The extent of nitrogen diffusion can be observed from the figure 4.1 above. The increase in the carbon composition for all nitriding temperature shows that carbon penetrated the outermost layer, probably in interstitial sites of the metallic network or in micro cracks resulting from the nitriding temperature.

Other element that present in the sample nitrided at 450°C was chromium. For samples nitrided at 480°C and 520°C, other elements that present in the sample were iron, manganese, chromium, vanadium, molybdenum, niobium and cobalt. These elements form hard and stable nitrides as soon as they come into contact with nitrogen atoms at the surface of the work piece.

SEM data confirm that the nitrogen diffusion presence in the all nitrided samples which are 450°C, 480°C and 520°C. The intensity of nitrogen increases with nitriding temperatures.

4.3 Linear Polarization Resistance (LPR)

The aim of this investigation was to determine the influence of the gas nitriding on the electrochemical behaviors of X-52 carbon steel in 3% NaCl. Linear polarization resistance measurement consist of the results for the system of 3% NaCl at 25^0C with 0 ppm of acetic acid and system of 3% NaCl at 25^0C with 100 ppm of acetic acid. The result for each experiment can be seen from all the figures below.

4.3.1 The systems of 3% NaCl solution at 25^0C with 0 ppm acetic acid

Figure 4.5 shows the corrosion rate for untreated X-52 carbon steel and nitrided X-52 carbon steels at 450°C, 480°C and 520°C for the system of 3 % NaCl at 25^0C with 0ppm of citric acid. All these systems have pH 4. All the experiments were conducted for 1 hour with one reading taken in every 15 minutes. The corrosion rate indicated below is the result of the last reading for each experiment which is after 1 hour.

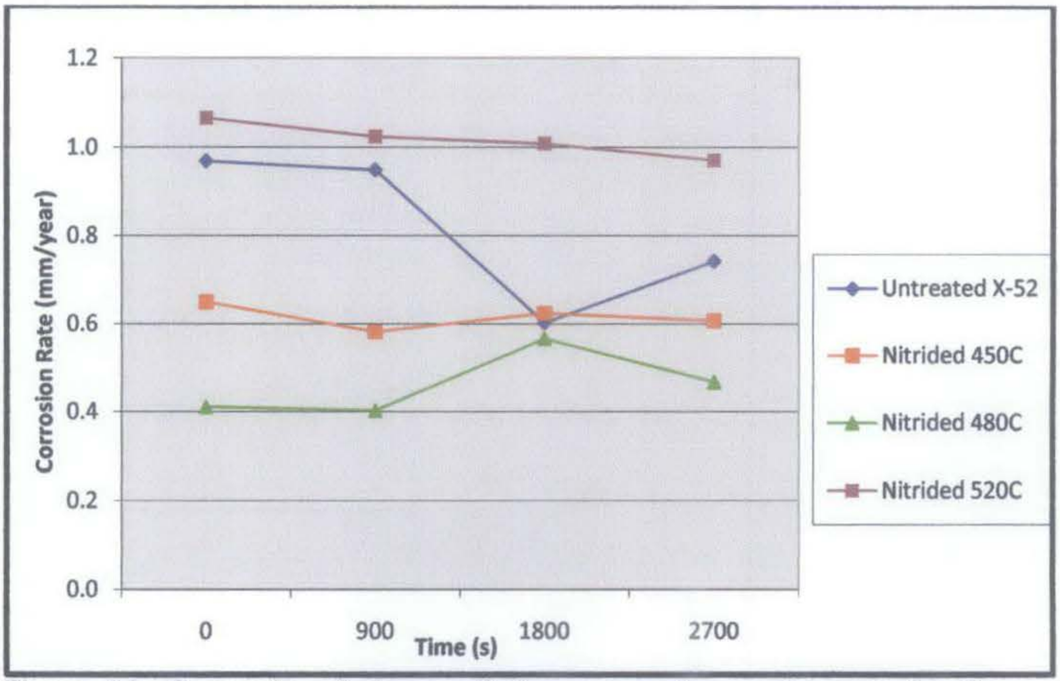

Figure 4.5: Comparison between all the measured corrosion rate for the system of 3% NaCI (25°C) with 0 ppm acetic acid in CO_2 environment

From the Figure 4.5 above, there are four plots of lines which are corrosion rate for untreated and nitrided X-52 carbon steel in 3% NaCI solution (25^0C) with 0 ppm of acetic acid in carbon dioxide environment. There is huge decrement in the corrosion rate for sample nitrided at 450°C and 480°C. For sample nitrided at 450°C, the mean corrosion rate decreased from 0.74 mm/year to 0.60 mm/year. For sample nitrided at 480°C, the mean corrosion rate decrease from 0.74 mm/year to 0.47 mm/year. Mean corrosion rate for sample nitrided at 520°C is higher than untreated sample. The corrosion rate increased from 0.74 mm/year to 0.97 mm/year

4.3.2 The systems of 3% NaCl solution at 25^0C with 100 ppm acetic acid

From Figure 4.6 shows the corrosion rate for untreated X-52 carbon steel and nitrided X-52 carbon steels at 450°C, 480°C and 520°C for the system of 3 % NaCl at 25^0C with 100 ppm of acetic acid. All these systems have pH 3.All the experiments were conducted for 1 hour with one reading taken in every 15 minutes. The corrosion rate is the result of the last reading for each experiment which is after 1 hour.

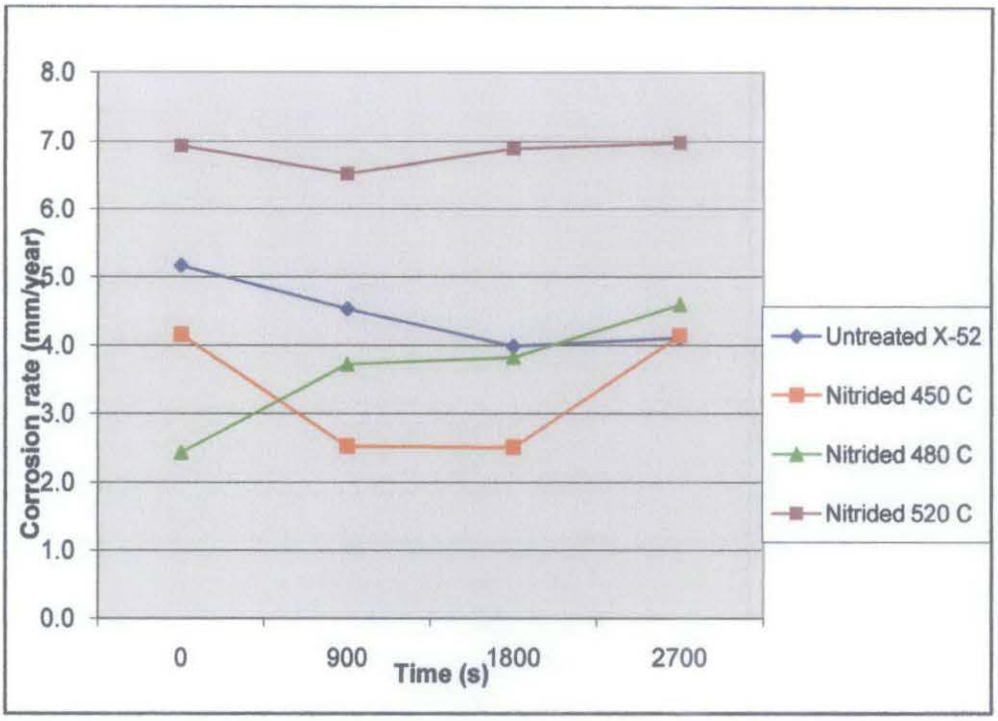

Figure 4.6: Comparison between all the measured corrosion rates for the system of 3% NaCI (25°C) with100 ppm acetic acid in CO_2 environment

From the Figure 4.6 above, there are four plots of lines which are untreated corrosion rate and corrosion rate for X-52 carbon steels at different nitriding temperature in 3% NaCI solution with temperature 25^0C and 100 ppm of acetic acid in carbon dioxide environment. Mean corrosion rate for all the samples higher than untreated sample. At 450°C, the corrosion rate happen is similar as the untreated sample which is 4.1 mm/year. For nitriding temperature of 480°C, the corrosion rate increase from 4.1 mm/year to 4.6 mm/year. At nitriding temperature of 520°C, the corrosion rate increased from 4.1 mm/year to 6.2 mm/year.

4.3.3 The efficiency result for each system with the current densities, I_{corr}, corrosion potential, E_{corr} and corrosion rate.

The effect of nitriding temperature on the corrosion behavior of gas nitrided steel is presented in table 4.1 and table 4.2. The values of associated electrochemical parameters such as corrosion potential (E_{corr}), corrosion current density (I_{corr}), corrosion rate and efficiency are presented. It has been proven that gas nitriding treatment decreases I_{corr} significantly with increase of temperature in comparison with the untreated steel. The decrease in I_{corr} indicates that the incorporation of nitrogen in the steel surface, which form dense layer after gas nitriding, can significantly improve corrosion characteristics. E (%) is calculated by I_{corr} with the following equation:

$$E\ (\%) = \frac{I^{o}_{corr} - I_{corr}}{I^{o}_{corr}} 100$$

Where I^{o}_{corr} and I_{corr} are the corrosion current density values of untreated and gas nitrided carbon steel respectively.

Table 4.1: Corrosion properties of untreated and gas nitrided samples with 0 ppm of acetic acid in CO_2 environment

Samples	R_p (Ohm.cm^2)	I_{corr} (mA/cm^2)	Corrosion rate (mm/year)	E (%)
Untreated	407	0.06	0.74	-
Nitrided 450°C	498	0.05	0.61	17%
Nitrided 480°C	647	0.04	0.47	33%
Nitrided 520°C	312	0.09	1.06	-50%

Table 4.2: Corrosion properties of untreated and gas nitrided samples with 100 ppm of acetic acid in CO_2 environment

Samples	R_p (Ohm. cm^2)	I_{corr} (mA/cm^2)	Corrosion rate (mm/year)	E (%)
Untreated	74	0.35	4.1	-
Nitrided 450°C	73	0.35	4.1	-
Nitrided 480°C	66	0.36	4.60	-3 %
Nitrided 520°C	43	0.60	7.00	-70 %

4.3.4 The effect of nitriding temperature and solution pH on the corrosion rate

At 0 ppm of acetic acid, the corrosion density for sample nitrided at 450°C and 480°C decreased due to the formation of iron nitride which was proven in the XRD patterns and SEM analysis. This nitride layer protected the surface of the sample from further corrosion. For sample nitrided at 520°C, corrosion density increased compared to untreated sample. The drastic increase in the corrosion rate of the sample can be due to the uneven distribution of nitride layer on the surface. Furthermore, high porosity of the sample also can allow the movement of solution into the sample, and the corrosion reaction proceeds. At 100ppm of acetic acid, the efficiency of the nitride layer decreases. This can be due to the low pH. The nitride layer will dissolve in the acidic solution. In the absence of the protective film, the metal surface is in direct contact with the acid solution, and the corrosion reaction proceeds at a greater rate than it does at higher pH values. Furthermore, it can be concluded that addition of acetic acid can increase corrosion rate due to decrease in the pH of the solution.

4.4 Electrochemical Impedance Spectroscopy (EIS)

The corrosion behavior of untreated and gas nitrided X-52 carbon steel in 3% NaCl solution of CO_2 environment was also investigated by the electrochemical impedance spectroscopy (EIS) at 25°C. The simulation for the EIS was completed using software Nova. Nyquist plots of untreated and treated X-52 carbon steel at different temperatures are given in figure 4.7 and figure 4.8.

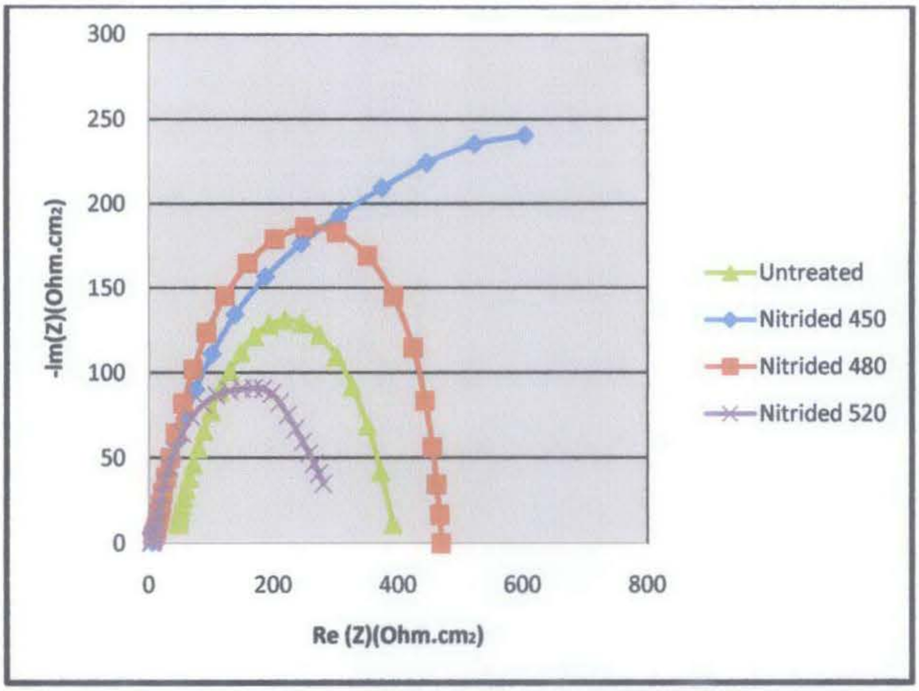

Figure 4.7: Nyquist diagram for Untreated and Gas nitride X-52 carbon steel with 0 ppm of acetic acid in co_2 environment

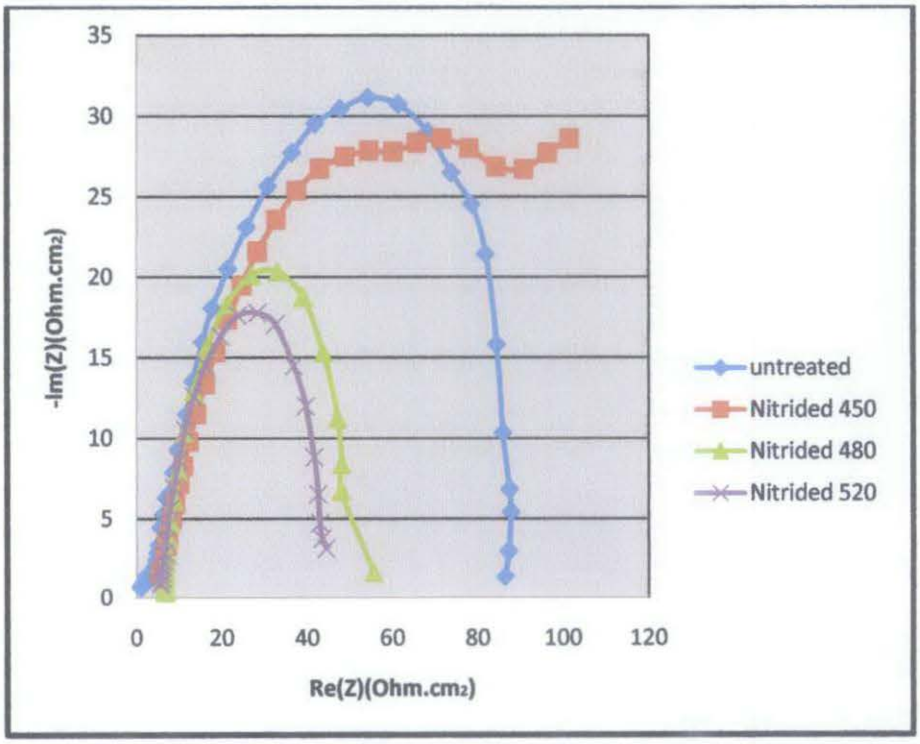

Figure 4.8: Nyquist diagram for Untreated and Gas nitride X-52 carbon steel with 100 ppm of acetic acid in co_2 environment

Figure 4.9, shows the electrical equivalent circuit employed to analyze the impedance spectra. In this equivalent circuit, R_s is the solution resistance, R_{ct} presents the charge transfer and CPE represents the capacitive element. Double layer capacitance, C_{dl} is not suitable for roughness and other in homogeneities of the metal surface. For this reason, the capacitance of the double layer at the metal/solution interface is modeled by CPE (constant phase element) to compensate for non-homogeneity in the system. CPE is introduced to give more accurate fit. Excellent fit with this structural model was achieved for all experiment data, are illustrated in figure 4.9.

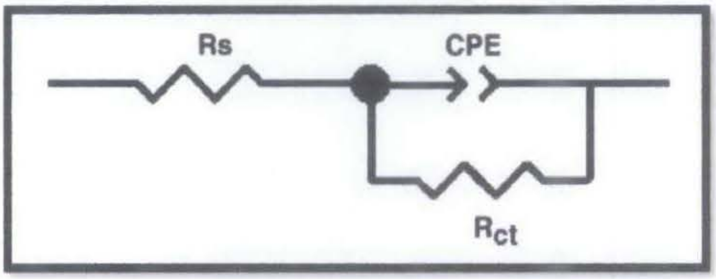

Figure 4.9: Electrical equivalent circuit used for modeling the interface of X-52 steel (untreated and nitride)

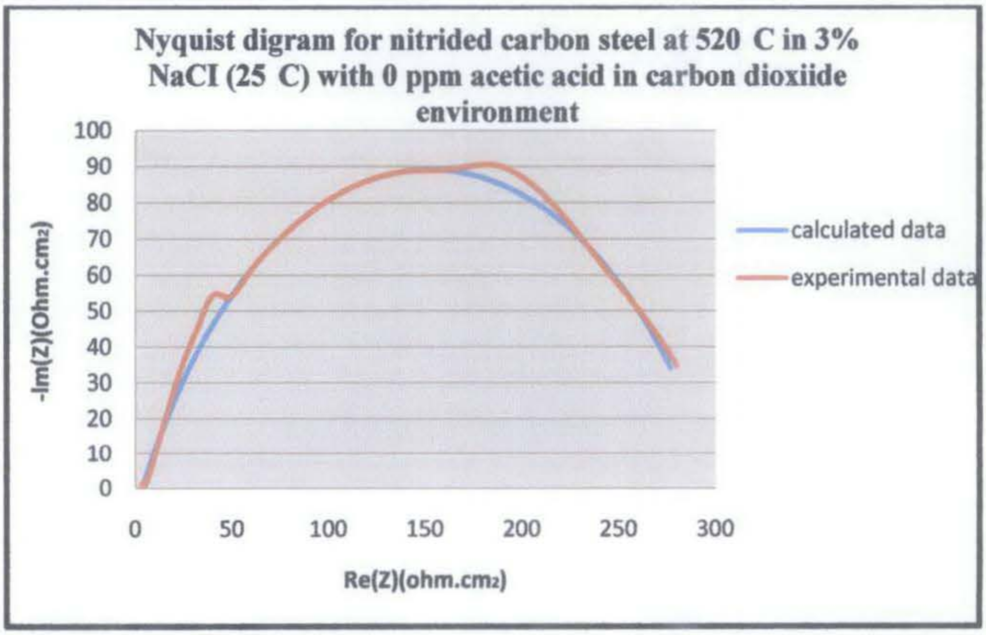

Figure 4.10: Comparison of the Nyquist diagram for Nitrided 520°C at 0 ppm acetic acid in CO_2 environment

4.4.1 The efficiency result for each system using AC Impedance

The efficiency is calculated by E% using equation below where R°_{ct} and $R_{ct}$are the charge transfer resistance values of untreated and gas nitride X-52 carbon steel"

$$E\ (\%) = \frac{1/R^{0}_{ct} - 1/R_{ct}}{1/R^{0}_{ct}} 100$$

In table 4.3 and 4.4, are show also the CPE parameters (A,n) and R_{ct} :

Table 4.3: Impedance parameters for untreated and gas nitride X-52 carbon steel with 0 ppm acetic acid in CO_2 environment

Sample	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	A ($\Omega^1 s^n cm^{-2}$)	n	E%
Untreated	42	378	0.0009	0.73	-
Nitrided 450°C	4	711	0.0060	0.73	47%
Nitrided 480°C	7	514	0.0003	0.74	26%
Nitrided 520°C	3	297	0.0030	0.69	-27%

Table 4.4: Impedance parameters for untreated and gas nitride X-52 carbon steel with 100ppm acetic acid in CO_2 environment

Sample	R_s (Ωcm^2)	R_{ct} (Ωcm^2)	A ($\Omega^1 s^n cm^{-2}$)	n	E%
Untreated	1	119	0.002	0.52	-
Nitrided 450°C	4	120	0.004	0.62	3 %
Nitrided 480°C	6	46	0.005	0.52	-150 %
Nitrided 520°C	5	40	0.004	0.88	-190 %

As it can be seen, the impedance response of carbon steel in sodium chloride has significantly changed after gas nitriding and the impedance of the treated system increased with the increase in the nitriding temperature (until 480°C) for 0 ppm of acetic acid.

For system with 100 ppm of acetic acid, the impedance response decreased for all the samples. The efficiency of the sample decreased indicating that nitriding is not suitable for corrosive environment.

4.4.2 The effect of nitriding temperature and pH effect on the corrosion rate

At 0 ppm of acetic acid, corrosion rate for sample nitrided at 450°C and 480°C decreased. At 100 ppm of acetic acid, the corrosion rate increased drastically compared to the untreated sample except for sample nitrided at 450°C. This can be due to corrosive environment. The layer on the surface did not protect the sample but dissolve in the solution allowing the corrosion to happen. The efficiency calculated from EIS study show the same trend as those obtained from LPR.

In the case of impedance study as expected the R_{ct} values increased with the nitriding temperature until certain level. Inspection of these results at 0 ppm shows that the R_{ct} vales obtained for nitrided samples at 450°C and 480°C greatly increased compared to that obtained for the non-treated samples, indicating a large increase in the protectiveness of the surface. This enhancement is caused by the formation of nitride phases on the steel surface. A large charge transfer resistance is associated with a slower corroding system. The result indicates that after gas nitriding, the nitride phases are formed on the steel surface to provide higher corrosion resistance.

The capacitance value parameters related to the CPE parameters which is A and n. The relationship is:

$$C_{dl} = (AR_{ct}^{1-n})^{1/n}$$

The increase of the values of n when compared to non nitride and nitride samples can be explained due to the diffusion of nitrogen in the steel surface, forming a dense nitrided layer.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 Conclusion

The objective of this project work as stated previously is to investigate the performance of different nitrided carbon steel in CO_2 environment. The properties of gas nitrided layers are evaluated in the context of gas nitriding temperature. It is proven that nitride layer formed on sample nitrided at 450°C, 480°C and 520°C from the XRD pattern and SEM pictures. At ph 4, corrosion rate of sample nitrided at 450°C and 480°C decreases. The highest corrosion rate recorded for sample nitrided at 520°C. This may be due to the poor surface preparation of the sample and uneven nitride layer fails to protect the sample. The metal in contact with acid solution results in high corrosion rate. At pH 3, the corrosion rates of sample nitrided at 480°C and 520°C higher than untreated sample. For the sample nitrided at 450°C, the corrosion rate was similar as the untreated sample. The slight decrease and increase in the corrosion rate at pH 3 indicate that the presence of nitriding layer was detrimental. This negative effect can be linked to porous nitriding layer that lead to galvanic coupling between the nitriding layer and bare metal. Further studies need to be conducted to confirm this possibility.

5.2 Recommendation

The recommendation is to further investigate the effect of other nitriding conditions which are time and gas composition on the corrosion rate of carbon steel in CO_2 environment. Time and gas composition are the two important factors that determine the volume fraction of nitride layer. The experiment also can be repeated for different nitriding temperatures.

Using the same nitrided samples in this project, the time for the corrosion testing can be increased. In this project, the corrosion data were recorded only for one hour. Further data can show the trend of the corrosion rate clearly and better conclusion can be made.

Other parameters that affect corrosion rate are temperature, partial pressure and pH. The variation of these parameters during corrosion testing can show the effectiveness of nitride layer in different CO_2 environment.

CHAPTER 6

REFERENCES

[1] Pye,David.(2003). *Practical Nitriding and Ferritic Nitro carburizing*. United States, US: ASM International.

[2] Mouri,L & Mabille,I. (2001). *Corrosion science. Improvement of the Corrosion resistance of a low Carbon Steel using a two step Plasma Treatment,* 44, 2089-2099

[3] Baranowska Jolanta, & Arnold Bozena (2006).Surface and coating technology. *Corrosion Resistance of nitrided layers on austenitic stee*l, 200(22-23), 6623-6628.

[4] Ashrafizadeh,F .(2003). Surface and coating technology. *Influence of Plasma and Gas Nitriding on Fatigue Resistance of Plain Carbon (Ck 45) Steel,* 174, 1196-1200.

[5] Basu,A., & Dutta Majumdar,J. (2008). Materials letter. *Corrosion resistance improvement of high carbon low alloy steel by plasma nitriding*, 62(17), 3117-3120.

[6] Bouanis,F.Z. (2008).Electrochemical test. *Enhanced corrosion resistance properties of radiofrequency cold plasma nitrided carbon steel,* 54(8), 2371-2378.

[7] Bouanis,F.Z., & Jama,C. (2010). Corrosion science. *Study of Corrosion Resistance of Properties of nitride Carbon Steel using Radiofrequency* N_2/H_2 *Cold Plasma Process,* 52(10), 3180-3190.

[8] Ensinger.W. (1992).Surface Coating Technlogy.52,217-221

[9] Kermani & Smith.(1997). CO_2 *Corrosion Control in Oil and Gas Production.* United Kingdom, UK: IOM Communications.

[10] Das,G.S. & and Khanna,A.K. (2004). Corrosion science and engineering. *Corrosion Behaviour of Pipeline in* CO_2 *Environment*, 57(3), 227-281.

[11] Nace Resource Center. Corrosion monitoring. *Linear Polarization Resistance.* Retrieved July 18,2011 from http://events.nace.org/library/corrosion/monitorbasics/lpr.asp

[12] Princeton Applied Research (2006). *Basics of Electrochemical Impedance Spectroscopy.* Retrieved July 18,2011 from http://www.fq.uh.cu/dpto/qf/docencia/pregrado/dinamica_1/laboratorio/impedancia/basics_of_eis.pdf

[13] Sridharan Vengkatasubramaniyan (2009). *Measurement of Carbon Dioxide Corrosion on Carbon Steel Using Electrochemical Frequency Modulation.* University of Saskatchewan

[14] Honarvar. (2010). Applied surface science. *Development of nitride-layer of AISI 304 austenitic stainless steel during high-temperature ammonia gas-nitriding.*doi:10.1016/j.apsusc.2010.05.100

CHAPTER 7

Appendix 1

1. **The systems of 3%NaCl solution with 25^{0}C and 0ppm citric acid**

Table 1: LPR result for untreated sample

Time (Sec)	LPR (ohm.cm²)	Icorr (mA/cm²)	Corrosion Rate (mm/year)	Potential (mV)
0	283.65	0.0919664	1.0658	-234.44
900	295.19	0.0883728	1.0242	-243.53
1800	299.7	0.087041	1.0088	-252.93
2700	311.5	0.0837443	0.9705961	-265.05

Table 2: LPR Result for samples nitrided at 450°C

Time (Sec)	LPR (ohm.cm²)	Icorr (mA/cm²)	Corrosion Rate (mm/year)	Potential (mV)
0	464.86	0.056117	0.6503956	-573.24
900	519.37	0.0502278	0.58214	-610.63
1800	484.21	0.0538747	0.6244075	-636.06
2700	497.99	0.0523845	0.6071358	-278.19

Table 3: LPR result for samples nitride at 480°C

Time (Sec)	LPR (ohm.cm²)	Icorr (mA/cm²)	Corrosion Rate (mm/year)	Potential (mV)
0	735.73	0.035457	0.4109469	-169.73
900	750.95	0.0347386	0.4026202	-171.48
1800	533.65	0.0488837	0.5665622	-172.83
2700	646.76	0.0403342	0.4674739	-176.77

Table 4: LPR result for sample nitride at 520°C

Time (Sec)	LPR (ohm.cm²)	Icorr (mA/cm²)	Corrosion Rate (mm/year)	Potential (mV)
0	287.58	0.0907108	1.0513	-497.87
900	314.04	0.0830675	0.9627528	-498.87
1800	302.22	0.0863161	1.0004	-497.58
2700	284.6	0.0916606	1.0623	-498.86

2. **The systems of 3%NaCl solution with 25^{0}C and 100 ppm acetic acid**

Table 5: LPR result for untreated sample

Time (Sec)	LPR (ohm.cm^2)	Icorr (mA/cm^2)	Corrosion Rate (mm/year)	Potential (mV)
0	58.468	0.4461713	5.1711	-312.7
900	66.696	0.3911282	4.5331	-328.08
1800	75.848	0.343934	3.9861	-342.31
2700	73.634	0.3542749	4.106	-347.26

Table 6: LPR Result for samples nitrided at 450°C

Time (Sec)	LPR (ohm.cm^2)	Icorr (mA/cm^2)	Corrosion Rate (mm/year)	Potential (mV)
0	72.731	0.3586767	4.157	-428.25
900	119.58	0.218152	2.5283	-431.26
1800	120.48	0.2165111	2.5093	-428.56
2700	73.019	0.3572616	4.1406	-330.86

Table 7: LPR Result for samples nitrided at 480°C

Time (Sec)	LPR (ohm.cm^2)	Icorr (mA/cm^2)	Corrosion Rate (mm/year)	Potential (mV)
0	124.22	0.2100042	2.4339	-621.81
900	81.262	0.3210228	3.7206	-645.2
1800	79.035	0.3300677	3.8254	-646.8
2700	65.78	0.3965758	4.5963	-648.81

Table 8: LPR Result for samples nitrided at 520°C

Time (Sec)	LPR (ohm.cm^2)	Icorr (mA/cm^2)	Corrosion Rate (mm/year)	Potential (mV)
0	43.604	0.5982608	6.9338	-350.52
900	46.342	0.5629203	6.5242	-361.59
1800	43.86	0.5947668	6.8933	-366.63
2700	43.305	0.6023967	6.9817	-372.41

3.6 Milestone

No	Detail/Week	1	2	3	4	5	6	7		8	9	10	11	12	13	14
1	Preparing samples for nitriding	▨	▨						Mid Semester Break							
2	Nitriding Process			▨	▨	▨	▨	▨								
3	Characterizations															
4	Submission of progress report II									●						
5	Corrosion Testing									▨	▨					
6	Interpreting result											▨				
7	Pre-EDX												●			
8	Work continue												▨	▨		
9	Submision of Draft Report													●		
10	Submision of Dissertation														●	
11	Submission of Technical Paper														●	
12	Oral Presentation															●
13	Submission of Project Dissertation (Hard Bound)															W15

● Suggested milestone

▨ Process