Electrochemical corrosion testing of boronized and unboronized steels

Kranthi K. Pallegar
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ABSTRACT

ELECTROCHEMICAL CORROSION TESTING OF BORONIZED AND UNBORONIZED STEELS

by
Kranthi K. Pallegar

Boronizing is a thermo-chemical surface coating technique with which surface properties of materials are enhanced substantially. One of these properties is corrosion resistance. Corrosion resistance testing has been performed in many ways right from the traditional weight loss methods to the latest electrochemical techniques. These electrochemical techniques are more reliable and less time consuming and hence are widely accepted for corrosion testing in the industry.

In the present work, direct current (D.C) corrosion testing studies of both boronized and unboronized steels have been discussed. Three types of steels, AISI 1018, AISI 4340 and AISI 304 stainless steel, were considered for this work. The steels were boronized and tested for corrosion resistance in the solutions 5% v/v HCl, 4% w/v NaCl, and 5% w/v KOH. These three solutions represent acidic, salt and basic media. Unboronized steels were also tested in these solutions. Linear Polarization, Tafel plots and Cyclic Polarization were the three techniques used to analyze the corrosion resistance of boronized and unboronized steels. Comparative studies revealed increase in corrosion resistance of AISI 1018 by 3-8 times, of AISI 4340 by 3-10 times, and of AISI 304 by 5-17 times. The results from Cyclic polarization experiments proved an increase in pitting resistance of the boronized specimens.
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APPROVAL PAGE

ELECTROCHEMICAL CORROSION TESTING OF BORONIZED AND UNBORONIZED STEELS

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I dedicate this work to my family

and friends for their encouragement and support.
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CHAPTER 1

INTRODUCTION

1.1 Objectives

The purpose of this thesis is to understand the corrosion properties of Boronized steels. Three types of steels, AISI 1018, AISI 4340, and AISI 304 were used for the current research. These steels have many applications in industry but they also suffer from corrosion.

1.2 Background

Corrosion is one of the oldest problems in materials science. Corrosion is a slow process to begin with but has a pronounced effect on the lifetime of product and hence on the economy. It can affect any metallic or sometimes non-metallic parts. Corrosion can be measured by either weight loss or potentiodynamic methods. The current research focuses on advanced and fast potentiodynamic methods of testing corrosion. Even though the potentiodynamic methods are relatively new, they are extensively used due to accuracy in measurements of corrosion rates. The potentiodynamic methods yield plots potential vs. the current density or current, which can be used to calculate the corrosion rates.
CHAPTER 2

CORROSION

2.1 Corrosion

Corrosion is a natural electrochemical process during which a metal returns to its native lowest energy state. Thus, for example, iron has a natural tendency to combine with other substances like water or oxygen to form rust, both of which are omnipresent in the environment. Rust is hydrated iron oxides, similar in chemical composition to the original iron ore.

Corrosion can be defined in many ways. Some definitions are narrow and concentrate on a particular form of corrosion, while others cover a good range of mechanisms. The word corrode is derived from Latin corrodere, which means "to gnaw into pieces." The general definition of corrosion is to eat into or wear away gradually, as if by gnawing\textsuperscript{[1]}.

In a broad sense corrosion can be defined as an electrochemical reaction between a material and its environment that leads to deterioration of the material and its properties.

2.2 Corrosion Mechanisms

Corrosion is an electrochemical process as nearly, all metallic corrosion processes involve transfer of electronic charge. Corrosion consists of two different types of reactions, i.e. anodic and cathodic, occurring simultaneously. Anodic reaction involves
losing of electrons or increase of oxidation state of the metal, while cathodic reaction involves the reduction of some other species like hydrogen or water.

For example, consider the corrosion of Zinc in Hydrochloric acid. The overall reaction is represented by:

\[ \text{Zn} + 2\text{HCl} \rightarrow \text{ZnCl}_2 + \text{H}_2 \]

Zinc reacts with the acid solution forming soluble Zinc chloride and liberating hydrogen bubbles on the surface. The anodic and cathodic reactions for the above reaction are:

\[ \text{Anodic reaction} \quad \text{Zn} \rightarrow \text{Zn}^{2+} + 2e^- \]
\[ \text{Cathodic reaction} \quad 2\text{H}^+ + 2e^- \rightarrow \text{H}_2 \]

The anodic reaction involves oxidation of Zinc from 0 to +2, liberating electrons, while the cathodic reaction involves reduction of hydrogen from +1 to 0, consuming electrons \( [2] \).

2.3 Forms of Corrosion

There are different mechanisms or forms in which corrosion can occur, they are:

- Uniform Corrosion
- Galvanic Corrosion
- Crevice Corrosion
- Pitting Corrosion
- Environmentally Induced Corrosion
• Hydrogen Damage
• Intergranular Corrosion
• Dealloying
• Erosion Corrosion

Uniform Corrosion occurs uniformly throughout the surface of the metal and accounts for greatest tonnage of metal consumed, while all other forms occur locally and are visible only at certain parts and are much more damaging and cause failures.

**Uniform Corrosion:**

A uniform and regular removal or degradation of metal from the surface is the general mode of corrosion \[^2\]. The corrosive environment should have same access to all parts of the metal and also the metal itself should be metallurgically uniform in order that uniform corrosion occurs. This kind of corrosion is preferred to other localized forms of corrosion because it can be easily predicted compared to other forms of corrosion.

**Galvanic Corrosion:**

Galvanic corrosion can be called as preferential corrosion of one metal over the other. When two dissimilar metals are coupled in the presence of a corrosive electrolyte, one of them gets preferentially corroded while the other is protected \[^2\]. This is due to the difference in their corrosion potentials. Figure 2.1 shows galvanic corrosion when two metals are connected.
Figure 2.1 Galvanic corrosion \[^{[3]}\].

A list of different alloys and metals is given arranged in the decreasing order of nobility of their corrosion potentials are shown in Table 2.1 which is called as the galvanic series.

The metals are noble to active in the direction from top to bottom in the table. Therefore, when two dissimilar metals or alloys are in contact with each other, the more active metal will corrode and the more noble metal will be protected.

Table 2.1 Galvanic Series \[^{[4]}\]
Crevice Corrosion:

When a metal is alloyed with another metal, small sheltered areas or crevices are formed. Usually corrosion is greater in these small crevices. This type of corrosion which is seen in metal-metal crevices is called crevice corrosion [2]. Crevice corrosion can be observed in metal parts like bolts, rivets, washers etc. Below is a schematic which shows the formation of crevices in metal-metal joints.

Figure 2.2 Crevice corrosion in metal-metal crevices [4].

Pitting Corrosion:

Pitting corrosion is a localized form of corrosion in which small or large pits are formed on the surface of the metal [5].

Almost every metal is susceptible to pitting corrosion. Pitting is generally observed when a certain area of metal becomes anodic over the other. It is the most intense localized form of corrosion and is always difficult to detect in lab tests. The formation of pits on the metal surface can be seen in Figure 2.3.
Environmentally Induced Cracking:

If a ductile metal or alloy undergoes brittle fracture in the presence of a corrosive environment, then it is called environmentally induced cracking. Further, this can be divided into three subgroups which are Stress Corrosion Cracking, Corrosion Fatigue Cracking, and Hydrogen Induced Cracking.

If an alloy undergoes static tensile stresses under the presence of a corrosive environment, then the phenomenon is called Stress Corrosion Cracking. Figure 2.4 shows stress corrosion cracking in a metal.

Corrosion fatigue cracking occurs when the metal or alloy undergoes cyclic stresses in the presence of a corrosive environment. Figure 2.5 shows Corrosion Fatigue Cracking.
Hydrogen induced cracking is a part of hydrogen damage which will be discussed in detail in the next section.

**Hydrogen Damage:**

When a hydrogen evolution reaction takes place, the atomic hydrogen diffuses into the alloy lattice causing Hydrogen Induced Cracking.

**Intergranular Corrosion:**

Grain boundaries are preferentially attacked over grains in intergranular cracking. Intergranular corrosion can be defined as selective dissolution of grain boundaries over grains \(^{[1]}\). There is a potential difference between the grains and grain boundaries due to which the selective dissolution of the grain boundaries is observed.
In Figure 2.6, the preferential corrosion of grain boundaries (the black region) to the grains (the region inside the black region) is observed.

**Dealloying:**

Dealloying is a corrosive process in which one of the metals which is more active is selectively removed leaving behind the porous deposits of the noble metal \(^{[1]}\). The most popular example of Dealloying is dezincification in which preferential leaching of zinc from brass is observed.

After Dealloying, the metal is spongy and porous loosing its strength, hardness and ductility.

**Erosion Corrosion:**

Erosion-corrosion is observed when there is a corrosion fluid involved \(^{[2]}\). Erosion-corrosion is usually observed in tanks, tubes etc., where in fluids flow. Depending upon the flow rate of the corrosion fluid the intensity of corrosion is high or less.

Thus, these are the different forms of corrosion which are observed in day to day life. There are many ways in which these corrosion reactions can be prevented.

### 2.4 Methods of Prevention

The five primary methods of controlling corrosion are:

- Material selection
- Coatings
• Inhibitors

• Cathodic protection

• Design

Protective coatings, both metallic and non-metallic, can be applied to the metals and alloys to protect them from corrosion.

There are many kinds of coatings, like Carburizing, Nitriding, Aluminizing, Chromizing, Carbonitriding etc., but boronizing (boriding) is the main subject of the present discussion which is further discussed in Chapter 3.
3.1 Boronizing

Boronizing is a thermo-chemical surface treatment in which hard borides are formed. This process can be applied to wide variety of ferrous, non-ferrous and cermet\textsuperscript{[5-11]}. Boronizing is a thermo-chemical treatment which means that it involves temperature and chemical reactions. Typically, Boronizing is carried out at high temperatures of 800\degree C-1300\degree C.

Based on the mode in which metal is treated with boron, there are different kinds of Boronizing such as powder, paste, liquid or gaseous boronizing. This work focuses on solid powder boronizing. Diffusion reaction takes place between the boron powder and the metal which needs to be boronized at high temperature. The two factors that affect the diffusion reaction are temperature and time. Varying these two factors, the thickness of the boride layer can be controlled.
3.2 Characteristics of Boronizing

Typically, boronizing is a surface hardening process by means of which several enhanced properties can be observed in the base metal. Some of these properties\(^5\) are as follows:

- The hardness of the boride layer is so high that it makes the surface of the base metal harder than it was previously.
- The corrosion resistance and the wear resistance are improved by boronizing.
- Boride layers also show a moderate oxidation resistance of up to 850\(^0\)C.
- Due to all the above enhanced properties, the service life of the metal is improved.

The following section describes the process of solid state boronizing.

3.3 Process of Boronizing

The base metal which needs to be boronized is ground on silicon carbide sand paper from 120 grit size up to 600 grit size. The boron powder mixture used for the boronizing comprises of boron carbide (B\(_4\)C), Alumina (Al\(_2\)O\(_3\)) and potassium tetra fluoro boride (KBF\(_4\)). This boron powder mixture is mixed well and is dried in the furnace at 250\(^0\)C for approximately 2 hours. After drying, the ground metal sample is packed in boron powder in a crucible such that the base metal remains in the center and is covered by the boron powder mixture from all sides. The crucible is covered with a lid.

This crucible is placed in the furnace and is heated to the desired temperature for the desired time in an atmosphere which is inert or under vacuum. Then the crucible is cooled to room temperature. The work piece is removed from the crucible and is used for various characterization techniques such as Optical Microscopy and X-Ray Diffraction.
(XRD) for the confirmation of the presence of the boride layer. Thus obtained work piece is tested for corrosion resistance and is compared with the corrosion resistance of the unboronized metal. The corrosion rate is calculated for both of them and the improvement in the corrosion rate can be observed and analyzed.

These corrosion measurements are discussed in detail in the subsequent chapters.
CHAPTER 4

CORROSION TESTING AND MONITORING

4.1 Classification of Corrosion Testing

Corrosion testing and monitoring studies are needed to control corrosion. Testing provides useful information about selection of existing materials, materials suited to a particular environment, alternative materials or new materials that can be used. Monitoring provides early warning regarding a corrosion failure and helps in preventing further damage.

American Standards for Testing Materials (ASTM), National Association of Corrosion Engineers (NACE), International Organization for Standardization (ISO), the Materials Technology Institute of the Chemical Process Industries (MTI), etc have designed certain tests for corrosion testing.

There are three general categories of corrosion tests:

- Laboratory tests

- Pilot-Plant tests

- Field tests
Laboratory Tests:

They can be used as screening tests prior to field tests. Laboratory tests are particularly useful for quality control, materials selection, and study of corrosion mechanisms.

Most laboratory tests are accelerated corrosion tests. The tests can range from a week to several months. The electrochemical methods can test in a matter of an hour. The goal of accelerated lab tests is to provide reliable information about the life of the materials or coatings.

The accelerated tests increase the severity of the exposed environment by increasing the concentration and temperature of solutions. The disadvantage of the lab tests is that the accelerated conditions may change the mechanism of corrosion; therefore, results should be used carefully.

Pilot-plant Tests:

Pilot-Plant tests are more effective than laboratory tests. These tests simulate the actual working conditions in a small-scale plant. As the pilot-plants can be modified constantly to suit the working environment, this can simulate actual working temperatures, pressures and velocities which can fluctuate during operation.

Field Testing:

This is the most reliable of all the tests as the tests are conducted short of actual working conditions. These so-called natural environments include exposure to cyclic effects of the weather, geographical influences, and bacteriological factors that cannot
be realistically duplicated in the laboratory. Field tests normally range in duration from several months to several years [12-16].

**Other Classification:**

These tests can be further classified as weight loss methods which are traditional and modern electrochemical tests. In traditional weight loss methods, the weight of the specimens are measured before the test, then the specimens are immersed in solutions to be tested. The specimens are periodically removed and cleaned to remove any corrosion products and weighed. The difference in weights gives the weight loss which is related to the corrosion rate as per the formula:

$$MPY = \frac{534 \times W}{D \times A \times T}$$ \[^2\]

**MPY** - Corrosion rate in mils per year  
**W** - Weight loss in milligrams  
**D** - Density in grams per cubic centimeter  
**A** - Area of the specimen exposed in square inches  
**T** - Time of immersion in hours.

All the corrosion reactions are associated with the exchange of electrons. Electrochemical test methods primarily focus on the control and measurement of the fundamental properties of electrochemical reactions. The greater the currents measured during the corrosion testing, the greater is the corrosion rate. This means, that the sample is polarized, or point cathodes and anodes are formed on the surface of the specimen.

The basics of all the electrochemical techniques lie in the mixed-potential principle. The theory demonstrates that uniform corrosion occurs when anodic and
cathodic reactions take place in constant change of location and time of the individual processes. Based on this theory, various experiments were designed to measure corrosion.

These can be broadly classified as:

- No applied signal- Open circuit or corrosion potential, dissimilar metal corrosion.
- Small-signal polarization- Polarization resistance (Linear Polarization), electrochemical impedance spectroscopy.
- Large-signal polarization- Potentiodynamic and galvanodynamic polarization, Potentiostatic and galvanostatic polarization.
- Scanning electrode techniques- Potential scans, Current scans, electrochemical impedance spectroscopy scans.

The Small-signal polarization, Large-signal polarization, and Scanning electrode techniques were used for the current research study as they are widely accepted and also due to their simplicity in interpreting the results.

4.2 Electrochemical Methods

Corrosion occurs via electrochemical reactions and therefore, electrochemical techniques are ideal for the study of the corrosion processes. In electrochemical studies, a metal sample with a surface area of a few square centimeters is used to model the metal in a corroding system. The metal sample is immersed in a solution typical of the metal’s environment in the system being studied. Additional electrodes are immersed in the solution, and all the electrodes are connected to a device called a potentiostat. A
potentiostat has the ability to change the potential of the metal sample in a controlled manner and measure the current that flows as a function of potential.

Although, there are large number of electrochemical tests that can be conducted using the potentiostat, the present discussion is confined to three basic methods namely:

- Polarization resistance method
- Tafel plots
- Cyclic polarization

**Polarization Resistance Method:**

This technique is used to measure the polarization resistance ($R_p$). Polarization resistance is defined as the resistance of the specimen to oxidation during the application of the external potential. The corrosion rate is directly related to the $R_p$. $R_p$ can be calculated from the formula:

$$R_p = \frac{\beta_a \times \beta_c}{2.3 \times i_{corr} \times (\beta_a + \beta_c)}$$ \[17-21\]

- $R_p$ - Polarization resistance in ohms ($\Omega$)
- $\beta_a$ - Anodic beta coefficient
- $\beta_c$ - Cathodic beta coefficient
- $i_{corr}$ - corrosion current in $A/cm^2$

In a Polarization Resistance experiment, the specimen is scanned in the range of ±20 mv about $E_{corr}$ (the open circuit potential). Open circuit potential is the potential at which rate of the anodic reaction is equal to rate of the cathodic reaction. The data are
plotted on a voltage vs. current density plot. A numerical fit of the curve yields a value for the Polarization Resistance, $R_p$. Polarization Resistance data does not provide any information about the values for the Beta coefficients. Therefore, to use above equation Beta values are required. These can be obtained from a Tafel Plot\textsuperscript{[22]}.

**Tafel Plots:**

Corrosion normally occurs at a rate determined by equilibrium between opposing electrochemical reactions. The first is the anodic reaction, in which a metal is oxidized, releasing electrons into the metal. The other is the cathodic reaction, in which a solution species (often $O_2$ or $H^+$) is reduced, removing electrons from the metal. When these two reactions are in equilibrium, the flow of electrons from each reaction is balanced, and no net electron flow (electrical current) occurs. The two reactions can take place on one metal or on two dissimilar metals (or metal sites) that are electrically connected.

Figure 4.1 describes this process. The vertical axis is potential and the horizontal axis is the logarithm of current density. The theoretical current for the anodic and cathodic reactions are shown as straight lines. The curved line is the total current, the sum of the anodic and cathodic currents. This is the current that is measured when the potential of the metal is swept with the potentiostat. The sharp point in the curve is actually the point where the current changes signs as the reaction changes from anodic to cathodic, or vice versa. The sharp point is due to the use of a logarithmic axis. The use of a log axis is necessary because of the wide range of current values that must be displayed during a corrosion experiment. Because of the phenomenon of passivity, it is
not uncommon for the current to change by six orders of magnitude during a corrosion experiment \cite{23}.

![Tafel Plot](image)

**Figure 4.1** Typical Tafel plot.

The potential of the metal is the means by which the anodic and cathodic reactions are kept in balance. Refer to Figure 4.1. Notice that the current from each half reaction depends on the electrochemical potential of the metal. Suppose the anodic reaction releases too many electrons into the metal. Excess electrons shift the potential of the metal more negative, which slows the anodic reaction and speeds up the cathodic reaction. This counteracts the initial perturbation of the system.

The equilibrium potential assumed by the metal in the absence of electrical connections to the metal is called the Open Circuit Potential, $E_{\text{corr}}$. In most electrochemical corrosion experiments, the first step is the measurement of $E_{\text{corr}}$.

The value of either the anodic or cathodic current at $E_{\text{corr}}$ is called the Corrosion Current, $i_{\text{corr}}$. If $i_{\text{corr}}$ is measured, it can be used to calculate the corrosion rate of the metal. $i_{\text{corr}}$ cannot be measured directly. However, it can be estimated using electrochemical techniques. In any real system, $i_{\text{corr}}$ and Corrosion Rate are a function of many system variables including type of metal, solution composition, temperature,
solution movement, metal history etc., $i_{corr}$ can also be determined from the polarization resistance experiment.

Once $i_{corr}$ is determined from the polarization resistance method and $\beta_a$ and $\beta_c$ from the slopes of anodic and cathodic part of the Tafel plot, these values are used to calculate the corrosion rate by the formula:

$$\text{Corrosion Rate (MPY)} = \frac{0.13 \times i_{corr} \times E.W}{A \times D}$$

$i_{corr}$ - Corrosion current (in A/cm$^2$)

$\beta_a$ - Anodic Tafel constant

$\beta_c$ - Cathodic Tafel constant

E.W - Equivalent weight

A - Area of cross section of specimen exposed in cm$^2$

D - Density of the specimen in g/cm$^3$

The equivalent weight of the specimen is calculated by the formula:

$$N_{eq} = \sum \frac{f_i \times n_i}{a_i} \quad [2]$$

Where,

$f_i$ is the mass fraction

$n_i$ is the electrons exchanged

$a_i$ is the atomic weight of the alloying element in grams

Equivalent weight = $1 / N_{eq}$
**Cyclic Polarization:**

This technique measures the pitting tendencies of the specimen in the given metal-solution system.

In a pitting experiment a potential scan beginning at $E_{corr}$ and continuing in the positive direction is applied until a large increase in current occurs. When the scan reaches the user-defined current density value, it reverses and begins a scan in the opposite direction. The threshold current density is typically 1 mA/cm$^2$. The resulting graph plots the applied potential vs. the log of the measured current.

The graph consists of a forward scan and a reverse scan. If the forward and reverse scans follow the same path, or reverse scan follows a current density direction that is less positive in values than the positive scan, this means that the material has less tendency to pit. If the reverse scan follows a more positive current direction as compared to forward scan, this indicates the easier tendency of the material to pit. The extent of pitting depends on the area of the hysteresis loop formed by the forward and reverse scans.

The above experiments give the indication of the corrosion behavior and pitting behavior of the samples in the selected environment, which can be used to determine the life of the specimen [24-27].
5.1 Experimental Description

The process of boronizing is comprised of sample preparation which includes grinding the sample surface and cleaning the surface. The next step is to pack the sample in the boron powder mixture and the final step of boronizing is the heat treatment of the boron powder with the sample packed in it. The samples thus obtained are subjected to a series of characterization techniques which includes corrosion testing.

Corrosion testing is conducted using electrochemical methods. Parstat 2263 and Flat cell K00235 are used to conduct the experiment, along with Powersuite software which is used to analyze the data.

5.2 Equipment Description

Corrosion testing is conducted using a Potentiostat Parstat-2263 manufactured by Princeton Applied Research. The potentiostat is connected to a computer on one hand and flat cell on the other hand. The flat cell is the actual part where the corrosion reactions occur. Currents and voltage produced due to the corrosion reactions are measured by the potentiostat and supplied to the computer. The computer with its unique software named Powersuite supplied by the Princeton Applied Research records the data. The data provided can be analyzed to get comprehensive information about the properties of the specimen. The block diagram of the experimental setup is shown in Figure 5.1.
Figure 5.1 Block diagram of the experimental setup.

Potentiostat:

The PARSTAT® 2263 is a potentiostat/galvanostat/FRA that consists of hardware that is capable of ± 10 V scan ranges, 200 mA current capabilities, and EIS measurements up to 1 MHz. The PARSTAT® 2263 is DC powered and can be operated with an AC/DC converter (included with the system) or with a DC power supply (i.e., 12V auto battery) for remote/field applications. The interface to the PC or laptop is USB. The potentiostat is connected with the computer using the USB port. The PARSTAT® family is operated by Powersuite® which can be used to perform many of the standard techniques (such as CV, LSV, Tafel Plots, EIS, etc.). The potentiostat is the link between the working flat cell and recording software. The potentiostat applies and measures the potential difference between the working and the reference electrode and the current generated during corrosion.
Figure 5.2 Potentiostat Parstat 2263.

The technical specifications of the Parstat 2263 are as follows:

Dimensions: 14.5"x16"x6", 16.5 lbs in weight.

Power requirements: 10-18 V DC

iR compensation: Positive feedback, Range-20 MΩ to 20Ω, 16 bit DAC potential error correction.

Impedance specifications: Frequency range: 10µHz-1MHz.

Flat Cell:

Flat cell is the actual sample chamber in which the corrosion reactions take place. The flat cell consists of a cylindrical glass tube with two end caps made of Teflon as shown in Figure 5.3. The end cap on the left hand side of the figure has a small opening in the middle. The specimen or the working electrode is placed at this end. The other end cap is fixed with a Platinum counter electrode. In the middle (more towards the working electrode) of the glass tube there is a glass insert where in the reference electrode (Ag-AgCl KCl) is placed. This is connected to the working electrode with a small plastic tube.
in order to establish a continuous flow of liquid between the reference electrode and working electrode.

**Figure 5.3** Flat cell (Model K0235).

The block diagram of the flat cell is shown in the Figure 5.4. The reference electrode is needed to complete the measurement circuit and provide a stable and reproducible potential against which the indicator electrode is compared.

**Figure 5.4** The block diagram of the flat cell.
Powersuite:

Powersuite is the software which records the data supplied by the potentiostat and plots the graphs. The data and graphs can be analyzed to calculate the corrosion rates and comment upon the life of the specimen in the given environment and its susceptibility to pitting corrosion.

Powersuite has two modules namely Powercorr and Powersine. Powercorr is used for DC measurements whereas the Powersine is used for AC corrosion techniques like the Electrochemical Impedance Spectroscopy (EIS). The present research mainly concentrates on DC measurements and therefore Powercorr was used for all the measurements.

5.3 Experimental Procedure

Boronizing:

The experimental setup was described in the previous section. Three steels namely AISI 1018, AISI 4340, and AISI 304 were selected for the experiments as they represent all the three classes of steel namely the plain carbon steel, high alloy steel, and stainless steel. They specimens were not subjected to any sort of heat treatment. The composition of the steels is shown in Table 5.1. The steels were boronized by using the pack boronizing procedure. The process consists of the following steps:

- The samples AISI 1018, AISI 4340, and AISI 304 are cut into 10 x 10 x 3 mm, 12 x 12 x 7 mm, and 12 x 10 x 6 mm, respectively.
- The samples are ground on SiC sand paper on 120, 220, 400 and 600 grit sizes. The ground samples are cleaned with acetone in an ultrasonic bath for 5 minute.
• The boron powder mixture (1% w/w KBF₄ (Potassium tetrafluoroborate of Alfa Aesar), 5% w/w Al₂O₃ (Aluminum oxide powder of Atlantic Equipment Engineers), and 94% w/w B₄C (boron carbide, technical grade of Electro Abrasives Corporation)), packed in the crucible is preheated at 250°C for 2 hours.

• The samples are tightly packed in the preheated powder mixture and are left in a desiccator connected to vacuum without covering the crucible with lid.

• Thereafter, the samples embedded in the boron powder mixture are heated to a temperature of 250°C for 2 hours without the lid on. The lid is then placed on and the temperature is increased to 850°C in inert atmosphere (argon gas grade 5 99.99% pure from SOS gases) and left at that temperature for 4 hours.

• After heat treatment the samples are cooled to room temperature and are taken out of the boron powder mixture. The samples are then cleaned with methanol.

**Table 5.1 Chemical Composition of the Steels AISI 1018, AISI 4340 and AISI 304**

<table>
<thead>
<tr>
<th>Steel</th>
<th>Chemical Composition, %</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>C</td>
</tr>
<tr>
<td>1018</td>
<td>0.2</td>
</tr>
<tr>
<td>4340</td>
<td>0.4</td>
</tr>
<tr>
<td>304</td>
<td>0.02</td>
</tr>
</tbody>
</table>

**Microscopy:**

The Surface images were taken using the AxioTech Microscope of Carl Zeiss with 10x eyepiece lens and 20x, 50x, 100x objective. The resulting microstructure images have been taken by using the digital camera (Pixelink PL-A662). The images were taken before and after the corrosion process to study the difference in surface because of corrosion reactions.
XRD:

The X-ray diffraction data for all the samples before and after corrosion were taken in order to observe the phases present. The experiments were performed with XRD Philips (PW3040 MPD DY715) using Cu K-α 1 at 45 kV and 40 mA. 1/4” diverging slit and 1/4” anti scattering slits were used for the divergence and scattering of X-rays. The scan range for 2θ was from 5° to 120°. The phases of the specimen were determined by the software called X’Pert high score.

Solution Preparation:

Three solutions that were used for the corrosion testing are 5% v/v HCl, 4% w/v NaCl, and 5% w/v KOH. These solutions were selected to represent acid, salt and base solutions respectively. They were prepared from 37%, 99%, and 99% pure chemicals respectively supplied by Acros Organics. The volume by volume measurement was used for HCl, while weight by weight was used for NaCl and KOH. For, 5% HCl preparation 5 ml of 37% concentration HCl was added to 100 ml of distilled water. 4% NaCl and 5% KOH were prepared by adding 4 g and 5 g of NaCl and KOH respectively to 100 ml of distilled water.

Corrosion Testing:

The experimental setup is similar for all the three corrosion tests performed. The only things that differ are the software modules and also experimental parameters. The scan rate is constant at 0.166 mV/sec for all the experiments [28-31].
The experimental procedure consists of the following steps:

- The sample is fixed to the flat cell.
- The reference electrode is placed into the reference electrode compartment and the solution prepared earlier is first poured into the reference electrode compartment and made sure that the liquid flows through the small pipe connection between working and reference electrode.
- Approximately 270 ml solution is poured into the flat cell.
- The flat cell is connected to the potentiostat. The connections are very important as there are five different colored leads coming out of the potentiostat. The connections are: red lead to counter electrode, green and gray leads to working electrode, white lead to reference electrode, and the black lead is grounded.
- Then the potentiostat is connected to the computer. The potentiostat is switched on.
- The open circuit potential experiment is run using the Powercorr software for 1 hour. The standard scan rate is applied. During open circuit experiment, the free currents generated during the exposure of sample to the corrosive environment are measured with respect to time.
- Then the polarization resistance experiment is run using the Powercorr software with the same parameters. The experiment scans the sample from ±0.02mV vs. the open circuit potential. The experiment takes approximately 20 minutes to complete.
- Then the sample is removed, cleaned and fresh solution is poured into the flat cell. After running the open circuit potential for 1 hour, the Tafel polarization experiment is run using the same Powercorr software. The experiment scans the sample in the range ±250 mV with respect to the open circuit potential. The open circuit potential is measured by the instrument itself. The experiment runs approximately for 1 hour.
- The sample is again removed and cleaned, the flat cell is cleaned and refilled with fresh solution and the Powercorr is used to run the cyclic polarization experiment after open circuit experiment is run for 1 hour. During the polarization experiment, the scan starts from the open circuit potential and continues into the anodic region till a sudden increase in the potential occurs. Then, it continues its journey a little longer and it reverses back. This is all controlled by the software parameters defined by the user.
- The values and graphs obtained are analyzed and calculations are discussed in Chapter 4.
6.1 Corrosion Testing of AISI 1018 Steel

The AISI 1018 steel was tested in 5% V/V HCl, 4% NaCl, and 5% KOH using polarization resistance, Tafel, and cyclic polarization experiments.

6.1.1 AISI 1018 Steel in 5% HCl

In all the graphs, the blue graph represents the boronized specimens while the green graph represents unboronized specimen.

![ Comparative linear polarization and Tafel graphs of AISI 1018 steel in 5% HCl. ]

**Figure 6.1** The comparative linear polarization and Tafel graphs of AISI 1018 steel in 5% HCl.
Figure 6.1 (a) shows the polarization behavior of boronized (blue) compared to the unboronized specimen (green) in 5% HCl. The graph shows more noble potentials of the boronized specimen as compared to the unboronized specimen. The $R_p$ value of the boronized specimen obtained from the graph is also higher as compared to the unboronized samples (Refer to Table 6.4). The $i_{corr}$ is calculated from the $R_p$ value as discussed in the theory.

Figure 6.1 (b) shows the comparative Tafel plot of AISI 1018 steel in 5% HCl. The unboronized sample shows a more noble open circuit potential. The current density value is similar for both unboronized and boronized samples, indicating better corrosion properties for unboronized graph. But, as anodic region is approached that is the top portion of the graph, the graph for the boronized sample pulls back more than unboronized graph. This gives more corrosion resistance to the boronized specimen as suggested by the calculations. The calculations are shown for this particular steel in HCl environment. The calculations for all other steels in all other environments are same and hence not shown but just tabulated.

### 6.1.1.1 Calculations.

Area of specimen exposed to the corrosive environment is similar for all the samples, as the aperture is constant for the flat cell.

AISI 1018 steel in 5% HCl:

The $R_p$ (Polarization resistance) value from the linear polarization curve

$$= 179.19 \, \Omega$$

$\beta_a$ value from the slope of anodic part of Tafel curve

$$= 74.535$$

$\beta_c$ value from the slope of cathodic part of Tafel curve
\( \beta_c \) value form the slope of cathodic part of Tafel curve

\[ = 174.15 \]

The \( i_{corr} \) value is calculated by substituting the above values in the equation:

\[ R_p = \beta_a \times \beta_c / \{2.3 \times i_{corr} \times (\beta_a + \beta_c)\} \]

After calculations \( i_{corr} \) value \( = 0.13 \)

Density of steel \( = 7.87 \text{ g/cm}^3 \)

Radius of the specimen exposed to the corrosive solution \( = 0.75 \text{ cm} \)

Area of specimen exposed \( = \pi r^2 \) (as the opening in the flat cell is circular)
\( = 0.44 \text{ cm}^2 \)

Equivalent weight of the specimen is calculated by the formula:

\[ N_{eq} = \sum \frac{f_i \times n_i}{a_i} \]

We need to consider all the elements present in the AISI 1018 steel neglecting trace elements

**Table 6.1 Equivalent Weight Calculations**

<table>
<thead>
<tr>
<th>Element</th>
<th>C</th>
<th>Mn</th>
<th>Al</th>
<th>Fe</th>
<th>Si</th>
</tr>
</thead>
<tbody>
<tr>
<td>% composition (f)</td>
<td>0.2</td>
<td>0.72</td>
<td>0.065</td>
<td>98.983</td>
<td>0.016</td>
</tr>
<tr>
<td>Valency (n)</td>
<td>2</td>
<td>2</td>
<td>3</td>
<td>2</td>
<td>4</td>
</tr>
<tr>
<td>Atomic weight(a) (grams)</td>
<td>12.01</td>
<td>54.94</td>
<td>26.98</td>
<td>55.85</td>
<td>28.09</td>
</tr>
</tbody>
</table>

By substituting all the values in the equation and reciprocating

Equivalent weight = 27.67

Corrosion rate can be calculated by substituting all the above values in the equation:
Corrosion Rate (MPY) = 0.13 \times i_{corr} \times E.W/(A \times D)

Corrosion rate = 0.13 MPY

All the corrosion rate values are obtained in mills per year.

AISI Boronized 1018 steel in 5% HCl:

The $R_p$ (Polarization resistance) value from the linear polarization curve

$$= 347.98 \ \Omega$$

$\beta_a$ value from the slope of anodic part of Tafel curve

$$= 154.03$$

$\beta_c$ value from the slope of cathodic part of Tafel curve

$$= 127.74$$

The $i_{corr}$ value is calculated by substituting the above values in the equation:

$$R_p = \beta_a \times \beta_c / \{2.3 \times i_{corr} \times (\beta_a + \beta_c)\}$$

After calculations $i_{corr}$ value = 0.09

After boronizing, the surface of the samples consists of Fe$_2$B and FeB. Boronized 1018 contains nearly 50% FeB and 50% Fe$_2$B, boronized 4340 contains nearly 100% Fe$_2$B, and boronized 304 contains nearly 100% FeB. After boronizing, surface density changes due to the presence of only borides on the surface. So, for AISI 108 steel, since equal amount of FeB and Fe$_2$B are present, taking the average of densities,

Density of Boronized 1018 steel = 7.09 g/cm$^3$
Table 6.2 Composition and Density of Boron Compounds \[30\]

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\text{Fe}_2\text{B})</th>
<th>(\text{FeB})</th>
</tr>
</thead>
<tbody>
<tr>
<td>Density</td>
<td>8.83</td>
<td>7.43</td>
</tr>
<tr>
<td>Boron %</td>
<td>16.23</td>
<td>6.75</td>
</tr>
</tbody>
</table>

Radius of the specimen exposed to the corrosive solution  
= 0.75 cm

Area of specimen exposed  
= \(\pi r^2\) (as the opening in the flat cell is circular)  
= 0.44 cm\(^2\)

Equivalent weight of the specimen is calculated by the formula:

\[
N_{eq} = \sum \frac{f_i n_i}{a_i}
\]

Since this is boronized 1018, 50% \(\text{Fe}_2\text{B}\) and 50% \(\text{FeB}\) are considered. \(\text{Fe}_2\text{B}\) contains 8.83% boron while \(\text{FeB}\) contains 16.23% boron, so total amount of boron present is 12.53%.

Table 6.3 Valency, Composition, and Atomic Weights of Boron and Iron \[30\]

<table>
<thead>
<tr>
<th>Element</th>
<th>B</th>
<th>Fe</th>
</tr>
</thead>
<tbody>
<tr>
<td>% composition</td>
<td>12.53</td>
<td>87.47</td>
</tr>
<tr>
<td>Valency (n)</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>10.81</td>
<td>55.85</td>
</tr>
<tr>
<td>(grams)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

By substituting all the values in the equation and reciprocating \(N_{eq}\)

Equivalent weight = 15.13
Calculations for boronized 4340 and boronized 304 are simple as they contain either Fe₂B or FeB.

Corrosion rate can be calculated by substituting all the above values in the equation:

\[
\text{Corrosion Rate (MPY)} = 0.13 \times i_{\text{corr}} \times E.W/(A \times D)
\]

\[
\text{Corrosion rate} = 0.06 \text{ MPY}.
\]

Table 6.4 Comparative Corrosion Properties of Plain and Boronized AISI 1018 Steel in 5% HCl

<table>
<thead>
<tr>
<th>HCl</th>
<th>Rp(Ω)</th>
<th>βa</th>
<th>Bc</th>
<th>Density (g/cm³)</th>
<th>Eq. Wt.(g)</th>
<th>Radius (cm)</th>
<th>Area (cm²)</th>
<th>Icorr</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1018P</td>
<td>179.19</td>
<td>74.54</td>
<td>174.15</td>
<td>7.87</td>
<td>27.67</td>
<td>0.75</td>
<td>0.44</td>
<td>0.13</td>
<td>0.13</td>
</tr>
<tr>
<td>1018B</td>
<td>347.97</td>
<td>154.03</td>
<td>127.74</td>
<td>7.09</td>
<td>15.13</td>
<td>0.75</td>
<td>0.44</td>
<td>0.09</td>
<td>0.06</td>
</tr>
</tbody>
</table>

The calculations indicate nearly two times decrease in corrosion rate of boronized sample.

6.1.1.2 Cyclic Polarization The cyclic polarization experiment gives the information regarding the pitting behavior of the sample in the selected corrosive environment.

The graph shows that the hysterisis loop for unboronized sample has more area than the boronized sample indicating more pitting resistance of the boronized sample. The reverse scan for the unboronized sample traces a more positive path compared to the forward scan indicating pitting corrosion, while, this is not the case with the boronized graph[33-35].
Figure 6.2 Comparative cyclic polarization graph of 1018 steel in 5% HCl.

6.1.1.3 Microscopy The specimens were observed under a microscope before and after corrosion and the surface images were taken.

Figure 6.3 Surface images of unboronized 1018 before and after corrosion in 5% HCl at 20x.
Figure 6.4 Surface images of boronized 1018 before and after corrosion in 5% HCl at 20x.

The uncorroded boronized sample looks dull due to the presence of borides on the surface which protect the metal and this can be clearly seen in the greater deterioration of the plain sample after corrosion compared to the boronized sample. The image also shows that there is more uniform corrosion on the surface of the boronized sample. More pitting corrosion is observed on the surface of the plain corroded sample.

6.1.1.4 XRD Data The X- Ray diffraction analysis of the unboronized specimen indicates the presence of the higher order oxides. Both, Fe₂O₃ and Fe₃O₄ indicate free corrosion of the substrate.

In the XRD analysis of the after corrosion boronized substrate, only FeO was detected as a corrosion product. Borides FeB and Fe₂B were detected confirming presence of the boride layer.
Figure 6.5 XRD of P1018 after corrosion 5% HCl.

Figure 6.6 XRD of B1018 after corrosion 5% HCl.
6.1.2 AISI 1018 Steel in 4% NaCl

The boronized and unboronized samples were subjected to the corrosion tests in 4% NaCl. The graphs obtained are shown in Figure 6.5.

![Graphs showing linear polarization and Tafel plots](image)

(a) Linear polarization  (b) Tafel plot

**Figure 6.7** The comparative linear polarization and Tafel graphs of AISI 1018 steel in 4% NaCl.

The linear polarization graph shows the more noble behavior of the boronized as compared to unboronized as per the Rp Values shown in the Table 6.5. \(i_{corr}\) is calculated from the Rp value.

The Tafel plot shows a more noble open circuit potential of the boronized sample compared to the unboronized sample. It also shows nobler current density at the open circuit potential. Even though the unboronized graph indicates a formation of passive layer, the calculations indicate greater corrosion resistance of the boronized sample.
6.1.2.1 Calculations  The calculations are tabulated in Table 6.5. The calculations show four fold increase in the corrosion resistance value of the boronized specimen.

Table 6.5  Comparative Corrosion Properties of Plain and Boronized AISI 1018 Steel in 4\% NaCl

<table>
<thead>
<tr>
<th>NaCl</th>
<th>$R_p(\Omega)$</th>
<th>$\beta_p$</th>
<th>$\beta_t$</th>
<th>Density (g/cm$^3$)</th>
<th>Eq. Wt (g)</th>
<th>Radius (cm)</th>
<th>Area (cm$^2$)</th>
<th>$i_{cor}$ (A/cm$^2$)</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1018P</td>
<td>$2.7 \times 10^3$</td>
<td>84.78</td>
<td>136.49</td>
<td>7.87</td>
<td>27.67</td>
<td>0.75</td>
<td>0.44</td>
<td>$8 \times 10^{-3}$</td>
<td>$9 \times 10^{-3}$</td>
</tr>
<tr>
<td>1018B</td>
<td>$6.5 \times 10^3$</td>
<td>89.63</td>
<td>274.39</td>
<td>7.09</td>
<td>15.13</td>
<td>0.75</td>
<td>0.44</td>
<td>$4 \times 10^{-3}$</td>
<td>$3 \times 10^{-3}$</td>
</tr>
</tbody>
</table>

6.1.2.2 Cyclic Polarization  The comparative cyclic polarization graph of boronized and unboronized specimens is shown in Figure 6.6.

The graph shows a hysteresis loop for the unboronized steel. In the boronized steel graph, the reverse scan almost retraces the path of the forward scan indicating pitting resistance.
6.1.2.3 Microscopy  

The microscopy studies show that the boronized specimen has less corrosion compared to the unboronized specimen. Lots of pits are visible on the surface of the plain sample after corrosion. More uniform corrosion is visible on the surface of the boronized specimen after corrosion giving support to the data from the cyclic corrosion graph.

**Figure 6.8** Comparative cyclic polarization graph of AISI 1018 steel in 4% NaCl.
6.1.2.4 XRD Data

The XRD peaks of the unboronized 1018 after corrosion in 4% NaCl indicate mainly the presence of Fe$_2$O$_3$ as the corrosion products.

The XRD peaks of the boronized 1018 after corrosion in 4% NaCl indicate mainly the presence Fe$_3$O$_4$ and Fe$_2$O$_3$. There were no traces of any boron oxides indicating the protectiveness of the boron coating against the oxidation.
Figure 6.11 XRD spectrum of unboronized 1018 after corrosion in 4% NaCl.

Figure 6.12 XRD spectrum of boronized 1018 after corrosion in 4% NaCl.
6.1.3 AISI 1018 Steel in 5% KOH

The corrosion studies of boronized and unboronized AISI 1018 steel in 5% KOH shows a five times decrease in the corrosion rate. The comparative linear and Tafel graphs are shown in the Figure 6.12.

![Figure 6.12](image)

(a) Linear Polarization  
(b) Tafel Plot

**Figure 6.13** Comparative linear and Tafel plot of AISI 1018 steel in 5% KOH.

The Linear polarization graph yields the $R_p$ value that is much more noble for the boronized graph as compared to the unboronized graph as shown in Table 6.6.

The Tafel plot shows the vast difference in open circuit potential of the boronized sample as compared to the unboronized sample. The graph shows that the open circuit potential of the boronized sample is much nobler than that of the unboronized sample. Even though the current density of the boronized sample at open circuit potential is more than that for the unboronized sample the huge difference in the open circuit potential leads to the decrease in corrosion rate of the boronized sample.
6.1.3.1 Calculations The calculations tabulated in Table 6.6. Show the five times increase in corrosion resistance value in the boronized sample. This is mainly due to the big difference in the polarization resistance values of the two specimens.

Table 6.6 Comparative Corrosion Properties of Plain and Boronized AISI 1018 Steel in 5% KOH

<table>
<thead>
<tr>
<th>KOH</th>
<th>Rp(Ω)</th>
<th>β</th>
<th>Be</th>
<th>Density (g/cm³)</th>
<th>Eq.Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm²)</th>
<th>Icorr (A/cm²)</th>
<th>Corr. rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1018P</td>
<td>3.4×10⁵</td>
<td>392.56</td>
<td>213.78</td>
<td>7.87</td>
<td>27.67</td>
<td>0.75</td>
<td>0.44</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>1018B</td>
<td>1.73×10⁴</td>
<td>285.91</td>
<td>288.03</td>
<td>7.09</td>
<td>15.13</td>
<td>0.75</td>
<td>0.44</td>
<td>4×10⁻³</td>
<td>2×10⁻³</td>
</tr>
</tbody>
</table>

6.1.3.2 Cyclic Polarization The comparative cyclic polarization graph is shown in Figure 6.12. The graph shows that the reverse scan for the boronized sample pulls back into a more negative current region compared to the unboronized graph indicating greater nobility to pitting corrosion of the boronized sample. Hysteresis loop exists for the unboronized specimen showing an increase in the pitting behavior.
Figure 6.14  Comparative cyclic polarization graph of AISI 1018 steel in 5% KOH.

6.1.3.3 Microscopy:

The microscopy analysis of the boronized and unboronized specimens before and after corrosion shows the resistance of the boronized specimen supporting the calculated data. The surface of the boronized specimen showed little or no corrosion at all which can be expected when testing in KOH solution. The surface of the plain specimen showed some pits. But it also had good resistance to corrosion.
Figure 6.15 Surface images of unboronized 1018 before and after corrosion in 5% KOH at 20x.

Figure 6.16 Surface images of boronized 1018 before and after corrosion in 5% KOH at 20x.

6.1.3.4 XRD Analysis

The XRD graph for plain specimen after corrosion shows presence of Fe$_2$O$_3$ as the only corrosion product. Boronized specimen showed the presence of both Fe$_2$O$_3$ and Fe$_3$O$_4$. Borides FeB and Fe$_2$B were also detected.
Figure 6.17 XRD spectrum of unboronized 1018 after corrosion in 5% KOH.

Figure 6.18 XRD spectrum of boronized 1018 after corrosion in 5% KOH.
6.2 Corrosion Testing of AISI 4340 Steel

The AISI 4340 steel, whose composition was mentioned in the previous chapters, was also tested in the three environments 5% HCl, 4% NaCl, and 5% KOH for the evaluation of corrosion properties. The surface of the specimen was characterized by microscopy and XRD before and after corrosion.

6.2.1 AISI 4340 Steel in 5% HCl  The comparative linear and Tafel plots of the boronized and unboronized 4340 steel in 5% HCl are shown in the Figure 6.7.

The linear polarization graph shows more positive potential of the graph and linearity indicates greater $R_p$ value as confirmed from Table 6.7.

The Tafel plot shows the nobler open circuit potential and also lower current density at open circuit potential indicating greater corrosion resistance of the boronized sample. There is a slight tendency of the part of the plain sample for the protective layer formation as indicated by the tip in the curve, but, it is very minimal.
6.2.1.1 Calculations  The calculations of the corrosion values are tabulated in the table below. The values show greater corrosion resistance of the boronized sample.

Table 6.7  Comparative Corrosion Properties of Plain and Boronized AISI 1018 Steel in 5% KOH

<table>
<thead>
<tr>
<th>HCl</th>
<th>$R_p$ (Ω)</th>
<th>$\beta_1$</th>
<th>$\beta_2$</th>
<th>Density (g/cm$^3$)</th>
<th>Eq. Wt.(g)</th>
<th>Radius (cm)</th>
<th>Area(cm$^2$)</th>
<th>$I_{cor}$ (A/cm$^2$)</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4340P</td>
<td>129.69</td>
<td>143.22</td>
<td>103.18</td>
<td>7.84</td>
<td>27.24</td>
<td>0.75</td>
<td>0.44</td>
<td>0.20</td>
<td>0.21</td>
</tr>
<tr>
<td>4340B</td>
<td>812.2</td>
<td>95.29</td>
<td>105.51</td>
<td>7.43</td>
<td>17.51</td>
<td>0.75</td>
<td>0.44</td>
<td>0.03</td>
<td>0.02</td>
</tr>
</tbody>
</table>

6.2.1.2 Cyclic polarization  The comparative cyclic polarization graph of the boronized and unboronized specimens is shown in Figure 6.18. The reverse scan in the graph for the boronized specimen traces the same path as forward scan and then traces a path more negative to the forward scan implying good pitting resistance. The graph for the

Figure 6.19  Comparative linear and Tafel plot of AISI 4340 steel in 5% HCl.
unboronized specimen has very small hysteresis loop but, the reverse scan traces a path more positive to forward scan implying pitting tendency.

![Graph showing cyclic polarization of AISI 4340 steel in 5% HCl](image)

**Figure 6.20** Comparative cyclic polarization graph of AISI 4340 steel in 5% HCl.

6.2.1.3 Microscopy  The boronized sample after corrosion shows negligible traces of corrosion in 5% HCl as compared to the unboronized sample. Figure 6.20 shows a clear picture of the above discussed point where there are hardly any traces of corrosion on the surface of the boronized sample indicating the protectiveness of the boron coating. Figure 6.19 shows how badly the plain sample is affected and the presence of large amount of pits.
Figure 6.21 Surface images of unboronized 4340 before and after corrosion in 5% HCl at 20x.

Figure 6.22 Surface images of boronized 4340 before and after corrosion in 5% HCl at 20x.

6.2.1.4 XRD Analysis  The X-ray diffraction analysis of unboronized 4340 is presented in Figure 6.21. The XRD shows the presence of Fe$_3$O$_4$ and Fe$_2$O$_3$ as the corrosion products indicating free corrosion of the sample. The XRD spectrum for the boronized specimen also indicates the presence of same oxides but optical microscopy and corrosion testing showed less corrosion of boronized sample. Presence of boride layer can be confirmed by the presence of Fe$_2$B and FeB in XRD spectrum of boronized sample.
Figure 6.23  XRD spectrum of unboronized 4340 after corrosion in 5% HCl.

Figure 6.24  XRD spectrum of boronized 4340 after corrosion in 5% HCl.
6.2.2 AISI 4340 Steel in 4% NaCl

The corrosion data for the boronized and unboronized 4340 in 4% NaCl is shown in Figure 6.23 below.

![Figure 6.25](image)

(a) Linear polarization  
(b) Tafel plot

Figure 6.25 Comparative linear and Tafel plot of AISI 4340 steel in 4% NaCl.

The linear polarization graph shows more positive potential for the boronized sample than the unboronized sample as in all other cases. The $R_p$ value obtained from the graph for both boronized and unboronized samples are tabulated in table 6.9.

The Tafel graph of the boronized steel shows a more noble open circuit potential than the unboronized specimen. Both show similar anodic behavior.
6.2.2.1 Calculations. The calculations of the corrosion values are tabulated in the table below. The values show greater corrosion resistance of the boronized sample.

Table 6.8 Comparative Corrosion Properties of Plain and Boronized AISI 1018 Steel in 5% KOH

<table>
<thead>
<tr>
<th>NaCl</th>
<th>$R_p$(Ω)</th>
<th>$\beta_r$</th>
<th>$\beta_s$</th>
<th>Density (g/cm³)</th>
<th>Eq. Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm²)</th>
<th>$I_{corr}$ (A/cm²)</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4340P</td>
<td>897.53</td>
<td>85.03</td>
<td>98.01</td>
<td>7.84</td>
<td>27.24</td>
<td>0.75</td>
<td>0.44</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>4340B</td>
<td>2.58×10⁷</td>
<td>68.3</td>
<td>349.79</td>
<td>7.43</td>
<td>17.51</td>
<td>0.75</td>
<td>0.44</td>
<td>9.6×10⁻³</td>
<td>6.71×10⁻³</td>
</tr>
</tbody>
</table>

6.2.2.2 Cyclic Polarization. Figure 6.24 shows the cyclic polarization behavior for boronized and unboronized samples in 4% NaCl.

From the figure, one can observe that the reverse scan for the boronized sample follows the same path as the forward scan showing good pitting resistance and in the end, it exhibits minor pitting behavior. The unboronized sample follows a positive path in the reverse scan exhibiting pitting behavior.

**Figure 6.26** Comparative cyclic polarization graph of AISI 4340 steel in 4% NaCl.
6.2.2.3 Microscopy  Figure 6.26 shows the surface images of the boronized 4340 before and after corrosion in 4% NaCl. The boronized sample shows traces of corrosion on the surface but is less when compared to the unboronized sample as shown in Figure 6.25.

![Figure 6.27](image)

Figure 6.27 Surface images of unboronized 4340 before and after corrosion in 4% NaCl at 20x.

![Figure 6.28](image)

Figure 6.28 Surface images of boronized 4340 before and after corrosion in 4% NaCl at 20x.

6.2.2.4 XRD Analysis  The presence of Fe₃O₄ and Fe₂O₃ as the corrosion product indicates free corrosion occurring in the unboronized sample.

The same corrosion products are observed even in the XRD spectrum of the boronized specimen after corrosion as shown by Figure 6.29 except for the presence of borides FeB and Fe₂B.
Figure 6.29 XRD spectrum of unboronized 4340 after corrosion in 4% NaCl.

Figure 6.30 XRD spectrum of unboronized 4340 after corrosion in 4% NaCl.
6.2.3 AISI 4340 in 5% KOH

The comparative linear and Tafel plots of the boronized and unboronized 4340 steel in 5% KOH are shown in Figure 6.30.

The unboronized sample shows more positive potential when compared to the boronized sample but the linearity for the boronized sample is more than the linearity of the unboronized sample.

The open circuit potential for the boronized sample is nobler than the unboronized sample. The $i_{\text{corr}}$ for the unboronized sample is less than the $i_{\text{corr}}$ for the boronized sample but calculations show better corrosion resistance properties for the boronized samples.

Figure 6.31 Comparative linear and Tafel plot of AISI 4340 steel in 5% KOH.
6.2.3.1 Calculations. The resistance to polarization and $i_{corr}$ values and their corresponding calculations are shown in Table 6.11.

Table 6.9  Comparative Corrosion Properties of Plain and Boronized AISI 4340 Steel in 5% KOH

<table>
<thead>
<tr>
<th>KOH</th>
<th>$R_p$(Ω)</th>
<th>$\beta_a$</th>
<th>$\beta_t$</th>
<th>Density (g/cm$^3$)</th>
<th>Eq.Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm$^2$)</th>
<th>$i_{corr}$ (A/cm$^2$)</th>
<th>Corr. Rate(MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>4340P</td>
<td>3.821.13×10$^4$</td>
<td>407.03</td>
<td>203.29</td>
<td>7.84</td>
<td>27.24</td>
<td>0.75</td>
<td>0.44</td>
<td>0.02</td>
<td>0.02</td>
</tr>
<tr>
<td>4340B</td>
<td>1.98×10$^4$</td>
<td>291.84</td>
<td>347.77</td>
<td>7.43</td>
<td>17.51</td>
<td>0.75</td>
<td>0.44</td>
<td>3.48×10$^3$</td>
<td>2.42×10$^3$</td>
</tr>
</tbody>
</table>

6.2.3.2 Cyclic polarization. The cyclic polarization graph for the boronized and unboronized samples is shown in Figure 6.32.

The unboronized sample forms hysteresis loop during the reverse scan towards the positive end showing the pitting tendency whereas the boronized sample exhibits the same path in both the directions. Though the boronized sample shows pitting tendency, it is very less when compared to the unboronized sample.
Figure 6.32 Comparative cyclic polarization graph of AISI 4340 steel in 5% KOH.

6.2.3.3 Microscopy The surface images of the unboronized 4340 sample before and after corrosion in 5% KOH is shown in figure 6.32. Compared to the boronized sample after corrosion as shown in Figure 6.33, more pronounced pits are observed in the plain sample supporting the cyclic polarization data.
Figure 6.33 Surface images of unboronized 4340 before and after corrosion in 5% KOH at 20x.

Figure 6.34 Surface images of boronized 4340 before and after corrosion in 5% KOH at 20x.

6.2.3.4 XRD Analysis Fe$_2$O$_3$ is the only corrosion product observed in unboronized specimen after corrosion while both Fe$_2$O$_3$ and Fe$_3$O$_4$ are observed in the boronized specimen. Fe$_2$B and FeB confirm the presence of boronized layer.
Figure 6.35  XRD spectrum of unboronized 4340 after corrosion in 5% KOH.

Figure 6.36  XRD spectrum of boronized 4340 after corrosion in 5% KOH.
6.3 AISI 304 stainless steel

AISI 304 was also tested in the three solutions 5% HCl, 4% NaCl, 5% KOH and the results are discussed below.

6.3.1 AISI 304 in 5% HCl

The Tafel plots and the polarization resistance plots are obtained for 304 stainless steel in 5% HCl, and Figure 6.36 shows the results.

![Graphs](image)

**Figure 6.37** Comparative linear and Tafel plot of AISI 304 steel in 5% HCl.

From the linear polarization graph, it can be concluded that the boronized sample has more positive potential than the unboronized sample. The $R_p$ values indicated in Table 6.12 show a better resistance to polarization for the boronized 304 than the unboronized 304.
The Tafel plot in Figure 6.37 shows a more noble open circuit potential for the boronized 304. At the same time, the pulling back tendency for the unboronized sample is better when it is compared with the boronized 304. From the graph, one can observe that the boronized 304 has a much low $i_{\text{corr}}$ than the unboronized sample. Better corrosion resistance of boronized steel AISI 304 in 5% HCl was also observed in the work done by R. Petrova et. al$^{[36-37]}$.

6.3.1.1 Calculation  The calculations for the boronized and unboronized 304 in 5% HCl are tabulated in Table 6.12. The values indicate a huge increase in the corrosion resistance value of the boronized sample.

Table 6.10  Comparative Corrosion Properties of Plain and Boronized AISI 304 Steel in 5% KOH

<table>
<thead>
<tr>
<th>HCl</th>
<th>Rp(Ω)</th>
<th>βa</th>
<th>Bc</th>
<th>Density (g/cm²)</th>
<th>Eq. Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm²)</th>
<th>$i_{\text{corr}}$ (A/cm²)</th>
<th>Corr. Rate(MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304P</td>
<td>997.01</td>
<td>141.22</td>
<td>142.54</td>
<td>7.94</td>
<td>25.03</td>
<td>0.75</td>
<td>0.44</td>
<td>0.03</td>
<td>0.03</td>
</tr>
<tr>
<td>304B</td>
<td>1.61×10³</td>
<td>40.13</td>
<td>307.39</td>
<td>6.75</td>
<td>12.87</td>
<td>0.75</td>
<td>0.44</td>
<td>9.6×10⁻³</td>
<td>5.4×10⁻³</td>
</tr>
</tbody>
</table>

6.3.1.2 Cyclic Polarization  From the cyclic polarization curve in Figure 6.37, the following points can be observed and compared between the boronized and the unboronized 304:

Unboronized 304 shows a wide hysteresis loop than the boronized sample indicating more pitting resistance for the boronized sample:

- Unboronized 304 shows a wide hysteresis loop than the boronized sample indicating more pitting resistance for the boronized sample.
Also for the boronized sample the reverse scan is more negative than the positive scan showing up good pitting resistance properties, while the unboronized sample has a more positive reverse scan than the forward scan.

Figure 6.37 Comparative cyclic polarization graph of AISI 304 steel in 5% HCl.

6.3.1.3 Microscopy  Figure 6.39 shows the surface images of the boronized 304 before and after corrosion in 5% HCl. Though the after corrosion image shows small instances of corrosion but when compared to 1018 and 4340, 304 corroded less in 5% HCl. Little larger pits are found in the surface of unboronized specimen after corrosion. The Figure 6.38 shows a part of large pit.
6.3.1.4 XRD Analysis

The presence of Fe$_2$O$_3$ only is observed in plain sample while all the three oxides of iron are observed as corrosion products in boronized 304. Further studies need to be conducted to analyze the corrosion products and why the reasons for their formation. FeB is the only boride observed in AISI 304 steel.
Figure 6.41 XRD spectrum of unboronized 304 after corrosion in 5% HCl.

Figure 6.42 XRD spectrum of unboronized 304 after corrosion in 5% HCl.
6.3.2 AISI 304 in 4% NaCl

Figure 6.43 Comparative linear and Tafel plot of AISI 304 steel in 4% NaCl.

Figure 6.42 shows the comparative linear polarization graph and Tafel graph for boronized and unboronized 304 in 4% NaCl.

From the linear polarization curve, it is clear that the boronized sample has a more positive potential than the unboronized sample. The $R_p$ values and the $i_{corr}$ values are tabulated in Table 6.13. The Tafel plot also indicates a more noble open circuit potential for the boronized 304. From the graph, it can be observed that the boronized sample has high resistance to corrosion in the anodic region as indicated by the pulling back of the anodic curve. The unboronized sample readily corrodes due to absence of the pull back behavior.
6.3.2.1 Calculations  The table below shows the calculations of the corrosion data for AISI unboronized and boronized 304 steel in 4% NaCl solution. The table gives an indication of the better corrosion properties of the boronized sample which can be attributed to the presence of boron coating.

**Table 6.11** Comparative Corrosion Properties of Plain and Boronized AISI 304 Steel in 4% NaCl

<table>
<thead>
<tr>
<th></th>
<th>Rp(Ω)</th>
<th>αa</th>
<th>βc</th>
<th>Density (g/cm³)</th>
<th>Eq. Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm²)</th>
<th>Icorr (A/cm²)</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NaCl</td>
<td>304P</td>
<td>1.02×10⁴</td>
<td>65.49</td>
<td>194.43</td>
<td>7.94</td>
<td>25.03</td>
<td>0.75</td>
<td>0.44</td>
<td>2.09×10⁻³</td>
</tr>
<tr>
<td></td>
<td>304B</td>
<td>2.27×10⁵</td>
<td>268.10</td>
<td>172.72</td>
<td>6.75</td>
<td>12.87</td>
<td>0.75</td>
<td>0.44</td>
<td>2.01×10⁻⁴</td>
</tr>
</tbody>
</table>

6.3.2.2 Cyclic Polarization  Figure 6.43 shows the cyclic polarization behavior for both boronized and unboronized 304 in 4% NaCl. The boronized sample shows better pitting resistance behavior than the unboronized sample. This is due to lesser area of the hysteresis loop for the boronized sample as compared to the wider area of the unboronized sample. The reverse scan for the boronized sample is more negative than the forward scan showing good pitting resistance behavior when compared to the unboronized sample.
Figure 6.44 Comparative cyclic polarization graph of AISI 304 steel in 4% NaCl.

6.3.2.3 Microscopy  304 being stainless steel should corrode less when compared to the other steels like 1018 and 4340. This behavior is obvious in Figure 6.44 and Figure 6.45. Very less traces of corrosion are observed on the surface of the sample.

The only difference between the boronized and unboronized specimens after corrosion is that the unboronized specimen has much larger pits compared to the boronized specimen.
6.3.2.4 XRD Analysis

The XRD analysis of the unboronized specimen is shown in Figure 6.46, and XRD analysis for boronized 304 after corrosion in 4% NaCl is shown in Figure 6.47. The analysis shows presence of all forms of iron oxide in the both specimens. Again FeB is the only boride observed. This was the reason why FeB was the only boride considered on the surface of 304 steel for calculations.
Figure 6.47 XRD spectrum of unboronized 304 after corrosion in 4% NaCl.

Figure 6.48 XRD spectrum of boronized 304 after corrosion in 4% NaCl.
6.3.3 AISI 304 in 5% KOH

Both plane and boronized 304 samples were tested in 5% KOH for obtaining the linear polarization and Tafel plots. Figure 6.48 shows the comparative graphs for boronized and unboronized samples. A different behavior is observed for the linear polarization curve where the unboronized sample showed a more positive potential when compared to the boronized sample. But the resistance to polarization value for the boronized sample was much higher than the value for the unboronized sample due to the more linear slope of the boronized sample. The graph also shows up a behavior for the unboronized sample where it readily corrodes. Boronized sample resists corrosion and exhibits a high $R_p$ value.

![Graph](image)

(a) Linear polarization  
(b) Tafel plot

**Figure 6.49** Comparative linear and Tafel plot of AISI 304 steel in 5% KOH.
The Tafel plot for the unboronized sample shows a noble $i_{\text{cor}}$ when compared to the boronized sample. But the huge difference in the open circuit potential dominates this point. The $R_p$ and $i_{\text{cor}}$ values are tabulated below in Table 6.14.

**6.3.3.1 Calculations** The calculations of the corrosion values are tabulated in the table below. The values show greater corrosion resistance of the boronized sample.

**Table 6.12** Comparative Corrosion Properties of Plain and Boronized AISI 304 Steel in NaCl

<table>
<thead>
<tr>
<th>KOH</th>
<th>$R_p$ ($\Omega$)</th>
<th>$\beta_a$</th>
<th>$\beta_c$</th>
<th>Density (g/cm$^3$)</th>
<th>Eq. Wt. (g)</th>
<th>Radius (cm)</th>
<th>Area (cm$^2$)</th>
<th>$i_{\text{cor}}$ (A/cm$^2$)</th>
<th>Corr. Rate (MPY)</th>
</tr>
</thead>
<tbody>
<tr>
<td>304P</td>
<td>3.89x10$^3$</td>
<td>117.15</td>
<td>550.08</td>
<td>7.94</td>
<td>25.03</td>
<td>0.75</td>
<td>0.44</td>
<td>0.75</td>
<td>0.01</td>
</tr>
<tr>
<td>304B</td>
<td>1.99x10$^4$</td>
<td>794.61</td>
<td>252.14</td>
<td>6.75</td>
<td>12.87</td>
<td>0.75</td>
<td>0.44</td>
<td>4.18x10$^{-3}$</td>
<td>2.35x10$^{-3}$</td>
</tr>
</tbody>
</table>

**6.3.3.2 Cyclic polarization** Figure 6.49 shows the comparative cyclic polarization graphs for both boronized and unboronized samples. Both the samples almost exhibit the same behavior in the forward and reverse scan except that the boronized sample deviates from the path and goes to the negative direction of current exhibiting pitting behavior resistance.
Figure 6.50 Comparative cyclic polarization graph of AISI 304 steel in 5% KOH

6.3.3.3 Microscopy  The surface images of unboronized and boronized 304 before and after corrosion are shown in Figures 6.50 and 6.51 respectively. No traces of corrosion are seen on the surface of boronized specimen expect for some coloration indicating occurrence of some reaction. The surface of unboronized specimen shows clear signs of pitting.
6.3.3.4 XRD Analysis  The presence of the corrosion products was confirmed by the XRD analysis. The peaks for the corrosion products are shown in Figure 6.52 and 6.53. Similar to most other XRD spectrum in the present discussion, the spectrum for 304 in 5% KOH also showed the peaks for the same iron oxides. Unboronized specimen showed peaks for FeO and Fe$_2$O$_3$. The boronized specimen in addition to the above two showed the peak for Fe$_3$O$_4$ and FeB. The XRD was conducted basically to observe any abnormality in corrosion products and to confirm the presence of borides, but no such abnormality in corrosion products was observed in all the experiments conducted.
Figure 6.53 XRD spectrum of unboronized 304 after corrosion in 5% KOH.

Figure 6.54 XRD spectrum of boronized 304 after corrosion in 5% KOH.
CHAPTER 7

CONCLUSIONS

The boronizing of steels was successful and the presence of boride layer was confirmed by the XRD results. From the comparison of corrosion properties of the boronized and unboronized steels, following conclusions can be drawn:

- The corrosion resistance of AISI 1018, AISI 4340, and AISI 304 steels in 5% HCl increased by nearly 3, 11, and 10 times respectively.

- The corrosion resistance of AISI 1018, AISI 4340, and AISI 304 steels in 5% KOH increased by nearly 8, 6, and 6 times respectively.

- The corrosion resistance of AISI 1018, AISI 4340, and AISI 304 steels in 4% NaCl increased by nearly 3, 4, and 17 times respectively.

- From the Cyclic Polarization graphs, it can be concluded that the boronized AISI 1018, AISI 4340, and AISI 304 steels show better pitting resistance compared to the unboronized steels.
This is the cyclic polarization graph of titanium alloy in seawater. This graph is used as a reference to predict the pitting behavior of the steel samples in the current research.

Figure A.1 Cyclic polarization graph of titanium alloy in seawater.
REFERENCES


23. N. G. Thompson and J.H. Payer, DC Electrochemical Test Methods, NACE, Houston, TX.


