ELECTROCHEMICAL INVESTIGATION OF THE CORROSION BEHAVIOUR OF MICRO ALLOYED STEEL AND COLD FORMED STEEL IN HCL SOLUTION

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ABSTRACT

This paper presents the development and the technical importance of the Micro alloyed steel for different microstructural conditions. Weight loss, Non Electrochemical method, and Electrochemical Impedance Spectroscopy (EIS) techniques, optical microscope and XRD have been used to study the electrochemical behavior. Steel is an alloy of iron and carbon. Steel is the most useful material for building structures with strength of approximately ten times that of concrete, Steel plays a fundamental role in the development of modern societies. Corrosion is the destructive attack of a metal by chemical or electrochemical reaction with its environment. Deterioration by physical causes is not called corrosion, but is described as erosion, galling, or wear. The influences of the low temperatures on the mechanical properties of micro steel and cold formed steel are compared and their differences are discussed. The corrosion patterns and rust characteristics of the corroded steel bars were examined

Key words: Micro alloyed steel, Electrochemical Impedance Spectroscopy & XRD.

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1. INTRODUCTION

Scope and Objectives

- The objective of this project is to compare the effect of corrosion rate on Microalloyed steel and Cold formed steel under industrial environment.
- To study the corrosion behaviour of Microalloyed Steel and Cold Formed Steel using Non Electrochemical methods and electrochemical methods.
Electrochemical Investigation of the Corrosion Behaviour of Micro Alloyed Steel and Cold Formed Steel in HCL Solution

- To study the microstructural variations in both Microalloyed Steel and Cold Formed Steel through corrosion product analysis tests such as Optical Micrographs, X-ray diffraction (XRD) method.

2. SPECIMEN DETAILS
The sample specimens used in the non electrochemical method are extracted in the form of hexahedral piece dimensions about 30mm x 20 mm with thickness of 2mm for Microalloyed steel and 0.8mm thick for Cold formed steel. The specimens used in the electrochemical method are cut in the form of 20mm square piece having same thickness as above mentioned for both the steels.

3. EXPERIMENTAL PROCEDURE
Corrosion Test
Corrosion testing refers to the processes conducted by laboratories in order to solve, prevent or mitigate problems related to corrosion. These processes can be applied in industrial materials and infrastructure products, and are often used in failure analysis.

Non Electrochemical Method
Non-electrochemically, the rate of corrosion is determined by the conventional weight loss technique. The simplest, and longest-established, method of estimating corrosion losses in plant and equipment is weight loss analysis. A weighed sample (coupon) of the metal or alloy under consideration is introduced into the process, and later removed after a reasonable time interval. The coupon is then cleaned of all corrosion products and is reweighed. The weight loss is converted to a corrosion rate (CR). Weight loss measurement is still the most widely used means of determining corrosion loss, despite being the oldest method currently in use.

The rate of corrosion is the speed at which a metal deteriorates in a specific environment. The rate, or speed, is dependent upon environmental conditions as well as the type, and condition, of the metal.

![Figure 1 Specimen at the Time of Immersion and After the Exposure Time](image)

4. ELECTROCHEMICAL CORROSION TESTING
Electrochemical techniques of corrosion measurement are currently experiencing increasing popularity among corrosion engineers, due primarily to the rapidity with which these measurements can be made. Long term corrosion studies, such as weight loss determinations, may take days or weeks to complete, while an electrochemical experiment will require, at
most, several hours. The speed of electrochemical measurements is especially useful for those metals or alloys that are highly corrosion resistant.

![AUTOLAB PGSTAT100](image)

**Figure 2 AUTOLAB PGSTAT100**

There are different electrochemical techniques can be employed to evaluate the state of a specimen from a corrosion point of view. These techniques were developed and have been used for lab measurements; however, civil engineers managed to adapt a number of them to be used in field applications. The following section provides an explanation of electrochemical techniques that were used in this study.

**Electrochemical Impedance Spectroscopy (EIS)**

Electrochemical impedance is usually measured by applying an AC potential to an electrochemical cell and then measuring the current through the cell. EIS measurements were carried out using Auto Lab PGSTAT 100 workstation (Fig. 7) provided with an electrochemical cell supporting 250 mL electrolyte (0.05 HCl solutions) at 298 K and controlled by NOVA 1.10 analysis software.

Detailed analysis of the data obtained during an electrochemical impedance measurement is usually performed by fitting the experimental data with an equivalent circuit. Many circuit elements can be used to fit the experimental data with a model. However, the equivalent circuit must be constructed carefully, since a given experimental data set can be fitted with more than one unique equivalent circuit.

The values of $C_{dl}$ were obtained at the frequency $f_{max}$, at which the imaginary component of the impedance is maximal $-Z''_{max}$. using the following equation

$$C_{dl} = \frac{1}{2\pi f_{max}R_{ct}}$$

According to the electrochemical theory, $R_{ct}$ is inversely proportional to the corrosion current density, so it is analogous to the use of polarization resistance in the Stern-Geary equation

$$i_{corr} = \frac{\beta a \beta b}{R_{ct} (2.303 (\beta a + \beta b))}$$

**Linear Polarization Resistance (LPR)**

The electrochemical technique of polarization resistance is used to measure absolute corrosion rates, usually expressed in millimeters per year (mpy). Polarization resistance measurements can be made very rapidly, usually in less than ten minutes. Excellent correlation can often be made between corrosion rates obtained by polarization resistance and
conventional weight loss determinations. Polarizations resistance is also referred to as “linear polarization”.

The Tafel slope analysis tool provides a quick estimation of the corrosion rate and the polarization resistance. The corrosion rate is calculated from the estimated corrosion current, $i_{corr}$, obtained from the intercept of the two linear segment of the Tafel slope.

The corrosion rate is calculated from following relation

$$\text{Corrosion rate (CR)} = \frac{K \times i_{corr} \times (\text{E.W})}{D}$$

where

$K = \text{corrosion rate factor (0.3272 for mm/y)}$

$i_{corr} = \text{corrosion current density (A/cm}^2\text{)}$

$\text{E.W} = \text{equivalent weight of the corroding species (g)}$

$D = \text{density of the corroding species (g/cm}^3\text{)}$

**Sample Requirements**

Samples for electrochemical corrosion testing must electrical conductors and must be small enough to fit in the polarization cell. Components can be tested as a whole or as a smaller section. Metal coupons are specially prepared for some tests. The steel sample material is extracted in the form of hexahedral piece dimensions of about 20 x 20 x 2 mm and 20 x 20 x 0.8mm for Microalloyed and cold formed carbon steel respectively. The samples are mirror polished and carefully fitted on the electrochemical cell.

![Electrochemical Cell](image)

**Figure 3 Electrochemical Cell**

In testing practice, a electrochemical cell is setup consisting of an electrolyte solution of 0.05M HCl, a reference electrode, a counter electrode(s), and the metal sample of interest connected to a specimen holder. (The sample is called the working electrode.) The electrodes are connected to an electronic instrument called **Auto Lab PGSTAT100**. The working, reference, and counting electrodes are placed in the electrolyte solution. All the techniques are conducted with static working electrode, naturally aerated electrolytes at a controlled temperature of 298 ± 1 K. Reading is taken for 1, 5, 10, 30 days. Automatic generation of graph is obtained and saved using **NOVA** software. The observed plot data’s are entered in the **Origin Pro** software to get both Nyquist and Tafel graph.
5. RESULT AND DISCUSSION

Non Electrochemical Method

The weight loss is measured after each experiment and the corrosion rate is calculated in millimeters per year. The Weight loss of steel in percentage with respect to time of exposure into aggressive chloride induced industrial condition is clearly shown in the table.

<table>
<thead>
<tr>
<th>Exposure time in days</th>
<th>1</th>
<th>5</th>
<th>10</th>
<th>30</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight loss in percentage</td>
<td>MA steel</td>
<td>0.92</td>
<td>1.39</td>
<td>1.56</td>
</tr>
<tr>
<td></td>
<td>CF steel</td>
<td>0.16</td>
<td>1.08</td>
<td>1.36</td>
</tr>
</tbody>
</table>

The results based on this test are given below:

- It was observed that considerable damage occurred for the Cold formed steel subjected to 0.05M HCl with respect to weight loss after 30 days of immersion when compared with weight loss of Microalloyed steel subjected to same solution. This is due to the effect of pH value present in the solution.

- In the case of Microalloyed steel, corrosion rate was initially higher and later it gradually reduced due to fast reaction of alloy element (titanium) with the HCl solution which made the solution neutral after few days of exposure.

- High weight loss (4.09%) occurred after exposure for 30 days in case of CF steel exposed to 0.05M HCl, whereas for the MA steel (2.45%) occurred after exposure for 30 days exposed to 0.05 M HCl. The percentage of weight loss obtained from the CF steel has 1.64% higher than the MA steel.

- While comparing both the steel, CF steel have more tendency of corrode in electrolyte solutions (0.05 M HCl).

![Figure 4 Weight loss of steel with respect to different time interval in presence of HCl solution](http://www.iaeme.com/IJCIET/index.asp 144 editor@iaeme.com)
Corrosion rate of steel with respect to different time interval in presence of HCl solution

- From Fig. 15, shows the corrosion rate of both steels exposed to 0.05M HCl solution. At initial stage, high corrosion rate (3.0223 mm/yr) occurred at the end of 1st day exposure time in the case of MA steel exposed to 0.05M HCl, whereas for CF steel the max. corrosion rate occurred when exposed to 0.05M HCl at the end of 5th day exposure time are 0.2906 mm/yr.

- Corrosion rate was gradually decreased in case of MA steel exposed to 0.05M HCl and reaches a rate of 0.2391 mm/yr after exposure time of 30 days. In case of CF steel, the corrosion rate are gradually increased upto 5 days of exposure and then starts to decrease and reaches 0.1792 mm/yr after exposure time of 30 days.

Comparing the results, that the Microalloyed steel has better corrosion property than the Cold Formed steel. It is better to use MA steel sections and bars for construction than CF steel under this industrial environmental.

**Electrochemical Method**

**EIS Measurement**

The corrosion behaviour of Microalloyed and Cold formed steel in 0.05M HCl solution was investigated by EIS technique after the different immersion time intervals. Nyquist plots are shown in Fig. 16 and Fig. 17 for both MA and CF steel respectively.

The experimental results obtained from EIS measurements may be interpreted as follows:

- It is clear from the plots that the impedance response of both steels in 0.05M HCl solution was significantly varied because of different molecules present in the steel.

- The impedance of the MA steel goes on increases as the exposure time increases, whereas in the CF steel impedance value gets reduced as the exposure time increases.

- For analysis of the impedance spectra containing one capacitive loop, the equivalent circuit (EC) was used. Various parameters such as solution resistance charge $R_s$, transfer resistance ($R_{ct}$), double layer capacitance $Cdl$ were calculated and listed in Table 7 and 8.

- since $R_{ct} \propto \frac{1}{C.R}$, which indicates that decrease of $R_{ct}$ will increase the corrosion rate in the case of CF steel and for the MA steel, increase of $R_{ct}$ will decrease the corrosion rate.
Both the steel has increase in double layer capacitance ($C_{dl}$), which can result from an increase in local dielectric constant and/or a decrease in the thickness of electrical double layer, proposes that corrosive

![Figure 5 Nyquist plot for Microalloyed Steel](image)

![Figure 6 Nyquist plot for Cold Formed Steel](image)

**Table 2** Data from the EIS measurements for MA steel

<table>
<thead>
<tr>
<th>DAYS</th>
<th>OCP</th>
<th>RS(Ω)</th>
<th>Ret(Ω)</th>
<th>Cdl</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.493</td>
<td>26.222</td>
<td>80.072</td>
<td>3.8404 x 10^{-5}</td>
</tr>
<tr>
<td>1</td>
<td>-0.494</td>
<td>53.410</td>
<td>44.532</td>
<td>1.8402 x 10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>-0.545</td>
<td>41.888</td>
<td>116.99</td>
<td>9 x 10^{-13}</td>
</tr>
<tr>
<td>10</td>
<td>-0.567</td>
<td>115.67</td>
<td>71.251</td>
<td>1.245 x 10^{-8}</td>
</tr>
<tr>
<td>30</td>
<td>-0.597</td>
<td>167.260</td>
<td>167.260</td>
<td>1.3863 x 10^{-5}</td>
</tr>
</tbody>
</table>

**Table 3** Data from the EIS measurements for CF steel

<table>
<thead>
<tr>
<th>DAYS</th>
<th>OCP</th>
<th>R_S</th>
<th>R_E</th>
<th>C_{dl}</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>-0.485</td>
<td>10.6</td>
<td>2792.2</td>
<td>3.0137x10^{-6}</td>
</tr>
<tr>
<td>1</td>
<td>-0.542</td>
<td>16.397</td>
<td>5927.9</td>
<td>1.1828x10^{-8}</td>
</tr>
<tr>
<td>5</td>
<td>-0.551</td>
<td>93.754</td>
<td>3361</td>
<td>3.3462x10^{-5}</td>
</tr>
<tr>
<td>10</td>
<td>-0.591</td>
<td>7.2793</td>
<td>1807.3</td>
<td>1.0869x10^{-7}</td>
</tr>
<tr>
<td>30</td>
<td>-0.580</td>
<td>312.42</td>
<td>1005.8</td>
<td>6.8131x10^{-5}</td>
</tr>
</tbody>
</table>
6. CONCLUSIONS
In this study, the effect of the presence of chloride ions in simulated industrial environmental condition of (0.05 M) HCl solution on the corrosion behavior of Microalloyed steel, Cold formed steel was investigated using Electrochemical and Non Electrochemical methods. In addition, the surface morphology of those steels was investigated.

Following are the conclusions of this study.

- Based on weight loss of the sample specimen, a rough estimation of corrosion rate is determined from which suitability of the steel for construction is determined. The percentage of weight loss obtained from the CF steel has 1.64% higher than the MA steel.
- From the advanced techniques EIS behaviour of both the steels were studied and also corrosion rate of both the steels are determined, where the corrosion rate of CF steel has 9% higher than the MA steel. It is clear that Microalloyed steel has better corrosion property than the Cold Formed steel.
- Microstructural studies for Microalloyed and Cold formed steel after immersion in HCl solution showed the surface with general, crack and pitting corrosion.
- The characterization of corrosion product of both the steels were studied by X-Ray Diffraction. Based on the observed pattern the main phase was Lepidocrocite, followed by ferric chloride occurred in both MA steel and CF steel. In addition with that magnetite compounds were detected in the products of CF steel and Goethite compounds in the products of MA steel.

It is clear that the Microalloyed steel has better corrosion property than the cold formed steel. It is better to use MA steel sections and bars for construction than the CF steel under this industrial environmental.

REFERENCES
Annapurani M, Sivaranjani S, Nalini S


