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Influence of Grain Size on Corrosion Resistance and Electrochemical behaviour of Mild Steel

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Abstract: Corrosion of mild steel is one of the biggest issues faced in today's world, and leads to huge losses every year. Mild steel, an alloy with a very vast range of applications, is very susceptible to corrosion and thus, it is important to study the factors that govern corrosion in mild steel and how to control this corrosion. In this study, the effect of heat treatment, microstructure, grain size and hardness of mild steel on its rate of corrosion under a natural environment is studied. The microstructures of mild steel that underwent heat treatment for various time periods were characterized using optical microscope and their grain sizes were determined by intercept method. The corrosion resistances of these samples were found using Electrochemical Impedance Spectroscopy (EIS). The study suggests that, as time of heat treatment increases, grain size increases, hardness decreases and corrosion rate decreases. The conclusion obtained from the results of this study is found to match with those predicted by theory.
Keywords: **Corrosion, Heat treatment, Optical Microscopy, Electrochemical Impedance Spectroscopy, Mild Steel with 0.07%C**

I. INTRODUCTION

Grain size and microstructure of a metal or alloy plays a very important role in determining its physical, mechanical and chemical properties. The strength, wear, ductility, toughness, hardness, corrosion resistance and various other properties depend to a large extent on grain size and microstructure. Grain refinement of an alloy, achieved through thermo-mechanical processing methods such as heat treatment etc., improves its properties such as strength, wear, corrosion resistance and ductility. [1] [2]

The Grain size of a material changes with heat treatment due to recrystallization, which is the process of formation of new, defect-free, equiaxed grains above a certain temperature, called recrystallization temperature. As the recrystallization temperature of mild steel is 400 – 700 ºC, at temperatures above this range, recrystallization occurs, with new grains formed. Higher the temperature and the time period allotted for this recrystallization, higher the grain size, as more grains join together to form new, bigger grains. [3]

Grain size can be obtained from images of microstructure of the alloy as given by optical microscope by the application of Intercept method, also called Average Grain Intercept or AGI method. In this method, Average Grain Intercept (AGI) is found as the ratio of number of times a randomly drawn line in an image of a microstructure intercepts with grain boundaries to the total length of the line. This ratio is obtained for multiple arbitrary lines and then corresponded against a standard table, which gives the approximate grain size of the sample. Alternatively, grain size can be obtained from images of microstructure using various specialised softwares designed for this specific purpose.

The Hardness of a material has a direct correlation with the grain size, and it is generally observed that, as grain size increases, hardness decreases. The Hall-Petch equation, given by E. O. Hall and N. J. Petch, gives that, for frictional stress σ_o where dislocation movement starts under standard conditions and average grain diameter d,

$$\sigma_y = \sigma_o + k(d)^{-1/2} \quad -(1)$$ [4]

Where k_y is a strengthening coefficient that is unique for a material. According to this equation, as grain size increases, yield strength σ_y decreases. As yield strength and hardness have been demonstrated as being directly proportional to each other, hardness decreases with an increase in grain size. [5]

Corrosion is one of the most important issues faced in today's world, and trillions of dollars are lost every year due to corrosion of various metal parts. Corrosion of a metal occurs due to the tendency of the metal to stay in its base state of least energy, and thus, more reactive metals such as Iron, Zinc etc. are more susceptible to corrosion than most other metals. As mild steel is an alloy of Iron, it is very susceptible to corrosion. This becomes a bigger issue as mild steel is one of the most commonly used materials in the present world, with its usage coming in all sectors, from construction to machinery. Corrosion in mild steel occurs mainly due to presence of higher energy sites, such as grain boundaries, with larger the grain boundary area, higher the rate of corrosion. Grains, being low energy sites with a lower strength and hardness, are not as susceptible to corrosion as grain boundaries under natural environmental conditions. Thus, increase in the grain size of the alloy due to heat treatment etc. would result in decreased grain boundary area, and thus, in decreased corrosion rates. As a result, higher the grain size of the mild steel, higher is the corrosion resistance displayed by it under normal environmental conditions. [6] [7] [8]

The heat treatment required to obtain a specific grain size depends on the microstructure and composition of the alloy. In the case of steel, this is mainly determined by the presence of carbon, as steel is an alloy of Iron and Carbon. However, as other alloying elements are usually present in small quantities in steel and affect the microstructure in similar ways to carbon, Carbon Equivalent (CE) of the steel is calculated to understand the effect of its constituents on heat treatment and grain size. CE is an empirical value that relates the combined effects of different elements present in the alloy in various quantities to an equivalent amount of carbon. This allows us to treat the steel as if it has the CE percentage of carbon and remaining Iron with no other elements present. [9]

CE, in terms of weight percentage of commonly found elements in steel, is calculated as:

$$CE = \%C + (\%Mn)/6 + (\%Cr + \%Mo + \%V)/5 + (\%Ni + \%Cu)/15 \quad – (2)$$

There are various ways to find the corrosion resistance of a material, but most of them involving destructive testing with a metal piece being exposed to corrosive environment to calculate the weight loss (corrosion rate) after a certain time interval. One of the most reliable, accurate, and non-destructive method of testing the corrosion rate of a material is by using Electrochemical Impedance Spectroscopy (EIS). [10] EIS gives a measure of Electrochemical Impedance of a material. Electrochemical Impedance is the response of an electrochemical system to an applied potential. It is the resistance offered to flow of charge and, thus, flow of mass between two electrodes due to an applied potential. By Faraday's law of electrolysis, the weight deposited by a material during electrolysis due to an applied current is directly proportional to the current used. Thus, higher the electrochemical impedance of a material, higher is its resistance to transfer of charge and current, and thus, lower is the weight deposited during electrolysis and the corrosion rate of the material. EIS uses this principle to characterize materials in terms of their electrochemical impedance and corrosion resistance, in comparison to a reference electrode. EIS typically consists of a working electrode (sample), a counter electrode (platinum electrode) and a reference electrode, in an ionic solution (typically 3.5 wt% sodium chloride solution in water). The potential passes between reference and working electrodes, and current passes between counter and working electrodes as a result. The potential difference between the applied potential at reference electrode and final obtained potential can help quantify the electrochemical impedance of the material.

The plots obtained in EIS can be in terms of:

1) Total Impedance value vs frequency of AC current applied to the electrodes
2) Current Density at the electrodes vs Potential applied at the electrodes

All these plots give a measure of the corrosion resistance of the material used as working electrode. [11]

In this study, we aim to calculate the effect that the grain size of mild carbon steel of a given composition has on its rate of corrosion and corrosion resistance when other factors are kept constant. We aim to study the extent of influence of grain size on the corrosion rate of the alloy and to check if this corresponds with the theoretical predictions based on Hall-Petch equation and previous experiments on various materials. One of the most important challenges in studying the influence of grain size on the corrosion rate of an alloy is the difficulty in isolating grain size effects from other microstructural changes due to thermo-mechanical process used to gain variation in grain size. To achieve this, in our study, we have kept all other factors such as temperature, cooling rate, composition etc. of samples with different grain size as constant, so that the influence of grain size on the corrosion rate of mild steel can be isolated.

II. EXPERIMENTAL

A. Material

Mild Steel sheet of thickness 3mm was bought from a commercial supplier and the composition of the particular sample are mentioned below- [12]

TABLE I. COMPOSITION of TEST SAMPLES

%C	%Mn	%P	%S	%Si	%Al	%N	%B	%Cr	%Cu	Carbon Equivalent
0.07	0.25	0.005	0.005	0.013	0.031	0.0042	0.0025	0.007	0.002	0.1153

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B. Methodology

The mild steel sheet of 3mm thickness was cut into 20mm x 20mm x 3mm slices. Three sets of 3 samples each were taken from these slices and then heat treated in three-zone tubular furnaces (OTF-1200X) at a temperature of 1000℃. Three different time durations were set for these three different sets, with one set heat treated for half an hour, second set for 2 hours and the third set for 5 hours.

After the heat treatment, these samples were allowed to normalize (air cooling performed at room temperature) with an approximate cooling rate of 10℃ per minute, these cooled samples were made to undergo grinding with the help of emery papers of different grades and polishing with aluminium polish to obtain a mirror-like surface finish.

The microstructures of these samples, after grinding and polishing, were observed with an optical microscope (Nikon Microscopes) at 200x magnification after etching with Nittal (98ml nitric acid in 5ml ethanol). The grain sizes of each sample were obtained from the image of the microstructures through intercept method. [13]

The electrochemical corrosion behaviours of the samples were studied using a potentiostatt corrosion measurement system (Electrochemical Impedance Spectroscopy). [14] Polarisation measurement was carried out in a corrosion cell containing NaCl using a standard three-electrode that are 'flat-cell' type. Ag/AgCl electrode was used as a reference, with a platinum electrode as counter electrode and the sample as working electrode.

The hardness of the samples was studied using Rockwell Hardness Testing machine (AFFRI System) at B-scale by applying 60 KgF load. The microstructure, rate of corrosion and hardness of a bare mild steel sample that was not heat treated were then obtained using the respective instruments to act as a reference.

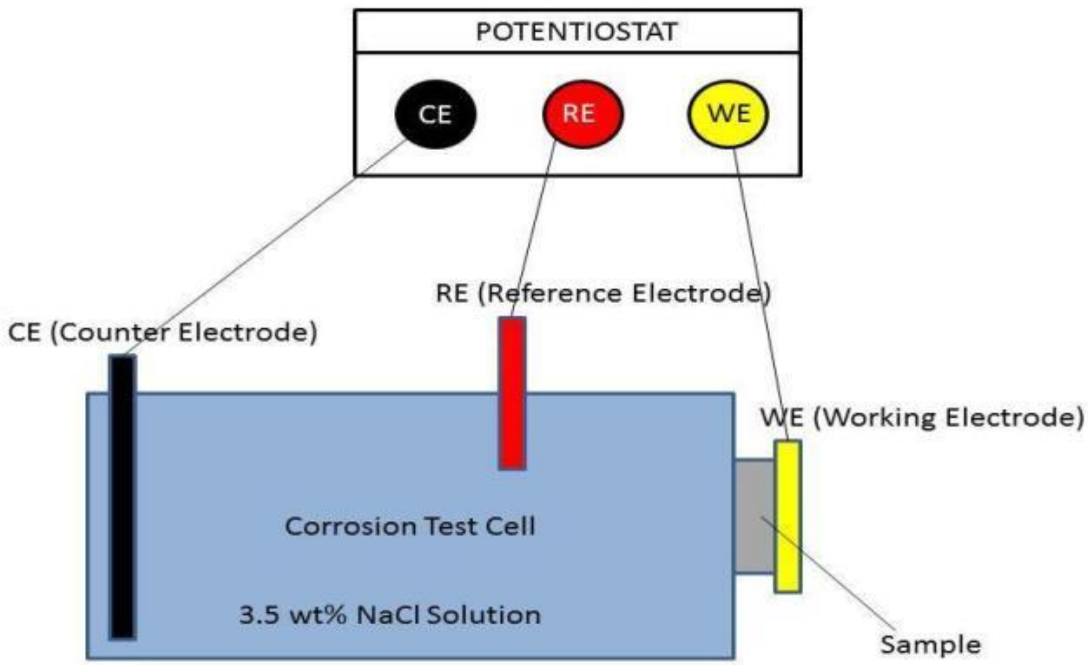


Fig. 1 Schematic diagram representing EIS study of mild steel

III. RESULTS AND ANALYSIS

A. Microstructures

The microstructures and average grain size of bare sample and samples heat treated for ½ h, 2h and 5h respectively are mentioned here. All the images of microstructures were taken at 200x magnification and the grain sizes were calculated from the images of the microstructures. [15][16]

At 1000 ºC full austenitic phase is obtained. When the cooling was takes place (normalizing) the austenitic phase changes into pearlite phase along the grain boundaries and rest is ferrite phase.

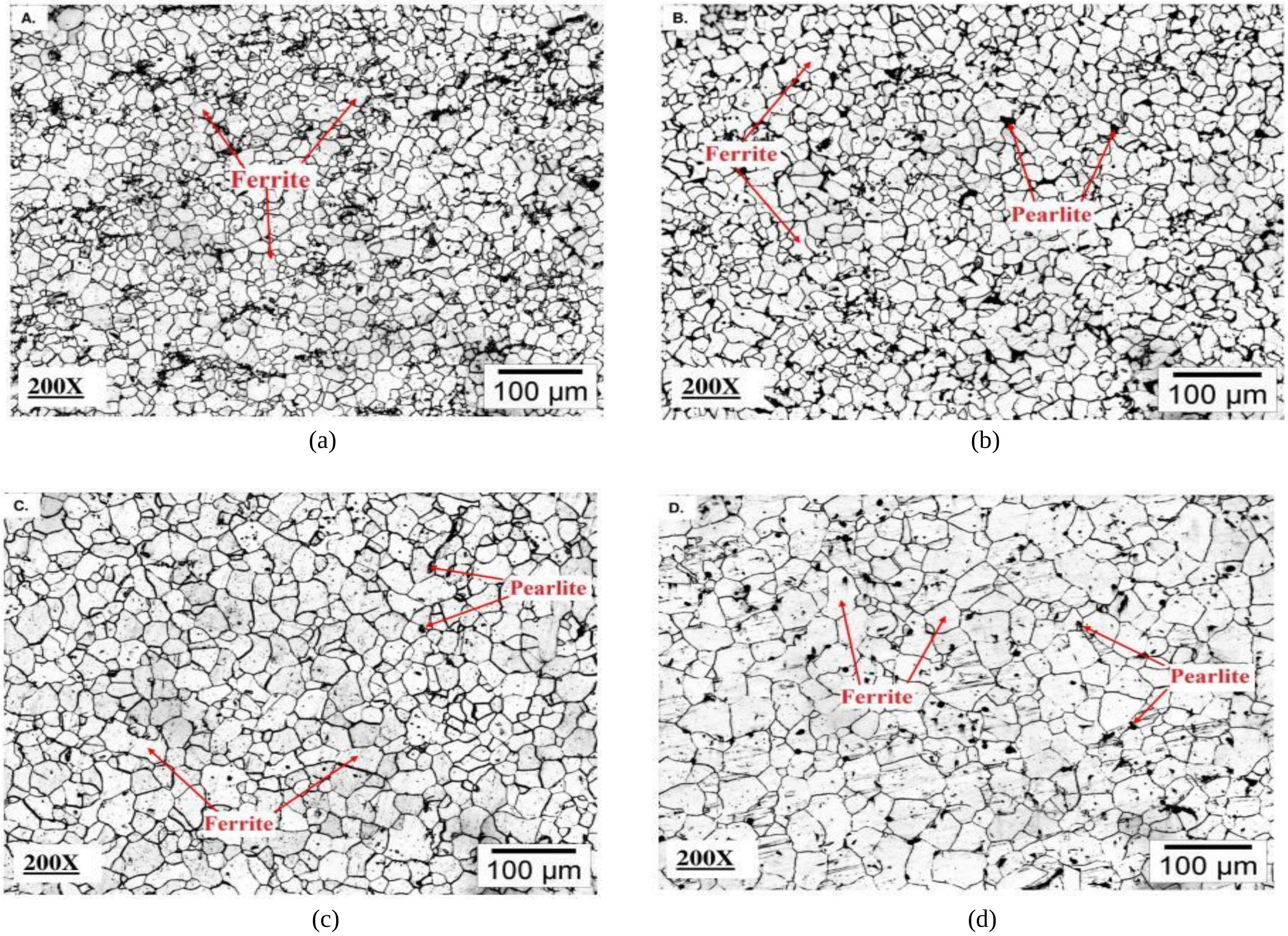


Fig. 2 Microstructures of **(a)** Bare sample, **(b)** Sample Heat treated for half an hour, **(c)** Sample Heat treated for 2 hours, **(d)** Sample heat treated for 5 hours

Grain size is measured with the help of linear intercept method, in which a straight line is drawn throughout the grain boundaries and number of grains which are intersected by the line were calculated and then by applying the formula of intercept method, average grain size is calculated. The length of the straight line is measured with the help of software used.

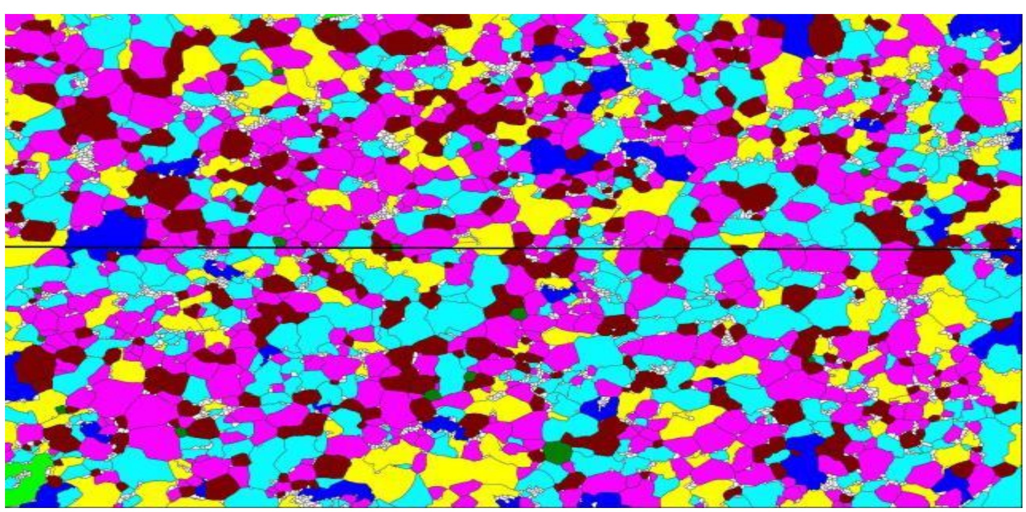


Fig. 3 Graphical representation of microstructure during calculation of grain size

Intercept formula is given by –
Average grain size = (length of the line) / (avg. number of grains) – (3)

TABLE II. AVERAGE GRAIN SIZE OF DIFFERENT SAMPLES

Sample	Bare (No Heat Treatment)	Heat treated for ½h	Heat treated for 2h	Heat treated for 5h
Average grain size (µm)	16.71 µm	19.16 µm	28.85 µm	30.90 µm

B. *Electrochemical Impedance Spectroscopy*

Electrochemical Impedance Spectroscopy (EIS) is a non-destructive testing method that is used to find the corrosion rate and corrosion resistance of a material under a given environment (usually alkali solution). EIS consists of a working electrode (sample), a counter electrode (platinum electrode) and a reference electrode, in an ionic solution (3.5 wt% sodium chloride solution in water). The potential passes between reference and working electrodes and current passes between counter and working electrodes, and, as a result, the potential difference between the applied potential at reference electrode and final obtained potential can help quantify the electrochemical impedance, and thus, the corrosion resistance of the material. [17][18]

To find out impedance/corrosion resistance, a curve is plotted between logarithm values of corrosion resistance (Ω) and frequency (Hz). If the value of impedance at lowest frequency is high then the material is considered to have better corrosion resistance.

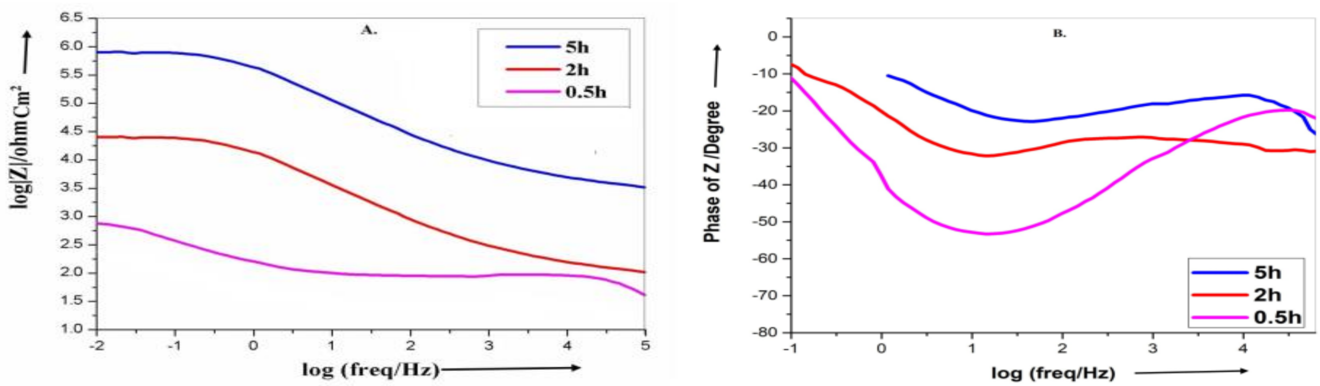
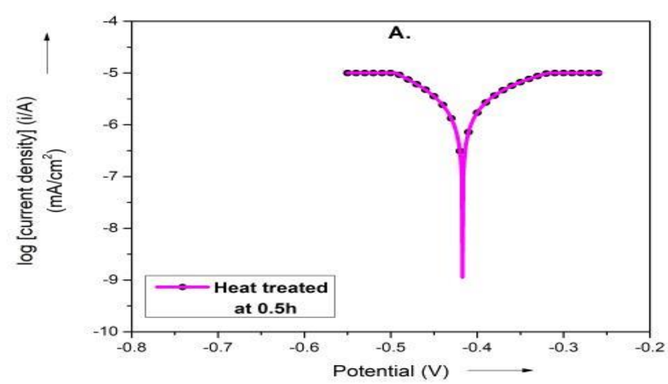


Fig. 4 EIS plots for mild steel samples heat treated for different time periods at 1000 ºC in terms of **(A.)** Impedance and **(B.)** Phase

In above graphical representation, in the impedance plot, the curve representing mild steel sample heat treated at 1000 ºC for 5 hours has highest value of impedance and the curve representing mild steel sample heat treated at 1000 ºC for ½ hour has the lowest value of impedance, which shows that the sample heated for 5h has a higher corrosion resistance as compared to mild steel sample that has been heat treated for ½h. From this, it is clear that corrosion rate decreases as time duration for heat treatment increases.



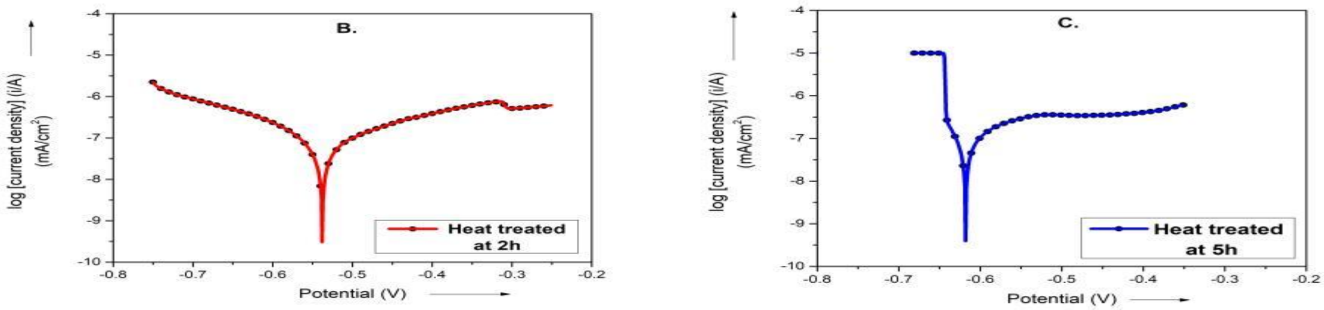


Fig. 5 EIS plots for mild steel samples heat treated for different time periods **(A.)**, **(B.)** and **(C.)** at 1000 °C in terms of current density and potential

In above graphical representation, in the current density and potential plot, the curve representing mild steel sample heat treated at 1000 ºC for 5 hours has highest negative value of potential and the curve representing mild steel sample heat treated at 1000 ºC for ½ hour has the lowest negative value of potential, which shows that the sample heated for 5h has a higher corrosion resistance as compared to mild steel sample that has been heat treated for ½h. From this, it is clear that corrosion rate decreases as time duration for heat treatment increases.

C. Hardness Test

The Rockwell hardness test is used to find out Rockwell hardness based on indentation on a material. The Rockwell test gives the information of hardness of a material by measuring the depth of penetration by an indenter under a large load as compared to the depth of penetration made by a much smaller preload.

There are different scales denoted by a single letter, which use different loads or indenters. The hardness values of the samples heat treated for different times as obtained from Rockwell Hardness Testing Method with Scale B and corresponding graphical representation is given below-

TABLE III. HARDNESS VALUES of DIFFERENT SAMPLES

Sample	Bare (No Heat Treatment)	Heat treated for ½h	Heat treated for 2h	Heat treated for 5h
Hardness (HRA)	37.225	34.7	24.95	22.65

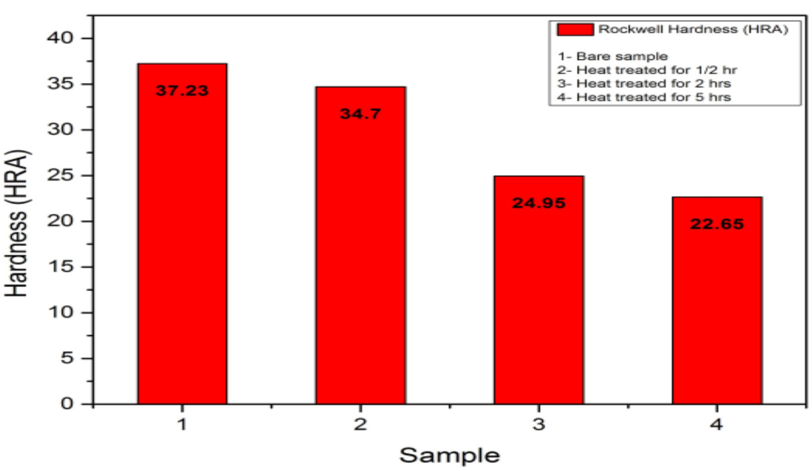


Fig. 6 Graphical representation of hardness values

IV. CONCLUSION

Through our study of the microstructure and grain size of bare mild steel that has not been heat treated, and mild steel samples heat treated at 1000ºC for 0.5h, 2h and 5h respectively, we can conclude that as the time given for heat treatment increases, average grain size also increases. This is in accordance with theoretical predictions based on past experiments. From the images of the microstructure obtained, we can conclude that all 4 samples have an equal proportion of ferrite and pearlite in their microstructure, which can help us reasonably rule out the influence of microstructural changes on the trends observed in hardness and corrosion resistance of the samples. By keeping other factors such as temperature etc. constant and only varying the heat treatment time and grain size, we have reasonably isolated the role of changes in grain size in the trends observed in corrosion resistance of a mild steel sample. The studies of hardness of these samples help us conclude that the hardness of the sample decreases as heat treatment time and grain size increases. This trend is in accordance to the theoretical predictions based on Hall-Petch Equation.

Our study of the corrosion resistance of the mild steel samples with the help of Electrochemical Impedance Spectroscopy revealed that, as the time given for heat treatment and grain size of the mild steel sample increases, corrosion resistance increases and tendency to corrode under natural environmental conditions decreases. This trend is in accordance to the theoretical predictions which anticipate that corrosion occurs preferentially in higher energy sites such as grain boundaries and will be less when grain area is large and grain boundary area is small.

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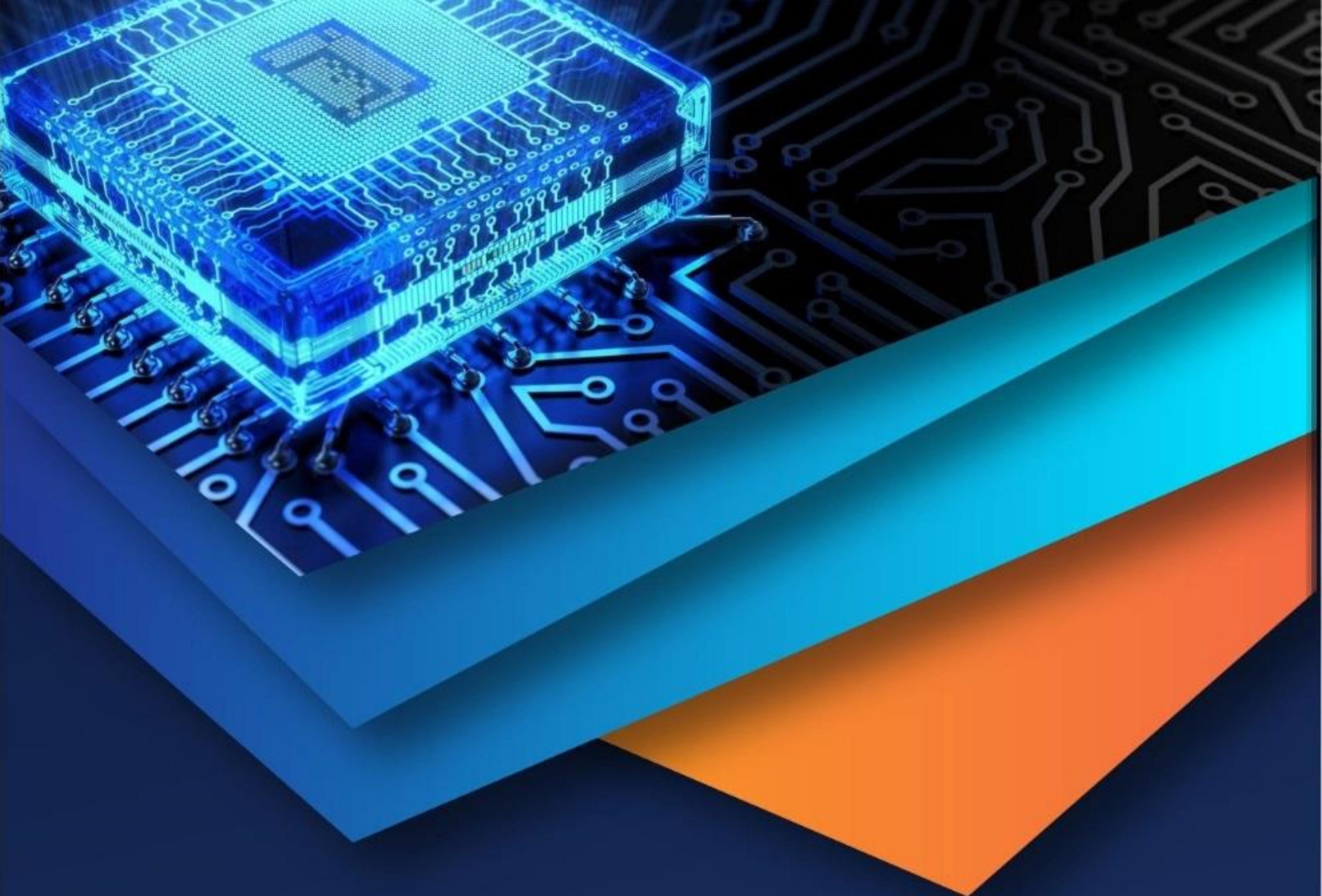

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