

Development and Characterization of Nickel-Graphene Nano Composite Coating for Corrosion Protection of Steel



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(2024)

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A thesis submitted to the National University of Sciences and Technology, Islamabad,

in partial fulfillment of the requirements for the degree of

**Master of Science in
Materials Engineering**

Supervisor: Dr. Muhammad Shahid

School of Chemical and Materials Engineering

National University of Sciences & Technology (NUST)


Islamabad, Pakistan

(2024)



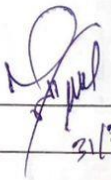
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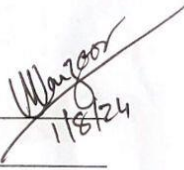
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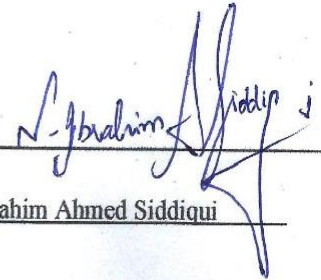
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I dedicate this thesis to My Parents & My Respected Teachers without whom I would not be here. Thanks for their endless Guidance and Support

ACKNOWLEDGEMENTS

Firstly, I would like to thank Almighty Allah, for letting me through all the difficulties. I have experienced your guidance day by day. You are the one who let me finish my degree. I will keep on trusting you for my future

I would like to acknowledge and give my warmest thanks to my supervisor **Dr. Muhammad Shahid** who made this work possible. His guidance and advice carried me through all the stages of writing my project. I would also like to thank my committee members for letting my defense be an enjoyable moment, and for your brilliant comments and suggestions, thanks to you.

I would also like to give special thanks to my family as a whole for their continuous support and understanding when undertaking my research and writing my project. Your prayers and assistance for me was what sustained me this far.

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LIST OF ABBREVIATIONS

EDX	Energy Dispersive X-Ray
SEM	Scanning Electron Microscope
XRD	X-ray Powder Diffraction
FTIR	Fourier-Transform Infrared Spectroscopy
MAO	Micro Arc Oxidation
nm	Nanometers
HVOF	High Velocity Oxy-Fuel
PEO	Plasma Electrolytic Oxidation
CVD	Chemical Vapor Deposition
PVD	Physical Vapor Deposition
ELD	Electrolytic Deposition
EPD	Electrophoretic Deposition
GO	Graphene Oxide
rGO	Reduced Graphene Oxide
mpy	Mils Per Year

ABSTRACT

Nickel is a common and abundantly found material. Nickel composite coatings have been useful in providing optimal protection against corrosion and one of the abundantly researched composite coatings. The primary focus of this research is to develop a composite coating which can provide optimal protection against corrosive environment. Graphene is a new age material and has impressive properties; incorporation of graphene nano particles in nickel matrix provides better corrosion resistance and surface roughness as compare to pure nickel coatings. Graphene oxide (GO) was first reduced by hydrazine hydrate and then used for developing composite coating. Reduction of graphene oxide to reduced graphene oxide (rGO) was confirmed by SEM, XRD and FTIR. Electrochemical deposition technique was used for developing nickel-graphene composite coatings on steel substrate. Composite coatings were developed at different deposition current densities 3.6Adm^{-2} , 9Adm^{-2} and 14.5Adm^{-2} at 45°C with constant stirring at 400 rpm. The developed coatings were characterized by SEM, EDX and XRD. Three application testing Polarization Testing, EIS and Two Dimensional Non-Contact Profilometry (roughness assessment) were carried out to find the efficiency of developed composite coatings. SEM results showed a spherical morphology and bulges which increased with an increase in deposition current density. Coating developed at higher deposition current density 14.5Adm^{-2} displayed more number of bulges as compared to others. EDX result showed an increase in amount of carbon content in coatings with increase in deposition current density. XRD results showed a reduction in grain size with increasing deposition current density and reduction in (200) peak. Corrosion rate of composite coating in 3.5% NaCl solution was found by electrochemical polarization testing; coating developed at high deposition current density showed low corrosion rate as compared to coatings developed at low deposition current densities. EIS was carried out in 3.5% NaCl solution and EIS spectra showed semi-circles of different diameters depending upon the deposition current density. Coatings developed at high deposition current density exhibited semi-circle of larger diameter indicating higher impedance of developed composite coatings. Roughness assessment of composite coating was done by Two Dimensional Non-Contact Profilometry and roughness in terms of R_q (root mean square roughness) and R_a (average roughness) were found and roughness increased with an increase in deposition current density.

CHAPTER 1: INTRODUCTION

1.1 Corrosion

No material can remain stable for long period of time; the rate of degradation of materials is influenced by the type of material and their environment [1]. Just as human body can't handle temperature above 50 degree Celsius or below 20 degree Celsius, significant variation from atmospheric pressure and exposure to harmful gases like H₂S, H₂ and CO; material also need protection [1, 2]. Such protection comes in the form of coatings, routine maintenance, design-specifications, and addition of alloys, inhibitors, routine inspections and refurbishments [3].

Increasing the life of material and minimizing their susceptibility to corrosion is very useful. Increasing the life of materials provides the optical performance for longer period of time and also minimizes the costs [4]. Potential hazards and premature failures can be prevented by keeping the materials corrosion-free and can ensure optical performance of materials. It is also beneficial in terms of environment friendly as waste product is reduced and need for time to time replacement [3, 4] .

Effects of corrosion are not just the simple degradation of material, it also affects the performance, durability, safety and dependability which leads to the need for replacement of material and results in economic loss. Even a slight degradation of material due to corrosion can cause functional disruptions and severe breakdown. With corrosion not only a concern regarding loss of material and its performance comes but also economic challenges play their role [4].

1.2 Types of Corrosion

1.2.1 Atmospheric Corrosion

The loss of material or the degradation of material when it interacts with the environment is known as atmospheric corrosion, this type of corrosion is most common and cost more than any other [5]. This form of corrosion effects wide range of materials such as metals, alloys and also polymers. Atmospheric corrosion occurs mainly due to the following reasons [6]:

1. High humidity
2. High moisture
3. Different pollutants in air
4. High temperature
5. Heavy rainfall
6. Presence of different salts in environment

For effective prevention of such type of corrosion it is very important to understand these factors. For prevention of such corrosion, protective coatings and paints can be developed, use of such materials which are corrosion resistance such as stainless steel or aluminum can be maximize, limiting the time of interaction of materials and equipment to harmful environment, regular maintenance and inspection of materials will also be useful for reducing corrosion and replacement of corroded part with fresh one is also useful but may cost more but can prolong the life of material [7, 8].



Figure 1.1: Atmospheric corrosion effects in industrial sector [9]

1.2.2 Galvanic Corrosion

This form of corrosion is also known as two-metal corrosion or bimetallic corrosion [1]. It is an electrochemical form of corrosion which occurs when two different metals

are in electrical contact with each other in the presence of an electrolyte and one metal corrodes faster than the other [10]. It is known to us that every metal has its own electrochemical potential and when two different metals comes in contact with each other the metal with the higher potential act as cathode and the one with lower potential acts as anode [11]. Oxidation process (corrosion) occurs at anode, which cause the release of metal ions and electron formation in the electrolyte. These electrons then flow towards cathode through electrical circuit where reduction (reduction of oxygen) process occurs. With occurrence of these things an accelerated corrosion takes place at anode [11, 12].

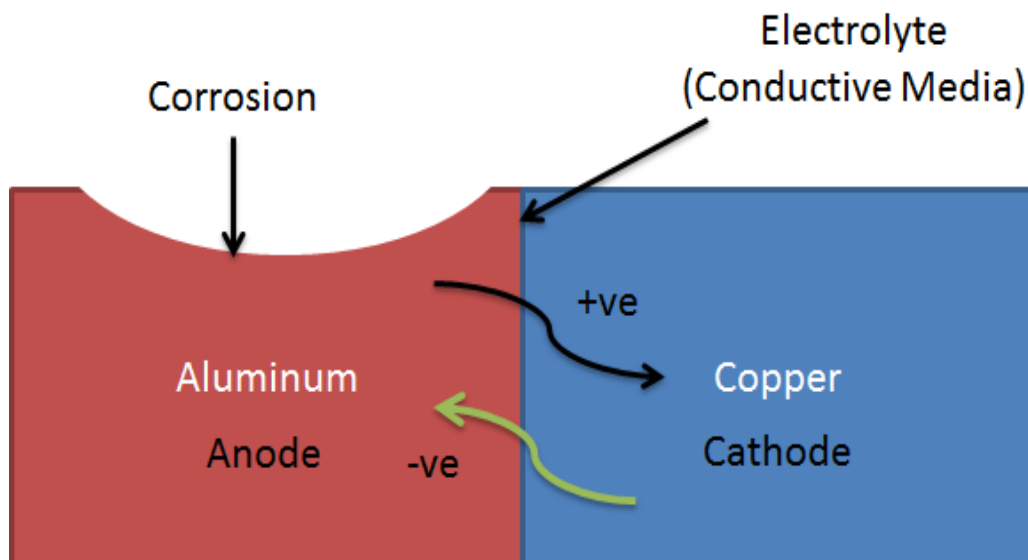


Figure 1.2: Mechanism of galvanic corrosion [9]

For prevention of galvanic corrosion non-conductive barriers such as gaskets, coatings or paints should be used to separate two materials, regular inspection should be carried out to inspect for the signs of galvanic corrosion, selection of materials should be made very carefully so that such metals which have high potential difference doesn't come in contact with each other and such designs where small anodic area are in contact with large cathodic areas should not be used [13].

1.2.3 Crevice Corrosion

It is a localized form of corrosion which happens in the areas of metals which are sheltered or in narrow gaps between the metals when the material is subjected to a corrosive environment [13, 14]. Crevice corrosion is very dangerous as it may initiate unnoticeably and propagates significantly which can lead to severe failure and damage of material.

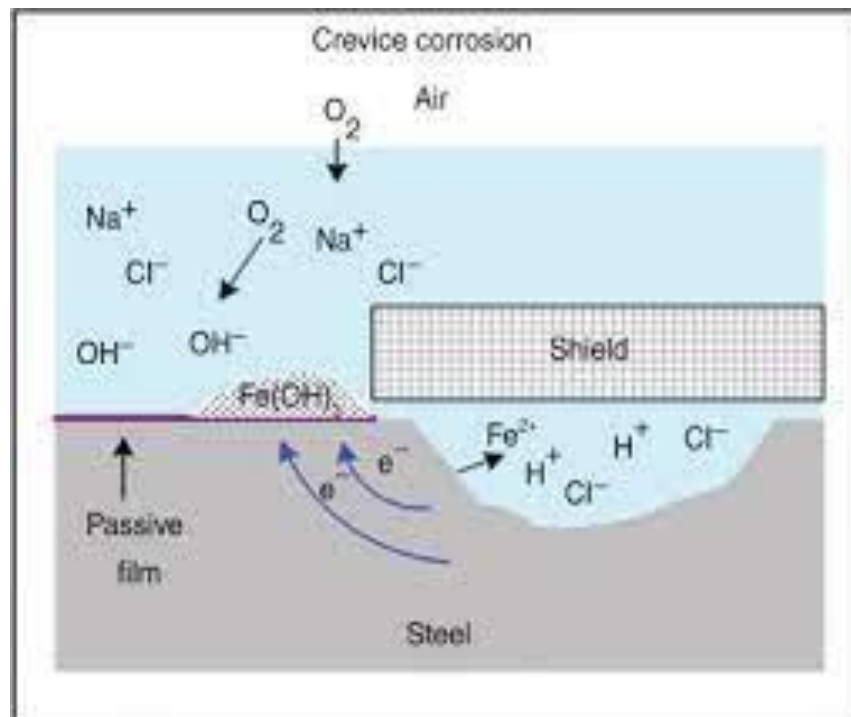


Figure 1.3: Mechanism of crevice corrosion [9]

Crevice corrosion mainly occurs due to the difference of concentration of ions and oxygen between the environment and the crevices (narrow gaps between two metals) [15]. An oxygen concentration cell is formed when metal is exposed to the corrosive environment and due to the formation of initial oxide layer by which depletion of oxygen occurs in the crevice areas. Outside of crevice area remains rich in oxygen and act as cathode while the inner area act as anode and has lesser oxygen concentration. This difference of oxygen concentration sets up the electrochemical cell and in the inner area other metal cations and anions start to accumulate which leads to faster corrosion rate [15, 16]. Crevice corrosion can be avoided or prevented

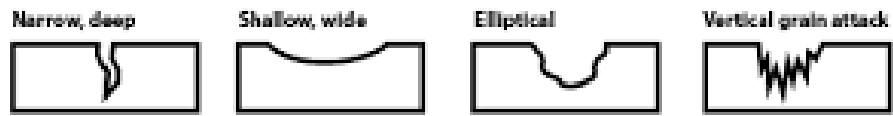
by using materials which are more resistant to such type of corrosion such as stainless steel, titanium and nickel alloys, by selecting the designs where there is no unnecessary gaps, undercuts, welds and overlaps, by developing coatings which offers more resistance and regular inspection and maintenance [17].

1.2.4 Pitting Corrosion

It is also another highly localized type of corrosion that can form small pits and holes on material surface [13]. Pitting corrosion affects the structural integrity of material with very less material lost which makes it more harmful than other forms of corrosion [18]. Pitting corrosion initiates from the defects and imperfections in the protective coating/film on the surface of material. The protective coating can be break down due to the presence of harmful anions and anodic sites will be formed [19]. Pits will be formed at that anodic sites and some of them can re-passivizes spontaneously and some of them can grow to become stable pits. Whenever a pit becomes stable the inside environment of pit is highly acidic which accelerates the dissolution of metal. After sometimes the concentration metal cations inside the pit starts to increase which can lead to crevice corrosion and may lead to reduction of pH and more aggressive environment is created inside the pit. The opening of the pit gets covered with corrosion product and this will also lead to further isolating the internal environment and pits will be grow continuously [20, 21].

TYPES OF PITTING CORROSION:

TROUGH PITS



SIDEWAY PITS



Figure 1.4: Different types of pitting corrosion [9]

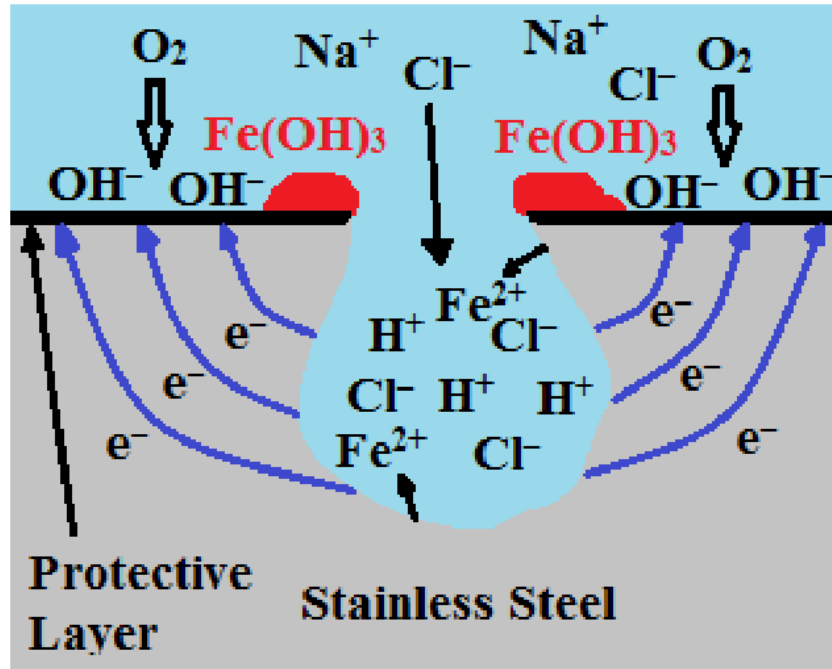


Figure 1.5: Mechanism of pitting corrosion [9]

1.3 Coating Methods

Depending upon the need of different industries there are various types of coating methods. These methods are different from one another in terms of their time of duration, materials structure, in terms of end results, how well it works and the effectiveness of coating produced [22]. There are some coatings which are developed to give protection against corrosion and wear. Due to corrosion material gets weaker and the corroded bits can create even more corrosive conditions [23, 24].

Different types of coatings are deposited in different ways and it is important for us to know their strength and limitations for some specific job [25]. There are various ways in which coatings are deposit, some of the best methods are PVD, CVD, MAO, Sol-Gel, Thermal spray and using polymers [25, 26]. Each of these methods is very good and they formed coatings of various thicknesses and are used for specific purpose. While choosing a coating it should be kept in mind that whether it will be useful or not ,will it be safe for medical use or not, will it prevent rust or not and will it improves material properties or not [27].

With the advantage of giving protection and other benefits to materials, there are some disadvantages. Like sometimes in high temperatures applications they react badly and it causes them to crack and peel off from the surface of material. If coatings are not well protected from air and environment dirt and other contaminations will get in and affect them. It is important for us to understand and know about the properties of various coatings before implementing them [28].

Material selection is the very important for getting a good coating in terms of performance and desired properties. Choosing the right material is the key for getting the optimal protection and desired performance. Different materials ranging from metals, ceramics and polymers are used to get protective coatings and they bring unique properties which are useful in various applications [29]. Metallic coatings offers durability and strength, ceramic coatings offer heat resistance and polymer coatings provide flexibility and adaptability. That is why it is very important to understand the requirements and need before developing the coatings [30].

1.1.1 Physical Vapor Deposition (PVD)

By PVD technique we can get a thin uniform protective layer on a material which can shield it from corrosion and wear. Besides giving only the protection this thin layer can also be used for decorative purpose [31]. PVD method is very versatile and its unique characteristic is its adaptability we can modify the strength, corrosion resistance, look of coating and also their properties depending upon our need. This technique is not limited it can be used on everything from decorative items to heavy duty industrial machinery. PVD method works in high vacuum environment in which first the material is converted into vapor phase and then this vapor is condensed to form a thin and dense coating on a material [32]. Two most common types of PVD methods are evaporation and sputtering. The coatings prepared by PVD technique are very thin in nature so there is always a need for multilayered coatings. Material selection is also the key of getting desired results. Many components coated by PVD method used in conditions where they face constant wear and tear. This constant friction can remove the protective coating and when this protective layer of coating is removed the resistance against wear and corrosion will be minimized and they are more prone to corrosion [32, 33].

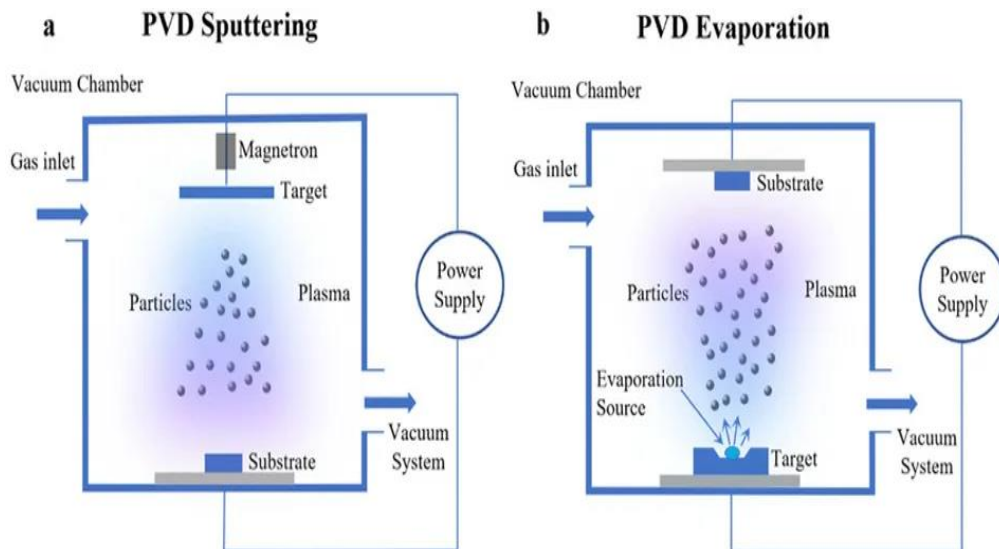


Figure 1.6: Sputtering and evaporation PVD process [28]

1.3.1 Chemical Vapor Deposition

It is another type of vapor deposition technique. This technique provides high resistance, high quality layer of coating on the material. CVD technique is mostly used on mechanical parts which are constantly in contact with each other and may wear out and corrode [34, 35]. CVD has wide range of applications in semiconductor industry as it provides uniform coating. In this method the material on which coating is needed is exposed to volatile material precursors and different chemical reactions occur on it. As a result of these chemical reactions a coated layer gets deposited on the substrate. Some by products are also formed due to the chemical reaction and these by products are removed by the constant air flow of the vacuum pump and remain in the chamber [36, 37]. CVD is carried out in three different categories which are [38]:

1. Atmospheric pressure CVD
2. Low pressure CVD
3. Ultra high vacuum CVD

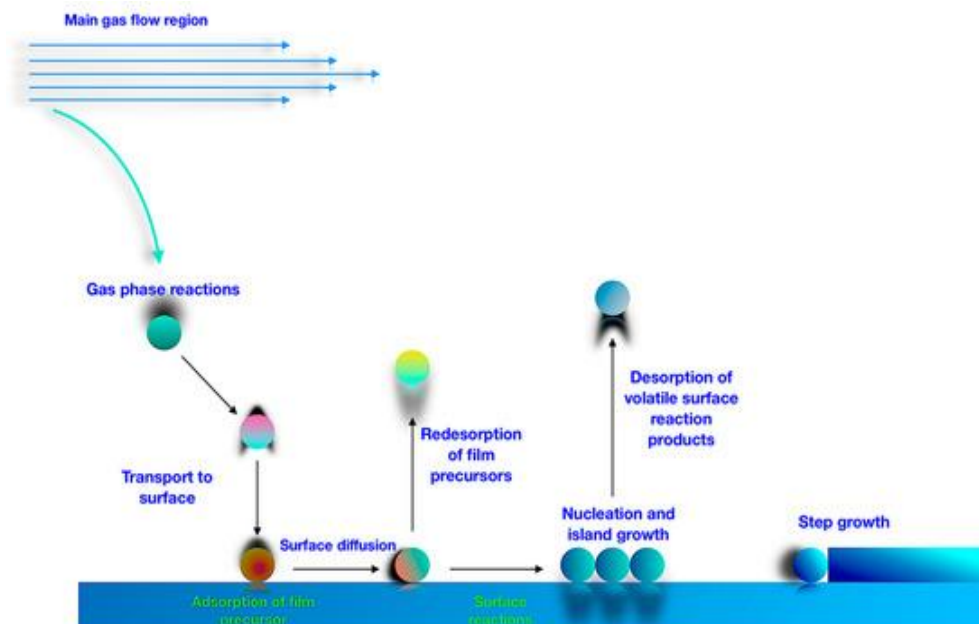


Figure 1.7: CVD coating process [28]

1.3.2 Micro-Arc Oxidation Coating (MAO)

It is a flexible coating process also known as plasma electrolytic oxidation (PEO). This process is used to develop ceramic coatings on metal surfaces, mainly aluminum,

magnesium and titanium. The coatings develop by this process increase the corrosion resistance, wear resistance and thermal resistance [39]. In MAO the metal substrate is first cleaned to remove any kind of contamination and impurity which will affect the adhesion of oxide coating and then it is submerged in an electrolyte bath which contains a mixture of chemicals. The metal substrate is connected with the external power supply and is acting as anode and another electrode as cathode, when high voltage is applied the oxide coating begins to form on the metal surface which is acting as an anode. Thickness of oxide layer increases with time and it starts acting as an insulator and when the oxide coating layer insulating properties reach a certain value, the voltage applied leads to dielectric failure and results in localized plasma (micro-arc) discharge [40, 41].

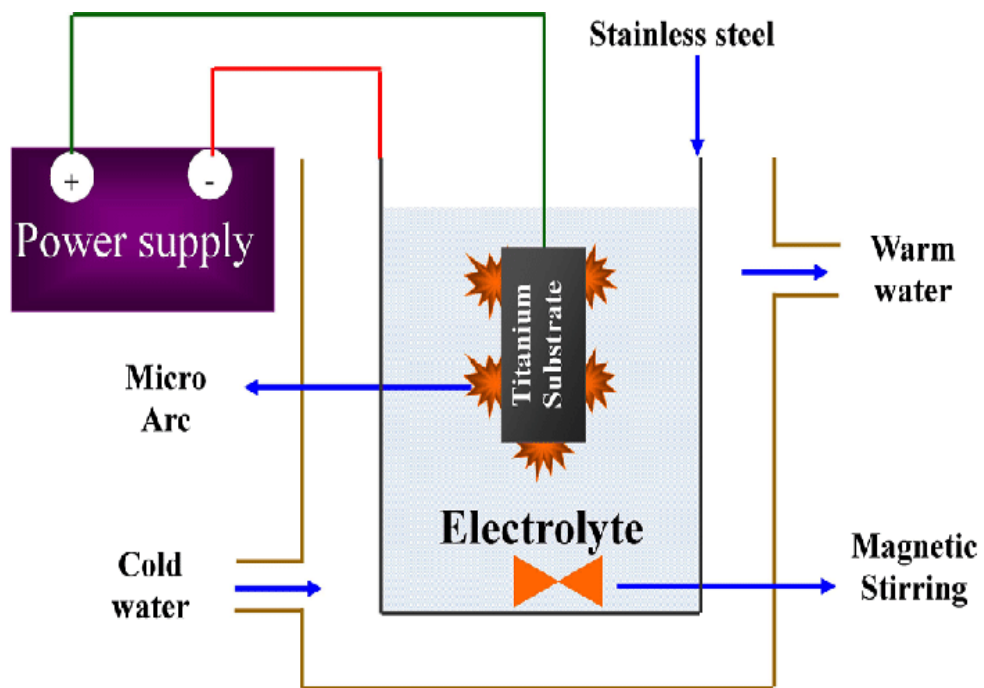


Figure 1.8: MAO coating setup [28]

1.3.3 Cold Spray Coating

This is solid state process. Cold spray is a coating technique which unlike other coating techniques does not require and kind of heat source to get the coating material in molten or semi-molten state. Coating material used in this method is in powder form and instead of heating, high velocity impact is used to achieve the bonding [42].

The material that is used to make coating is in powder state and is introduced in a high velocity gas stream. The gas can be helium, nitrogen or air. This high velocity gas stream is first preheated to increase the acceleration of particles but temperature is kept below melting point of particles. These accelerated particles are then propelled towards the substrate at supersonic speed, where upon impact they undergo plastic deformation which leads to adhesion of these particles on the substrate [43]. The coatings developed by this process are useful for protection against wear and corrosion, for enhancement of conductivity and repairing of components [44].

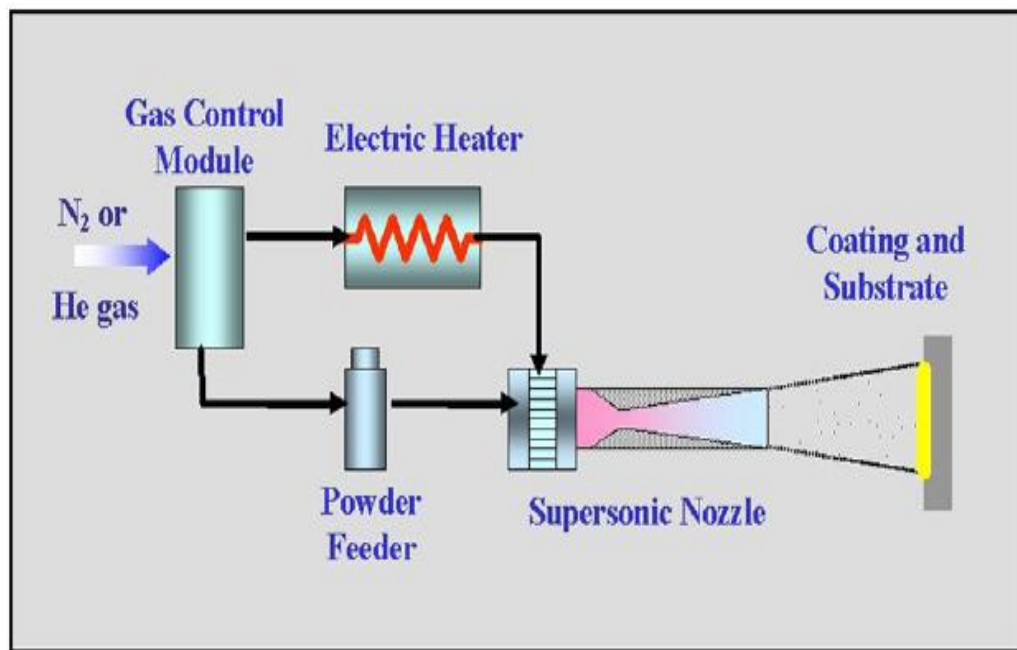


Figure 1.9: Cold spray coating process [28]

1.3.4 Sol-Gel Coating

For developing inorganic and hybrid organic-inorganic coating sol-gel is very versatile and widely used method [45]. In this method there is transition from liquid phase (solution) into solid phase (gel). Sol-gel process starts with the preparation of a colloidal suspension by mixing a metal oxides or metal chlorides in a solvent generally alcohol. After which water is added, due to which hydrolysis reactions starts up and metal precursors reacts to form metal hydroxides. Then poly-condensation reaction occurs which leads to the formation of three dimensional networks of metal–oxygen-metal bonds which converts the solution in to gel [46]. With various methods like spin coating, dip coating or by spray coating this solution is applied is applied on

to the substrate and after evaporation of liquid the solution starts to become gel and forming a continuous coating/thin film on to the substrate. This gel is then dried to remove the remaining liquid and after drying it starts to become dense. This process allows us to develop coatings which are uniform in nature and defect free in nanometer range [47, 48].

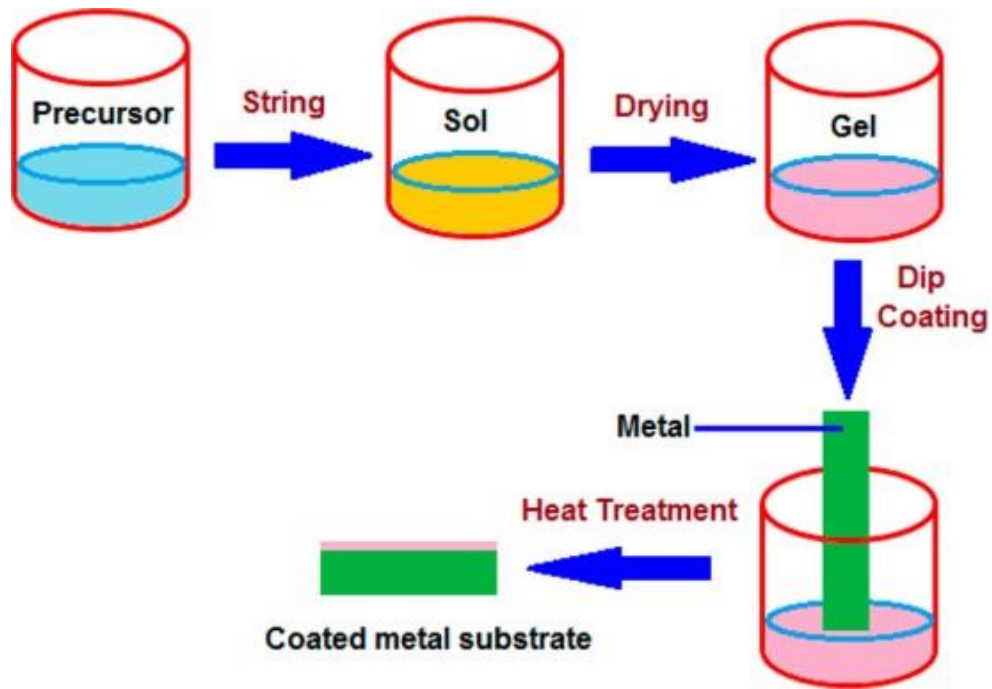


Figure 1.10: Sol-Gel coating flow diagram [28]

1.3.5 High Velocity Oxy Fuel Coating (HVOF)

High velocity oxy-fuel (HVOF) coating is the type of thermal spray process which is used to develop coatings with high level of adhesion, low porosity and very dense which makes them very useful for wear resistance and corrosion resistance [49]. HVOF is very helpful in restoring and improving components surface properties or dimensions. This method has wide range of applications in oil and gas industry, aerospace industry, paper and printing industry and automotive industry etc. In this method the mixture of fuel (gases like hydrogen, propane, propylene, acetylene or kerosene) and oxygen are ignited in the combustion chamber where high temperature and high pressure combustion gases are produced [50]. The coating material which is in powder form is introduced into the stream of high temperature gases. This stream of high velocity gases accelerates the semi-molten particles from the nozzle towards

the substrate. On bombardment with the substrate these semi-molten particles forms splats, these splats interlock and grow upon one another to form the coating [50, 51].

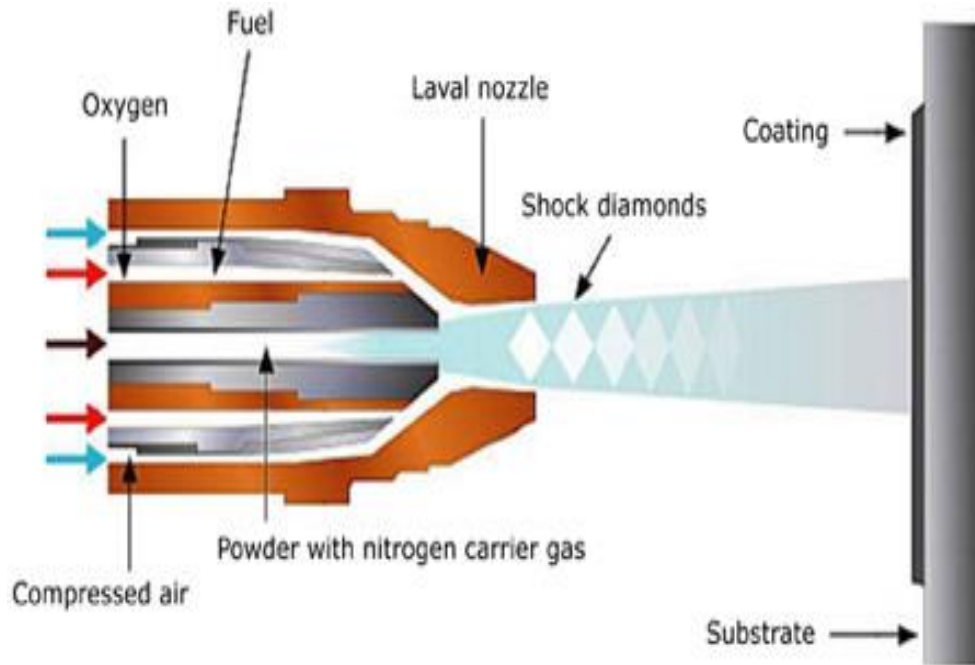


Figure 1.11: HVOF coating mechanism [52]

1.3.6 Plasma Spray Coating

This type of coating is done under vacuum or atmospheric conditions. Plasma spray coating is a very flexible process which can facilitate the different kinds of feedstock such as powder, slurry, liquid and suspensions [53]. The coatings developed by this process are of very high corrosion and wear resistance and are very strongly adhere to the surface of substrate due to high surface tension and very high temperature [54, 55]. In plasma spray coating a plasma gun can provide very high temperature up to 10000k which can easily melt polymers, ceramics and refractory metals. The materials which are used for the stabilization of plasma can be gas or water and the mixture of these two which is known as hybrid plasma. The coating material or feedstock is fed into the stream of high temperature plasma where they are melted and due to the high velocity of plasma stream at the tip of converging nozzle the molten droplets are deposited on to the substrate, where they cool down and form a denser coating [56, 57].

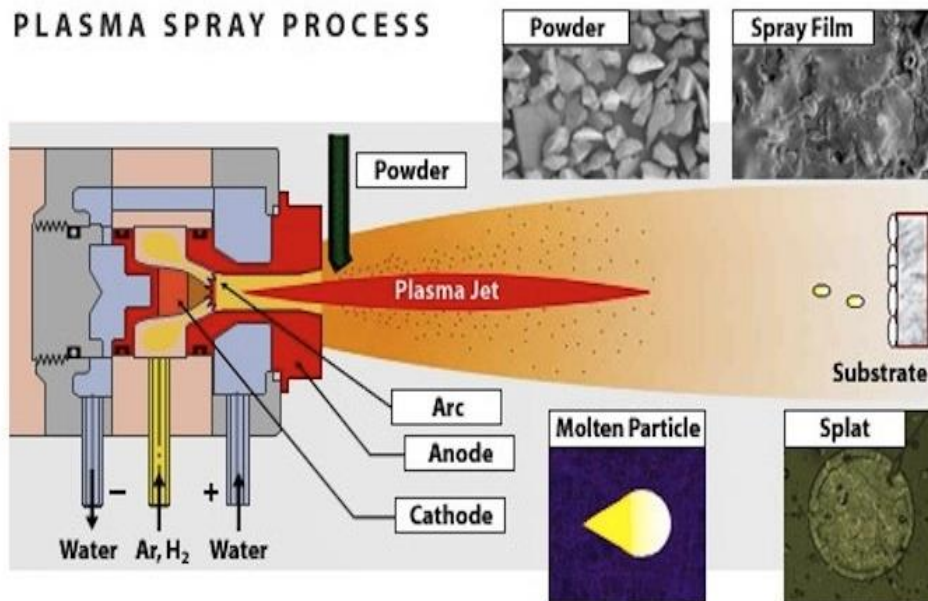


Figure 1.12: Plasma spray coating process [52]

1.3.7 Arc Wire Spray Coating

Arc wire spray coating is the type of thermal spray coating. In this method two wires of coating materials which are electrically charged and have opposite polarity are introduced into the spray gun. When these wire of oppositely charged come together at the tip to the gun an electric current arcs between them which generates a significant heat which melts the tip of the wire [58]. During this process feedstock (wire) are continuously fed into the gun and an atomizing gas introduced around the arc which propels the molten metal towards the substrate at high velocity. When these molten particles bombard with the substrate they flatten and solidify on the surface of substrate to form the coating layer. This process is very useful as it is very economical in terms of feedstock, deposition rate is very high, low input heat is generated and variety of metal and metal alloys can be applied by using this method [59, 60].

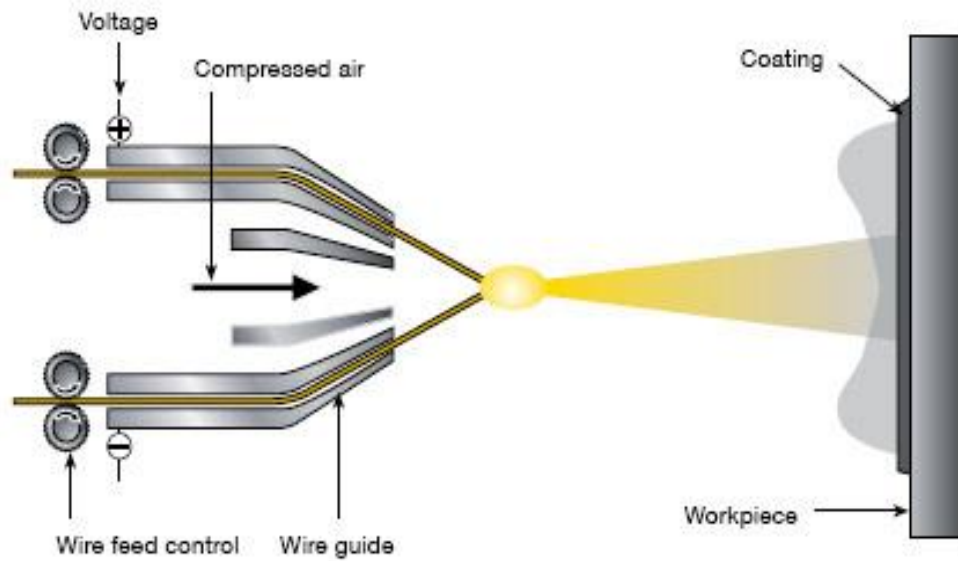


Figure 1.13: Arc Wire Spray coating technique [52]

1.3.8 Electrochemical Deposition Coating

This method is also known as electroplating or electro coating, in this method we use electric current to reduce the cations of desired material from the solution and coat a conductive substrate with the thin layer of material. In this technique the substrate which is to be coated is known as cathode which is connected to the negative terminal of electrical power supply, is dipped into the electrolytic solution which contains different metal ions depending upon the coating which we want to develop. Another electrode which is also immersed into the electrolyte and connected to an electrical circuit at positive terminal is called as anode. When electric current flows in the circuit, metal cations start to reduce at the cathode from the solution and are deposited as a thin layer on the cathode surface. Anode may also be consumed during the process depending upon the metal being used and the purpose of plating [61-63].

Electro-deposition method can be used to develop highly uniform coatings, even in recessed areas. If current and time are controlled then the thickness of deposited coating can be carefully controlled. By this method we can develop coating with enhanced corrosion resistance, wear resistance, reflectivity, electrical conductivity and appearance [64].

There are two types of electro-deposition techniques which are commonly used:

1. Electrolytic deposition (ELD)

2. Electrophoretic deposition (EPD)

1.3.8.1 Electrolytic Deposition (ELD)

During this process metal ions present in the solution or electrolyte are reduced to their metallic form with the application of electric current through the solution. And then this metal starts to deposit on the electrode which is acting as cathode in the process [65]. Electrolytic deposition is a process which is widely used in industries to coat on metal over another to increase the aesthetic appearance, corrosion resistance, wear resistance, reduced friction and other properties which are needed. This process is very versatile and has high deposition rate than many others and is currently used in many industries like automotive, electronics, jewelry, aerospace, semiconductors and many more [66, 67].

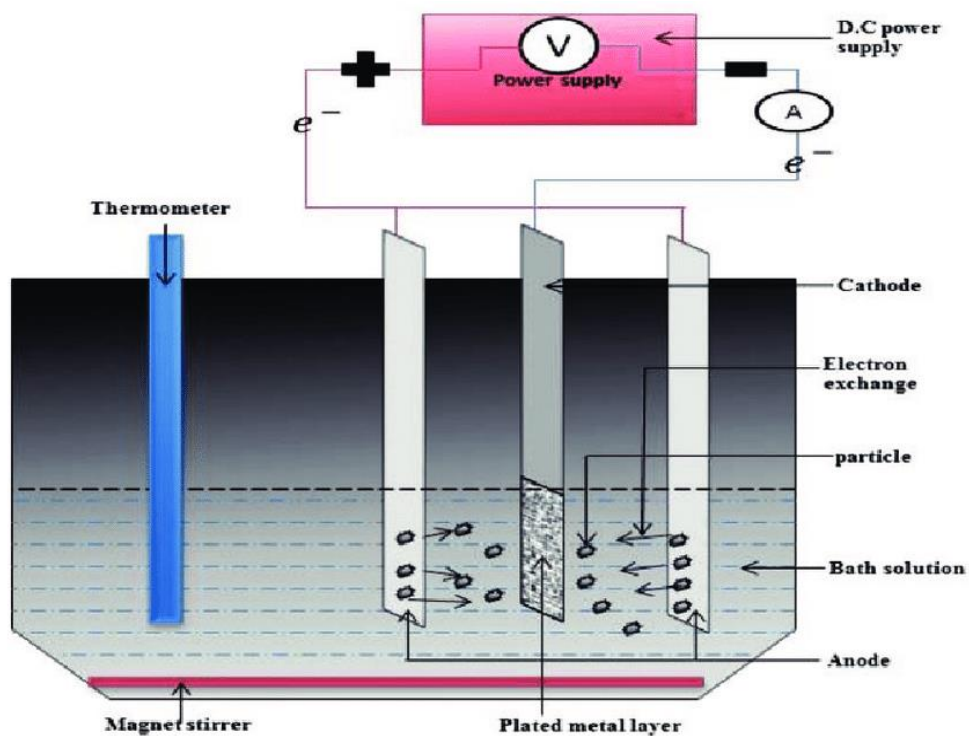


Figure 1.14: Electrolytic deposition setup [68]

1.3.8.2 Electrophoretic Deposition (EPD)

Electrophoretic deposition (EPD) is a type of electroplating technique in which charge particles are suspended in some liquid and when electric current is applied they

deposited on the electrode surface which is acting as cathode in the circuit. This process is different from the electrolytic deposition in a way that there is charge particles are suspended in the solution unlike electrolytic deposition where metal ions from the solution gets reduce to form metallic coating on electrode [69, 70]. A suspension of colloidal particle which can be metals, ceramic, polymers or even the combination of either is made in some suitable liquid. These particles are charged because of the ionization of functional groups of surface. Similarly, two electrodes one as cathode on which coating is needed and other as anode are placed in the suspension. When voltage is given to the system the charge particles in the suspension migrate towards the cathode and lose their charge and layer of coating will developed on it. After the deposition the coated substrate may undergo heat treatment and post processing procedure to improve the properties coating [71].

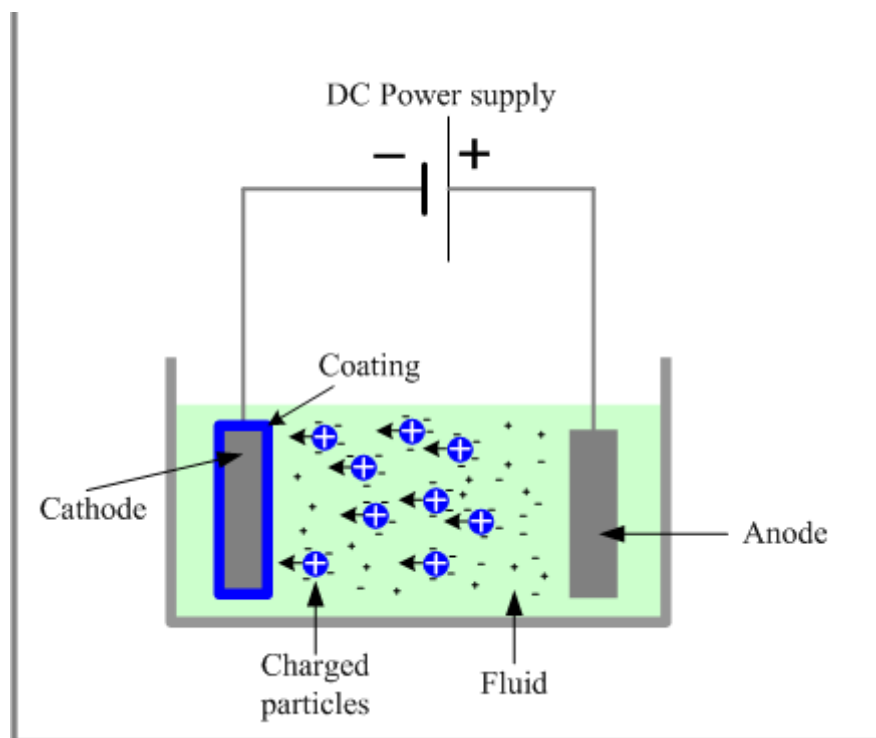


Figure 1.15: Electrophoretic deposition setup [68]

1.4 Research Gap

As we already know that nickel is a very useful material for corrosion resistance. Nickel coatings have been developed many times before for giving optimal protection to materials against corrosion and wear. Now a day nano composite coatings are developing and these coatings provide not only protection but also other properties which are beneficial to proper functioning of that material. Graphene is the modern era material which has excellent properties. The combined effect of nickel and graphene in the field of corrosion protection haven't been properly explored yet and very limited data is available in scientific research. The effect of nickel-graphene nano composite coating in terms of corrosion resistance and effect of deposition current density on corrosion resistance, carbon content, surface roughness and surface morphology are investigated in this research.

1.5 Research Objectives

The process of developing an efficient nickel-graphene nano composite coating for corrosion resistance of steel is very interesting and multi-functional. The first thing that needs our focus is to prepare a well-balance mixture of nickel and graphene which should be suitable and used as an electrolyte in electro deposition method for coating of steel. The electrolyte should be of good quality and consistency as it will lay down the foundation of coatings which we will make. After the preparation of electrolyte steel substrate will be immersed in electrolyte and electrochemical deposition process will be started. Steel sample will be connected to external power supply and coating will be carried out at different current densities. With changes in deposition current density it is assumed we can vary the overall composition, surface morphology, surface roughness and corrosion resistance of coated samples.

By following this procedure we will be able to develop nickel-graphene nano composite coated samples and they would be able to give optimal protection against corrosion. It will be our primary focus of study to analyze that whether preparing coated samples at different deposition current density shows improvements in resistance against corrosion or not. Similarly, we will measure carbon content in each coated samples. It is known to us that graphene is primarily made up of carbon and its bonds with other elements, so by measuring the carbon content of coated samples it will provide as with insight whether or not current density affect the amount of carbon

content. Microscopic assessments of each coated sample of different deposition current density will be carried out to observe variations in terms of smoothness, uniformity, structure and patterns which will be very important in determining optimal conditions/parameters for deposition current density.

After getting optimal corrosion resistance, analyzing the amount of carbon content which is required and determining surface roughness and morphology we can be able to recommend the most effective deposition current density and other parameters which by our believe will helps in preparing robust and efficient nickel-graphene nano composite coating for corrosion protection.

1.6 Objectives

1. Preparation of nickel-graphene nano-composite coating on steel substrate by electro deposition technique.
2. Electrochemical Tafel plots for bare and coated samples
3. Electro chemical impedance spectroscopy (EIS) and polarization testing (Tafle curves) of coated and uncoated samples.
4. Roughness measurements of nano composite coatings.
5. XRD and FTIR analyses to characterize the coatings
6. Determination of Carbon content in coated samples and surface morphology of these samples.

CHAPTER 2: LITERATURE REVIEW

2.1 Applications of Steel

Steel has excellent mechanical properties and wide range of applications in numerous industries. Strength and wider range of properties makes it very important material. Despite of these characteristics when it interacts with environment of high humidity, high pH and high temperature it becomes vulnerable to corrosion attack [72]. There is a protective layer on steel which protects it from corrosion but in such harsh conditions this layer gets compromised and optimum protection is not provided by this layer. For this reason, to take preventive measurements there should be some kind of protective coating layer on steel structures which can provide optimum protection, increase the life span and structural integrity should be maintained [73, 74].

Steel is a very versatile material in terms of its excellent mechanical properties and cost effectiveness which makes its first choice of material for outdoor structures. Many outdoor equipment of our daily usage are being made by steel such as benches, lamp posts and sports equipment. Now a day we can see steel is being used in construction of bridges, railway lines, skyscrapers, highway infrastructure and automobile production [75].

Due to the extensive use of steel in outdoor applications there will be the large ratio of the steel structures which will be subjected to the harsh environmental conditions. In urban areas pollution level is high which can cause accelerated corrosion of steel and makes it more pronounce. Corrosion process gets accelerated by emission of sulfur compounds from automobiles and harmful industrial waste which is emitted out in atmosphere [75, 76].

Some of the widely use types of steels are enlisted in table 1 along with their properties and applications [77].

Table 2.1: Applications and properties of various types of steel

Type of steel	Properties	Applications
Carbon steel	Varying carbon content affects hardness.	<ul style="list-style-type: none"> • Building construction • Dies • Springs • Punches • Car body parts
Stainless steel	Resistant to corrosion due to chromium content	<ul style="list-style-type: none"> • Aircraft construction • Tankers • Vessels • Food and catering industry
Alloy steel	Contains additional elements like nickel, chromium, or molybdenum	<ul style="list-style-type: none"> • Pipes • Offshore structures • Railway lines • Aerospace bodies
Electrical steel	Optimized magnetic properties	<ul style="list-style-type: none"> • Electromagnetic device cores • Transformers • Generators
Spring steel	High yield strength, returns to original shape after bending.	<ul style="list-style-type: none"> • Coils • Compression springs • Leaf springs • Surgical tools
Mild steel	Ductile, can be welded and not very hard.	<ul style="list-style-type: none"> • Machinery parts • Fencing • Gating • Cookware
Manganese steel	Extremely high toughness and wear resistance	<ul style="list-style-type: none"> • Rock crushers • Shovel buckets • Elevators • Cement mixers
Tool steel	Hard, resistant to abrasion, and able to hold a sharp edges.	<ul style="list-style-type: none"> • Dies • Gears • Vinyl window frames

		<ul style="list-style-type: none"> • Metal stampings
High speed steel	Retains hardness at high temperatures.	<ul style="list-style-type: none"> • Drill bits • Tool bits • Cutters • Blades • Punches and dies
Weathering steel	Forms a protective rust layer when exposed to weather.	<ul style="list-style-type: none"> • Coal mining machines • Construction machines • Engineering machines • Bridges • Containers

2.2 Corrosion of Carbon Steel

Carbon steel has impressive mechanical strength and inherent properties which makes it very good choice of material for safely handling and storing of radioactive waste materials. Carbon steel can bear high stress, pressure and wear which is the main reason for using carbon steel container for storing radioactive waste as it will prevent any leaks and breaches [78]. Radioactive waste contains chemicals and compounds which are very aggressive in nature and can cause corrosion of material with time, but carbon steel has superior corrosion resistant properties which are very important in such applications. These properties of carbon steel makes it primary choice for such applications where radioactive waste is stored safely and both human health and environmental risk is reduced [78, 79].

Over the time many researchers have penned various article and segments regarding the degradation of carbon steel because of corrosion. About half of the world's total population lives in the coastal areas and many developing and industrial countries setup their production plants in areas which are close to sea. Carbon steel tends to corrodes in many atmospheric exposures [80]. The preference of carbon steel over other materials is not due to its corrosion resistance property but because of economic benefits, ease of fabrication, robustness, mechanical strength and cost effectiveness [81]. Carbon steel when comes in interaction with nitrates, ammonia, hydrogen

sulfide and hydroxides there is a risk of stress corrosion cracking and also the presence of evolved hydrogen may cause carbon steel to become weak and form blisters [82, 83].

According to Tiwari et al. carbon steel has excellent strength but it is also susceptible to corrosion attack. This limitation of carbon steel becomes very prominent when it comes in contact with substances which are reactive in nature such as alkalis, hydrochloric acid (HCl), and sodium chloride (NaCl) [84]. Interactions with such substances may lead to corrosion of carbon steel and create a doubt about environmental conditions in which carbon steel can be used safely. With their experience and research the author has given a solution for corrosion of carbon steel by developing a specialized conversion coating which not only provides the optimum protection but also ensures the strong adherence to the carbon steel surface which will increase the life span and also its usage in challenging environment [84, 85].

The damage and potential failure of carbon steel during its operational phase especially in harsh environment according to Panagopoulos et al. raise doubt regarding the trustworthiness of material. According to the author selection of alloying materials and electrochemical deposition technique can be very useful in minimizing the corrosion attack. By adjusting the parameters such as current density, pH balance and undergoing the electrochemical deposition of carbon steel will not only enhance the corrosion resistance but also increase the wear resistance and increases hardness. This method is very cost friendly and provides the optimum solution for the corrosion attack [86, 87].

2.3 Graphene

Graphene is a remarkable material in modern times. It is two dimensional thin sheet made up of carbon atoms which are organized in regular sp²-bonded hexagonal lattice. Graphene can be thinks of as an extremely thin sheet of graphite with thickness of just around single atom [88, 89]. Graphene belongs to the family of carbon-based materials which includes charcoal, graphite, advanced materials like carbon nanotubes and ball shaped like material known as fullerenes. Beyond just the physical structure, graphene can be considered as a huge flat molecule [90, 91]. In chemistry there is a family of molecules which is known as polycyclic aromatic

hydrocarbons, graphene belongs to this family and is most extreme and biggest member of this family [90].

Graphene is extremely thin and very versatile material which is made up of carbon atoms. Graphene is a thin sheet of carbon atoms which is so thin that all atoms on both sides of this sheet are exposed and due to which the edges of this sheet become very active and interact readily [92]. As compared to other materials which are made up of carbon atoms such as carbon nanotubes (CNTs) graphene has more number of active edges which makes it very interesting material and we can use it for various interactions and experiments [93].

One of the properties of graphene that really makes it unique is its exceptional strength. It is many times stronger than steel and also way more stronger than Kevlar which is used to make bullet proof jackets [94]. It may come in our mind that with all that strength that graphene has it must be very heavy but it is quite opposite in reality. Graphene is extremely light material. Imagine a sheet made as big as the size of football ground if that sheet is made up of graphene it will be only as heavy as the small packet of sugar. In simpler words graphene is both super light and super strong material [95].

Graphene is not only known by its strength and light weight another interesting property of graphene that makes it different from other material is its significant elasticity. Graphene is very stretchy in nature and can revert back to its original shape after it is being pulled or bent. In 2007 an experiment was conducted by the scientists where they placed graphene sheets over a base and pushed over it. They were shocked to observe that these graphene sheets acted like very strong stretchy springs. These attributes can only be achieved when flawless graphene is made. On big scale making a perfect graphene is very expensive and difficult but with passage of time it might be possible for us to make perfect graphene [96, 97].

Graphene falls in the category of either semi- metal or a zero-gap semiconductor. Graphene is very unique material which can conduct electricity very well [98]. It is different from other materials because both holes and electrons can assist to move electricity through graphene, which make graphene an excellent conductor of electricity. Due to properties like excellent strength, light weight and good conduction of electricity graphene can be game changer in electronic industry in near future. As

we have already known that graphene is extremely thin and has thickness of just one atom but despite of that graphene can absorb 2.3% of white light. This happens because of the ability of electrons to move around. This percentage of absorption is not because of how graphene is made but is connected to a universal science number. If add another layer of graphene on top it will again absorb another 2.3% of white light and this keeps adding up for every layer we put. This characteristic of graphene makes it very unique and interesting for optical and electronic devices [99-101].

2.4 Synthesis of Graphene Oxide (GO)

The technique of converting graphite chemically into graphene by using liquid mixture is not only very helpful but also simple. Through this process mass production of graphene can be accomplished. As a result of this process we get oxidized form of graphite which is graphene oxide (GO) which can be used for various applications [102].

In the mid of 19th century the process of converting graphite into its oxidized form first took place. In the year 1859, Brodie et al. invented the process of oxidizing graphite into graphene oxide (GO) by using powerful combination of nitric acid and potassium chlorate [103]. For over the century this process was considered as the only reliable method for conversion of graphite into its oxidized form. After the much development and research over this process Hummers et al. and Offeman et al. proposed a new and novel synthesis method in 20th century [104]. This method incorporated the use of potassium permanganate (KMnO_4) and highly concentrated sulfuric acid as oxidizing agents. This new technique of them was not only the best alternative approach but also it proved to be more efficient than the previous one. This process is later named as Hummers method, and few modifications were made in it and it then emerged as the dominant and most widely used method for producing graphene oxide (GO) in many research works and industrial applications [104, 105].

The Hummers method is the best approach for getting graphene oxide (GO) from raw graphite. Over the time modifications have been made in this process but basic fundamental procedure remains same. In Hummer's method, natural raw graphite in powder form is taken into the flask and concentrated sulfuric acid (H_2SO_4) is added in it. This mixture is then place on an ice bathed to cool down and to ensure low temperatures. After agitation of this mixture potassium permanganate (KMnO_4) is

added in it, due to low temperature and gradual addition of it prevents exothermic reactions. After proper mixing this mixture is allowed to reach the room temperature and continuous stirring is done for some time. This reaction is generally exothermic in nature so water is added cautiously to neutralize it by release of steam or gas. A bit of hydrogen peroxide (H_2O_2) may be added to further neutralize the effect of potassium permanganate. Now the product in flask is referred as graphene oxide. This graphene oxide can be purified by doing multiple washing by using blend of water, hydrochloric acid and ethanol to remove any kind of salts or acids. After washing the following mixture is filtered and allowed to dry. To obtain the single sheet graphene oxide or few layered graphene oxide the dried graphene oxide is mixed with water and ultrasonication is carried out. Ultrasonication is helpful in separation of layered graphene oxide. The end product which is graphene oxide (GO) is then collected in powder form and is characterized by various characterization techniques such as SEM, AFM, EDX, XRD, FTIR and Raman spectroscopy to determine its structural quality. It is important to keep in mind the hazardous nature of oxidizing agents and this method should be carried out under a fume hood and protective gears should be used for safety [105-108].

Graphene oxide (GO) has oxygen containing functional groups both on its smooth surface and edges according to, Lerf et al. and his associates. It is known that smooth surface or basal plane have hydroxyl groups or epoxy groups and edges contains carbonyl or carboxylic acid groups [109]. Till now the exact chemical composition of graphene oxide (GO) remains unknown and a subject of continuous study. As compared to graphene the oxygen groups in graphene oxide (GO) leads to structural deviation. The carboxylic acid group on the edges allows graphene oxide (GO) to achieve electrostatic stability in polar solvents, high pH water, without depending on surfactants. To get a well dispersed graphene oxide (GO) mixture certain processes such as ultrasonication and centrifugation must be carried out [109, 110].

2.5 Synthesis of Reduced Graphene Oxide (rGO)

Graphene oxide (GO) can be converted into reduced graphene oxide (rGO) through chemical reduction or thermal reduction method. By these reduction techniques most of the oxygen containing functional groups can be remove from graphene oxide. After the reduction of graphene oxide to reduced graphene oxide (rGO), the electrical and

thermal properties of reduced graphene oxide becomes quite similar to pure graphene. By the latest developments in this century there are number of methods for reduction of graphene oxide to reduce graphene oxide with high level of efficiency and more precision. Each of these methods aims to achieve properties of pristine graphene [111].

One of the main methods which are used for reduction of graphene oxide to reduced graphene oxide is high temperature thermal reduction method. In this method reduction is carried out at very high temperature generally above 200°C, in vacuum environment or in the presence of inert gasses like argon and nitrogen. Reduction is carried out at such high temperatures because it can be very useful to remove or eliminate specific oxygen containing functional groups more effectively and easily from graphene oxide [111, 112].

Other method which is commonly used is chemical reduction method which is carried out at low temperature with the use of various chemical agents that are capable to get desired reduction of graphene oxide. Such type of reduction can be done in both liquid and gaseous phase [111]. Common reducing agents such as hydrazine, metal hydrides like sodium hydride (NaH) and sodium boron hydride (NaBH₄) are used. Natural compounds like ascorbic acid are also used in this method [113]. Other chemical agents such as hydroquinone, hydrogen iodide (HI) and p-phenylene diamine are also being used for desired reduction results [111].

Aside from these two methods of reduction of graphene oxide alkaline treatment is another way for getting reduced graphene oxide. In this, alkaline substance such as potassium hydroxide (KOH) and sodium hydroxide (NaOH) are used and this treatment is usually carried out at high temperature or in super critical water conditions [111, 114].

In modern era due to the advancements in technology, the other technique through which reduction of graphene oxide is possible is ultraviolet (UV) assisted photocatalytic reduction. In this technique power of ultraviolet radiation is used to carry out reduction process [111, 115].

Reduction of graphene oxide to reduced graphene oxide through microwave driven reduction is another type of advance method where the energy from microwaves is

being used to effectively carry out reduction process. If there is a need to achieve more effective reduction of graphene oxide then various methods which are discussed above should be combined in a step wise manners [111, 116].

Across the primary plane of reduced graphene oxide (rGO) there are many limitations or flaws. When thermal reduction is carried out some structural changes occurs within the basal plane of reduced graphene oxide. These changes occurs when carbon atom is liberated in the form gases like carbon monoxide (CO) or carbon dioxide (CO₂), which leaves the voids or gaps in their place. Similarly in chemical reduction of reduced graphene oxide which is facilitated by reducing agents there are some irregularities and flaws which occurs. Chemical reduction method not only produces defects on the surface of reduced graphene oxide but also prompts the formation of the multilayered structure. These structural changes introduced outsider molecules and atoms to the material; such phenomenon is called as unintentional doping. This unintentional doping occurs in those areas where defects are prominent. Due to this unintentional doping, electronic and chemical properties of reduced graphene oxide may vary [111].

2.6 Differences between GO and rGO

Following table shows the difference in properties of graphene oxide (GO) and reduced graphene oxide (rGO) [94].

Table 2.2: Differences between graphene oxide and reduced graphene oxide

Properties	Reduced graphene oxide (rGO)	Graphene oxide (GO)
Molecular structure	Restoration of π -conjugation to some extent. More sp ² hybridized carbon	Disrupted π -conjugation due to the presence of oxygen functionalities. Sp ³ hybridized carbons.
Composition	Has fewer oxygenated groups, but not entirely free from defects and heteroatoms.	Contains oxygen in the form of epoxides, hydroxyls, and carboxyls attached to the graphene sheet.

Mechanical properties	Enhanced mechanical properties compared to GO but still not at par with pristine graphene.	Weaker mechanical strength due to the presence of functional groups that disrupt the carbon network.
Surface functionalities	Less reactive than GO due to reduced number of functional groups but still can undergo certain surface modifications.	Presence of oxygen functionalities makes it highly reactive and suitable for chemical modifications.
Dispersibility	Reduced dispersibility compared to GO due to removal of polar functional groups.	Can be easily dispersed in water and various solvents due to polar functional groups.
Optical properties	Darker dispersions (brown to black); changes in UV-VIS spectrum indicative of restored π -conjugation.	Brownish-yellow dispersions in water and some organic solvents; characteristic absorption peaks in UV-VIS spectroscopy.
Thermal stability	Improved thermal stability compared to GO but might still have residues from reduction process.	Lower thermal stability due to the presence of oxygen functionalities.
Electrical conductivity	Conductivity is significantly improved but doesn't match pristine graphene.	Highly insulating because of the disruptions caused by oxygen functionalities.
Barrier properties	Reduced barrier properties compared to GO due to removal of functional groups.	Due to its functional groups, can act as a barrier in certain composites.
Production method	Produced by reducing GO using chemical agents (like hydrazine, ascorbic acid), thermal methods, or other techniques.	Produced by oxidizing graphite using strong oxidizing agents (often via Hummers' method).

Applications	Conductive inks, super-capacitors, batteries, gas sensors, catalysis, composite materials.	Barrier films, biosensors, drug delivery systems, water purification, as a precursor for rGO
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2.7 Nickel based Composite Coatings

Composite nickel based coatings are under research because of their interesting properties such as mechanical strength, corrosion resistance, wear resistance and lubrication proficiency. These properties make coatings having nickel as the integral part very important for wide range of applications and especially in environments where materials degrade due to wear, corrosion and friction. Other particles are also co-deposited in nickel based composite coatings to enhance the properties depending upon the application. These particles are embedded into the nickel matrix and they ensure durable and robust surface [117]. Some of the particles which are added in nickel matrix are:

Zirconia (ZrO₂): It provides resistance against high temperature and is known for its toughness. Durability of the coating is increased when it is combined with nickel [118].

Titanium Oxide & Titanium Nitride: Both these nano-particles are known for their hardness and wear resistance [119, 120].

Alumina (Al₂O₃): It is used to improve the hardness and wear resistance of surfaces [121, 122].

Cerium Oxide (CeO₂): With addition of this potentially soother coatings are formed with enhanced optical and frictional properties. It is also used in polishing agents [123].

Silica (SiO₂): This is another hard particle that can lend additional strength and durability to the nickel matrix [124-127].

Tungsten Carbide (WC): It is very hard and often used in cutting tools. Addition of it increases wear resistance [128].

Niobium: This nano-particle is known for its toughness and resistance against corrosion especially at elevated temperature [129, 130].

Carbon Nanotubes (CNTs): These nano particles are famous for their strength and flexibility. When they are added in nickel coating they significantly enhance the mechanical properties and bring useful electrical and thermal characteristics [131-133].

The basic purpose of adding these nano particles is to achieve synergy between nickel and the added particles, which results in a composite which has enhance properties as compared to individual components of composite. The ultimate purpose of co-deposition is to produce coatings which can function in harsh environment, have longer operational life span and should provide economical favor [134].

2.8 Previous Developments in Nickel based Composite Coatings

2.8.1 Addition of silicon carbide (SiC)

Addition of different amount of silicon carbide (SiC) nano particle in nickel based composite coatings were studied by Gul et al. and his team and they observed the change in characteristics of coating. They studied the coatings which were developed by electrochemical deposition method, which is one of the precise and most adaptable methods for developing uniform coatings. Study shows that with the addition of silicon carbide there was increase in the wear resistance, friction resistance and better lubrication properties and such coatings will perform better in harsh environment. It was also observed that the coating shows reasonable hardness which makes them more resistance to scratches and dents. According to, Gul et al. this hardness in coating comes due to the evenly/uniform distribution of silicon carbide nano particles in the nickel matrix which makes the whole structure stronger and due to the smaller grains in coatings which makes it harder and stronger. By this research of Gul et al. and his team we can create coating which can perform better on industrial level [135].

2.8.2 Addition of Carbon Nanotubes (CNTs)

Nickel is famous for its anti-corrosive nature, while carbon nanotubes (CNTs) are modern materials which contain exceptionally high strength and better conductivity [136]. Composite coatings of nickel (Ni) and carbon nanotubes (CNTs) were

developed and studied by Chen et al. and his team for better corrosion resistance. The basic aim of their in developing these coatings was to evenly/uniformly mix carbon nanotubes (CNTs) in nickel matrix which will makes them more stronger. They compare the corrosion resistance of pure nickel coating and Ni/CNT composite coating in salt water and acid rain. Results indicated that the composite coating of nickel and carbon nanotubes (CNTs) exhibits higher corrosion resistance as compared to pure nickel coating. This enhancement in corrosion resistance of composite coating resulted due to the addition on carbon nanotube (CNTs) in nickel matrix which changed the structure of nickel and bonded in a special way with nickel. This work of Chen e al. paved way for development of such type of coatings in future which will combine different material for obtaining various properties and characteristics [137].

2.8.3 Effect of Surfactant on Ni/CNT Composite Coating

Surfactants are vital chemicals for any type of coatings they insure better dispersion. The effect of addition of sodium dodecyl surfactant (SDS) in nickel and carbon nanotube composite coating was studied by Guo et al. and his fellow researchers [136]. In this type of coating properties of nickel was blended with strength and conductivity of carbon nanotube (CNT) which was very useful for various industrial applications. The addition of sodium dodecyl surfactant (SDS) influences the corrosion resistance, inner structure and appearance of the coating. With the addition of sodium dodecyl surfactant (SDS) these coatings showed more hardness, smaller grain size and increased corrosion resistance. The overall result of this research indicates that with the addition of surfactant like sodium dodecyl (SDS) in coatings we can achieve characteristics which are useful and are helpful in various applications [136, 138].

2.9 Incorporation of Graphene in Composite Coating

With taking in account the recent development in the field of nano composite coatings, graphene nanosheets can be incorporated in the composite coating [139, 140]. With the addition of graphene tribological properties show enhancements along with fracture toughness [141], hardness [142], wear resistance [143] and also corrosion resistance [144-147] of coatings increase significantly.

1.1.1 Graphene and Polyaniline Composite Coating

We already know graphene is a single layer of carbon atom having high strength and electrical conductivity and polyaniline is a type of polymer which is good at providing resistance against corrosion [88, 89]. Graphene and polyaniline composite coating was developed and tested by Chang et al. and his team and was compared with coatings which were prepared just from polyaniline and clay. Clay is used in coatings to provide polymer a better strength and it can be spread uniformly. They made composite coating of graphene and polyaniline hoping to get a super protective coating. The composite coating of graphene and polyaniline was effective at blocking water and oxygen and provides higher corrosion resistance as compare to the other. According to Chang et al. this composite coating of graphene and polyaniline could provide optimal protection to steel for longer period of time which is vigorously used in building materials and various industrial applications [148].

2.9.1 Graphene and Nickel Composite Coating

Nickel is a very good anti corrosive material and many coatings have been developed in past which consists of nickel and they have shown good efficiency against resisting corrosion. Graphene on the other hand is a new material and is a single layer of carbon atom which has high electrical conductivity and impressive strength. Kumar et al. and his group studied nickel graphene composite coatings and compared them with pure nickel coating. Purpose of their investigation was to see whether adding graphene with nickel gave high resistance against corrosion, provides high resistance against wear, hard and long lasting coatings or not. It was observed that composite coating of nickel and graphene were more effective than pure nickel coating in corrosive environment due to the addition of stronger layer of carbon atoms into nickel matrix. It was clearly observe that with the addition of thin layer of graphene structure of nickel was changed. The substrates which were coated with composite coating of graphene and nickel lasted longer than nickel coated substrate in highly corrosive environment. This type of coating is very suitable for automobile industry, construction, industry and in ship manufacturing. With such developments of adding new material to already known materials new composite coatings can be developed which could provide better resistance against environments which can lead to rusting

of vital components, better performance, less need of repairing and life span of components can be increased [149].

2.9.2 Graphene and Chromium Composite Coating

Steel is the most important material and is widely used in industries, but it is prone to rusting [72]. Rekha et al. and her team worked on composite coating of graphene and chromium. Chromium coatings are very famous for their anti-corrosive nature and providing a shiny and lustrous finish. Their main objective was to develop such coating which provides optimal protection against harsh environment and reduce the cost of repairing by increasing life span. They developed graphene chromium composite coatings for mild steel which work better than their expectations in high salt and acid environment. They successfully enhanced the resistance of steel against corrosion by composite coating of graphene and chromium. In comparison with chromium coating this composite coating proved to be the most reliable one in terms of optimal protection, hardness and wear resistance [150].

CHAPTER 3: MATERIALS & METHODOLOGY

3.1 Synthesis Technique for Coating

Coating technique chosen for steel substrate was electrochemical deposition. By carefully adjusting the parameters like deposition current density, pH of electrolyte, temperature and time of deposition uniform and consistent layer of coating on steel substrate can be obtain. By using electrochemical deposition surface properties of materials can be enhanced. Properties like corrosion resistance, wear resistance and hardness are increased by this synthesis route. Coating efficiency of electrochemical deposition process is very high, which means that high percentage of metal ions in electrolyte can be deposited on the objected being coated and with very minimal waste. By varying the parameters of electrochemical deposition, we can get coatings of varying grain size, morphology, textures and this can allow us to change or enhanced the material properties. Step by step procedure of our experimental work is shown in figure 16 and process flow chart is given in figure 17.

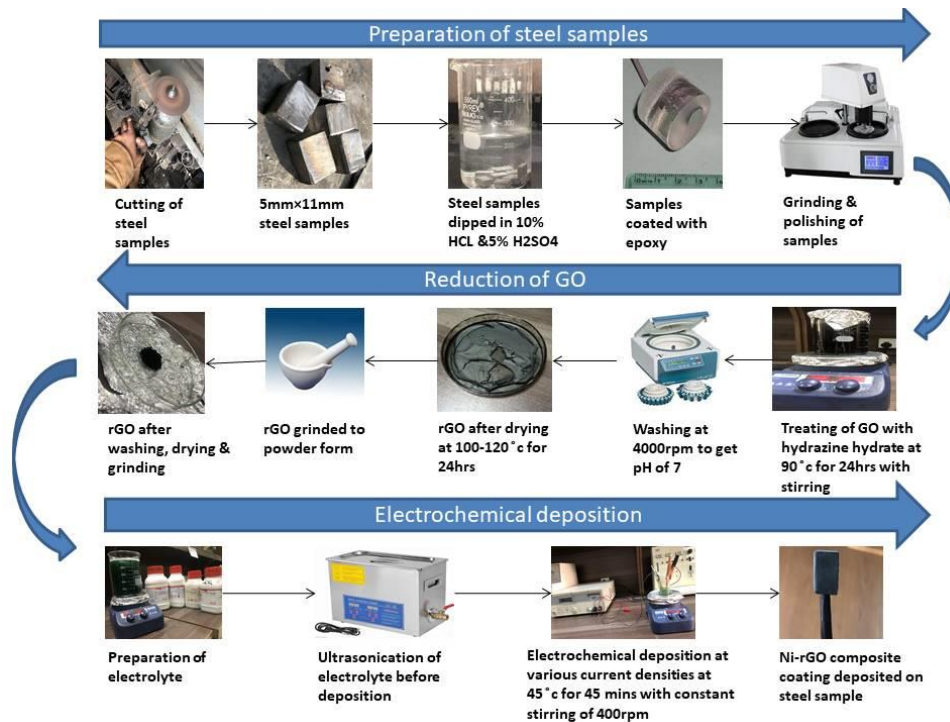


Figure 3.1: Fabrication route of composite coating

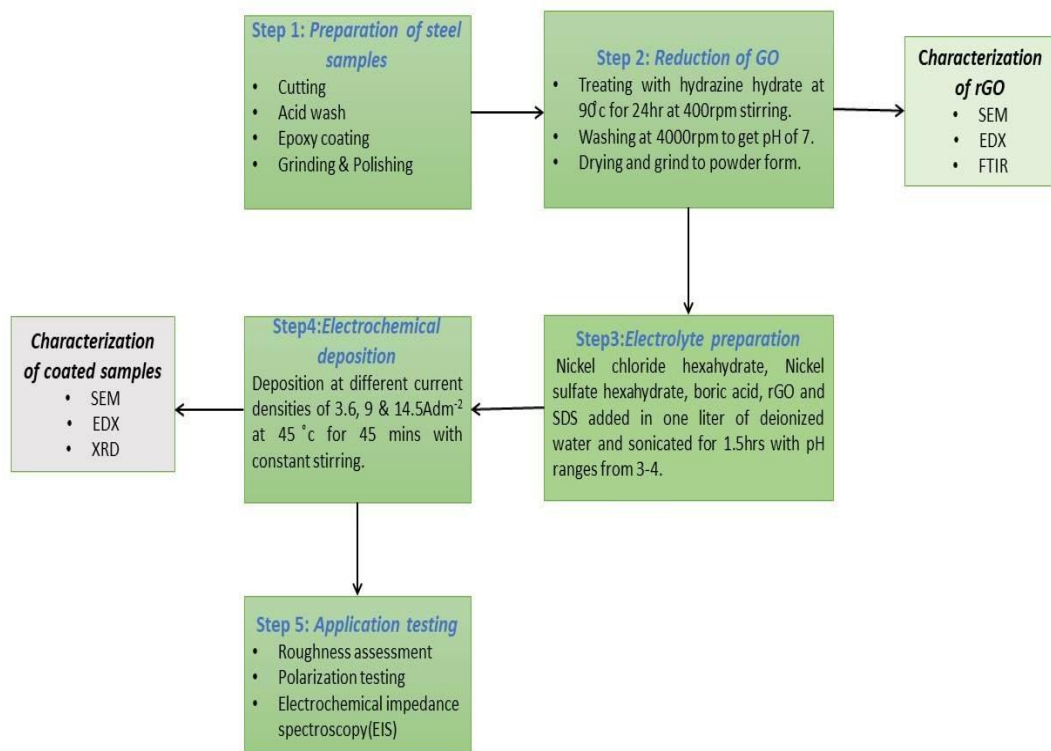


Figure 3.2: Flow chart of complete fabrication process

3.2 Materials

1. Nickel Chloride Hexahydrate
2. Nickel Sulfate Hexahydrate
3. Boric Acid
4. Sodium Dodecyl Sulfate (SDS)
5. Graphene Oxide (GO)
6. Nickel Plates
7. Sodium Chloride (NaCl)
8. De-Ionized water

Other materials and laboratory used materials such as:

1. Beakers
2. Magnetic Stirrer
3. Thermometer
4. Aluminum Foil
5. Mortar and Pestle

6. Petri Dishes
7. DC Variable Power Supply
8. Hydrazine Hydrate
9. Electrical Wires
10. Terminals/ Holders (for holding electrodes)
11. Hot Plate
12. Oven
13. Sonicator
14. Centrifuge Machine



Figure 3.3: Materials used in preparation of electrolyte

3.3 Synthesis of rGO

3.3.1 Reduction of GO:

The conversion of graphene oxide (GO) to reduced graphene oxide (rGO) was achieved by chemical reduction method. Hydrazine hydrate was used as reducing agent and was added in 1:1 ratio by weight along with GO in distilled water. After which this mixture was subjected to heat at 90 °C for 24 hours with constant stirring of 400rpm. At the completion of this procedure graphene was precipitated out and

settled out of the solution. The obtained black solid was then taken for washing with distilled water in centrifuge machine to get pH of 7. Figure 19 shows the heat treatment of GO with hydrazine hydrate and figure 20 shows rGO before washing and grinding.



Figure 3.4: Reduction of graphene oxide



Figure 3.5: rGO before grinding & washing

3.3.2 *Washing of rGO:*

The product which was gathered after reduction was washed with distilled water to get the pH around 7 in centrifuge washing machine at the rpm of 4000. After washing, the obtained black substance was dried in oven at the temperature of 100-120 °c for 24 hours period and grinded to powder form, which is shown in figure 21.



Figure 3.6: rGO in powder form

3.4 Preparation of steel substrate

1.1.1 Cutting of steel:

Carbon steel was cut in the size of 5mm width and 11mm length on a grinder. Multiple samples of same size were cut and then they were cleaned and polished for coating purpose. Figure 22 and 23 shows cutting of steel samples of desire size.



Figure 3.7: Cutting of steel samples



Figure 3.8: 5mm×11mm of steel samples

3.4.1 Acid Wash:

10% HCL and then 5% H_2SO_4 solution was prepared and steels samples were dipped in it to remove any kind of surface impurity, oil and oxide layers from substrate that will contaminate the coating, which is shown in figure 24.

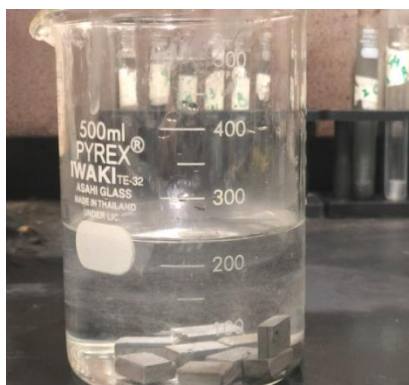


Figure 3.9: Acid wash of steel samples

3.4.2 Grinding and Polishing:

Different grades of emery papers (240#, 320#, 600# and 1200#, respectively) were used to obtain flat and uniform surface. After this samples were polished to obtain a mirror like surface.

3.4.3 Preparation of Cathode:

After grinding and polishing a wire was connected to the steel substrates through soldering and only that surface on which coating was required left and all the sides were covered with epoxy.

3.5 Preparation of Electrolyte

Nickel chloride hexahydrate, nickel sulfate hexahydrate, boric acid, sodium dodecyl sulfate and graphene was added in one liter of deionized water and was ultrasonicated for about 1hour and 30 min. Every time ultra-sonication was carried out before electrochemical deposition to get well dispersion of graphene in electrolyte. The composition of electrolyte is shown in table 3. SDS was added in electrolyte for the well dispersion of graphene sheets. Electrolyte used for coating is shown in figure 25.

Table 3.1: Chemical composition of an electrolyte

Chemicals	Amount [gL^{-1}]
$\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$	95-110
$\text{NiCl}_2 \cdot 6\text{H}_2\text{O}$	15-23
H_3BO_3	30-40
Surfactant (SDS)	0.409
Reduced graphene oxide (rGO)	0.23

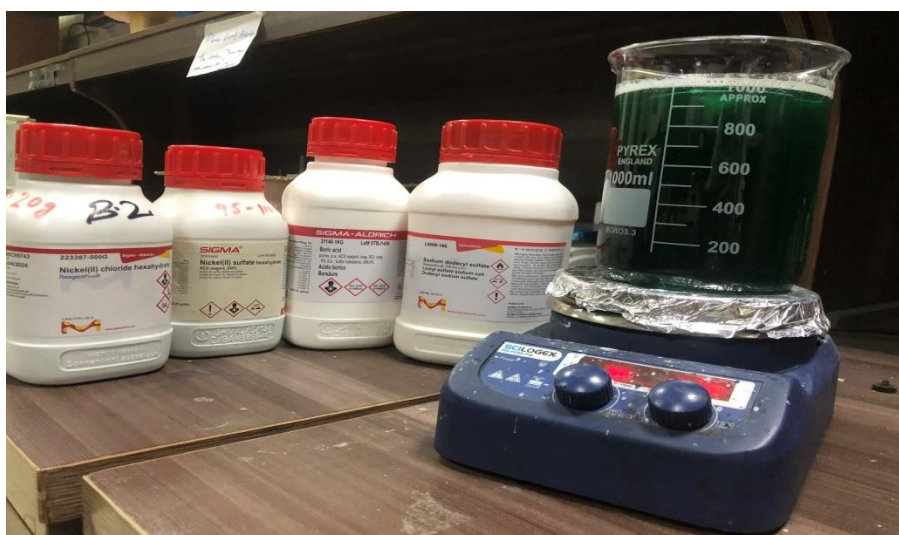


Figure 3.10: Electrolyte used for coating

3.6 Apparatus required for electrochemical deposition

1. DC variable power supply
2. Hot plate
3. Mechanical stirrer
4. Wires
5. Beaker
6. De-ionized water

3.7 Electrochemical deposition

Nickel plates were used as anode and steel samples as cathode for deposition of coating. Two nickel plate of 70 mm length, 40 mm width and 1mm thick were placed parallel to both sides of steel substrate. Anionic surfactant sodium dodecyl sulfate (SDS) was used in electrolyte for well dispersion of graphene sheets within the deposition solution. Sodium dodecyl sulfate (SDS) adheres to graphene sheets which leads to electrostatic repulsion between the graphene layers. Electrolyte was ultrasonicated every time for about 1 hour before deposition. Other conditions were varied for deposition process such as temperature, pH range and stirring. Temperature was set at 45 degree, pH of electrolyte was between 3 and 4 and stirring was carried out at 400 rpm. The nano-composite coatings were deposited on steel substrate at different current densities 3.6Adm^{-2} , 9Adm^{-2} and 14.5Adm^{-2} . For each sample deposition was done for about 45 minutes. Fig 26 shows electrochemical deposition of Ni-rGO coating on steel substrate.



Figure 3.11: Coating setup

3.8 Washing of coated samples

After deposition the coated samples were rinsed with deionized water and kept for sometimes to dry up and then cleaned with ethanol. These coated samples were carefully wrapped in clean and soft cloth to ensure coating on substrate remains uncontaminated and can be used for further testing. Fig 27 shows difference in coated and uncoated sample and fig 28 shows coated sample at peak deposition current density.



Figure 3.12: Difference between plane and coated sample



Figure 3.13: Coating deposited at peak current density

CHAPTER 4: CHARACTERIZATION TECHNIQUES

4.1 X-Ray Diffraction Techniques

A non-destructive method is employed to ascertain the lattice spacing in crystalline solids. This approach can determine elastic attributes, residual stresses, and assist in the identification of unfamiliar materials. The lattice spacing is gauged when X-rays of a known wavelength and angle penetrate the material, refracting through its atomic planes and subsequently being measured by a diffractometer. By directing X-rays at varying angles towards the sample, planes at different orientations are illuminated, facilitating the accurate identification of these atomic planes. Using X-rays to irradiate powder samples typically helps in identifying their Miller indices (hkl) and atomic spacing. The measured intensity corresponds to specific elements or phases, and if the sample comprises multiple elements or phases, numerous intensity peaks will be evident.

X-rays are produced when electrons, emitted from a heated filament, strike a copper target, causing the displacement of the target's inner shell electrons. The resulting X-rays are then focused and aimed at the sample. Upon hitting the sample, the X-rays are deflected based on Bragg's law through constructive interference and are captured by a diffractometer. This device translates these signals into counts (or peaks) that are displayed on a computer screen.

X-Ray Diffraction is employed to identify the crystalline phases and their specific orientations. Additionally, it aids in determining structural attributes such as grain size, strain, lattice measurements, atomic configuration, the composition of the existing phase, and assessing the thickness of thin films and multi-layered materials.

To identify the structure and phase of nanoparticles using XRD, a minute quantity of finely milled nano powder is subjected to an XRD apparatus adjusted to a 2θ angle, sweeping from 0° to 75° in increments of 0.04 over 50 minutes. The gathered data is then cross-referenced with the JCPD reference file to discern the phase. The crystallite size is ascertained using the Scherrer formula

Crystallite size (nm)

$$= \frac{\text{Shape Factor}(K) \times \text{Xray wavelength}(\lambda(\text{nm}))}{\text{COS}(\theta(\text{radians})) \times \text{Full Widht at Half Maximum}(\text{FWHM}(\text{radians}))}$$

Equation 1: Debye Scherrer formula for calculating crystallite size

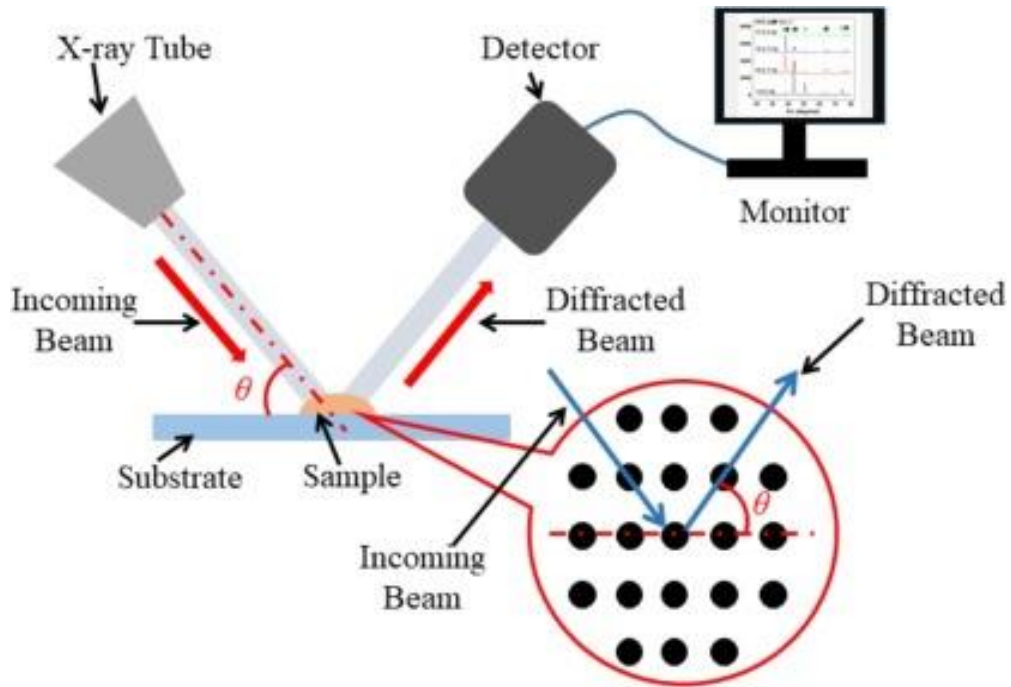


Figure 4.1: Experimental setup of X-ray Diffraction technique

4.2 Scanning Electron Microscopy

In the described technique, high-energy electron beams are utilized to produce a variety of signals. When these electrons interact with a sample, they yield valuable information about the sample's properties, including its surface morphology, orientation, chemical composition, and crystalline structure.

Typically, the outcome of this interaction is visualized as a two-dimensional image that depicts the surface attributes of the material in question. Such imaging, made possible by a scanning electron microscope (SEM), can cover areas as extensive as 5 microns. Notably, SEMs are characterized by their impressive resolution capabilities, which range from 50 to 100 nm. This enables the detailed magnification of samples, from a lower limit of 20X to an upper range of 30,000X.

Furthermore, SEMs have a unique feature that allows for selective analysis of the sample. For instance, the chemical composition of a specimen can be precisely determined using an auxiliary technique called Energy Dispersive X-Ray (EDX) spectroscopy. When integrated with SEM, EDX facilitates the identification of the elemental makeup of the sample by analyzing the X-rays emitted due to the electron beam-sample interaction. This combined approach enhances our understanding of the sample beyond just its physical structure, delving into its chemical intricacies.

When accelerated electrons come into contact with a sample, they produce a range of signals. Among these signals are secondary electrons, which offer insights into morphology and topography; backscattered electrons, which provide compositional contrast; and photons, which are essential for elemental analysis. The interaction also yields visible light and heat. Notably, SEM is viewed as a "non-destructive" method because the generation of these diverse signals doesn't result in any loss of material volume. As a result, the same sample can be examined multiple times without degradation.

For nanoparticle characterization, the samples underwent preparation through sonication in deionized water for duration of 1 to 2 hours. Subsequently, a droplet of this mixture was dispensed onto a glass slide and allowed to dry at 60°C for an hour. The slide was then mounted on a stub and gold-coated to enhance its conductivity. Following this, the sample was positioned in a low-vacuum chamber for examination via the SEM method. Images were captured at varying magnifications and resolutions, using an accelerating voltage set at 20 kV.

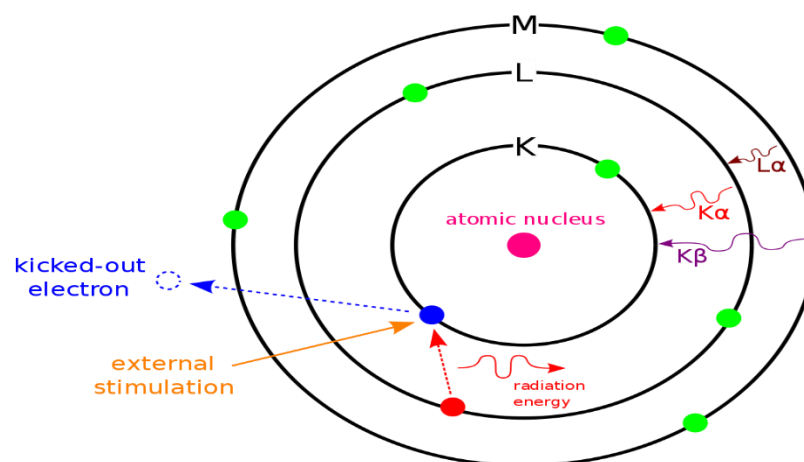


Figure 4.2: SEM mechanism

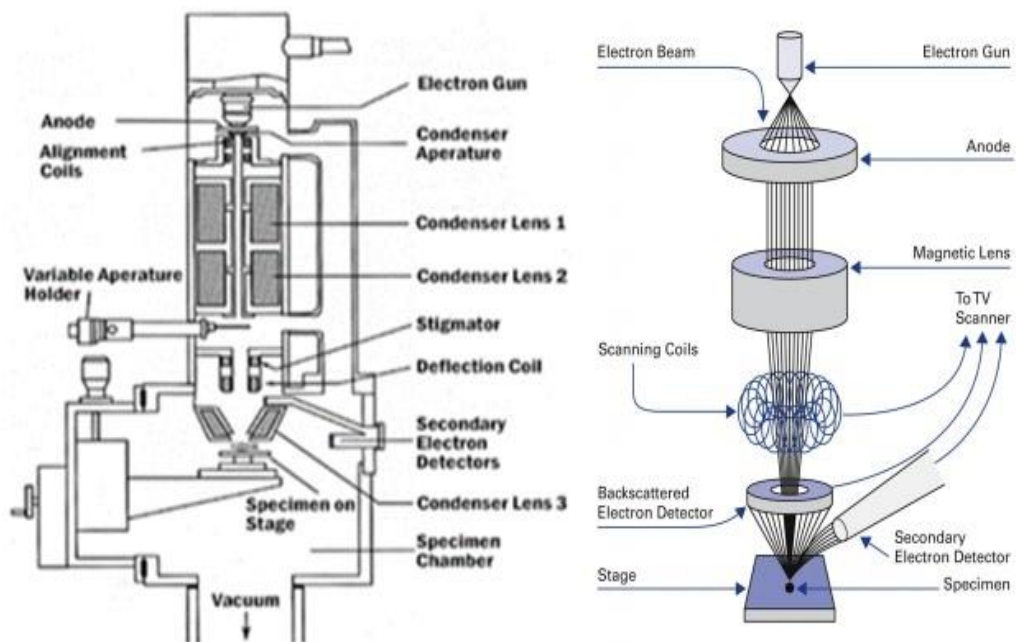


Figure 4.3: Experimental setup for Scanning Electron Microscopy

4.3 Fourier-Transform Infrared Spectroscopy (FTIR)

FTIR (Fourier Transform Infrared Spectroscopy) method generally works on the basic principle that at a specific wavelength materials can absorb infrared rays (IR). This behavior of materials to absorb infrared rays is due to materials composition and molecular structure which anchors like unique footprint for the substance. The materials can absorb infrared radiations at different wave lengths, and this can tells us about very important information regarding materials atomic arrangement and molecular make-up.

One of the major applications of the FTIR spectroscopy is to tell us about the different functional groups present on the surface on a sample. FTIR spectroscopy can be conducted in the spectral range of typically, between 4000cm^{-1} and 400cm^{-1} . In this method the spectrometer releases infrared rays which interact with the sample. These interactions of infrared rays with a sample yield a spectra that provide vital insights about various molecular structure and functional groups present within the sample.

For FTIR, the sample preparation is done by combining nanoparticles of substrate material with a common matrix which is used for infrared analysis which is potassium bromide (KBr). Once they are mixed, pressure is applied to this blend mostly with

uniaxial press to form a compact pellet. After all this the pellet will have uniform and constant texture and composition. This pellet will then be placed into the FTIR apparatus for testing. The reliability of spectral results depends upon the uniformity of pellet. The results can be accurately interpreted to understand the nature of the nanoparticles.

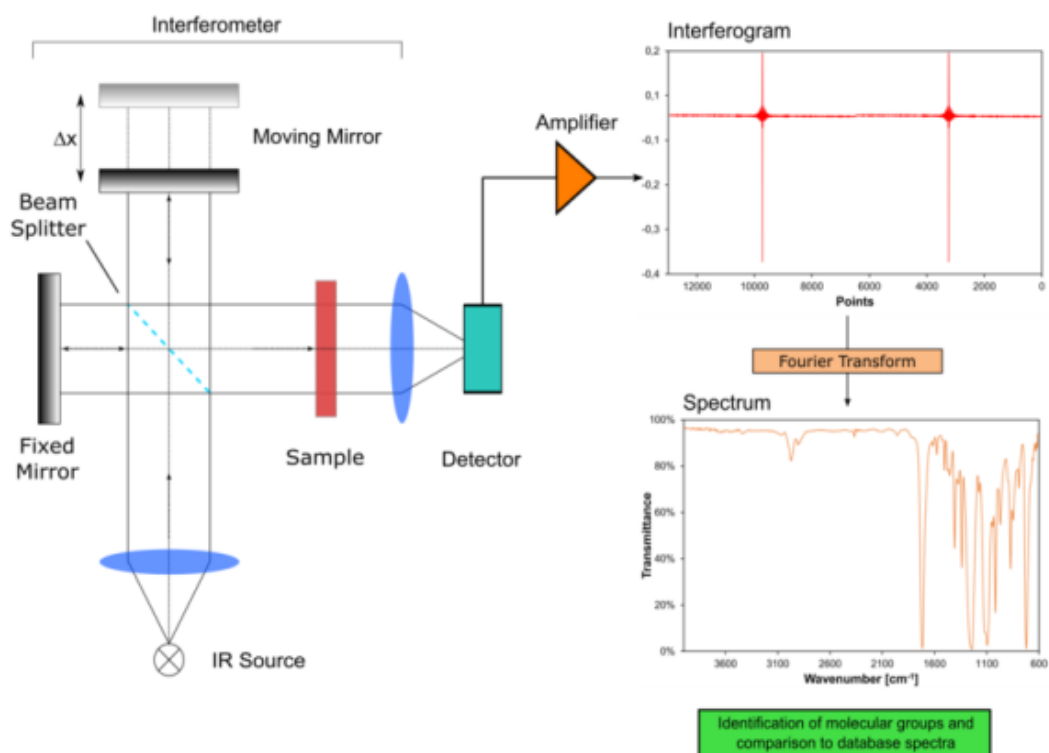


Figure 4.4: FTIR setup

4.4 Electrochemical Impedance Spectroscopy (EIS)

Electrochemical Impedance Spectroscopy (EIS) is a very powerful method which is used to determine the electrochemical properties of a system by measuring the impedance of a system across the range of various frequencies. Impedance can be understood as some resistance which system shows to the flow of current. In EIS spectroscopy, direct current (DC) is used so impedance will be resistance to flow of direct current in the circuit.

In this technique, minimum amplitude of AC voltage is given to an electrochemical cell, and the resulting AC current is measured. This technique is different from other electrochemical testing which are very traditional and involve the application of a direct current and voltage. The AC voltage which is given to the system gives wide range of frequencies which are usually from MHz to mHz. The system response varies with the applied signal frequency. The ratio of voltage to the current at each frequency is determined which show us the impedance, Z . Impedance of a system is very unique and complex quantity it has both magnitude and phase.

Nyquist or Bode plots are used to show the data obtain after electrochemical impedance testing. In bode plot impedance can be easily measured and it shows the magnitude of phase angle and impedance as a function of frequency. In bode plot real part is on x-axis and imaginary part is on y-axis.

EIS is applicable in different s fields like testing for corrosion resistance of coatings, knowing the behavior of conductive polymer, study about different mechanism of corrosion, calculating the performance of fuel cell, battery performance information and degradation of it and for analyzing electrochemical sensors.

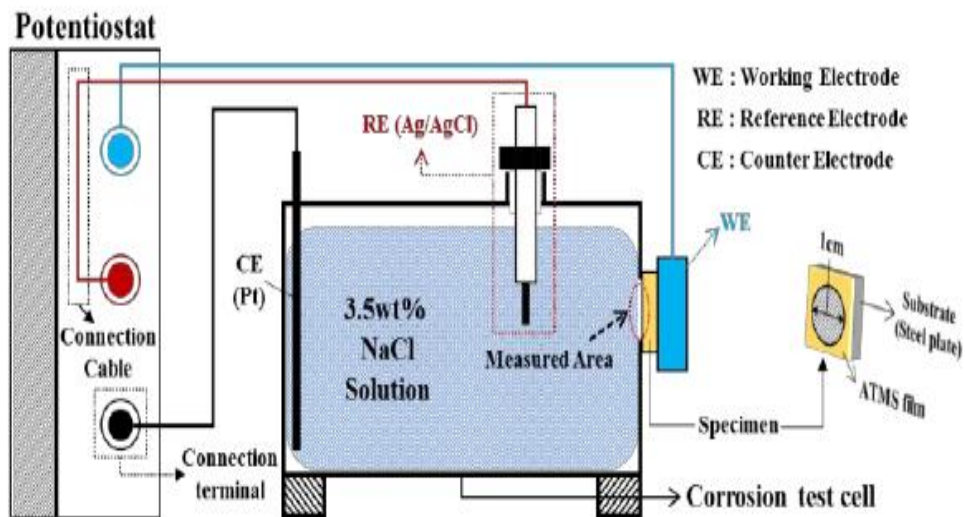


Figure 4.5: EIS setup

4.5 Tafel polarization

Tafel polarization is a technique through which we can determine the electrochemical kinetics of electrode reaction generally for corrosion mechanism. This technique is named after Julius Tafel, who first proposed his work in this context. In such type of testing we come to know about the relationship between current density and the electrode potential through linear region of the polarization curve. In this method the current which is passing through the electrode potential can be measured as the function of applied voltage (potential). When this potential goes beyond some specific range then current potential curve shows different zones of increasing and decreasing current.

The zone where current varies linearly with the applied potential is known as Tafel region and the slope of that region is called as Tafel slope or Tafel constant. Tafel slope shows the relationship between the logarithm of the current and potential and the properties of specific electrochemical reactions which are occurring at electrode. By extrapolation of the linear portion back to the potential axis we can determine the corrosion potential (E_{corr}). Corrosion potential can tell us how rapidly the material can degrade under specific corrosive environment.

This test is widely used in many industrial sectors for corrosion testing and to study the effects of various aggressive environments on the material. Three electrode system is used in this test, where a working electrode (behavior of which we want to know), a reference electrode and the counter electrode are immersed in an electrolyte of corrosive environment. These electrodes are connected to the potentiostat which can control the applied potential and can measure the resulting current.

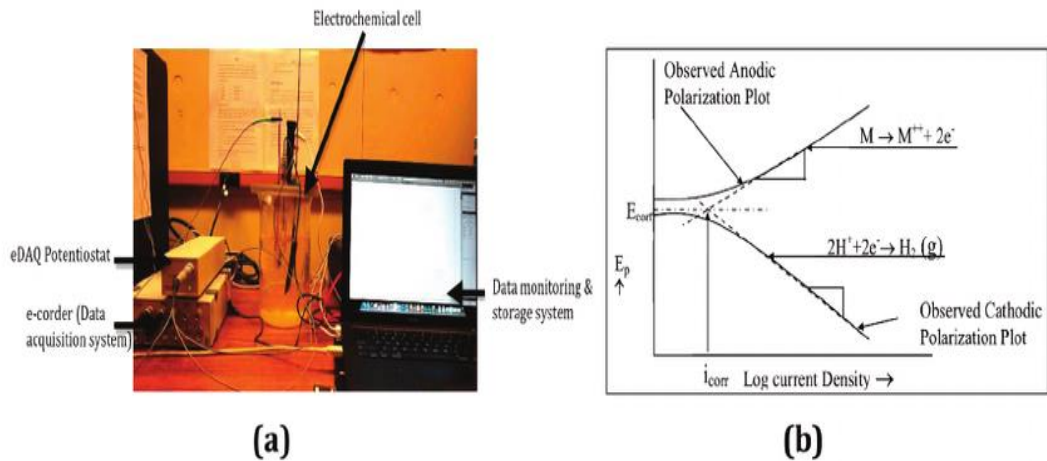


Figure 4.6: Polarization testing setup (a), Polarization curves (b)

4.6 Two Dimensional Non-Contact Profilometry

It is a method which is used to measure the surface topography or surface profile of an object without physically touching it. This type of characterization techniques are widely used in manufacturing processes, quality control engineering and in research works. The most commonly used methods for two dimensional non-contact profilometry are:

- 1) Optical Profilometry
- 2) Laser Scanning Profilometry
- 3) Atomic Force microscopy
- 4) Electrostatic Profilometry

All of the methods mention above have basic theme of work that is by the use of optics, lasers and other non-contact means to get the information about surface of an object and constructs its surface profile. In these methods an incident beam of light is projected on the surface of an object or by using sensors objects surface is scanned and then by analyzing the scattered or reflected light information about variations in height of an object surface is obtained. The interaction between incident light and surface of an object provides us the data that can be used to make 2 dimensional and three dimensional representation of the surface profile.

Surface roughness is a term which means any type of irregularities and deviations that are present on the surface of an object. Height variations are analyzed at very fine

scale in two dimensional non-contact profilometry methods to measure surface roughness. The parameters of roughness are quantified as Ra (average roughness), Rq (root mean square roughness) and Rz (maximum height).

Non-contact profilometry is widely used in quality control of manufactured products and components by inspecting the surface of products for any kind of defect and deviation which affects the overall functionality of product. Precision is critical aspect in semiconductor manufacturing, non-contact profilometry methods are also widely used to inspect and give characterize features on wafers. In many research works non-contact Profilometry is used to study the surface properties of different materials, determining the roughness of developed coatings and also the environmental conditions on the surface. This technique is also used in biomedical research works to study tissues and helps in developing understanding surface features at micro and nano scale.



Figure 4.7: Profilometer

CHAPTER 5: RESULTS & DISCUSSION

5.1 X-Ray Diffraction (XRD) Of Graphene

Reduction of graphene oxide (GO) to reduced graphene oxide (rGO) was confirmed through XRD.

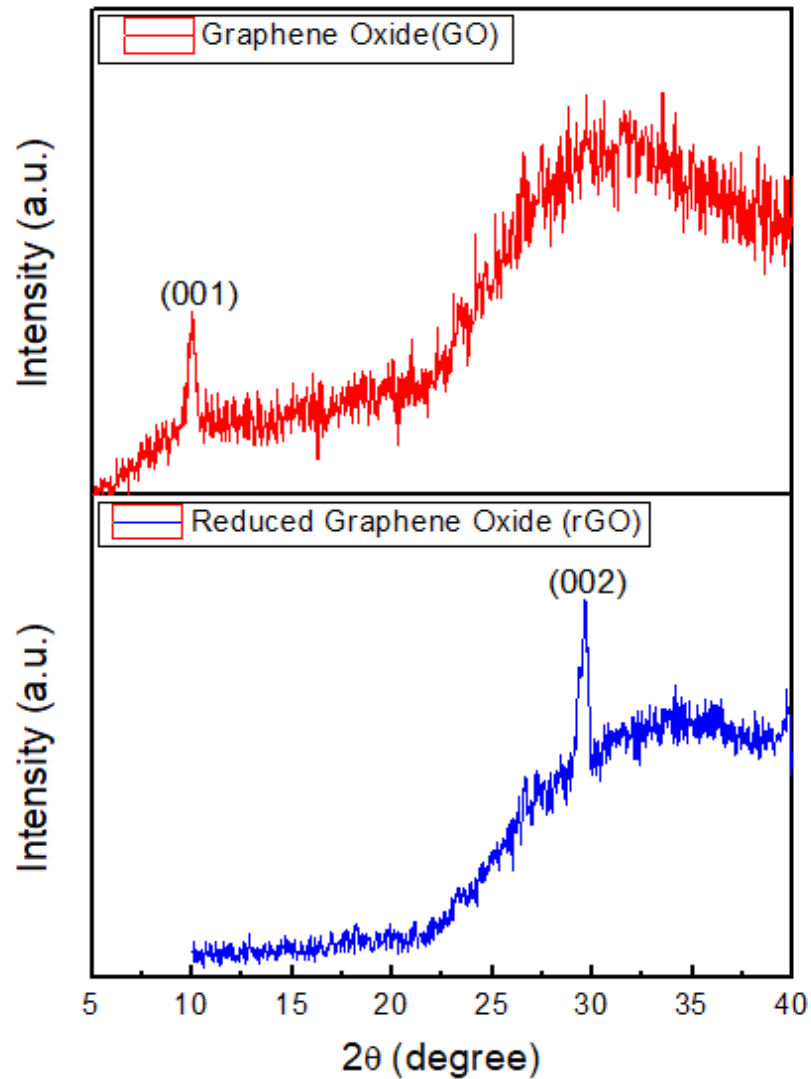


Figure 5.1: XRD pattern of GO and rGO

Figure 5.1 shows the XRD patterns of graphene oxide (GO) and reduced graphene oxide (rGO). For graphene oxide (GO) characteristic carbon peak (001) was observed at 10.00489° with corresponding d-spacing of 0.88412nm . After the reduction process (001) peak disappeared and a new peak (002) was observed at 29.66° with corresponding d-spacing of 0.30112nm , which were very close to literature values.

Graphene oxide showed large layer to layer distance due the oxygen containing functional groups between the layers and after the reduction process reduced graphene oxide (rGO) showed small layer to layer distance because of the removal of oxygen containing functional groups which confirmed the reduction of graphene oxide. Further, to confirmed the structural changes in reduction of graphene oxide (GO) to reduced graphene oxide (rGO) FTIR spectroscopy was carried out.

5.2 Fourier Transform Infrared Spectroscopy (FTIR) of Graphene Oxide (GO) and Reduced Graphene Oxide (rGO)

FTIR spectroscopy is very useful characterization technique which shows presence of various functional groups. After reduction process of graphene oxide with hydrazine hydrate both graphene oxide (GO) and reduced graphene oxide (rGO) were characterized by FTIR to confirm the reduction of graphene oxide. Both the samples were scanned in the range of 400 to 4000 cm^{-1} to obtain the FTIR spectra.

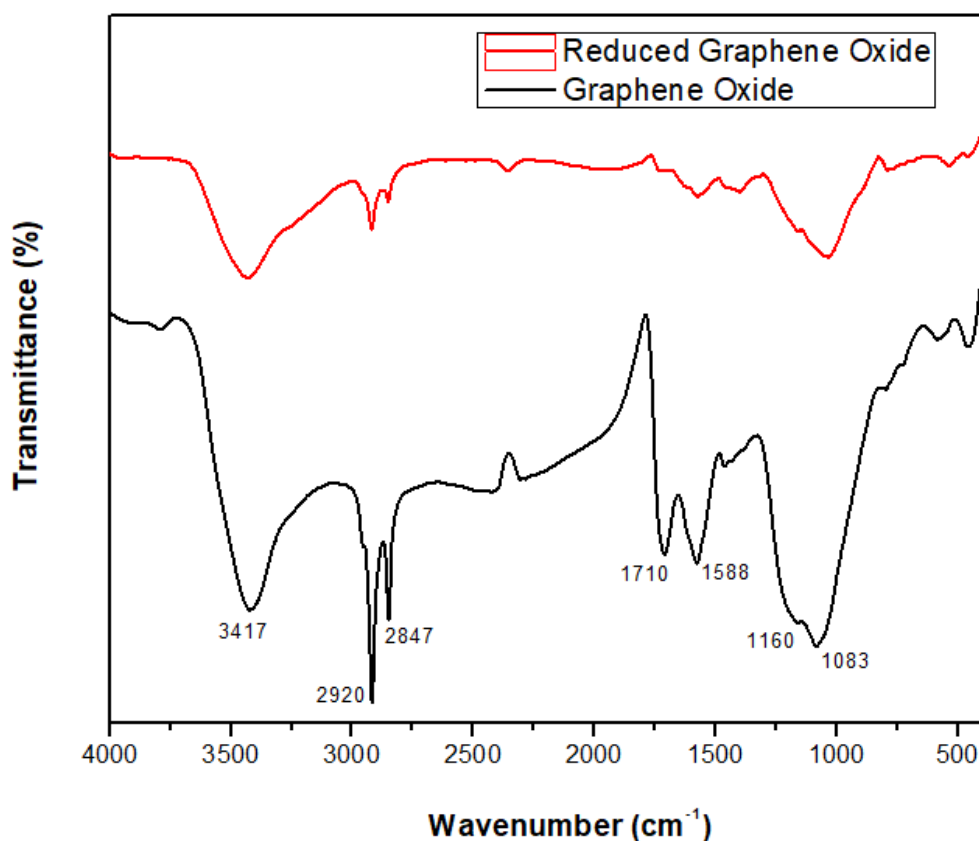


Figure 5.2: FT-IR spectra of GO and rGO

Figure 5.2 was obtained after FTIR spectroscopy. In FTIR spectra of graphene oxide (GO) functional groups such as O–H, C–OH, COOH and C–O were observed which were similar in literature. Broad peak between 3500 cm^{-1} and 2500 cm^{-1} in IR spectra of graphene oxide (GO) was due to the carboxyl O–H stretching mode. Peak 3417 cm^{-1} was due to the presence of absorbed alcohol and water molecules. The peaks of 2920 cm^{-1} and 2847 cm^{-1} were due the asymmetric and symmetric CH_2 stretching of GO respectively. The peak of 1710 cm^{-1} was due to C=O stretched of carboxyl group. The peak of 1588 cm^{-1} was attributed to C=C stretching from un-oxidized graphitic domain. Peak 1160 cm^{-1} indicated C–OH stretch of alcohol group and peak of 1083 cm^{-1} was attributed to C–O stretching vibrations of C–O–C.

Reduction of graphene oxide (GO) to reduced graphene oxide (rGO) was confirmed by FTIR spectra as it can be seen that the intensities of all the peaks that have oxygen functional groups were decreased in IR spectra of reduced graphene oxide (rGO) as compared to graphene oxide (GO). This shows the successful reduction of graphene oxide by hydrazine hydrate.

5.3 Scanning Electron Microscopy (SEM) of Graphene Oxide (GO) and Reduced Graphene Oxide (RGO)

Figure 5.3 shows SEM images of graphene oxide (GO) at various magnifications. Graphene oxide showed 3-dimensional interconnected well defined graphene sheets structure which looked very similar to loose sponge due to porous network system. As there were various oxygen functional groups present in graphene oxide so, it showed thick layered structure as compare to reduced graphene oxide (rGO).

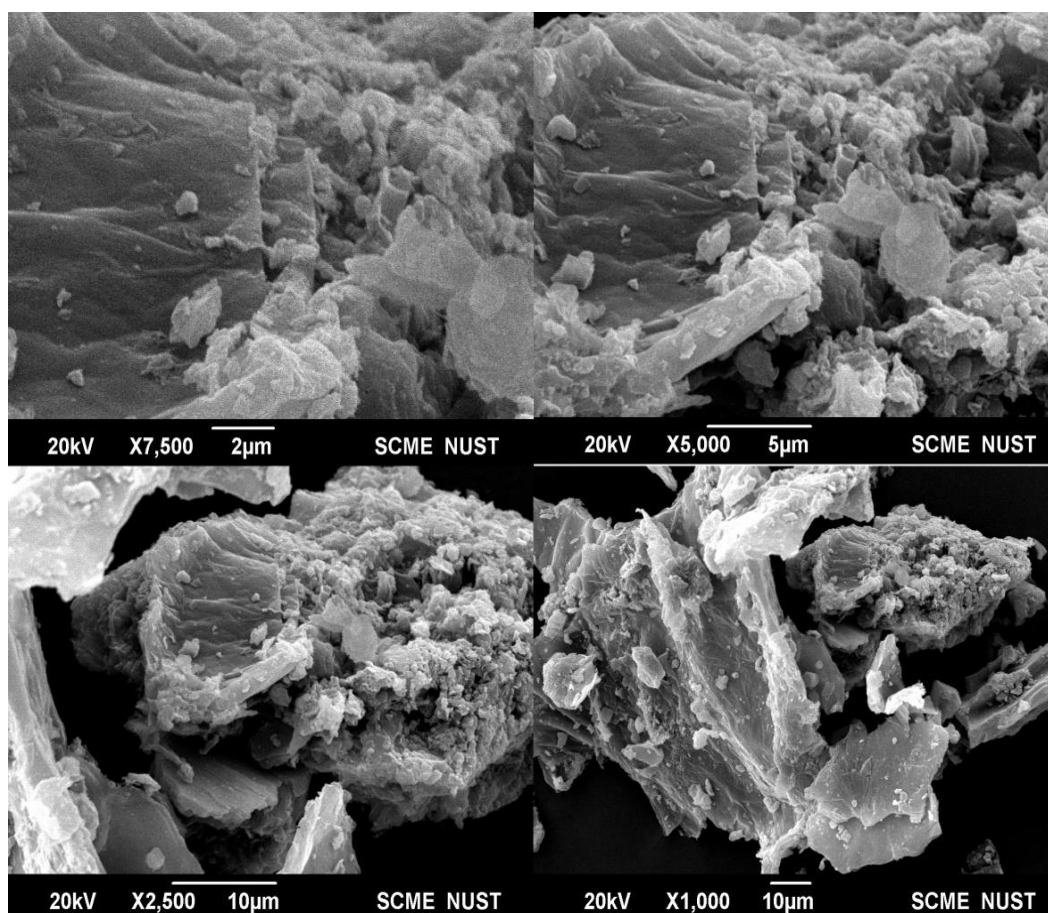


Figure 5.3: SEM images of GO at different magnifications

After the reduction of graphene oxide many oxygen functional groups were removed or decreased in number so, SEM images of reduced graphene oxide (rGO) showed light weight and wrinkled structure. SEM images of reduced graphene oxide (rGO) at different magnifications are given in figure 5.4.

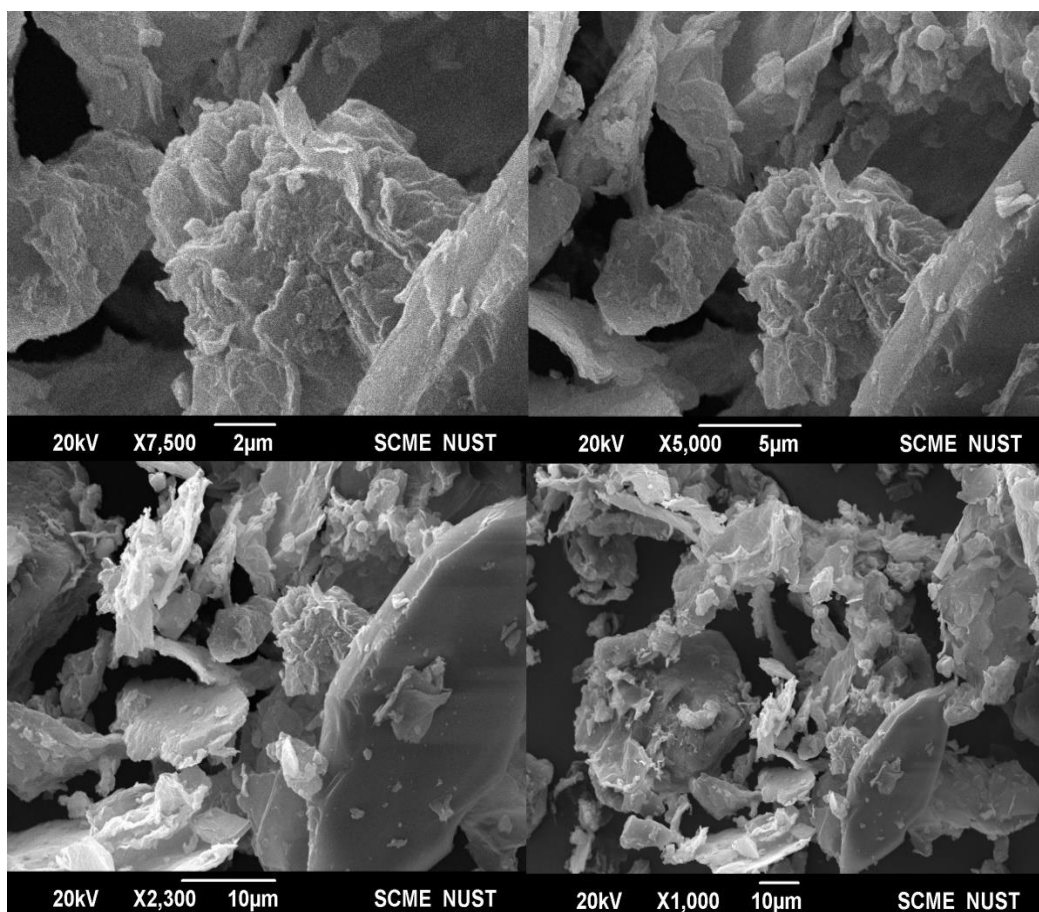


Figure 5.4: SEM images of rGO at different magnifications

5.4 SEM of Coated Samples

The surface characteristics of Ni-rGO nano composite coatings are shown in figure 5.5. These coatings were made on different deposition current densities specifically 3.6Adm^{-2} , 9Adm^{-2} and 14.5Adm^{-2} by electrochemical deposition technique. During the electrochemical deposition process graphene nano sheets were equally dispersed with in the nickel matrix which means that during the formation of coatings integration of graphene nano sheets into the layer of nickel occurred in a consistent manner.

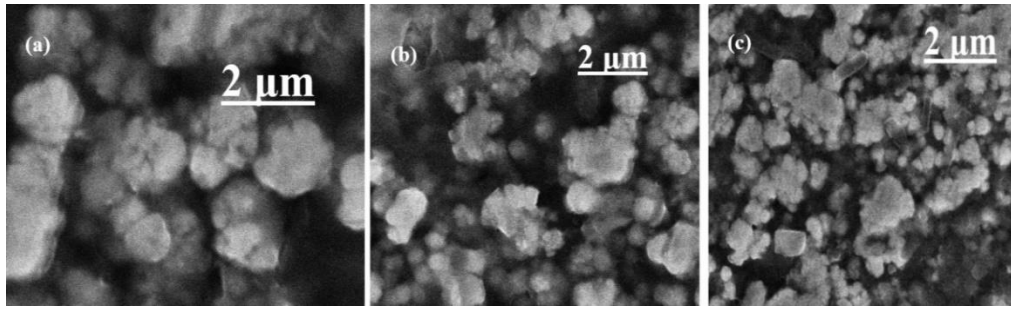


Figure 5.5: SEM morphology of coated samples (a) 3.6Adm^{-2} , (b) 9Adm^{-2} and (c) 14.5Adm^{-2}

With the increase in deposition current density bulges or protrusions can be observed on the surface of deposited coating. These bulges or protrusions were influenced by the level of deposition current density during the electrochemical deposition process.

In scanning electron microscopy the spherical shape of nano composite were observed. It was evident from the surface morphology that the coatings produced at lower current density had flat surface and uniform structure to some extent and less bulges on its surface as compare to coatings produced at high current density. At high current density 14.5Adm^{-2} bulges distribution were increased and it can be seen in figure 5.6.

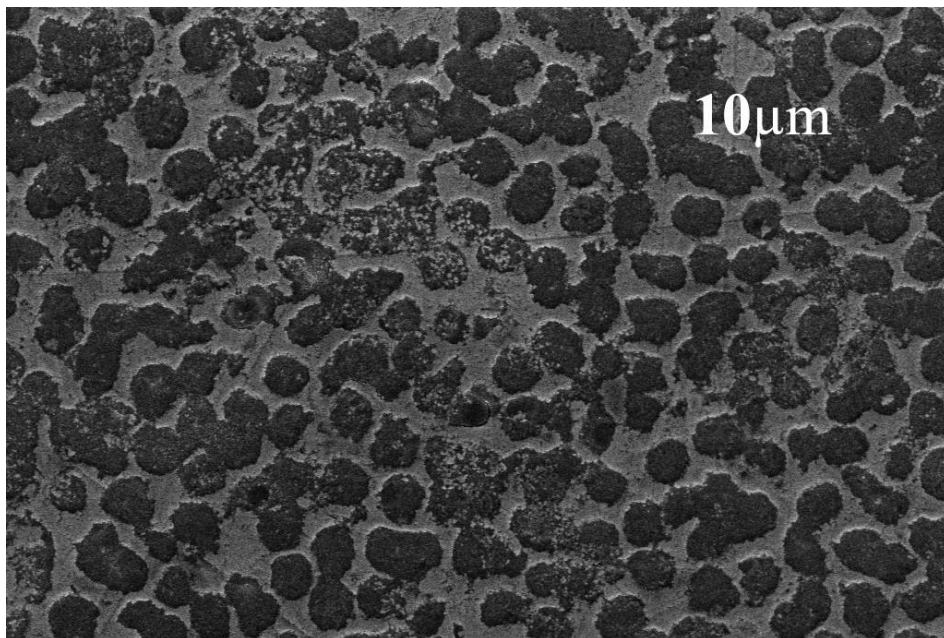


Figure 5.6: SEM image showing bulges in coated sample at peak deposition current density

5.5 Energy Dispersive X-ray (EDX) Composition Analysis

Energy dispersive x-ray (EDX) compositional analysis was carried out for Ni-rGO nano composite coatings developed at different deposition current densities and results showed that amount of carbon increased with increased in deposition current density. Coating which was developed at high deposition current density had high carbon content as compared to other which was developed at low deposition current density.

Reason for this increased in amount of carbon content in coating at high deposition current density was due the fact that graphene is more conductive as compare to nickel. The coating which we developed at high deposition current density indicated more amount of carbon content because at high current density there was fast reduction of nickel ions on the surface of cathode and a thin layer of metal deposited on the cathode. As graphene is more conductive then nickel so, due to the reduction process of nickel ions around graphene nano sheets the graphene nano particles started to incorporate into the nickel matrix. As we increased the deposition current density the reduction rate of nickel ions increased and more graphene nano particles were adding up in the nickel matrix.

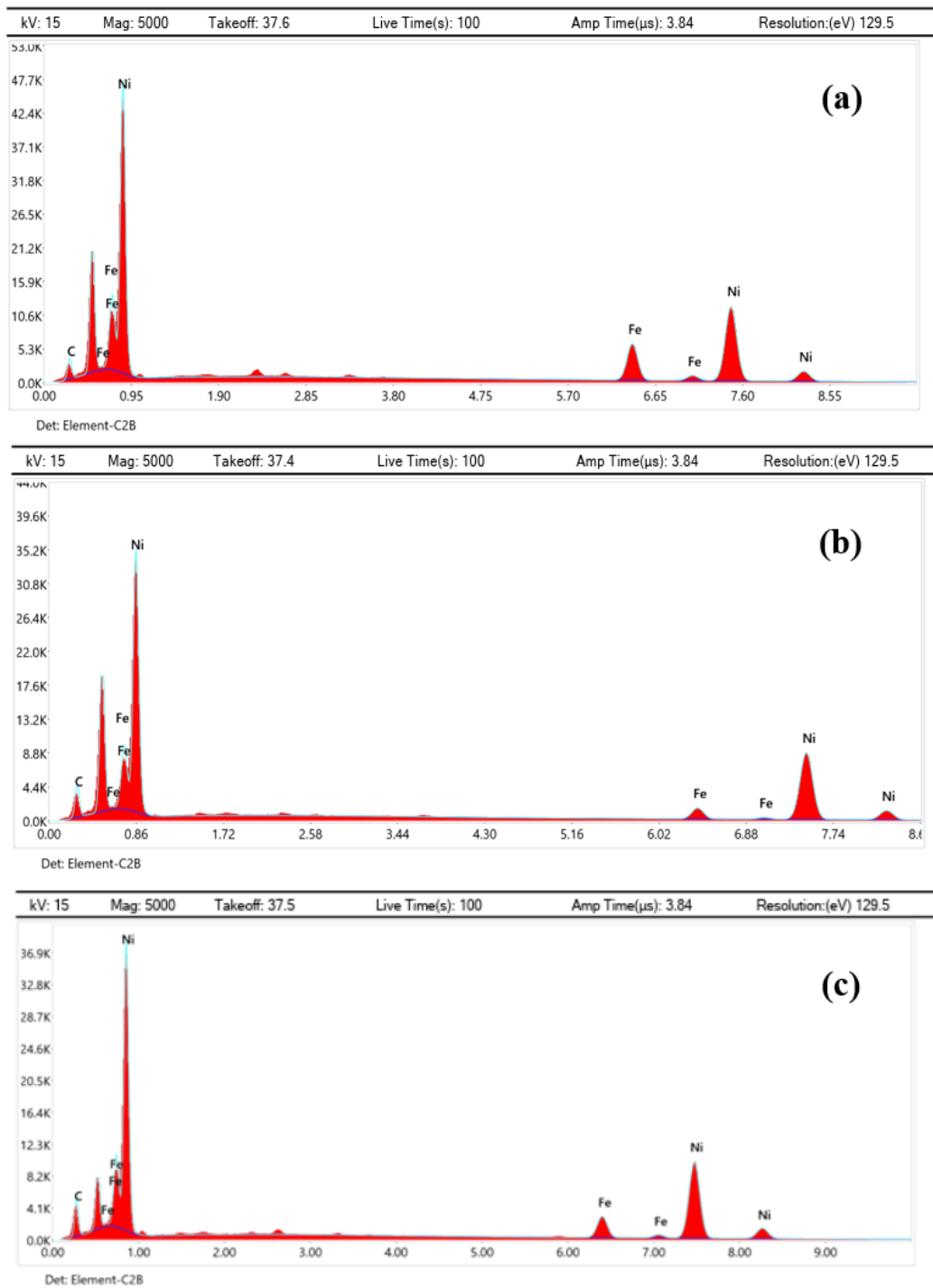


Figure 5.7: EDX analyses of coated samples (a) 3.6Adm⁻², (b) 9Adm⁻² and (c) 14.5Adm⁻²

Through energy dispersive x-ray (EDX) analysis it was confirmed that the amount of carbon content in coating increased with increased in deposition current density. Figure 5.7 shows the energy dispersive x-ray (EDX) analysis of Ni-rGO nano composite coatings developed at different deposition current densities. Effect of deposition current density on carbon amount in coatings is listed in table 5.1.

Table 5.1: Effect of deposition current density on carbon content

Deposition current density (Adm⁻²)	Weight percent of carbon (%)
3.6	6.34
9	10.81
14.5	12.77

It was observed that the coating developed at 3.6Adm⁻² showed 6.34 weight percent of carbon in it and coating which developed at 9Adm⁻² showed 10.81 weight percent of carbon while coating which developed at peak deposition current density of 14.5Adm⁻² showed 12.77 weight percent of carbon content in it which was higher than others. Figure 5.8 represents the graphical demonstration of effect of deposition current density on carbon content.

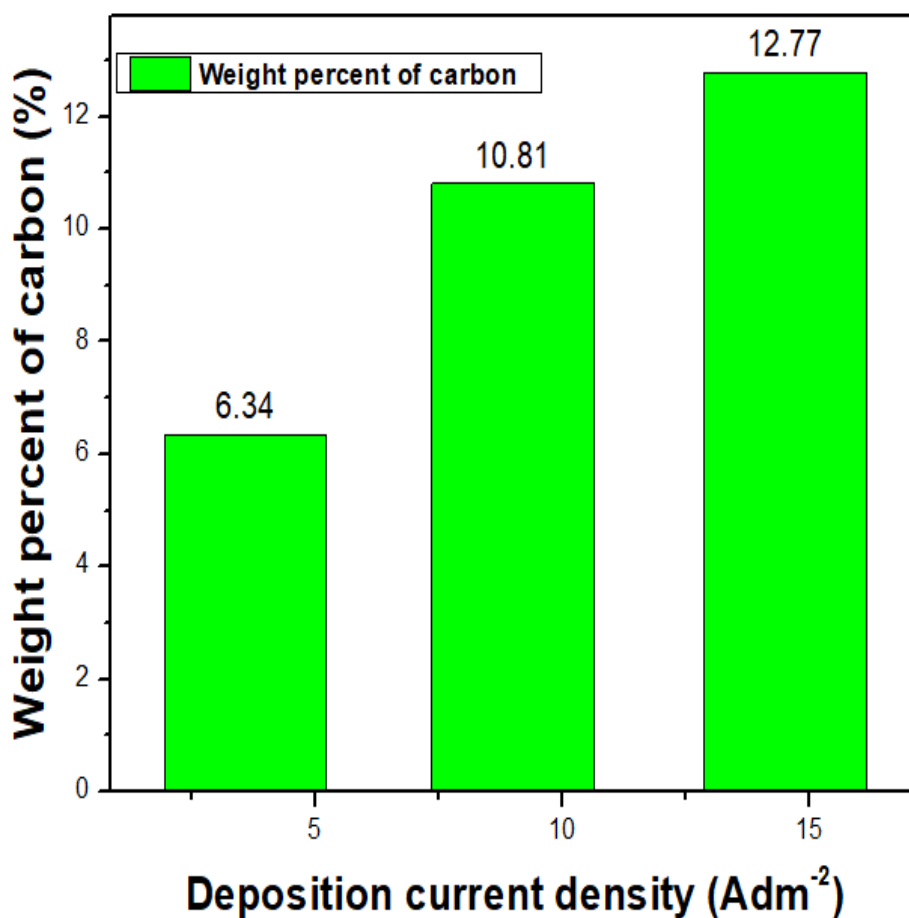


Figure 5.8: Effect of deposition current density on carbon content

5.6 X-Ray Diffraction (XRD) Results

XRD results of Ni-rGO nano composite coatings are given in figure 5.9, which showed peaks at (111), (200) and (220) planes which were similar in literature. It can be clearly observed that there was reduction in the intensity of (200) peak which was due to the addition of graphene in the nickel matrix and because of the increased in deposition current density. Coating which was developed at highest deposition current density showed maximum reduction in the intensity of (200) peak.

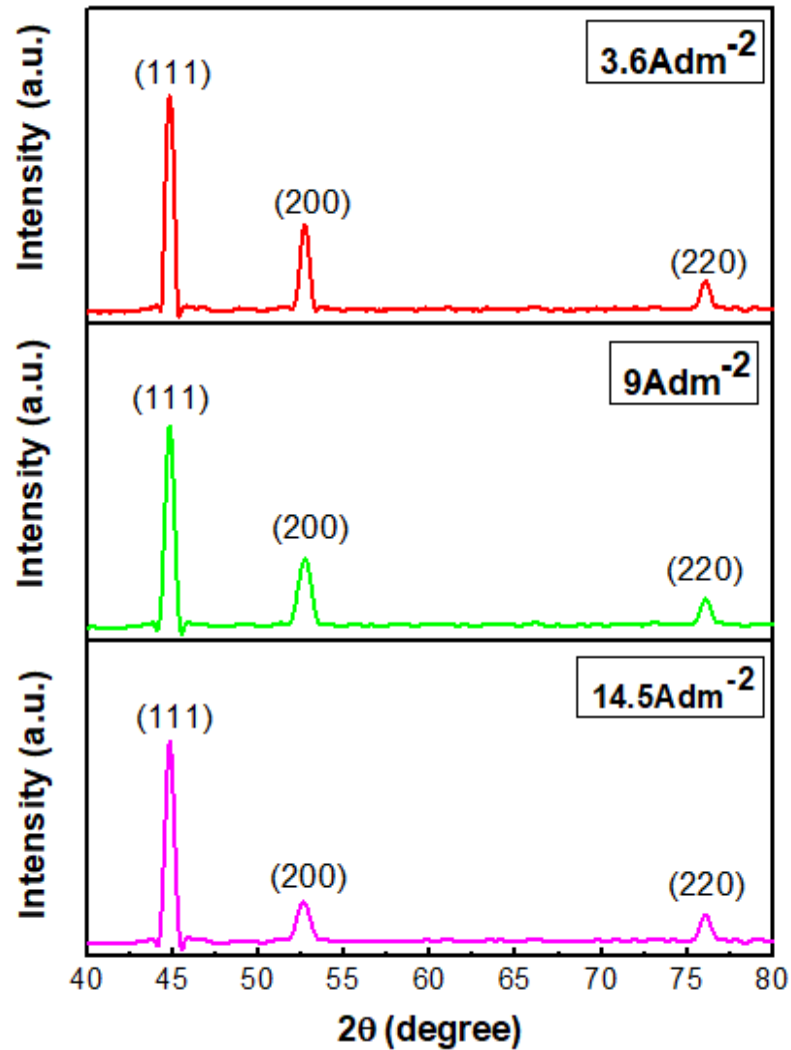


Figure 5.9: XRD patterns of coated samples

By these results of XRD it can be seen that the width of peak (200) became broader as deposition current density was increased from 3.6 Adm^{-2} to 14.5 Adm^{-2} . High deposition current density can influence the preferred orientation of crystallite within the coating and favoured the growth of crystallites with orientation other than the (200) plane, leading to decreased intensity of (200) peak. Increased defect formation within the coating occurred at high deposition current density also disturbs the long range ordering and contributed to decreased (200) peak intensity.

5.7 Roughness Assessment of Composite Coatings

Ni-rGO nano composite coatings fabricated at different current densities of 3.6, 9 and 14.5Adm^{-2} were assessed for roughness via 2-Dimensional Non-contact Profilometry. Main reason for roughness in composite coating was the formation of bulge morphology which was observed in SEM images. Roughness profiles of coated samples are shown in figure 5.11.

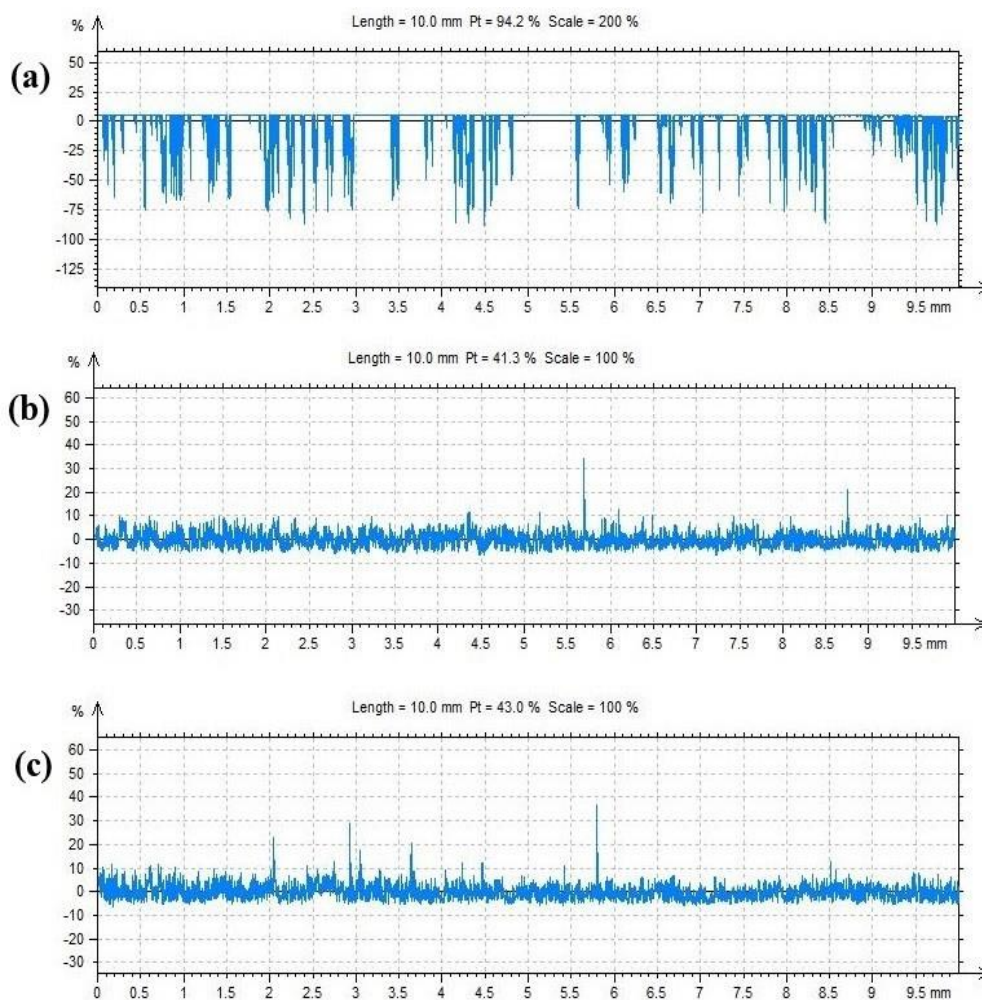


Figure 5.10: Roughness profiles of coated samples (a) 3.6Adm^{-2} , (b) 9Adm^{-2} and (c) 14.5Adm^{-2}

Graphene was added in nickel matrix by electrochemical deposition method and there was even distribution of graphene nano particles. Roughness of Ni-rGO nano composite coatings varied with the variation in carbon content in them and also due the bulges which were present randomly on the surface of our composite coating.

With increased in deposition current density there was increased in amount of carbon and bulge morphologies in composite coating and it was evident through EDX and SEM. Figure 5.12 shows the effect of deposition current density on roughness of nano composite coatings.

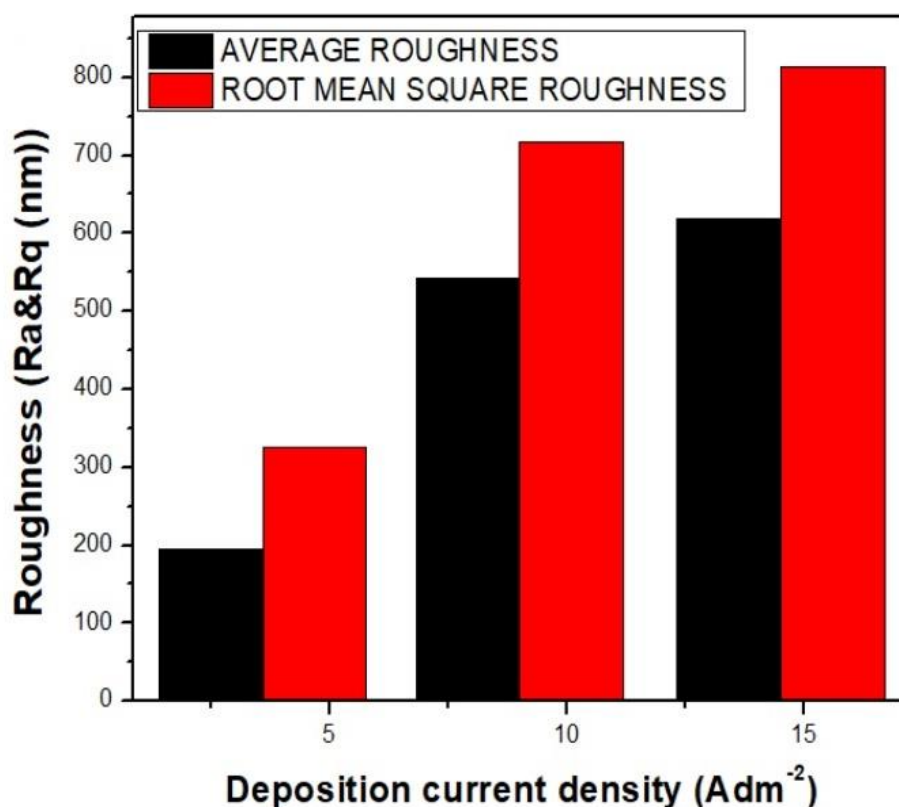


Figure 5.11: Effect of deposition current density on roughness

In our case of Ni-rGO nano composite coating, graphene had more electrical conductance than nickel and during formation of coating by electrochemical deposition high electric field was applicable on graphene and there was high reduction rate of nickel ions on surface of graphene which caused the bulge morphology in our coating due to the large difference in depositing rates around graphene nano particles and in other areas. It was observed that at low deposition current density, coating had flat surface up to some extent while at high deposition current density number of bulges increased due to which roughness of composite coating increased. High numbers of bulges were formed at peak deposition current density of 14.5 A dm^{-2} as

compare to 3.6Adm^{-2} and 9Adm^{-2} , so roughness of composite coating developed at 14.5Adm^{-2} was more. Table 5.3 shows the roughness assessment of nickel-graphene nano composite coatings developed at different current densities.

Table 5.2: Roughness profile of Nickel-Graphene nano composite coatings

DEPOSITING CURRENT DENSITY (Adm^{-2})	ROUGHNESS	
	AVERAGE ROUGHNESS	ROOT MEAN SQUARE ROUGHNESS
	Ra (nm)	Rq (nm)
3.6	195	325
9	543	718
14.5	619	813

5.8 Potentiodynamic Polarization Curves Measurements of Composite Coatings

Corrosion testing of Ni-rGO nano composite coatings fabricated at different deposition current densities was carried out in 3.5% neutral NaCl solution with graphite rod as counter electrode and saturated calomel electrode (SCE) as reference electrode. Before carrying out polarization testing open circuit potential (OCP) of all the samples were first stabilized. Polarization testing showed the effect of deposition current density on corrosion rate of composite coatings. Coating prepared at high deposition current density showed high corrosion resistance then others. Along with coated samples plane sample was also tested to show comparison of both in terms of corrosion rate. Tafel plots of coated samples and plane sample are shown in figure 5.13.

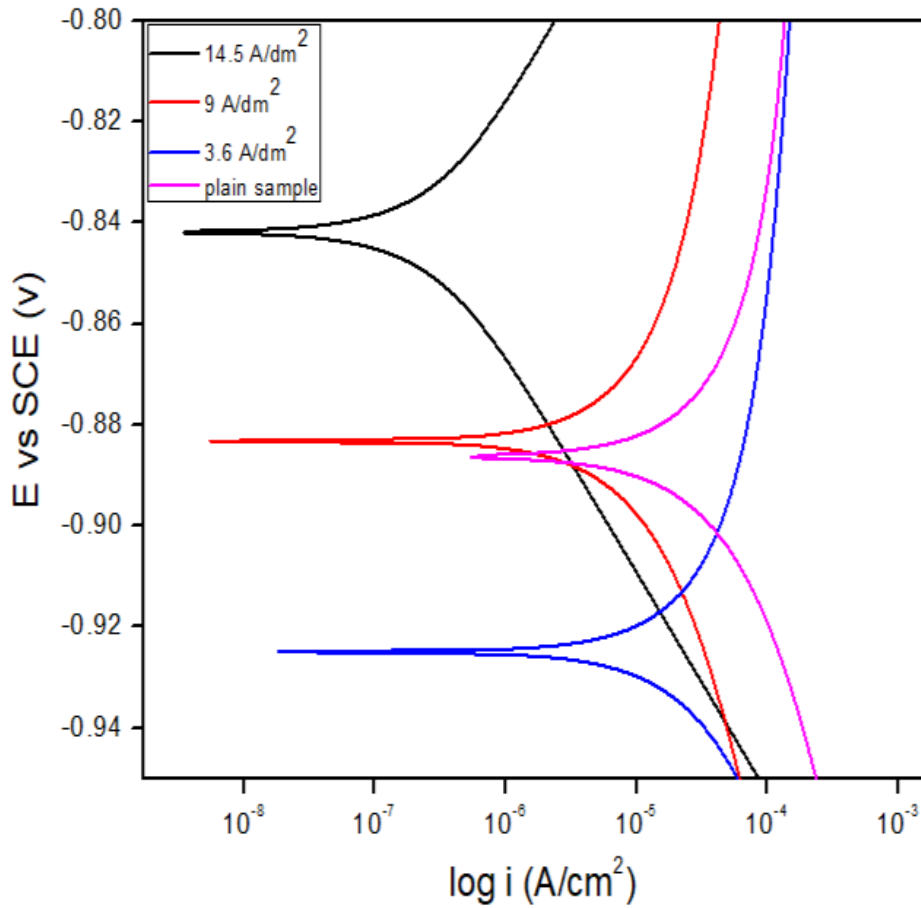


Figure 5.12: Polarization curves for coated samples and plane sample

Corrosion current density (I_{corr}) provides us the kinetic information and it is directly related to corrosion rate. Corrosion current density (I_{corr}) provides us the rate at which coatings are oxidizing (corroding). Higher values of I_{corr} are indicating fast corrosion rate and similarly smaller values indicates slow corrosion rate. I_{corr} in tafel plots are direct values which can provide us information regarding corrosion rate and it is directly proportional to corrosion by faradays law.

Corrosion potential (E_{corr}), is not a quantity which tell us directly about corrosion rate, it only tells about thermodynamic tendency of material to corrode.

It was clearly observed in our case as shown in table 5.4 that nano composite coating of Ni-rGO which had smaller corrosion current density (I_{corr}) gave smaller corrosion rate. Mechanism of corrosion mainly depends upon the addition of graphene in the composite coating. Homogeneous distribution of graphene in nickel matrix during

electrochemical deposition process increased the corrosion resistance of composite coating because graphene filled the pores/cavities in nickel matrix which decreased the possibility of defects in coating. There was also the large difference of potential between graphene and nickel which supported in passivation of coating and increased the corrosion resistance of composite coating. As graphene nano particles were strengthening phase in nickel matrix which was also one of the reason which increased the corrosion resistance of composite coating. And due to the higher deposition current density grain size of Ni-rGO nano composite coating was reduced, which enhanced the corrosion resistance of coating. Table 5.5 shows the corrosion current density, corrosion potential and corrosion rate of plane sample.

Table 5.3: Effect of deposition current density on corrosion current density, corrosion potential and corrosion rate of coated samples

Deposition Current Density (A dm⁻²)	Corrosion Current Density (I_{corr}) (A cm⁻²)	Corrosion Potential (E_{corr}) (mV)	Corrosion Rate (mpy)
3.6	2.13×10^{-4}	-0.925	84.125
9	3.2×10^{-5}	0.883	26.62
14.5	2.8×10^{-7}	-0.842	0.2635

Table 5.4: Corrosion current density, corrosion potential and corrosion rate of plane sample in 3.5% neutral NaCl solution

Plane steel sample	Corrosion Current Density (I_{corr}) ($A\ cm^{-2}$)	Corrosion Potential (E_{corr}) (mV)	Corrosion Rate (mpy)
	1×10^{-4}	-0.886	176.931

5.9 Electrochemical Impedance Spectroscopy (EIS) of Composite Coatings

Electrochemical impedance spectroscopy (EIS) of Ni-rGO nano composite coatings prepared at different deposition current densities was also carried out in 3.5% neutral NaCl solution to get information regarding corrosion resistance of these coatings.

Figure 5.14 shows the impedance spectra (EIS) of coatings developed at different deposition current densities and of plane sample. Result of EIS spectra indicated the high impedance value for composite coating developed at high deposition current density $14.5\ Adm^{-2}$ and low impedance value for uncoated/plane sample. The EIS spectra showed semi circles of different sizes for composite coating prepared at different deposition current densities and plane sample. Large diameter of semicircle indicated high resistance to corrosion and it was observed in the case of coating developed at peak deposition current density of $14.5Adm^{-2}$.

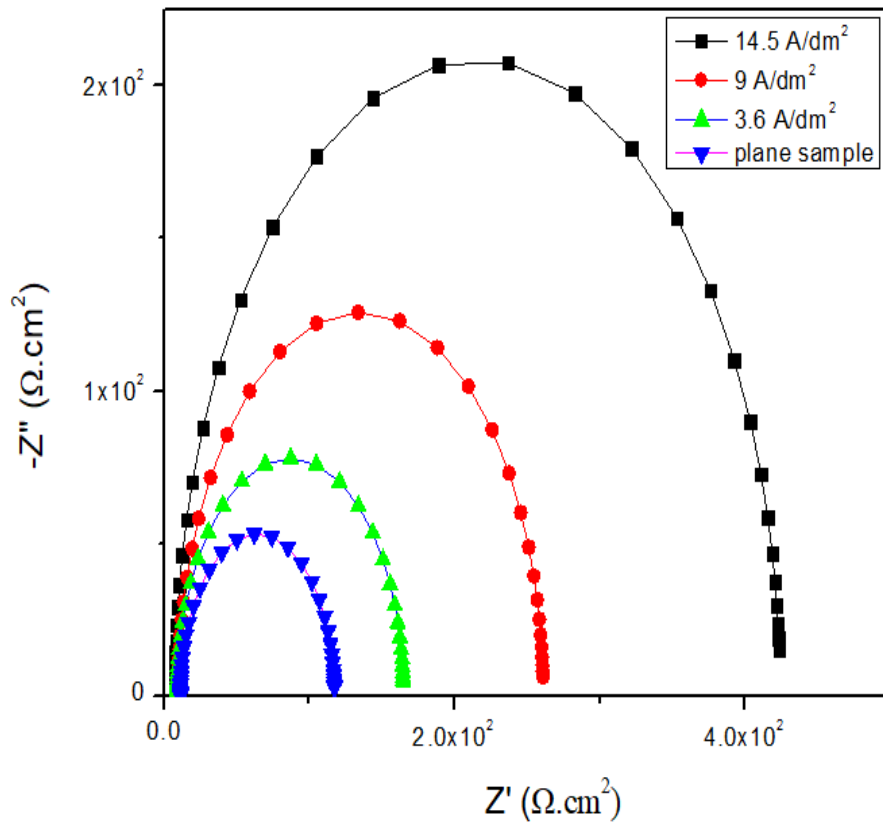


Figure 5.13: EIS spectra of coated samples and plane sample

CHAPTER 6: CONCLUSIONS

In this research work nano composite coatings of nickel-graphene were made by electrochemical deposition method on different deposition current densities on steel substrates for getting better corrosion resistance against aggressive environment. XRD and EDX results confirmed the formation of nano composite coating on steel substrate by showing relevant reduction in specific peak and showing increase in amount of carbon content with the increase in deposition current density. Then nano composite coating fabricated different deposition current densities were spherical in nature observed by SEM. Nano composite coatings developed at peak value of deposition current density 14.5Adm^{-2} showed high amount of carbon content 12.7 weight percent and more reduction in (200) peak then other coatings fabricated at low deposition current densities. Results showed that the roughness of nano composite coating fabricated at peak value of deposition current density 14.5Adm^{-2} was higher in comparison to low deposition current density coatings, root mean square roughness (Rq) and average roughness (Ra) were noted to be 813 nanometers and 619 nanometers respectively. As observed by SEM there were more number of bulge formation with increasing the deposition current density up to 14.5Adm^{-2} that was the reason for increase in roughness of nano composite coating developed at peak value of deposition current density. Tafel plots were made by carrying out polarization testing in 3.5% NaCl solution for observing the corrosion resistance of these coatings and plane sample. Results showed that corrosion rate ranges from 0.2635-176.931mpy (mils per year). Plane sample showed corrosion rate of 176.931mpy and sample with nano composite coating fabricated at peak value of deposition current density showed corrosion rate of 0.2635mpy which was much lowered then all others. EIS carried to get information regarding corrosion resistance of composite coatings fabricated at different current densities and plane sample. EIS spectra showed high impedance value for coating developed at peak value of deposition current density 14.5Adm^{-2} . Semicircles of different diameters were observed in EIS spectra and they gave indication of corrosion resistance. Large diameter semicircle was observed for composite coating prepared at peak value of deposition current density and indicated high corrosion resistance similarly, smaller diameter semicircle was observed for plane sample and indicated low corrosion resistance.

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