

**Development of Chromium and Chromium-Nickel
Electro Coated Mild Steel to Enhance Corrosion
Resistance Comparable to 304 Stainless Steel in 3.5%
Chloride Water**

A Thesis submitted in partial fulfillment of the requirements for the award of degree of

MASTER OF ENGINEERING IN METALLURGICAL ENGINEERING

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Declaration of Originality and Compliance of Academic Ethics

I hereby declare that this thesis contains literature review and original research work by the undersigned candidate, as part of his "*Development of Chromium and Chromium-Nickel Electro Coated Mild Steel to Enhance Corrosion Resistance Comparable to 304 Stainless Steel in 3.5% Chloride Water*" studies.

All information in this document have been obtained and presented in accordance with academic rules and ethical conduct.

I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work and taken from different resources.

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Certificate

This is to certify that the entitled '*Development of Chromium and Chromium-Nickel Electro Coated Mild Steel to Enhance Corrosion Resistance Comparable to 304 Stainless Steel in 3.5% Chloride Water,*' has been carried out by **Mr. Rakesh Kundu (Examination Roll No: M4MET19015, Registration No: 140893 of 2017-18)** under my guidance and supervision and accepted in partial fulfilment for the degree of Master of engineering in Metallurgical Engineering from Jadavpur University. To the best of our knowledge the contents of this thesis or any part thereof have not been previously submitted for the award of any degree or diploma.

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The foregoing thesis is hereby approved as a creditable study of an engineering subject and presented in a manner satisfactory to warrant acceptance as pre-requisite to the degree for which it has been submitted. It is understood that by this approval the undersigned do not necessarily endorse or approve any statement made, opinion expressed or conclusion drawn there in but approve the thesis only for which it is submitted.

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Chapter1 : Introduction



Introduction :

304 austenitic stainless steel is a very high corrosion resistant construction material widely used in aqueous and open atmosphere. The presence 18% Cr imparts passivity to it and 8% Ni gives it strength , ductility and toughness. This alloy steel is much costlier than mild steel which has the greatest use as structural material in tonnage basis, being very cheap, available, good strength and ductility . Since corrosion initiates from the surface and Cr imparts passivity to steel, an attempt has been made to coat mild steel with Cr and investigate, if its corrosion resistance can be increased close to the level of 304 stainless. Ni was also co deposited with Cr to enhance its corrosion property further .

Corrosion properties, namely corrosion potential , corrosion current density , pitting potential and passivity were determined electrochemically by potentiodynamic polarization and cyclic polarization. These corrosion properties were compared with those of stainless steel. Cr % and Ni-Cr % were varied to obtain the best corrosion resistance material.

To investigate further, the electrochemical phenomenon occurring at Steel-Solution interface Electrochemical Impedance Spectroscopy (EIS) studies were performed . Polarization resistance, Impedance and double layer capacitance were computed and compared with those of stainless. The R-L-C circuit evaluated from EIS studies helped to understand the fundamental science of enhancing corrosion resistance By Cr and Ni coating.

The constituents of coating and the difference phases were analyzed by X ray diffraction study. It helped to investigation passivity and passivity breakdown .

Electro coated mild steel so developed will have much less cost compared to that of stainless steel but exhibit high corrosion resistance in aqueous body such river, seawater and underground soil. So the cost of construction materials such as pipe lines, rods , plates etc. can be brought down, still maintaining very good life of structures in corrosive environments.

Chapter 2 : Literature Review

2.1 MILD STEEL

Steel is an alloy of carbon and iron containing carbon up to maximum of 1.5- 2 % .The carbon presents in the form of iron carbide which results in increase the hardness and strength of the steel. certain amounts of silicon, phosphorus, sulphur and manganese are also present which provide desirable properties to carbon steel. Most of the steels produced recently is the plain carbon steel or carbon steel.

A carbon steel is defined as a steel which has its properties mainly due to its carbon content and does not contain more than 0.5% of silicon and 1.5% of manganese [2]. The plain steels are usually classified in their carbon content,

There are mainly two types of carbon steel i.e. plain carbon steel and alloy carbon steel. Plain carbon steel contains carbon and iron in addition with notably amount of sulphur, silicon, phosphorus and manganese. Plain carbon steel can be grouped into the followings-

- Low carbon steel : contains 0.05-0.3 % carbon
- Medium carbon steel : contains 0.3-0.9 % carbon
- High carbon steel : contains 0.9-1.1% carbon
- Ultra high carbon steel: contains 1.1-2% carbon

Plain carbon Steel containing small percentage of carbon (almost less than 0.2%) is known as mild steel. The presence of less amount of carbon provides the malleable and ductile property to it. Mild steel is the most common form of steel as the cost of it is relatively low while it provides the material properties which are acceptable for many applications. Though , it does not have very good tensile strength but it is cheap and easy to form. The surface could be hardened by heat treatment.

As the carbon content rises in the plain carbon steel , it becomes very harder and shows less ductility.

In applications where large cross sections are used to minimize deflection , failure by yield is not a risk , low carbon steel or mild steel are choosen, for example as structural steel. The density of mild steel is 7.87 g / cm^3 and the young's modulas is 200 GPa.

2.11 corrosion of mild steel

Corrosion is defined as the destruction or degradation of metal by direct chemical and electrochemical reaction with its environment. Corrosion can also be defined as the reverse phenomenon of electroplating.

plain Carbon steel is the most widely used as engineering material. Despite its relatively limited corrosion resistance, carbon steel is used in large tonnages in marine applications, nuclear power and fossil fuel power plants, transportation, chemical processing, petroleum production and refining, pipelines, mining, construction and metal-processing equipment [1].

The cost of metallic corrosion to the total economy must be measured in hundreds of millions of money per year. Because carbon steels represent the largest single class of alloys in use, both in terms of tonnage and total cost, it is easy to understand that the corrosion of carbon steels is a major problem of practical importance. This is the reason for the existence of entire industries devoted to providing protective systems for irons and steel [1].

Carbon steels are usually less than 2% by weight for total of additions. Unfortunately, these levels of addition do not generally produce any remarkable changes in general corrosion behavior. One possible exception to this statement would be weathering steels, in small additions of copper, chromium, nickel and phosphorus produce significant reduction in corrosion rate in certain environments [1].

2.12 Factors Influencing Corrosion Of Plain Carbon Steels

Generally, the factors which affect the rate of corrosion of plain carbon steels depends on either material or environment or a combination of both . Some of the factors which are associated mainly with metals are:

- Chemical and physical homogeneity of the metal surface [2].
- pH in the solution
- Ability to form a thin protective layer
- presence of oxygen in the solution adjacent to the metal
- Rate of flow of solution in contact with metal [2].
- Presence of corrosive ions such as chloride ions etc.

2.2 stainless steel

'Stainless' is a term coined early in the development of these type of steels for cutlery applications [3]. It was adopted as a generic name for these steels and now covers a wide range of steel types and grades for corrosion or oxidation resistant applications.

Stainless steel is an alloy steel containing iron, carbon, chromium and two or more chemical elements. Stainless steel is used in a wide range of applications. It has excellent resistance to stain i.e. corrosion due to its chromium content, usually from 12 to 20 % of the alloy.^[4] Other alloying elements are added to enhance or provide their structure and properties such as formability, strength and toughness. Such alloying elements which are added to it are Nickel, Molybdenum, Titanium, Copper. Non-metal inclusions are also made, such as: Carbon, Nitrogen [3].

The required property for stainless steels is that they should be corrosion resistant in particular environment so that they can be used for a specified application. The selection of a particular type of stainless steel must be initially depended on fulfillment of the corrosion resistance property. Additional properties such as mechanical, metallurgical or physical properties also need to be considered to meet the overall service performance requirements.

There are more than 57 stainless steels which are recognized as standard alloy steel produced by different stainless steel producers [4]. These various types of steels are used in an endless number of applications and industries such as materials handling equipment, automobile components (exhaust, trim/decorative, engine, chassis, fasteners, tubing for fuel lines), chemical processing plants (scrubbers and heat exchangers), petroleum refining, water supply piping, consumer products, marine and shipbuilding, pollution control and transportation (rail cars) [4].

2.21 Raw Materials

Stainless steels are the alloys made of some of the basic elements such as iron, chromium, silicon, nickel, carbon, nitrogen, and manganese. Properties of the alloy (stainless steel) are achieved by varying the amounts of these elements. For example, Nitrogen improves tensile properties of stainless steel like ductility [4]. Chromium improves corrosion resistance.

2.22 The Manufacturing Process

The production of stainless steel involves a series of processes.

- The raw materials are first melted together in an electric furnace. This is a time consuming process. Almost 10 hours could be required for melting. When the melting is finished, the molten steel is cast into semi-finished forms. These include blooms, billets, slabs, rods.

Blooms have the rectangular shapes while billets are round or square shapes.

- Then the steel goes through forming operations, beginning with hot rolling. In hot rolling, the steel is heated and passed through rolling operations. Blooms and billets are formed into bar and wire, while slabs are formed into plate, strip, and sheet [4]. Plate, bar, strip, sheets of different sizes are also produced.
- Then, it must go through the heat treatment process. Annealing is a heat treatment process in which the steel is heated and cooled inside the furnace under the controlled conditions to relieve internal stresses and soften the metal. Further heat treating may take place to achieve the desired properties of the steel.
- Heat treating causes scale formation on the surface of the steel. The scale can be removed using several processes. Two methods are generally used for descaling of steel. One is acid pickling where nitric-hydrofluoric acid is used and the other process is known as electro cleaning.
- Cutting operations are usually required to obtain the desired shape or size to trim the part to final product with proper dimension. Mechanical cutting is accomplished by a variety of methods, including straight shearing, circle shearing (using horizontally and vertically positioned circular knives), shearing using high speed steel blades of hacksaw. Blanking uses metal punches and dies to punch out the desired shape by shearing with the application of hydraulic or mechanical forces.
- Surface finish is an important parameter for stainless steel products and is hard to achieve in such applications where appearance is also important. However surface finishes also make stainless steel easier to clean, which is obviously important for sanitary applications [4].
- Further shaping is accomplished using different forming methods. For joining stainless steel, welding is being the most common. Fusion and resistance welding are the two basic methods generally used with many variations for both the process. After parts are welded together, they must be cleaned around the joined area.
- In addition to precise control in temperature, time and other parameters during manufacturing and fabrication, stainless steels must meet specifications developed by the American Society for Testing and Materials (ASTM) with regard to mechanical properties such as toughness and corrosion resistance [4]. Metallography can sometimes be correlated to corrosion tests to help monitoring the quality of the stainless steel [4].

2.23 Types of stainless steel

There are mainly four types of stainless steel, which are primarily classified by their crystalline structure; austenitic, ferritic, martensitic and duplex.

Austenitic stainless steel

Austenitic stainless steel is the largest family of stainless steels, making up about two-thirds of all stainless steel production. They possess an austenitic microstructure i.e face-centered cubic crystal structure. This type of microstructure is achieved by alloying with sufficient nickel and manganese and nitrogen to maintain an austenitic microstructure at all temperatures [12]. Austenitic stainless steels contain at least 6 percent nickel and austenite. Thus austenitic stainless steels are not hardenable by heat treatment since the same austenitic microstructure should be maintained at all temperatures.

Austenitic stainless steel can be strengthened by cold working [12]. They also have good corrosion resistance and show high ductility even at cryogenic temperatures.

They can be further divided into two sub-groups, 200 series and 300 series:

- 200 Series are the stainless steels containing chromium, manganese, nickel. Manganese and nitrogen are used in large proportion to minimize the use of nickel. Due to their nitrogen addition, 200 series stainless steel provides approximately 50% higher yield strength than 300 series stainless steels. Decreasing nickel content and increasing manganese results in weak corrosion resistance [5].
- 300 Series are the stainless steels containing mainly chromium and nickel. This type of stainless steels achieves its austenitic microstructure almost exclusively by the addition of nickel [12]. 300 series is the largest group and the most widely used.

example: The best grade of austenitic stainless steel is type 304, also known as its composition 18/8 and 18/10. The composition of 304 stainless steel contains 18% chromium and 8% or 10% nickel, respectively for 18/8 and 18/10. The second most common austenitic stainless steel is Type 316. The addition of 2% molybdenum provides greater resistance to acids and to localized pitting corrosion caused by chloride ions. 316L or 304L are the examples of Low-carbon versions of austenitic stainless steel. They are used to avoid corrosion problems caused by welding [12].

Ferritic stainless steels

Ferritic stainless steels achieve a ferrite microstructure like carbon steel. Ferrite has a body-centered cubic structure. Ferritic stainless steels contain 10.5% - 27% chromium with very little or no nickel. This microstructure is possessed at all temperatures due to the chromium addition. Ferritic stainless steels are not hardenable by heat treatment like austenitic stainless steels to maintain its microstructure at any temperatures. They cannot be strengthened by cold work to the

same degree as austenitic stainless steels[12]. They are magnetic like carbon steel. They have better resistance to stress corrosion than austenitic stainless steel, but they are difficult to weld [6].

Martensitic stainless steels

Martensitic stainless steels provide a wide range of properties and are used as stainless engineering stainless tool steels, creep resisting steels. Martensitic stainless steel can be heat treated to achieve different types of mechanical property. The heat treatment of martensitic stainless steel is a 3-step process.

First, it is heated to the temperature of 980°-1500° C. Thus austenitic microstructure is achieved. Then, it is quenched in air, oil or water medium which results in body centred tetragonal structure i.e forms martensite. Martensite is too brittle to use for most of the applications. So, it is further heat treated. It is heated at 500° C and held at the temperature for a long period of time and then air cooled. This process is known as tempering. The mechanical properties such as yield strength, ultimate tensile strength, Impact resistance depend on the tempering temperature.

They are grouped into 4 sub-categories [12] :

1. **Fe - Cr - C grades:** They were the first grades used and they are still widely used in wear-resistant applications.
2. **Fe-Cr-Ni-C grades:** In these grades, some of the Carbon is replaced by Nickel. They provide a higher toughness and a higher corrosion resistance.
3. **Precipitation Hardening grades:** Grade 17/4PH, the best known grade, combines martensitic hardening and precipitation hardening which results in achieving high strength and good toughness. These type of stainless steels are used in aerospace engineering.
4. **Creep-resisting grades:** small additions of V, B, Co increase the strength and creep resistance up to about 650 °C.

Martensitic stainless steel are not as corrosion resistant as the common ferritic and austenitic stainless steels due to their low chromium content [12]. This problem is partially solved by recent development. Some of the Carbon in martensitic stainless steels are replaced by Nitrogen. The limited solubility of Nitrogen has been increased by the Pressure Electroslag Refining process in which melting of steel is carried out under a high nitrogen pressure [8]. Up to 0.4% N contents have been achieved which results in higher hardness/strength and higher corrosion resistance. As the PESR process is expensive, comparatively lower but significant N contents have been achieved using the standard AOD process [7].

Duplex stainless steel

Duplex stainless steels have a mixed microstructure of austenite and ferrite. They generally contain equal amounts of ferrite and austenite, although in commercial alloys the ratio may be 40:60 [12]. They also contain large amount of chromium (19–32%) and molybdenum (5%) and much lower nickel contents than austenitic stainless steels. Mixed microstructure of duplex stainless steels provide improved resistance to pitting and crevice corrosion in most environments in comparison to austenitic stainless steels Types 304 and 316. They also have superior resistance to cracking due to chloride stress corrosion[12]. Therefore, duplex stainless steels are widely used in the chemical industry in refineries, gas-processing plants, pulp and paper plants, and sea water piping installations[12].

Duplex grades are characterized into groups based on their alloy content and corrosion resistance.

Precipitation hardening stainless steels

Precipitation hardening stainless steels have corrosion resistance comparable to austenitic varieties, but can be precipitation hardened to even higher strengths than the other martensitic grades.

There are 3 types of precipitation hardened steel:

- Martensitic : contains about 17% Cr, 4%Ni, 4%Cu and 0.3% Nb [9].Solution treatment at about 1000°C is followed by quenching in water or oil . As a result a relatively ductile martensitic structure is achieved. Then ageing treatment at 475°C is performed which helps to precipitate Nb and Cu-rich phases that increase the strength up to above 1000MPa yield strength[12]. Another major advantage of this steel is that ageing. Unlike tempering treatments, it is carried out at a temperature that can be applied to finished parts without distorsion. .So, there is no risk of internal stressing. This type of steel finds uses in high tech applications such as aerospace [12].
- Semi Austenitic : contains about 17% Cr, 7.2% Ni and 1.2%Al[9] . First ,solution treatment and quenching are performed . Though the microstructure remains austenitic. It is then transformed into martensite either by a cryogenic treatment or by severe cold work usually by cold rolling or wire drawing. Ageing at 510°C is followed then which precipitates the Ni₃Al. Yield stress reaches above 1400MPa[12].
- A286 is another type of hardened precipitation stainless steel which contains Cr 15%, Ni 25% Ti 2.1% Mo 1.2% V 1.3% and B 0.005% [10].

The structure remains austenitic at all temperatures. At first, solution treatment and quenching is performed, followed by ageing at 715°C. Ageing results Ni₃Ti precipitates and increase the yield strength to about 650MPa. Unlike the above steels, the mechanical properties and creep resistance of this PH steel remains unchanged upto a certain temperature.

A286 is in fact a Fe-based superalloy, used in jet engines and gas turbines, turbo parts, etc.

The designation "CRES" is used in various industries to imply to corrosion-resistant steel [3].

2.3 Corrosion property of stainless steel

Stainless steel is mainly known for its corrosion resistance property. In such environments where other plain carbon steels corrode easily, stainless steel possesses good corrosion resistance. Corrosion resistance property of stainless steel is the reason for the widespread use of it. Stainless steels provide good corrosion resistance because a thin protective layer spontaneously forms on their surfaces due to the presence of chromium and reduces the rate of corrosion to almost negligible levels. This protective layer can heal itself very fast if any scratches are made under normal conditions. If stainless steels only suffered from uniform corrosion, they could survive for literally millions of years.

Passivity

As mentioned earlier, the main reason for the good corrosion resistance property of stainless steels is the formation of a very thin protective film on the surface. This surface layer is an oxide of chromium that protects the steel from attack in a corrosive environment. As chromium is added to the stainless steel, a rapid reduction in corrosion rate is achieved because this protective layer or passive film is formed on the surface. In order to obtain a thin but compact and continuous passive film, almost 18% chromium content is required in steels [13].

Therefore, it can be said that the most important alloying element of stainless steel to achieve good corrosion resistance is chromium. But other alloying elements such as molybdenum, nickel and nitrogen may also contribute to the corrosion resistance of stainless steels. Some of the alloying elements may help to achieve corrosion resistance property in specified environments, for example copper in sulfuric acid or silicon, cerium and aluminum in high temperature corrosion in some gases [14].

A stainless steel must be oxidized in order to form a passive film as the film is made of chromium oxide. The more corrosive the environment, the more oxidizing agents are required to combat against the corrosion. Stainless steels have such a strong tendency to passivate that very small amounts of oxidizing species are required for formation of the passive layer. As the passive film is self-healing, i.e. the passive layer can be healed automatically if there are any mechanical scratches or chemical damages, it is better to use than a layer of paint on plain carbon steel surface. In order to achieve the repassivation of the surface film, chromium content of the stainless steel must be high. So it can also be said that stainless steels are most suitable in oxidizing, neutral or weakly reducing environments because of the formation of the oxide layer to protect the material against a corrosive environment. The corrosion rate is much higher when stainless steels are used in hydrochloric acid as it possesses a highly reducing environment so that the passive layer can't be formed [15].

To Corrode stainless steel , the passive film on the surface has to be broken down. corrosion can occur by different mechanisms depending on the conditions of use and the nature of the environment. The most common types of corrosion are:

Uniform corrosion: Uniform corrosion of stainless steels can take place in acidic or hot alkaline solutions as the environment is highly reducing in nature. It results in uniform degradation of material.

Generally corrosion protective passive layer is formed with high chromium content which results in good corrosion resistance. In some specified case , other alloying elements can play a role to the corrosion behavior of the stainless steel. For example, Sulfur in solid solution is caused difficulty to form passive layer. So, sulphur is generally undesirable for good corrosion properties.

Nickel is generally used as austenitic stabilizer in stainless steel of grade 300 i.e it helps to retain the austenite phase of stainless steel at any temperature. But it is noticed that nickel can significantly improve the corrosion resistance property of stainless steels. Therefore , the austenitic stainless steels series achieve better corrosion resistance than the martensitic or ferritic stainless steels which contain no nickel [15].

Pitting corrosion: Pitting corrosion is occurred due to the local destruction of the passive film which leads to the subsequent degradation of material on that place. chloride, halide or bromide ions are the main culprit of this phenomenon. Pitting corrosion involves two step such as initiation of pitting and the propagation of pitting. In order to the occurrence of pitting corrosion , the passive layer on the surface of the stainless steel should be destructed. The destruction of that layer takes place because of the surface defect which leads to the local degradation of the passive film. It leads to a build-up of positively charged ions which starts dissolved in the solution just below the degraded passive layer. This build-up of positively charged metallic ions attracts the negatively charged ions to that place . In chloride environment , chloride ions are migrated to the place where the passive layer is degraded. The pH of the solution also reduced locaaly to 2-3 which leads to prevent the repassivation.

In the passive condition, the current density is too low, generally in the range of 10 microamperes/cm² to 100 nanoamperes/cm². In the pitting corrosion, the current density may be above 1A/cm².

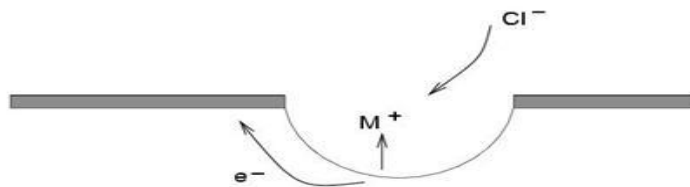
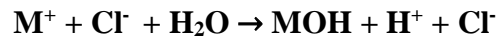


Figure 2.1: Schematic illustration of pitting corrosion

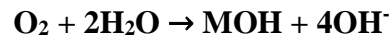
The Figure 2.1 illustrates the pitting process:

The local degradation of passive layer leads to the anodic dissolution of the steel which further results in inclusion of M^+ in solution. The anodic reaction takes place in the following :



This causes the drop of pH which prevents in repassivating the local surface where the film is destructed.

The cathodic reaction, on the surface near the pit follows:



The propagation phenomenon of pitting is well accepted, but the mechanism of pit initiation is still in debate. The propagation of pitting takes place after the initiation of pitting. This results in micro porous channel in the structure which further leads to the formation of crack or formation of holes. In marine applications, pitting corrosion is a serious concern as the environment possesses a rich amount of chloride. 316 grades of stainless steel are used in this application because of its good pitting resistance property.

The pitting resistance property of a stainless steel is dependent on the composition of the steel. Increasing the Chromium content or adding both the molybdenum and the nitrogen improves the pitting resistance.

2.4 Difference in corrosion properties between mild steel and stainless steel

Plain Carbon steel containing 0.1-0.3% carbon is known as mild steel. Mild steel does not contain any other alloying elements. So, it can be said that the properties of mild steel or any of the plain carbon steel depend on its carbon content. Carbon steel makes up the largest part of steel production and is used in a vast range of applications.

Stainless steel is defined as a steel alloy with a minimum of 11.5 -18% chromium content. Other alloying elements such as nickel, molybdenum, manganese, silicon, nitrogen are also added to achieve specified property.

The main property which makes stainless steel stand unique is the corrosion resistance property. This makes it different from other steels, specially from plain carbon steels. Stainless steel does not corrode in the environment where mild steel corrodes easily. Mild steel has no corrosion resistance property because it doesn't contain any alloying element which could help it combat against corrosion. Whereas stainless steel contains almost 18% chromium which can significantly improve the corrosion resistance. High Chromium content leads to the formation of a passive layer on the surface of the stainless steel in presence of oxidizing agent. This thin film acts as shield against corrosion in those environments. This thin, invisible, protective layer is self-healing so that it can repassivate whenever it requires. But in highly reducing environment such as strong acid

solution or strong alkaline solution , this passive layer can't be generated to protect the stainless steel so that the corrosion rate is much higher in these environments than that in the oxidizing, neutral , less reducing environment. Other alloying elements such as nickel, molybdenum , nitrogen may also take part in protecting stainless steel against the corrosion. As a result of those combined effect from the alloying elements , stainless steel posses good corrosion resistance.

When the passive layer is broken down and is unable to repassivate , corrosion is occurred in stainless steel. Stainless steel is mainly affected by pitting corrosion by chloride ions. Mild steel is mainly corroded by uniform corrosion , though pitting could also take place in mild steel as there is no shield of passive layer. The corrosion rate of stainless steel is generally in the scale of nanoampere/cm². When it is subjected to pitting corrosion , the corrosion rate enhances in the scale of ampere/cm². Whereas the corrosion rate of mild steel is normally in the scale of milliampere/cm² , when pitting started , the rate also increases rapidly.

2.5 Coating of mild steel— methods and technology :

As mentioned in earlier section , mild steel is very prone to corrosion. But it has so many applications as the cost of mild steel is relatively low. To use mild steel for longer time span , it is necessary to achieve corrosion protection. Though, there are various methods which can help mild steel combating against corrosion. if A shield can be made which will protect the mild steel surface , then the problem can be solved. As a protective shield ,metallic coating or non-metallic coating could be the possible solution. It is discussed in details in the following sections :

2.51 Metallic coating

Metallic coatings are the most common solution to protect mild steel from corrosion. It contain a metallic element or alloy. A thin film of metallic element or alloy can be applied electrochemically, chemically or mechanically. This thin layer works as shield of protection against corrosion which helps mild steel withstand in aggressive environment. Metallic coating leads to formation a layer on the substrate, which can change the surface property of the substrate. Therefore, coated mild steel exhibits some extraordinary properties, which can't be achievable by using other materials. The coating improves the surface property i.e corrosion resistance while the metal on which the coating is applied gives the load bearing capacity and other mechanical property.

Beside improving the corrosion resistance property, metallic coating accomplishes some others advantages such as abrasion resistance , lustrous appearances of the surface.

2.52 Process of metallic coating

- **Metal spraying :** Metal spraying or thermal spraying is a common process of coating on the surface of the material. It is widely used to provide coating on the ferrous material. It is performed to provide a corrosion resistance property as well as wear resistance. Metal spraying is done by projecting molten metal or softened particles to the prepared surface of the substrate. To generate coating by metal spraying a heat source, feed material of which spray will be projected on the substrate and projection method are required. With the help of heat source, the feed material turns into molten stage and it is projected to the surface. First, these particles bond with the rough surface of the substrate mechanically. Then they start bonding on each other and the coating is achieved. No alloy formation takes place in this process.
- **Hot dipping :** Hot dipping is the process of coating where the metal is dipped into the molten metal pool. Liquid metal bonds with the substrate and provides a good coating on the surface. A very common process of hot dipping is known as galvanizing. Galvanizing is the process of providing zinc coating on the steel surface. The surface is prepared first by acid pickling. Then it goes through the flash pool of 3% HCl, ZnCl₂, NH₄Cl to energize the surface. Then it goes into the pool of molten zinc. Alloy is formed in this process such as FeZn₇ (containing 11% Fe), FeZn₃ (containing 22% Fe). But more amount of coating material is required for the process to provide such type of coating.
- **Metal diffusion coating :** Diffusion coating is a process of producing a coating on the surface of a substrate metal based on the diffusion saturation of the surface of the substrate metal or alloys. This type of coating is done for achieving the high temperature oxidation resistance. Metal which is to be coated is kept in powder form inside a furnace and high amount of heat is applied. As a result of this, it vaporizes and diffuses on the surface of the substrate. Dimension remains almost same for the coated material. But complete alloy formation is accomplished.
- **Electroplating :** Electroplating is also known as electrodeposition. Electric current is passed through an electrolytic solution which leads to reduction of the dissolved cations present in the electrolyte. Thus a coating is formed on the substrate which is kept as cathode. A cell is formed during the electroplating, where the anode is generally a graphite rod and the metal surface on which the coating should be formed acts as cathode. Certain amount of current leads to the accumulation of electrons on the cathode which further attracts the cations present in the solution. Metal ions are reduced and deposited as metal on the cathode. DC power source is required to flow the current in the electrolyte. It is one of the cheapest ways to produce coating on the surface to combat corrosion in an aggressive environment. Costly metal is also deposited by this process. Coating of uniform thickness can be formed by this method. Every type of coating can be produced by this method such

as hard coating, soft coating, coarse coating, fine coating, powder coating, nano coating, lusturous coating, dull coating. Fig 2.2 shows the illustration of electroplating.

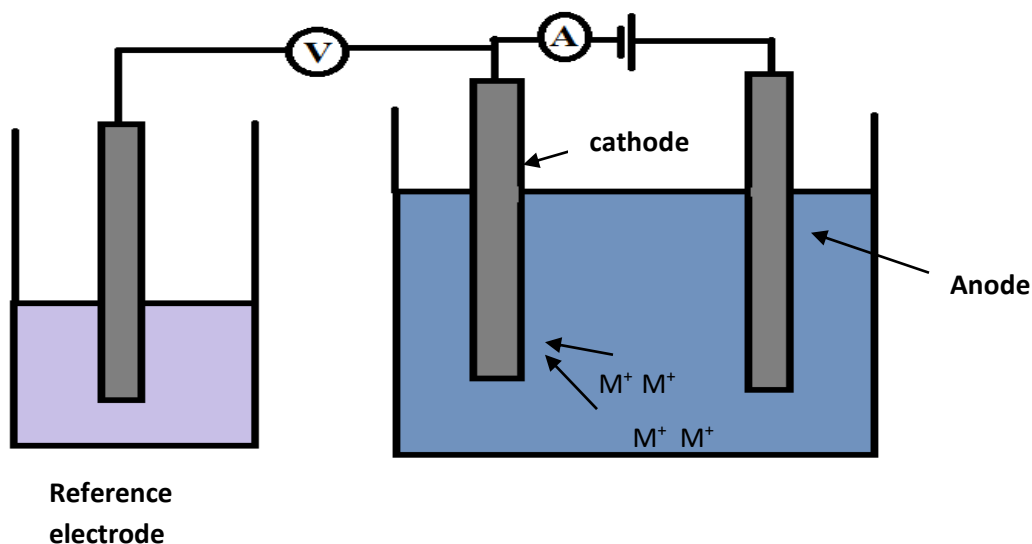


Fig 2.2 : illustration of electroplating

- **Pulse electroplating:** Normal electroplating is simply modified into the pulse electroplating. This process involves the alternation of current between two different values. This alternation results in a series of pulses of equal amplitude, duration and polarity. As a result of this modification, composition and thickness of deposited layer can be varied.

A maximum value of current is preset for the electroplating which is known as Peak current. A certain period of time is given for electroplating with the peak current. This effective portion of time in certain electroplating period with the current or potential applied is known as duty cycle [16].

Pulse electroplating improves the quality of electroplated film. the internal stress built up during fast deposition could be relieved during pulse electroplating. Changing the parameters will give us different quality of the produced surface. Power supply is required to provide high peak current and fast switching. The factors such as temperature, gap between the electrode, stirring effect are also counted in the process of pulse electroplating. Sometime, electroplating is done on anode which may create further problems.

- **Electroless deposition:** Electroless coating process required only one electrode on which the metal will be deposited while electroplating requires two electrodes and one reference electrode. Power source for current generating is not required in the electroless deposition process but a reducing agent is necessary for the deposition [18].

The redox potential of the reducing agent should be high as the energy barriers should be overcome by that of the reducing agent [17]. Generally hydrogen based reducing agents are used in electroless coating. Aldehydes, hypophosphite are also used to produce electroless

coating on the surface of the substrate.

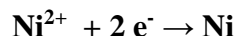
Eliminating power sources and plating baths i.e electrolyte solution which are mandatory in the electroplating process, electroless deposition reduce the cost of production. But the drawback of the process is that it can't produce a thick layer and the process is much slower than electroplating. It is mainly used for decorating purpose.

2.6 Previous works related to electro coating on mild steel :

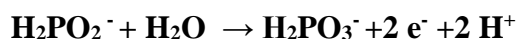
2.61 Electroless nickel plating:

Electroless nickel plating requires a source Nickel ions i.e electrolytic solution of nickel salts , a reducing agent, a complexing agent , stabilizer. The process involves dipping the substrate in a bath of plating solution, where the reducing agent, hydrated sodium hypophosphite ($\text{NaPO}_2\text{H}_2 \cdot \text{H}_2\text{O}$), reacts with the Ni^{2+} to deposit the nickel on the surface of the substrate [18]. Phosphorus may also deposited with nickel in this process which results in alloy deposition . The metallurgical and mechanical properties of the deposited alloy depend on the percentage of phosphorus. There is no requirement of passing current through the solution for the deposition.

The reduction reaction is :



The oxidation reaction is :



Overall reaction is :



The function of complexing agent is to prevent rapid decrement of pH of the solution, prevent precipitation of Nickel salt, reduce concentration of free Nickel ions. The function of stabilizer is to prevent decomposition of the deposited electroless nickel. Thio urea is used as stabilizer. The surface where the electroless coating has to be produced , should be cleaned properly. First it is treated with different chemicals to prepare the surface and then it is rinsed in water for 2-3 times to clean those chemicals. Then the electroless coating is made by using the reducing agent sodium hypo phosphate to achieve corrosion and wear resistance nickel deposited surface.

2.62 Electroplating of nickel :

Nickel deposition on mild steel by electroplating is a very common method to produce a good corrosion resistance and wear resistance coating. To produce a good nickel coating, the surface should be prepared well. First, the surface is cleaned and polished using emery paper having different grades. After getting mirror finished surface, it should be cleaned with ethyle alcohol and acetone to remove the oxide. Acid pickling is also used to prepare the surface. After preparing the surface, it is dipped into the electrolytic solution as cathode.

Different methods are used for nickel deposition by electroplating.

Watts bath:

Watts bath for nickel deposition involves the nickel sulphate ($\text{NiSO}_4 \cdot 6\text{H}_2\text{O}$), nickel chloride ($\text{NiCl}_2 \cdot 7 \text{H}_2\text{O}$), boric acid to make the electrolytic solution for nickel deposition. This bath provides a unrefined gray pitted appearance of nickel on the surface [20]. All the components have different functions in nickel deposition.

The nickel sulfate uses for the main source of nickel ions which will be deposited on the cathode after being reduced. So, the proper concentration of nickel is required for obtaining good deposits. The nickel chloride increases the anodic corrosion and leads to harder deposits and increases the conductivity of the solution which subsequently helps in deposition of nickel at much lower voltage. The boric acid acts as a buffer for pH control and helps in ductile deposition. The pH should be in the range of 3-3.5.

The addition of small amount of additives causes a change in appearances on the deposited nickel. It results in bright deposition of nickel. The additives are mainly responsible for grain refining which results in brightening the deposition. It also helps the deposition to remain ductile. Sodium dodecyle sulphate, benjonic sulphonic acid mainly used as the additives [20]. They actually reduce the surface tension and helps in pit free deposition of nickel.

The operating conditions required for nickel deposition are as follows [20]:

Nickel chloride: 250-300 gm/L, Nickel sulphate : 100-150 gm/L, Boric acid : 37-52 gm/L, Additives : 1.5 gm/L

pH : 3-3.5, temperature : 60° C, current density : 300 mA/ cm²

nickel sulphamate bath :

Nickel Sulphamate is another method to deposit nickel. A highly precise and quality surface treatment can be achieved by this process. Nickel Sulphamate bath is used for electroplating on electronic components, diamond cutter, metal musks etc [19]. It is also used for producing good corrosion resistance, wear and abrasion resistance on the surface. High efficient coating on the mild steel surface can be achieved.

High speed plating is possible and it is more than general Nickel bath (Watts bath). As the electroplating bath composition is simple, so further control is easy. As the solubility of the salt is high, high concentration can be used to make the bath and high current can be passed through to the solution. The coating thickness will be also high in this modification. Internal stress on the deposition is generated due to the presence of impurities in the solution. Fine grained surface is achieved by the deposition from sulphamate bath [19]. The deposition is often used as undercoating for chrome coating.

Nickel sulfamate with high solubility should be used for the source of nickel ions. Nickel Chloride and aNickel Bromide are used as an anode corroding agent. It has been seen that nickel bromide gives less internal stress when anode corroding agent is used in large quantity. Inorganic and organic impurities increases the risk of internal stress, gives brittle deposition of nickel. So the layer produced by the deposition achieves worse property. To reduce this risk, sulfamate bath should be prepared carefully.

The operating conditions are as follows [20]:

Nickel Sulfamate 250 to 650 g/L

Nickel Bromide : 0-30 g/L

Boric acid : 30- 50 g/L

pH : 4.0

Bath temperature: 50°C

Current density : 500 mA/cm²

Other nickel plating processes :

Beside these process of deposition of nickel which are maintained in the earlier section, there are more methods of nickel deposition. Though, these process are almost similar to the process maintained above as the solution chemistry is mainly changed and other parameters almost remain same.

All chloride bath for nickel deposition is used sometime to reduce the cost. It involves nickel chloride and boric acid only to make the electrolytic bath for nickel deposition [20]. It generally produces thick coating as nickel chloride increases the anodic corrosion. But internal stresses on deposited nickel is much higher in this process.

To reduce the internal stresses on the deposited nickel, chloride sulfate bath is used. It involves nickel chloride, nickel sulfate and boric acid [20]. The deposition rate of this electrolytic bath is higher than that of the watts bath.

All sulfate bath is also used for nickel deposition. It is used mainly for deposition of nickel on the surface inside a pipe. It used where the anode is insoluble [20].

Hard nickel coating is also produced by making a little change in the bath. The bath for hard nickel plating requires nickel sulfate, ammonium chloride, boric acid. The produced nickel film gives corrosion resistance as well as good hardness and tensile strength [20].

Black nickel coating is also a method of nickel electroplating. Though, the nickel film produced by this method, does not achieve good corrosion resistance property. It is mainly used for decorating purpose. The bath requires nickel ammonium sulfate, zinc sulfate, sodium thiocyanate [20].

2.63 Chromium plating :

Chromium plating , also known as Chrome plating is very common method of electroplating on mild steel surface. produced layer of chrome provides good corrosion resistance to mild steel. Also a hard coating of chromium has been developed to provide abrasion resistance , wear resistance, corrosion resistance.

The process involves some stages of surface preparation. first, all residual traces of dirt and impurities on the surface should be cleaned manually. Then it should be polished by emery paper. Then it is required to clean the oxide present in the surface by using diluted acid or acetone. Then it is dipped into the electrolytic solution as cathode. A certain amount of current is applied to the cell to achieve the desired deposition.

Two types of chromium oxide can be used for chromium plating. Chromium trioxide provide the source of hexavalent chromium. It is used for hard chrome plating and also for bright chrome plating. Chromium bath contains chromium trioxide (CrO_3) and sulfuric acid. The ratio of chromium oxide and sulfuric acid varies from 75:1 to 250 :1 [21]. The temperature and current density plays a great role for the deposition of chromium. The pH of the bath is in the range of 0.5-1. The temperature may vary between 45° - 60° C [21].

The disadvantage of this process is low cathode efficiency which leads to non-uniform coating. More deposition takes place on the edges and less on the inside corners and holes. To solve this problem , auxiliary anode may be used. Another disadvantage is that the hexavalent chromium salt is human carcinogenic. The toxicity may cause serious health issues.

Another type of chrome plating is done by trivalent chromium. Chromium sulfate, chromium chloride or chromium oxide (Cr_2O_3) may use as the source of trivalent chromium. Only the bath chemistry of trivalent chrome pating is different from the hexavalent chrome plating and other parameters are almost same. It is used as the alternative of hexavalent chromium plating. Hard coating and decorative bright coating can be produced by this method. The thickness of the deposition is much more than that of the hexavalent chrome plating. Also the uniformity of the coating is achieved by using this type of trivalent bath [21].

It has the advantages over the hexavalent chrome plating. It has higher cathode efficiency which results in better throwing power. Thus, it leads to the higher rate of the deposition. It also takes low voltages. So, the energy consumption is also less with a better result. It provides uniform coating throughout the cathodic surface.

It is also less toxic than hexavalent chromium. So, less hazards are involved in this process of chrome deposition. But the colour of the produced film is not satisfactory for the decorating purpose [22]. Currently, additives are used to solve this problem and produce coating with desired bright colour. The corrosion resistance property is also not good as the deposited layer by hexavalent chrome plating.

Two types of chrome plating is generally produced.

Bright chrome coating are generally produced for durability of the coating. It is mainly used for decorative purpose. The thickness of this coating is also less. But it provides good corrosion resistance on the surface of mild steel. To produce bright chrome coating, a thin film of nickel is deposited first [22]. Then, the chrome plating is performed on the surface.

Triple plating is also done sometimes. First, copper is deposited on the surface, then nickel is deposited and followed by chrome deposition. It is costly process but provides a better result.

Hard chrome plating is also known as industrial chrome plating. Hard chrome is generally thicker than decorative chrome. The thickness of hard chrome is ranging from 0.02 to 0.04 mm (20 to 40 μm). Hard chrome coating is used to reduce wear and abrasion, improve durability, improve corrosion resistance.

Increasing the thickness of the coating tends to various surface defect. It is the limitation of this type of coating. To solve the problem, thicker plating is required and then it is grinded into the desired dimension. Irregular shapes require more deposition to eliminate the non-uniform deposition and when it is grinded to its proper dimension, much of the deposited chrome is wasted.

Hard chrome coatings are often replaced by modern engineering coatings which has no such drawbacks. It also reduce the labors cost. The replacement of hard chrome also provide improved properties such as corrosion resistance and wear resistance. Also, the hardness of the produced coating by its replacement is much higher than that of the hard chrome deposition. Uniform thickness is achieved by applying spray deposition. No further polishing or grinding is required to get the desired dimensions.

2.64 Nickel chrome plating :

One of the good corrosion resistant coating is a nickel-chromium alloy. It can be electroplated on the surface of steel to increase the corrosion resistance. The film produce by electroplating is thin but it provides a major change in surface property of steel. Aesthetic appearance can also be changed by this electroplating.

The primary element in this type of coating is nickel which provides the coating thickness. Whereas nickel gives a higher composition, Chromium only accounts for around 2 percent of the coating composition [23]. Nickel provides some properties associated with the coating, such as hardness and resistance to corrosion. Chromium is mainly coated to protect the nickel coat but it also provides corrosion resistance. So, the overall corrosion resistance property of the deposited coating is improved. This type of deposition is known as layer by layer deposition.

Nickel alloys can be deposited by different methods also. Nickel alloys containing 22% chromium can be prepared by depositing chromium carbide particles with nickel and heat treating for 24 hours at higher temperature in hydrogen rich atmosphere [23]. Alloy hardness is increased after the heat treatment. Alloys containing 19% cobalt in addition to chromium are also produced by depositing chromium carbide from a nickel-cobalt based solution [23].

Production of different coatings with different levels of corrosion resistance can be achieved. Required hardness is also achieved by controlling the parameters of the electroplating. For simpler applications, where required corrosion resistance is much less, the coating specifications can be controlled so as to provide the right balance of chromium and nickel. Selecting appropriate amounts of each component of the deposition is mainly dependent on the purpose of the finished product. This should be the efficient way to provide a perfect alloy deposited coating depending on their purpose.

2.7 new technologies for electroplating :

Currently different technologies are invented which could replace conventional electroplating in future. Some of those are discussed in the following section.

2.71 Laser plating

Laser is the monochromatic and coherent source of light beam. The surface property can be improved by using these features of laser beam. Microstructure of the surface and subsequent surface property such as corrosion resistance, wear resistance can be improved [24].

Conventional electroplating method requires two or three electrode system. Two electrodes such as cathode and anode are immersed into the electrolyte solution containing metal ions to be deposited on the surface of the substrate. An external power source is used to provide current passing through the electrolyte solution. The metal ions are reduced and subsequently deposited on the cathode surface. This deposition of metal ions can be improved by some processes such as [27]:

- a) Increasing the temperature to increase the mobility of the ion
- b) Stirring the solution
- c) Increasing the concentration of the ions
- d) Reducing the anode cathode distance

Laser plating improves some of these factors maintained above. Laser energy is absorbed by the cathode when it is applied. As a result, the temperature of the adjacent area is raised and become more electrochemically active. Thus the deposition rate is enhanced greatly. This is the thermal model explanation of laser plating [27].

Another theoretical model is used to explain the phenomenon. It is known as optical method of explanation. It is based on photolysis effect. The laser energy promotes the self decomposition of the electrolyte so, the reaction rate is increased [27]. In other word, the concentration of metal ions are increased in the solution which results in increasing the deposition rate.

Not only the plating rate is improved by the addition of laser in electroplating , the quality of the film is also improved. Laser energy can improve the rate of nucleation so that the particles could form a dense structure.

Thermal model also helps in cleaning the substrate's surface so that a tight coating can be achieved.

2.72 Dry plating technology :

Dry plating is currently developed process of coating. Conventional electroplating is a wet process and accomplishes wet surface finishing whereas dry plating technology gives dry finishing. The waste of the conventional electroplating is often dangerous for the environment. It is found on EPA study that the effluents from conventional electroplating is the largest source of water contamination [26].

To eliminate this problem , dry plating is chosen over electroplating. It eliminates the wet surface finishing by eliminating liquid bath, wastewater, hazardous waste associated with electroplating.

Dry plating involves the concept of vapour bath in place of conventional liquid bath. Metal is heated to achieve the vapour form in a vaccum, where the metal film is deposited on the substrate. Subsequent recycling may be achieved by this process [26].

Dry plating is divided into two such as physical vapor deposition and chemical vapor deposition.

In Physical vapor deposition process, vaccum is required for the deposition. Metal is heated and vaporized under vaccum conditions which results in deposition of metal on the substrate.

In chemical vapor deposition , metallic deposition is achieved by increasing the temperature of the substrate and the plating space. Metal is vaporized and injected under low vaccum conditions. It leads to chemical reaction which results in deposition of the metal film.

Dry plating involves a sealed container which helps to protect from emission of hazardous vapor and wastes. This process involves less chemical to produce the metallic layer. It consumes less amount of energy and reduce water consumption in comparison to the conventional liquid bath electroplating [26]. It also reduce the labor cost. Eliminating the hazardous waste and water contaminants make the process more acceptable.

2.73 Nano technology :

Nano technology with electroplating has a great impact on metal deposition and enhancement of surface property. Electrodeposition in addition with nanotechnology involves deposition of metallic layer at the nanoscale level. Nano particles have diameter in the range of approximately 1 to 100 nanometers [25]. Nanocrystalline metallic surface are harder, more wear-resistant, and corrosion-resistant than ordinary metal surfaces. They are also lighter in weight and require only a thin coating for adequate protection.

The synthesis of nano particles requires an atomistic deposition and extreme tailoring over the deposition [25]. The advantages of the conventional electrodeposition method are high deposition rate, low cost, free from porosity and impurities, no post deposition treatment, uniformity etc.

The nucleation of nano materials on the electrode substrate during electrodeposition is affected by the crystal structure of the substrate, surface energy, orientation of the electrode surface and mismatch of orientation at the nucleus-substrate interface [25]. Nucleation rate is also important to get the proper size of the deposited metal.

The electrodeposition technique consists of an electrochemical cell containing electrolytic solution and two electrode. External power source is used to apply voltages and flow of current. The cathode is used as substrate on which electro deposition of the nanomaterials. Desired nanostructure can be produced by using cathode as template for the deposition. Such a template-assisted electrodeposition process can be broadly divided into two types: active template-assisted and restrictive template-based deposition.

The deposition of nanomaterials depends on the growth of the nuclei of the material [25]. Electrodeposition initiates at the dislocations, defect sites, edges of the electrode surface. The subsequent growth is responsible for the different morphologies of the deposited surface. So, an electrode should be selected for achieving desired surface for desired application. Highly oriented pyrolytic graphite (HOPG) is used extensively as an electrode substrate for the electrodeposition of silver, gold, molybdenum, palladium and platinum nanostructures.

2.8 Characterization technique :

2.8.1 Electrochemical characterization:

Electrochemical characterization of developed material gives a proper idea about the electrochemical behaviour of the material. They help to understand basic of the electrochemical property. The techniques frequently used for electrochemical characterizations are potentiodynamic polarization, cyclic polarization , electro chemical impedance studies etc. The basic of those technique are discussed in the following section :

a) Potentiodynamic polarization :

Potentiodynamic polarization test is often used for the corrosion study of the material. This technique provides important information about corrosion mechanisms, corrosion resistance property of the material, corrosion rate and susceptibility in corrosive environment. Polarization involves the change of potential from stabilized state [29].

Potential of the electrode is varied at a selected rate by application of current through the electrolyte which results in change in current. It is also a function of the working area of the electrode. the current is divided by the working area of the electrode to achieve the current density.

Anodic polarization

Anodic polarization involves change in potential in the positive direction [28]. It is a result of current passing through electrode to electrolyte. So, change in anode potential from initial value results in flow of current at anode. This leads to the corrosion of the electrode so that the electrode behaves as anode while the counter electrode behaves as anode.

The change in the potential of an electrode during electrolysis takes place in such a way that the potential of an anode becomes more noble, and potential of a cathode more active than their reversible potentials respectively [29].

Anodic polarization provides the measurement of corrosion rate as well as the protection. It acutely provide the potential regions where materials shows corrosion resistance and where materials are corroded rapidly.

Cathodic polarization

Cathodic polarization involves the potential change takes place in the negative direction [28]. As a result of this cathodic reaction will occur at the cathode. potential shift to the negative direction makes the working electrode behave like cathode and the counter electrode will behave like anode at that time.

Cathodic polarization involves the change of potential from its initial value. After achieving a certain value of potential, the cathodic reaction starts. Hydrogen gas bubbles are formed at the cathode indicating the reduction reaction [29].

Cathodic polarization provides the reduction in corrosion rate in aqueous environment. Cathodic protection is the application of cathodic polarization to protect a material from corroding.

Corrosion potential :

During corrosion, two electrodes are formed simultaneously. Corrosion potential is the potential of electrode which is acquired automatically on the metal surface.

Corrosion potential is measured by finding the potential difference between an appropriate reference electrode and the potential of material's surface immersed in an electrolyte. Corrosion potential gives us the idea about the effectiveness of the surface of a developed coating material as well as the surface of the substrate.

It is measured by the intersection of the cathodic and anodic polarization [29]. Potential below the corrosion potential indicates the change of potential in the negative direction i.e. cathodic polarization. Potential more than the corrosion potential gives anodic polarization.

b) Cyclic polarization

Cyclic polarization is the change in potential in both positive and negative direction in a cyclic manner [30]. In other words, cyclic polarization is the measurement technique of cathodic and anodic polarization in a cyclic manner. It provides the electrochemical characteristics of the material developed as well as the mechanism of the corrosion of the material. This technique actually measures the pitting tendency of the material and the potential of repassivation.

The potential is swept in a single cycle and a hysteresis loop is created [28]. It is described with the difference between open circuit corrosion potential and the repassivation potential. The size of the loop gives an idea about the amount of pitting. Higher value of pitting potential provides the idea about the pitting resistance of the material. The repassivation potential provides the idea about the self-healing capability of the passive film. Cyclic polarization is performed to achieve these properties of the developed material.

Pitting takes place simultaneously after the reaching of the pitting potential. Higher repassivation potential gives the pitting resistance of the passive layer.

c) Electro chemical impedance studies :

Electrochemical impedance spectroscopy is a perturbed dynamic characterization to obtain the electrochemical property. a sinusoidal test potential or current (ac potential or current) is applied to the sample to measure its impedance over a suitable frequency range. It is a powerful technique to investigate the electrochemical properties as well as equivalent electrical properties of materials. The electrochemical phenomenon occurring in the electrode surface which is immersed into the electrolyte, can be represented by an equivalent electrical RLC circuit. The measured impedance curve is generally fitted with an equivalent electrical model which gives us the unique equivalent electrical properties due to the electrochemical phenomena in the electrode-electrolyte interface and subsequently gives an idea about the behavior of the material or deposited film.

Impedance is also a measure of the ability of a circuit to resist the flow of electrical current but unlike resistant. It is expressed as 'Z'. It has two parts, real and imaginary. When the real part is plotted on the x axis and imaginary part is plotted on y axis, the resultant curve is 'nyquist plot'. The resultant curve is a semicircle for the simplest circuit with one time constant.

Another type of representation method is the Bode Plot. The impedance is plotted with log frequency on the X-axis and both the absolute values of the impedance and the phase-shift on the Y-axis. Unlike the Nyquist Plot, the Bode Plot does show frequency information [31].

EIS plots are commonly analyzed by fitting to an equivalent electrical model. Most of the elements in the model are common electrical elements such as resistors, capacitors, and inductors.

The impedance value of resistor i.e resistance, $R = E/I$

The impedance of inductor i.e inductance, $Z = \omega L$

The impedance of capacitor i.e, $Z = 1/ \omega C$

It can be said that the inductance is linearly proportional to the frequency while the capacitance is inversely proportional to the frequency.

Solution resistance is often a significant factor in the electrochemical impedance spectroscopy of an electrochemical cell. solution resistance between the reference electrode and the working electrode must be considered when the equivalent circuit is made.

An electrical double layer may exist on the electrode electrolyte interface. This layer is formed as ions from the solution adsorb onto the electrode surface. The charged electrode is just separated from the charged ions by a very thin insulating space [31]. So, eliminating the separation, double layer will behave like capacitance.

The change in potential from its initial value is known as polarization. When the working electrode is polarized, it will result current to flow through electrode surface. the amount of the

current is controlled by kinetics of the reactions , the diffusion of the ions present in the electrolyte solution. The factors which resists in the flow of this current in the process, is known as polarization resistance.

Diffusion also can create an impedance called a Warburg impedance [31]. The impedance depends on the frequency of the potential perturbation. At high frequencies, the reactants can't diffuse fast so the Warburg impedance is small. At low frequencies , the value of Warburg is high.

Besides these parameters , coating capacitance may become a factor in the electrochemical impedance spectroscopy.

Capacitors in EIS experiments often do not behave ideally. Instead, they act like a constant phase element.

The impedance of a capacitor can be expressed as:

$$Z_{CPE} = \frac{1}{(j\omega)^\alpha Y_0}$$

where,

$Y_0 = C =$ The capacitance

$\alpha =$ An exponent equaling 1 for a capacitor

For a constant phase element, the exponent α is less than one.

Simplified Randles Circuit

The Simplified Randles cell is one of most common cell models. It includes a solution resistance, a double layer capacitor and a polarization resistance.

The equivalent circuit for a Simplified Randles Cell is shown in Figure 2.31

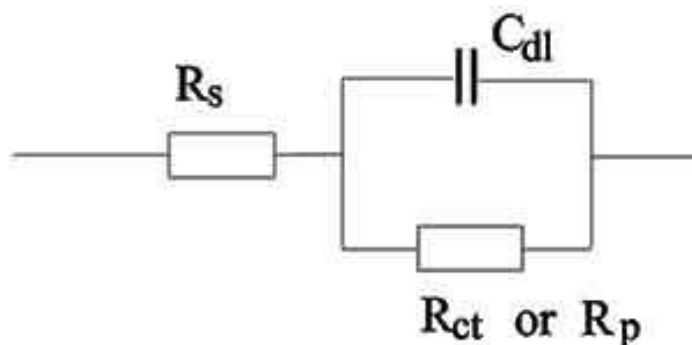


Fig 2.31 : Simplified Randles Cell Schematic Diagram

Figure 2.32 is the Nyquist Plot for a typical Simplified Randles cell.

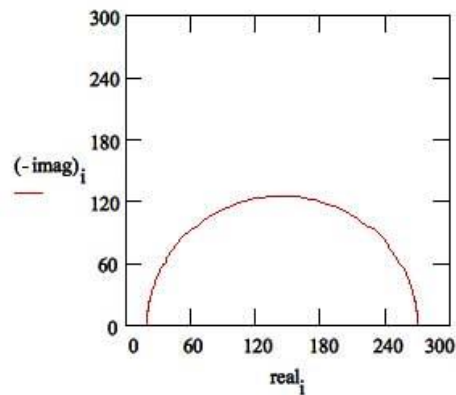


Fig 2.32 : Nyquist Plot for randle circuits

The Nyquist Plot for a Simplified Randles cell is always a semicircle [31].

The real axis value at the other (low frequency) intercept is the sum of the polarization resistance and the solution resistance. The diameter of the semicircle is therefore equal to the polarization resistance.

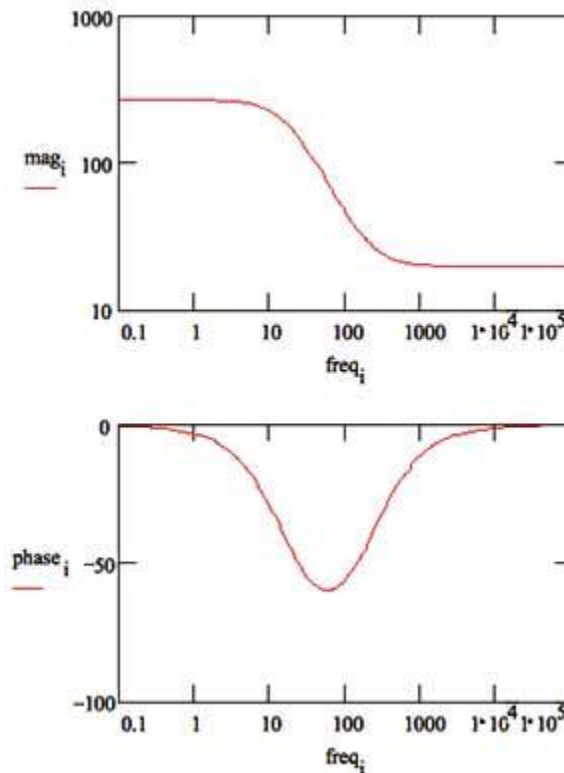


Fig 2.33. Bode Plot for randle circuit

Warburg model

Consider a cell where semi-infinite diffusion is the rate determining step, with a series solution resistance as the only other cell impedance.

A Nyquist Plot for this cell is shown in Figure 2.34

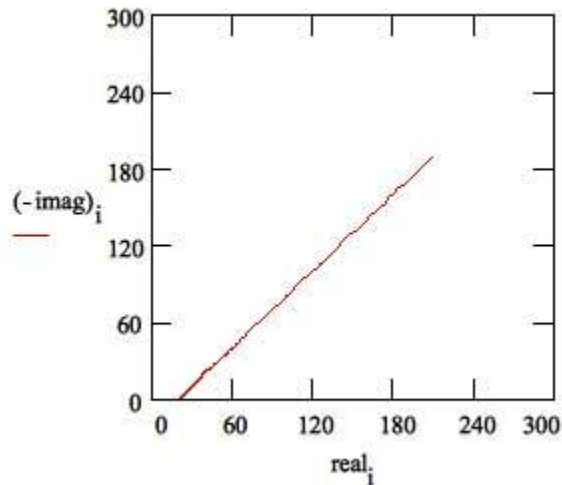


Fig 2.34 : Nyquist Plot for a Warburg Impedance

The same data is plotted in the Bode format in Figure 2.34. The phase angle of a Warburg impedance is 45° .

Adding a double layer capacitance and a charge transfer impedance, we get the equivalent circuit in the following figure. Since there is no simple element to model a Warburg impedance, it isn't possible to construct a dummy cell that models the Randles Cell [31].

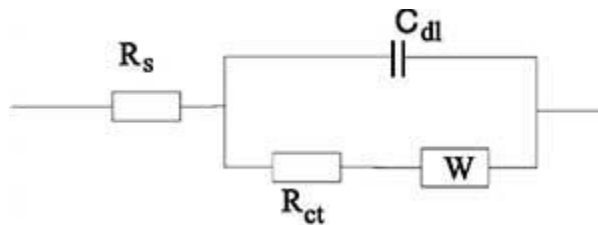


Fig 2.35 : Randles Cell: Equivalent Circuit with Mixed Kinetic and Charge-Transfer Control (Warburg model)

This circuit models a cell where polarization is due to a combination of kinetic and diffusion processes. The Nyquist Plot for this circuit is shown in Figure 2.36

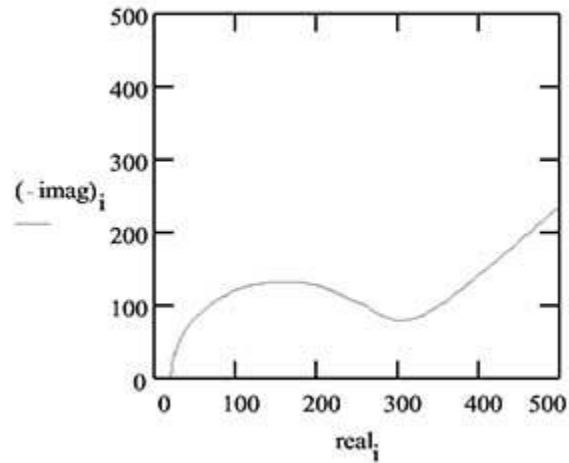


Fig 2.36 : Nyquist Diagram for Warburg model

The Bode Plot for the same data is shown in Figure 2.37. The lower frequency limit was moved down to 1 mHz to better illustrate the differences in the slope of the magnitude and in the phase between the capacitor and the Warburg impedance [31].

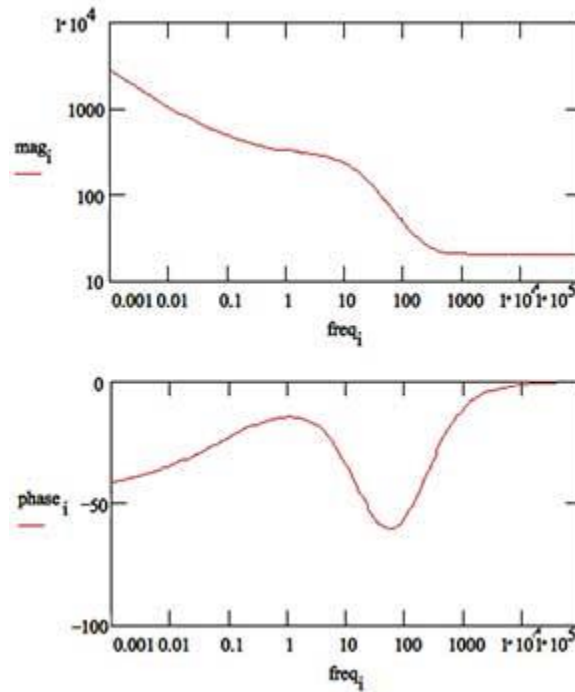


Fig 2.37 : Bode Plot for Warburg model

2.82 Material characterization

After finding the electrochemical properties of the developed material, it is necessary to understand the material's composition which is responsible for providing such properties. Material characterization is necessary to understand their composition and subsequent effect on the electrochemical characteristics.

XRD:

X-ray diffraction technique is an analytical process to analyze the composition and their phases present on the material. XRD is capable of providing the morphological informations such as unit cell dimensions , phases , grain size of crystalline material [32].

Xrd is a non-destructive test for material characterization. The principle of x-ray diffraction is based on constructive interference of monochromatic x ray beams. First, x ray is generated from a cathode ray tube and filtered to create monochromatic ray. It is directed towards the sample with known angle. When it satisfies bragg's law , we got the constructive interference.

Bragg's law relates the wavelength of x-ray to the diffraction angle and the lattice spacing of the sample.

$$n\lambda = 2d \sin\theta$$

when this condition satisfies , constructive interference is achieved. X ray diffraction technique provides the peak for the different composition or phases present in the sample which is subsequently compared to the reference data. Thus the desired result is obtained from the x ray diffraction technique.

SEM :

Scanning electron microscopy is material characterization technique which provides the magnified view of the surface and the clear idea about the morphologies of the surface. it is also a non destructive method for material characterizing. A scanning electron microscope uses electron beams for imaging. It uses the electron that are reflected and knocked out by the sample surface. as the wavelength of electron is much shorter than visible light, it will provide better resolution than optical microscope.

A schematic representation of a SEM is illustrated in Figure 2.4 below. first, electrons are generated at the top of the column by the electron source. These are emitted from the source. They are then accelerated and attracted by the positively-charged anode.

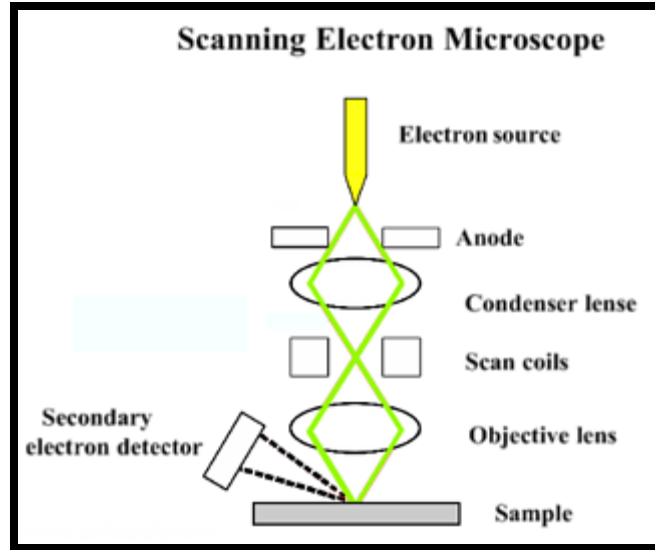


Figure 2.4: schematic representation of the basic SEM components

The entire electron column needs to be under vacuum because the path of electron can be diffracted easily by a minor magnetic field. The electron source is sealed inside a special chamber in order to preserve vacuum. Although the vacuum protects the electron source from vibration and noise, it also provide a high-resolution image. In the absence of vacuum, other atoms and molecules may be present in the column. Their interaction with electrons causes the electron beam to deflect and reduces the image quality.

As electrons cannot pass through glass, the lenses that are used in SEM are electromagnetic [33]. When current passes through the coils inside the lenses , a magnetic field is generated. The sensitivity of electron to the magnetic field , the lenses are used to control the path of the electrons by changing the current [33].

The condenser lens is the first lens in the predetermined path of the electron. This lens converges the beam before the electron beam cone opens again and is converged again by the objective lens before hitting the sample. The condenser lens defines the size of the electron beam as well as resolution, while the objective lens leads the beam to focus onto the sample.

The scanning electron microscope's lens system also contains the scanning coils, which are used to raster the beam onto the sample.

The electrons with high energy strike the sample. This interaction of electrons with sample results in the generation of many different types of electrons, photons or x ray emission . SEM uses two types of electron for imaging such as secondary electron and back scattered electron.

Backscattered electrons are reflected back after elastic interactions between the electron beam and the sample. Secondary electrons are originated from the atoms of the sample from inelastic interactions between the electron beam and the sample [33].

BSE provides the information of the deeper regions as it comes from deeper regions of the sample while Secondary electrons are originated from the surface. BSE can able to identify different material. The higher the atomic number , brighter the image of the materials by BSE. Secondary electron are used to form 3-D image of the sample surface.

The secondary and back scattered electrons are detected by different types of detectors. Solid state detectors are used to detect BSE [33]. The detector is placed concentrically to the beam to maximize the collection of back scattered electron.

To detect secondary electron, the Everhart-Thornley detector is mainly used [33], which is positively charged results in attracting the secondary electron. Secondary electron detector is placed at an angle to increase the efficiency [33].

Chapter 3 : Electrodeposition Methods And Experimental Procedure

3.1 Raw materials :

Raw material which is used as substrate in the experiments is mild steel.

Composition : 0.2% carbon,

99.98% Fe

Geometry : cylindrical

Dimension : 5 mm x ϕ 1cm

Density : 7.87 gm/cm³

The developed material i.e coating on mild steel is compared with 304 stainless steel to analyze the corrosion resistance property.

Composition: 18% chromium

8% nickel

0.08% carbon

Geometry : rectangular

Dimension : 1.2 cm x 0.3 cm x 0.6 cm

Density : 8 gm/ cm³

3.2 Electro deposition technique

3.21 Surface treatment :

In the following experiments mild steel is used as substrate to develop different type of coating. Mild steel is rapidly corroded when it is kept even in the open atmosphere as it does not have much corrosion resistance. Therefore , it is necessary that the surface on which the coating will be developed, is properly cleaned to produce non-porous, uniform coating. Surface preparation of mild steel for developing a uniform and compact coated surface involves a series of process. Those processes are discussed in the following

- First, the rusts present on the surface and pits are cleaned out by using a belt with emery paper of 100-120 grades.
- This process maintained above could be replaced by acid etching. Generally diluted sulphuric acid or nitric acid is used to control the degradation of material. For more precise

tailoring, inhibitor may be used.

- Then, the cleaned surface is polished with Silicon carbide paper of grades 400, 600, 800, 1000 subsequently to make sure that there is no scratches on the surface to be electroplated.
- After polishing properly, it is necessary to remove the oxide layer on the surface if it presents on the surface to be coated.
- This is done by using ethyle alcohol and acetone.
- The surface is rinsed with ethyle alcohol, followed by acetone to make sure that there is no oxide present on the desired surface.
- Now, the surface of the mild steel is ready for electrodeposition.

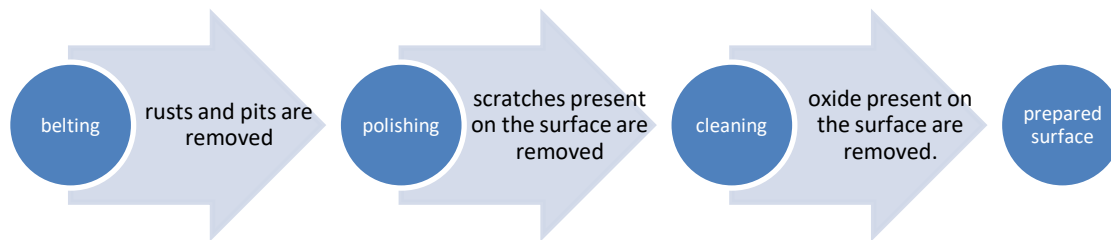


Fig 3.1 Illustration of processes of surface preparation

3.22 Electrodeposition :

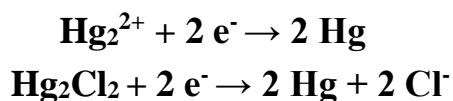
After the surface of mild steel is being prepared by polishing and cleaning with ethyle alcohol and acetone, it is ready to be electrodeposited. An electrolytic cell has to be formed properly for the deposition on the surface of mild steel which is prepared to remove any scratches, rust or oxide. Electrodeposition is the process where cathode electrode will attract metal ions by the influence of current provided by external power source. The entire electro deposition process involves a series of process. Those are discussed in the following sections.

3 electrode system cell

Generally, an electrolytic cell consists of two electrode such as cathode and anode. Mild steel surface on which the coating should be generated is used as cathode while a graphite rod is used as

anode in these experiments. In the cathode metallic ions are reduced and deposited on the surface. To find the cathode current density, the cathode are should be calculated before dipping into the solution. In the anode, oxidation reaction is occurred. Both the anode and the cathode are dipped in the electrolyte. This type of system is known as 2 electrode system. In 3 electrode system, another electrode is used, known as Reference electrode. It is used to measure the potential of the cathode. The potential of cathode is measured with respect to the potential of reference electrode.

In the following set of experiments, saturated calomel electrode has been used as reference electrode. The reaction takes place between elemental mercury and mercury chloride. The redox reactions are given bellow.



The reference electrode i.e saturated calomel electrode is kept in saturated potassium chloride solution. A salt bridge is used to build a connection between the reference electrode and the electrolytic solution. Salt bridges are made of saturated potassium chloride solution and agar agar powder. Thus the 3 electrode system of electrolytic cell is formed.

Formation of the electrical circuit

An electrical circuit is to be formed properly to make sure that the current is passing through the electrolyte solution. This current will help to reduce the metallic ions which results in deposition of the metal.

- DC power source has two terminals , one is positive and another is negative. Cathode is connected with the negative terminal while anode is connected with positive terminal.
- The anode for electrodeposition, graphite is used in the following experiments.
- To measure the cathode current for calculating the cathode current density, an ammeter is connected between cathode and the negative terminal of the power source.
- To measure the deposition potential, a voltmeter is connected between the reference electrode and the cathode electrode.
- Connector are used to connect one terminal to another terminal, the working electrode or the counter electrode. connectors are made of a copper wire attached with two alligator clip on the both terminal.
- The alligator clips which are used to connect one terminal to another, should be rust free otherwise the rate of electron flow could be affected.

Preparation of electrolytic solution

The electrolytic solution is required for the deposition of material on the surface of mild steel. It consists of metallic ions so that they could be reduced resulting deposition on the surface of cathode which is mild steel in these set of experiments. So, it is necessary to add metallic salts to make the solution to obtain the coating of that metal.

The solution chemistry i.e the salts and the other chemicals which are used to make the solution for the deposition of chromium and nickel-chromium on the surface of mild steel is provided in a tabulated form in the following sections of this chapter.

The processes for making the proper electrolyte are given below:

- The solution is made on a 250 ml borosil beaker. The beaker is properly cleaned to make sure that there is no trace of any other salts or contaminants which are not desired for the deposition of chromium and chromium-nickel on the surface of mild steel.
- 50 ml of distilled water is taken to make the electrolytic solution. The pH is checked with pH meter to make sure that it is around 7.
- The required amount of chemicals are measured in gram in the weighting equipment. The weighed amount of chemicals which are known to record the molar concentration of the specified chemicals are poured into the distilled water taken on the borosil beaker.
- A glass rod or magnetic bead for magnetically stirring on the magnetic stirrer is used to make sure that the chemicals, poured into the distilled water are entirely dissolved in the solution i.e the chemicals present in the prepared solution is in ionic conditions.
- Thus, the electrolyte is ready for electro deposition. Desired amount of sulfuric acid may be used for increasing the conductivity of the solution. It is also responsible for lowering the pH of the solution and anodic corrosion. Final pH of the solution is measured and recorded for further use.
- The temperature of the electrolyte is checked with the thermometer. Then the electrolytic solution is heated if required, to raise the desired temperature for electro deposition.

Other parameters

For deposition of chromium and chromium-nickel on mild steel, there are various parameters which has influence on the property of coating. Those parameters are pH of the solution , the temperature of deposition, cathode current density, stirring effect etc. The set of experiments are performed by varying one parameter at a time while the other parameters are kept constant.

A thermometer is used to measure the temperature of deposition and to hold the temperature magnetic stirrer (heater) is used. For the entire set of experiments for depositing different type of coating, the time period of deposition is kept fixed. The time for deposition on mild steel is kept 15 minutes for every coating.

The electrolyte solution is heated to obtain the desired temperature in micro-oven or in a heater. Once the temperature is reached, the continous heat source is powered off. To hold at same temperature , the magnetic stirrer is used to provide certain heat which is required. The stirring effect may be used for a better deposition because it increases the ionic movement.

3.3 Experimental procedure :

Experimental procedures for different coatings to be developed are discussed in the tabulated form in the following sections.

3.31 Solution chemistry and other parameters used for chromium coating :

Solution chemistry	Potential vs SCE (volt)	Current density (mA/cm ²)	Temperature(°c) ± 2°	Time (min)	Additives (if any)
1.5 M CrO ₃ , 0.5 ml H ₂ SO ₄	0.9	450	45	15	
1.5 M CrO ₃ , 0.5 ml H ₂ SO ₄	1.1	310	45	15	

1.5 M CrO_3 , 0.5 ml H_2SO_4	1.15	150	45	15	
1.5 M CrO_3 , 0.5 ml H_2SO_4	1.2	300	45	15	
1.5 M CrO_3 , 0.5 ml H_2SO_4	1.25	300	60	15	
1.5 M CrO_3 , 0.5 ml H_2SO_4	0.9	300	35	15	

3.32 Solution chemistry and other parameters used for chromium-nickel deposition :

Solution chemistry & the ratio of Ni-Cr concentration	Potential vs SCE (volt)	Current density (mA/ cm ²)	Temperature (°C)	Time (min)	Additives (if any)
1.5 M CrO ₃ , 0.525 M NiCl ₂ .6H ₂ O, 0.225 M NiSO ₄ .7H ₂ O, 0.65 M H ₃ BO ₃ , 0.5 ml H ₂ SO ₄ (1 : 2)	1.2	300	45	15	1.5 gm/lit CH ₃ (CH ₂) ₁₁ SO ₄ Na
1.5 M CrO ₃ , 0.35 M NiCl ₂ .6H ₂ O, 0.15 M NiSO ₄ .7H ₂ O, 0.65 M H ₃ BO ₃ , 0.5 ml H ₂ SO ₄ (1:3)	1.24	300	45	15	1.5 gm/lit CH ₃ (CH ₂) ₁₁ SO ₄ Na
1.5 M CrO ₃ , 0.21 M NiCl ₂ .6H ₂ O, 0.09 M NiSO ₄ .7H ₂ O, 0.5 M H ₃ BO ₃ , 0.5 ml H ₂ SO ₄ (1:5)	1.32	300	45	15	1.5 gm/lit CH ₃ (CH ₂) ₁₁ SO ₄ Na

3.33 Solution chemistry and other parameters for chromium-nickel coating with pre-deposited chromium on the surface :

Obtaining an interesting result of chromium nickel deposition on mild steel , different methods are tried to find the best quality material which is more corrosion resistant than the other developed material. For the electro deposition of chromium nickel on mild steel, an innovative method is used. The entire deposition process is splitted into two parts. Chromium is predeposited on the surface of the mild steel. The experiment is performed for 5 minutes. Then the electrolytic solution of nickel is mixed with chromium solution and the deposition takes place on the surface of the mild steel for another 10 minutes. The developed materials have shown some interesting surface properties. The details about the parameters and solution chemistry is provide in the following table.

Solution chemistry		Solution ratio of Ni-Cr concentration in the final solution	Potential vs SCE (volt)	Current density(m A/cm ²)	Temperature (°C)	Time (min)	
Initial (for pre deposition of Cr)	Final (for deposition of Ni-Cr)					Time for pre deposition of Cr (min)	Time for deposition of Ni-Cr (min)
1.875 M CrO ₃ , 0.5 ml H ₂ SO ₄	1.5 M CrO ₃ , 0.21 M NiCl ₂ .6H ₂ O, 0.09 M NiSO ₄ .7H ₂ O, 0.9 M H ₃ BO ₃ , 1.5 gm/L CH ₃ (CH ₂) ₁₁ SO ₄ Na, 0.6 ml H ₂ SO ₄	1:5	1.35	300	60	5	10
1.875 M CrO ₃ , 0.5 ml H ₂ SO ₄	1.5 M CrO ₃ , 0.21 M NiCl ₂ .6H ₂ O, 0.09 M NiSO ₄ .7H ₂ O, 0.9 M H ₃ BO ₃ , 0.6 ml H ₂ SO ₄ , 1.5 gm/L CH ₃ (CH ₂) ₁₁ SO ₄ Na	1:5	1.4	300	45	5	10

3 M CrO ₃ , 0.3 ml H ₂ SO ₄	1.5 M CrO ₃ , 0.21 M NiCl ₂ .6H ₂ O, 0.09 M NiSO ₄ .7H ₂ O, 0.9 M H ₃ BO ₃ , 0.6 ml H ₂ SO ₄ , 1.5 gm/L CH ₃ (CH ₂) ₁₁ SO ₄ Na	1:5	1.36	300	45	5	10
3.75 M CrO ₃ , 0.2 ml H ₂ SO ₄	1.5 M CrO ₃ , 0.21 M NiCl ₂ .6H ₂ O, 0.09 M NiSO ₄ .7H ₂ O, 0.9 M H ₃ BO ₃ , 0.6 ml H ₂ SO ₄ , 1.5 gm/L CH ₃ (CH ₂) ₁₁ SO ₄ Na	1:5	1.38	300	45	5	10

3.34 Cleaning

Obtaining the desired coating after performing the experiments for 15 minutes, it is necessary to clean the obtained surface. the surface is generally cleaned and rinsed with alcohol to remove the contaminants and other electrochemical impurities.

3.35 Precautions should be taken

Some precautions should be taken for performing the experiments of electro deposition. Those are :

- When the surface is prepared, it should not have any deep scratches which will affect the coating.
- Before dipping the surface of the mild steel into the electrolytic solution, it is required to make sure that other surfaces on which any electrochemical change is not desired, should be protected from the electrolyte. To protect other surfaces, Teflon is usually wrapped on those surfaces and only the desired and prepared surface is kept open for electro deposition.

- The chemicals which are used to make the electrolytic solution, are human carcinogenic. So , care should be taken when it is measured and dissolved in the distilled water.
- The power source should provide steady current. Fluctuation in current density can affect the surface property of developed material.
- The alligator clips which are used for the test should be free from rust. If , there is any rust present on those connector clips, it will affect the current passing through the entire circuit.
- Special care should be taken when the solution is heated. More amount of heat than required could lead to vaporization of the solution. The vapor is not good for human health.
- Care should be taken when the concentrated sulfuric acid is poured into the solution to increase the ionic conductivity of the solution.

3.4 electrochemical characterization :

Developed materials i.e the various chromium and nickel-chromium coating produced by different methods with different variables which are maintained in the above sections are subsequently taken for electrochemical characterization. The materials are subjected to some electrochemical corrosion tests to study the corrosion mechanism, corrosion resistance and other electrochemical properties of those developed materials. Then the results are compared to that of the 304 austenitic stainless steel.

3.41 potentiodynamic polarization test :

The developed materials are subjected to the potentiodynamic polarization test. This test is performed to find the corrosion rate i.e corrosion current density. Potential of the electrode is varied at a selected rate by application of current through the electrolyte which results in change in current. It is also a function of the working area of the electrode. To perform the test equivalent sea water is required. Here , 3.5% chloride solution is used to provide the corrosive environment for the developed materials.

This experiment is done in the ‘versastat 3’ system. The machine set up consists of a monitor , control unit and the connecting cable. The connecting cable is used to make a connection between the control unit and the electrochemical cell. The developed material is dipped into the 3.5% chloride solution as the working electrode. Graphite rod is used as counter electrode in the cell. Saturated calomel electrode is used as reference electrode. A salt bridge is used to make connection between the cell and the saturated potassium chloride solution where the reference electrode is kept. The connecting cable has 4 terminals such as working electrode, counter electrode, reference electrode and working sense. The working sense terminal is connected to the terminal which connects working electrode.

The control unit is the most important part of the system. It provides power to the electrochemical cell to perform cathodic and anodic polarization subsequently. It also generates the

data. The change in potential which causes the change in current is recorded by this unit directly from the electrochemical cell. Those data are sent to the monitor unit.

The monitor shows the generated curve by changing current with the change in potential. The polarization curve is being plotted in the monitor so that the corrosion potential and the corrosion current density can be found from the experiment.

The generated data can be taken in tabulated form and further it can be used for different plotting and comparing with other materials and 304 stainless steel.

3.42 Cyclic polarization test :

Cyclic polarization is the test on which the anodic and cathodic polarization is performed in a cyclic manner. This test provides the corrosion resistance property, passivity, pitting potential and repassivation potential of the developed materials.

To perform a cyclic polarization test for a developed material, the equivalent sea water is required for corrosive environment. 3.5% chloride solution is used for that purpose. The developed material is used as working electrode. graphite rod is used as the cathode and saturated calomel electrode is used as reference electrode.

It is also performed on the versastat 3. The set up is similar like that of the potentiodynamic test which is maintained in the above. The functions of the connecting cable, monitor unit and control unit are also discussed in the earlier section.

The range , other parameters are entered manually. The scan rate of the experiment is similar with the ASTM standard (1 mv/sec). In the cyclic polarization test, there is a peak potential which should be maintained before the starting of the experiment. This peak potential reverses the direction of change of potential. Thus the loop is formed. That loop provides the repassivation potential which indicates the self healing property of the passive layer formed on the surface of the developed material undergoing the test.

3.43 Electrochemical impedance spectroscopy :

Electrochemical impedance spectroscopy is performed to find the electrochemical property as well as equivalent electrical properties of the surface developed by the electroplating. The electrochemical phenomenon occurring in the electrode surface which is immersed into the electrolyte, can be represented by an equivalent electrical RLC circuit. The measured impedance curve is generally fitted with an equivalent electrical model which gives us the unique equivalent electrical properties due to the electrochemical phenomena in the electrode-electrolyte interface and gives information about the behavior of the material or deposited film.

EIS is performed in the 'gamry potentiostat'. It also has a connecting cable, control unit (analyzer) and the monitor. The connecting cable has 6 terminals. To perform the experiment, 5 terminals are

connected. 3 terminals are connected with 3 electrodes of the cell i.e working electrode, counter electrode, reference electrode. other terminals are the working sense, counter sense and connected with the terminals connecting working electrode and counter electrode respectively.

The connecting cables connects the cell to the analyzer unit. The experiment is performed between the frequency of 100 KHz to 0.01 Hz. The curves are generated as nyquist plot and bode plot. Echem analyst software is used to find the equivalent electrical circuit of the plot. Then the informations such as polarization resistance, warburgh resistance, solution resistance, generation of electrical double layer, capacitor or constant phase elements can be obtained from the equivalent circuit and the nature of the plot.

3.5 material characterization :

After electrochemical characterizing , it is required to understand the reason behind such type of surface properties discussed in the earlier section. Material characterizations are done by x-ray diffraction technique and scanning electron microscopy.

3.51 X-ray diffraction :

X-ray diffraction technique is the material characterization process to analyze the composition and their phases present on the material. After obtaining different type of electrochemical properties, the developed materials should be gone through the xrd test. It will provide the reason for showing such kind of electrochemical properties. The best materials are subjected to this test to understand their composition and phases which are responsible for their electrochemical behavior.

The range of the experiment is generally between 20° to 80° with a scan rate of 2°/min. The test is performed in the ‘Rigaku Ultima III X-ray diffractor’.

3.52 Scanning Electron Microscopy :

Scanning electron microscopy is material characterization technique which provides the magnified view and the complete idea about the morphologies of the developed surface. After performing all the electrochemical characterization tests, it is necessary to know about the surface in details. This is only possible through electron microscopy as it provides the magnified image of the surface. the best performing materials are gone through this test. The morphologies of the surface is obtained from this characterization technique.

The samples are mounted properly on a sample holder and then scanned by the electrons in vaccum condition to generate the detail morphologies with changing the magnification. This test is performed in SEM (model- JUNST-JSM 6360).

CHAPTER 4: RESULT AND DISCUSSION

4. RESULT AND DISCUSSION :

The results of the series of experiments of corrosion study , electrochemical impedance study as described in section 3 of plain carbon steel , nickel chromium electro coated carbon steel , 304 stainless steel are elaborately discussed in the following section. The following paragraphs consists of electrochemical corrosion studies of coated and uncoated carbon steel , electro chemical impedance spectroscopy , material characterization by XRD and Scanning electron microscopy. The computed electrochemical corrosion data are given in tabular form for comparison with those of 304 stainless steel. The Impedance data of capacitance , impedance and polarization resistance are also tabulated.

4.1 potentiodynamic polarization studies :

To measure the corrosion rate, corrosion mechanism , corrosion resistance of a material, potentiodynamic polarization studies are used. The results of the set of the experiments are discussed in the following section and compared to the corrosion resistance property of the 304 stainless steel.

4.11 Comparison of mild steel and stainless steel (potentiodynamic polarization test in 3.5% NaCl solution)

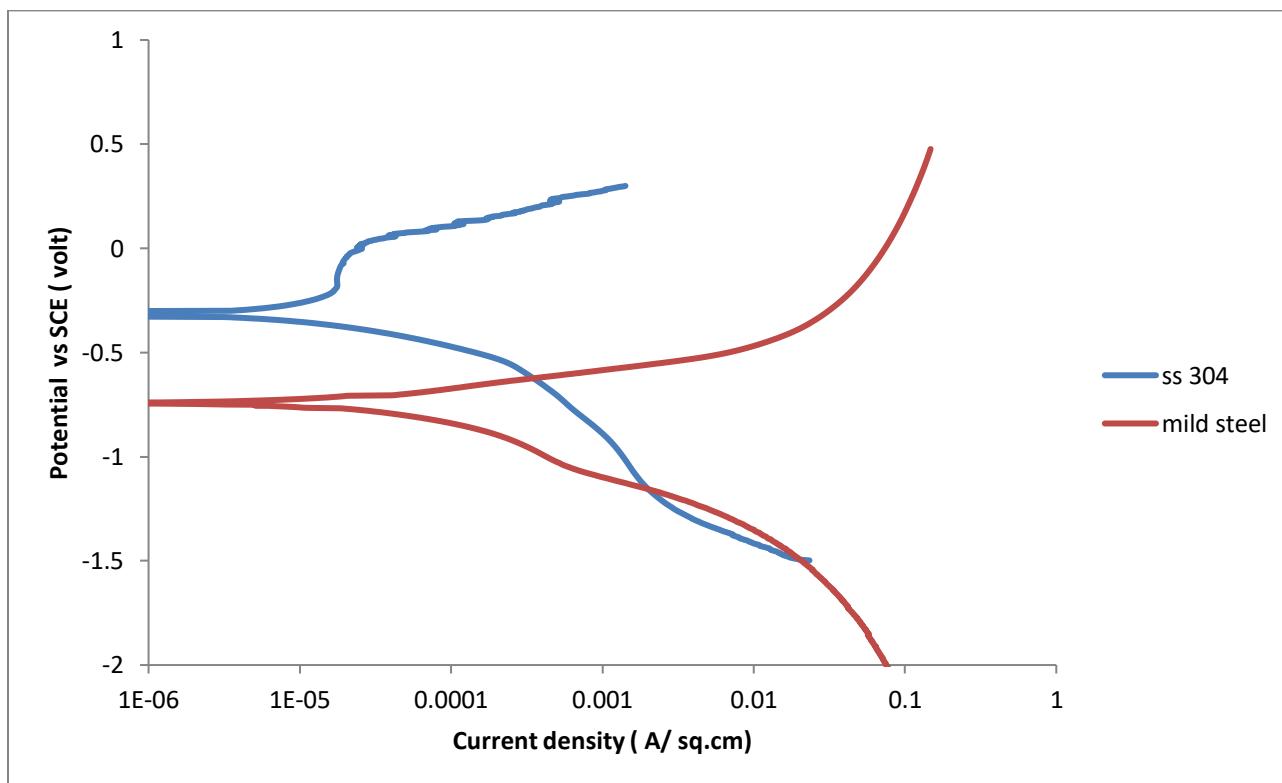


Fig 4.11 : comparison of corrosion property (potentiodynamic polarization)of mild steel and 304 stainless steel

Fig 4.11 shows that potentiodynamic polarization of carbon steel and 304 stainless steel in 3.5% nacl solution at temperature 28° C at pH 8.1 . Although it is known the stainless steel has got higher corrosion resistance compared to carbon steel and the figure exactly shows that and stainless steel also exhibits passivity .

It will be interesting to find that how a chromium coated mild steel behave in comparison to 304 stainless steel.

4.12 comparison in corrosion property of developed Cr coating with mild steel and stainless steel

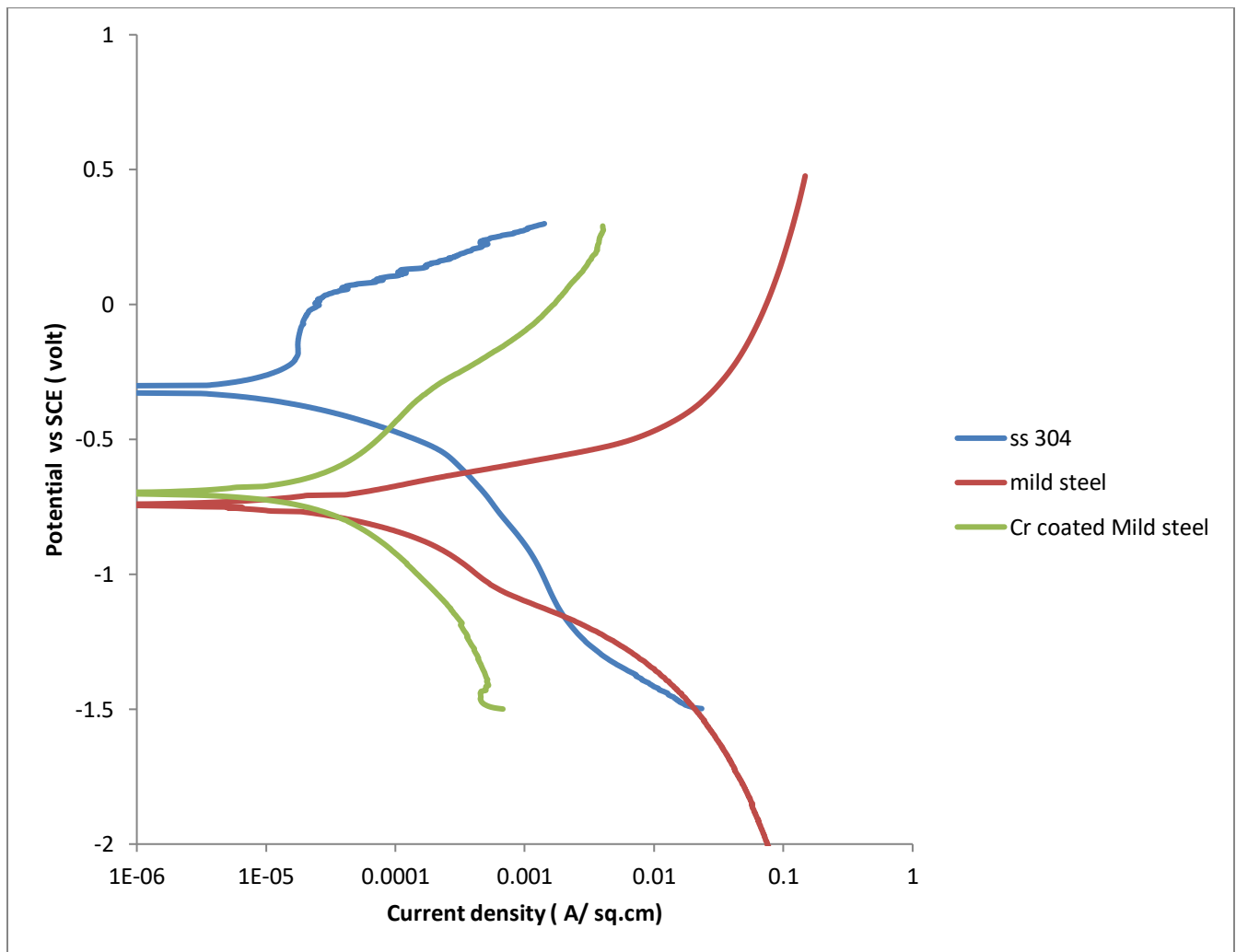


Fig 4.12 : comparison of corrosion property of mild steel, 304 stainless steel, Chromium coated mild steel

Fig 4.12 shows that comparative corrosion behavior of mild steel , Chromium coated mild steel and 304 stainless steel. It is interesting to find out that chromium coated mild steel gives much higher corrosion resistance than that of mild steel. Though it's corrosion rate is somewhat higher than 304 stainless steel . A small thin coating of Cr consuming few mg of Cr / cm² can drastically change the corrosion property of mild steel whereas in 304 stainless steel , Cr is present thoroughly from surface to centre into the whole body with 18 % of chromium consumption.

It will be interesting to see if a low cost variety chromium coated mild steel can be produced to combat aquas corrosion in Chloride environment.

4.13 effect of coating parameters on corrosion behavior of chromium electro coated mild steel

Having obtained interesting results of decreasing the corrosion rate of Cr coated carbon steel in 3.5 % cl environment endeavors have been taken to vary the coating parameters viz. coating current density, temperature, chemistry of solution so as to obtain the best coated high corrosion resistance material.

4.13a effect of temperature of electrolyte solution of chromium

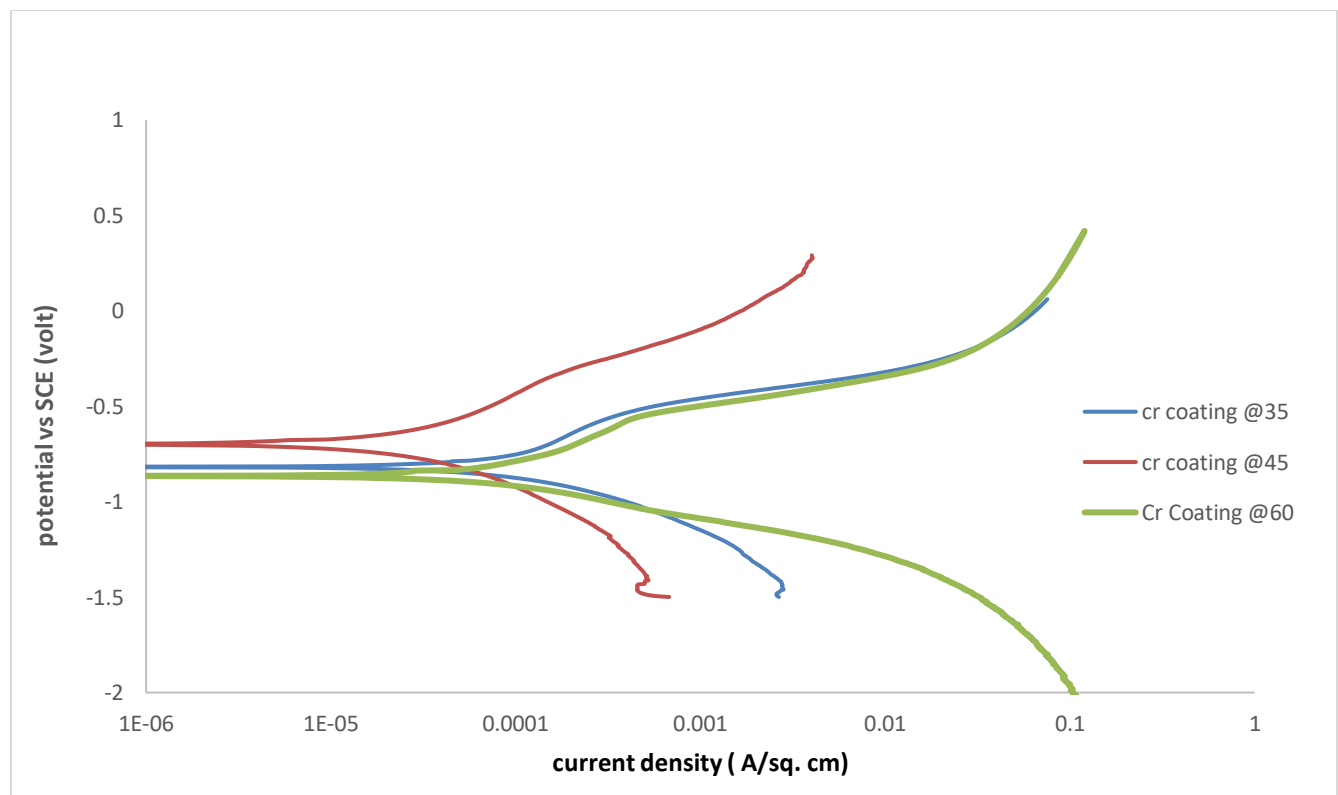


Fig 4.13a : comparison of corrosion property of developed Cr coating at different temperatures

Fig 4.13a shows that the effect of coating temperature of Cr coating on mild steel in 3.5% NaCl solution at 28° C.

It is seen that coating temperature has a strong effect on corrosion resistance of the electrocoated carbon steel. The best coated corrosion resistance is found at the coating temperature 45° C. It is found that I_{corr} value of chromium coated at 45° C is about half than the I_{corr} value of chromium coated at 35° C and 60° C at a fixed current density of 300 mA/ cm² . It shows that there is an optimum temperature of coating below which or above that corrosion rate increases.

Higher the temperature, faster is the mobility of ions so cr ions can reach the interface of solution and electrode at faster rate.

The deposition potential is given by the following equation —

$$E_{\text{dep.}} = E^{\circ}_{\text{cr}} + \frac{RT}{nF} \log [\text{Cr}] + \eta_{\text{act.}} + \eta_{\text{conc.}} + IR_{\text{drop}}$$

$\eta_{\text{conc.}}$ Will be less at higher temperature since the thickness of stagnant diffusion layer decreases and mass transfer increases with increase in temperature. Again at higher temperature more no. of cr ions will be available at the electrode interface. This will give rise to coarser and irregular deposition. The morphology of such deposit increases the corrosion rate. Thus there is an optimum temperature where the corrosion current is minimum.

4.13b effect of cathode current density of chromium deposition

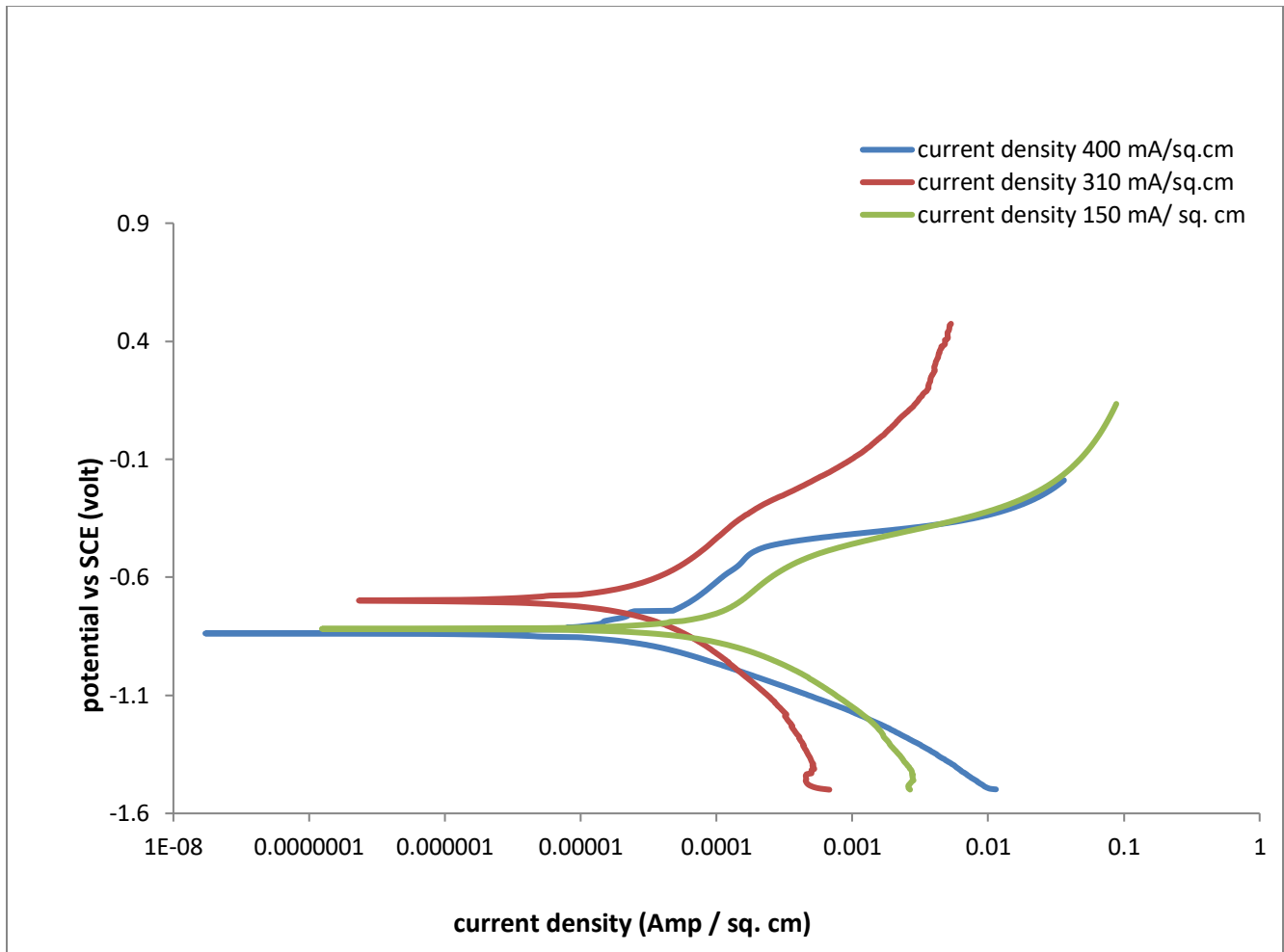


Fig 4.13b : comparison of corrosion properties of developed Cr coating at different current densities

Fig 4.13b shows the effect of current density on corrosion behavior of chromium coated carbon steel at temperature 45° C.

It is seen that high corrosion resistance material can be produced by depositing chromium at a current density of 310 mA/ cm².

More is current , faster the rate of electron transfer from the power source to the electrode surface . If cr ions is available at the electrode , they will be discharged by accepting free electron at electrode and can be deposited in the mild steel. The speed at which electron travels from power source to the electrode is much higher than the speed of which cr ions diffuse through the solution and reach the electrode surface. So, if current is increased more and more than what is

required for chromium deposition, the electrode surface will be overcharged and it will absorb unwanted impurities from the solution as well as from the environment by electrostatic deposition.

4.14 comparison of developed Cr coating by varying parameters to obtain the best quality material

The coating parameters for chromium coating has been varied to develop different type of cr electro coated mild steel. To find the best quality material , it is necessary to compare the corrosion rate of all the developed materials together so that the condition for optimization is achieved.

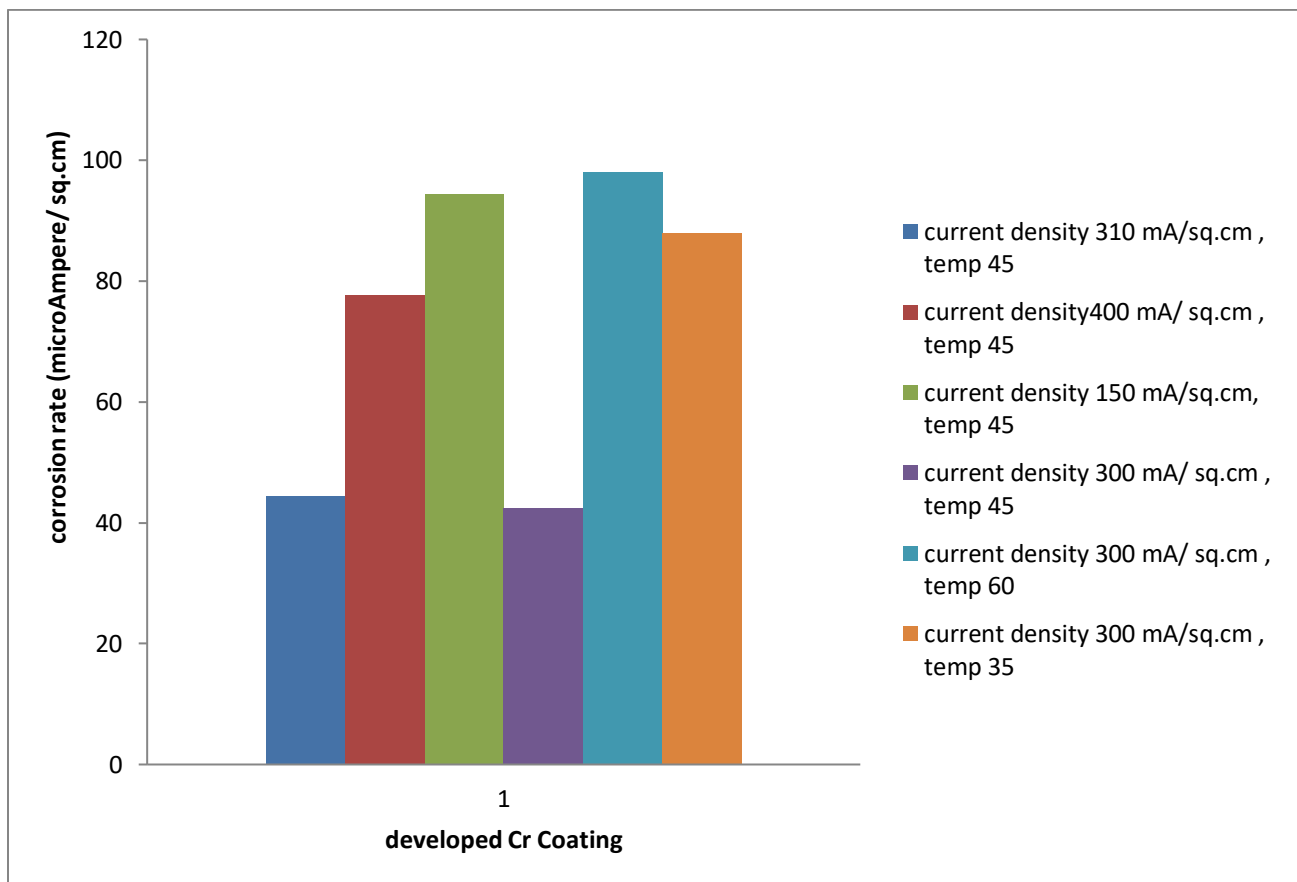


Fig 4.14 : the corrosion rate of developed chromium coating by variation of parameters

Fig 4.14 shows the corrosion rate of differently developed Cr coating on mild steel. From the bar chart, the optimized condition for Cr electro coated mild steel is clearly achieved. The optimized condition for developing best quality material is :

- Current density : 300 mA/ cm²
- Temperature : 45° C

4.15 comparison of corrosion property of developed Ni coating with mild steel and stainless steel

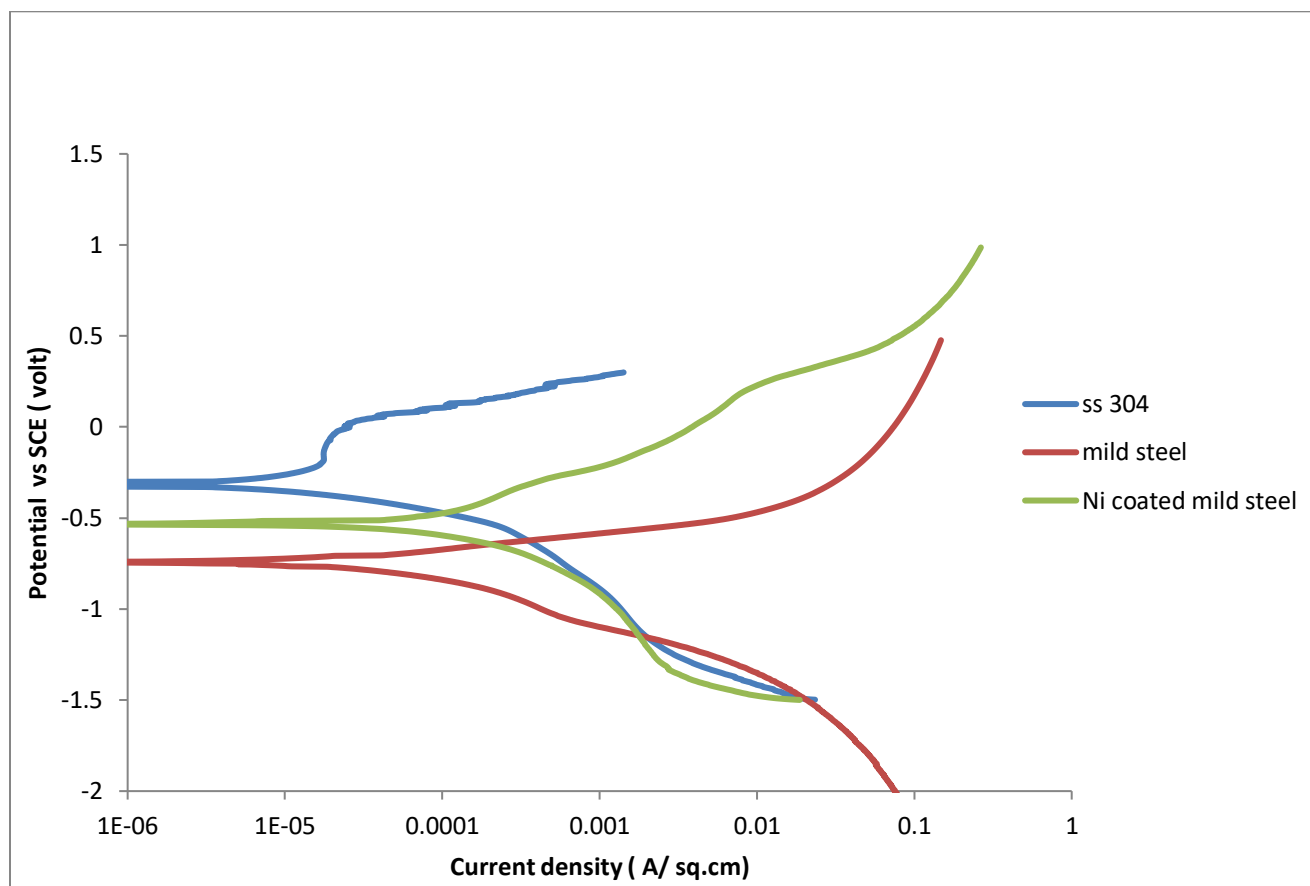


Fig 4.15 : comparison of potentiodynamic polarization of 304 stainless steel , mild steel and Ni coated mild steel

Fig 4.15 shows that the comparative corrosion study of mild steel , stainless steel 304 and Ni coated mild steel. Though it does not exhibit passivity and provides lower corrosion resistance than 304 stainless steel, it also gives an interesting result as Ni coated mild steel gives much higher corrosion resistance than mild steel. Almost 8% Ni is present thoroughly from centre to surface to provide austenitic stability and strength in stainless steel.

As a thin coating of Ni consuming few mg of Nickel per square cm gives a better result than mild steel ,It will be interesting to find out if a low cost coated material with good strength and passivity can be produced to combat aquas corrosion in chloride environment by using Nickel and chromium.

4.16 comparison of nickel-chromium electro coated material with mild steel and 304 stainless steel

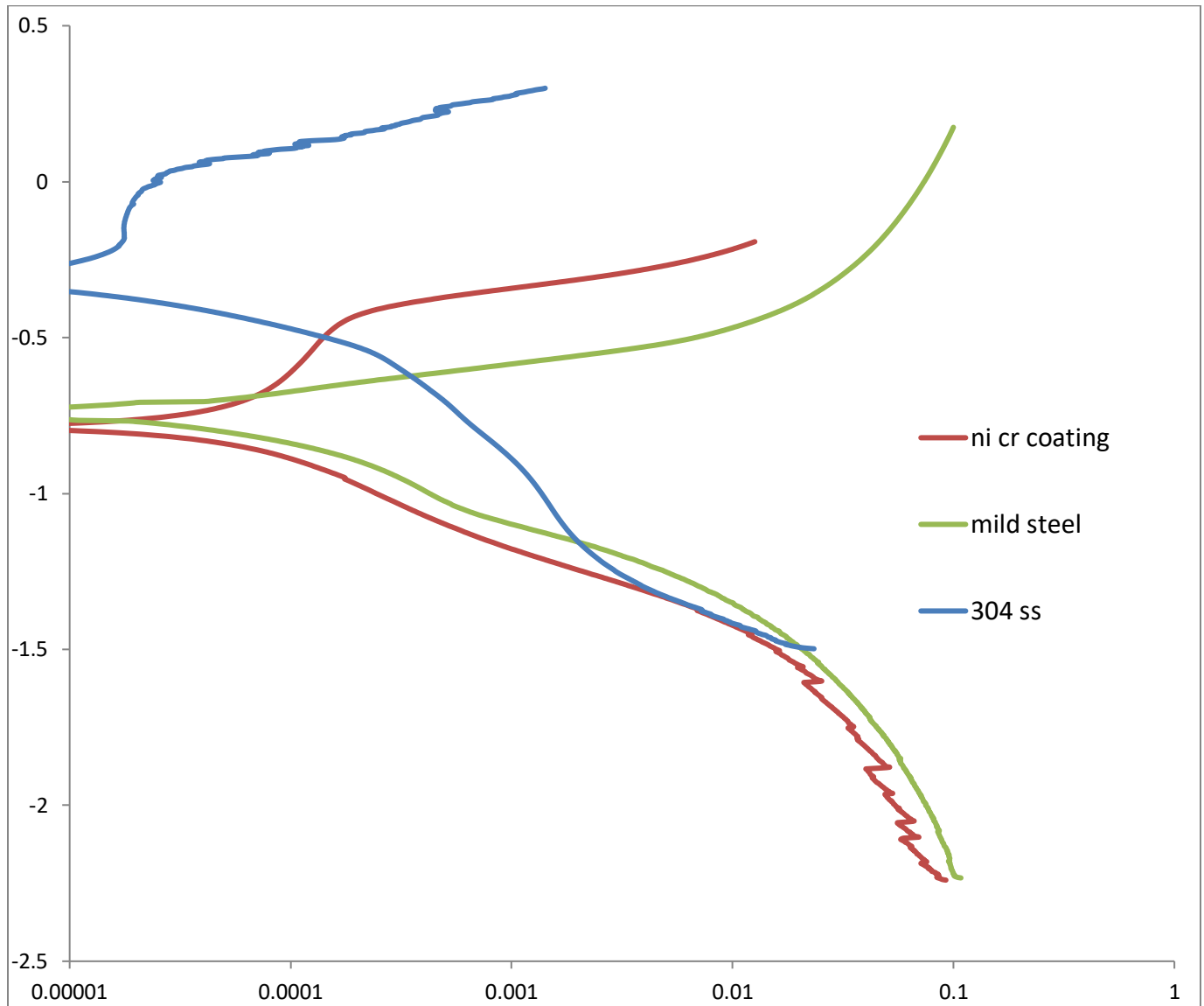


Fig 4.16 : comparison of corrosion property of Cr-Ni coated ms with 304 stainless steel and mild steel

Fig 4.16 shows that the comparative corrosion study of mild steel , stainless steel 304 and Cr-Ni coated mild steel. Though the corrosion rate is not so low but it shows better corrosion resistance than mild steel. It also shows the tendency to have passivity in the potentiodynamic polarization curve. It will be interesting to vary some parameters to get a better result for Cr-Ni coated mild steel.

4.17 effect of coating parameters on corrosion behavior of nickel -chromium electro coated mild steel

Having obtained interesting results of decreasing the corrosion rate of Cr-Ni coated carbon steel in 3.5 % cl environment, endeavors have been taken to vary the coating parameters viz. coating current density, temperature, chemistry of solution so as to obtain the best coated high corrosion resistance material.

4.17a effect of solution ratio of chromium-nickel

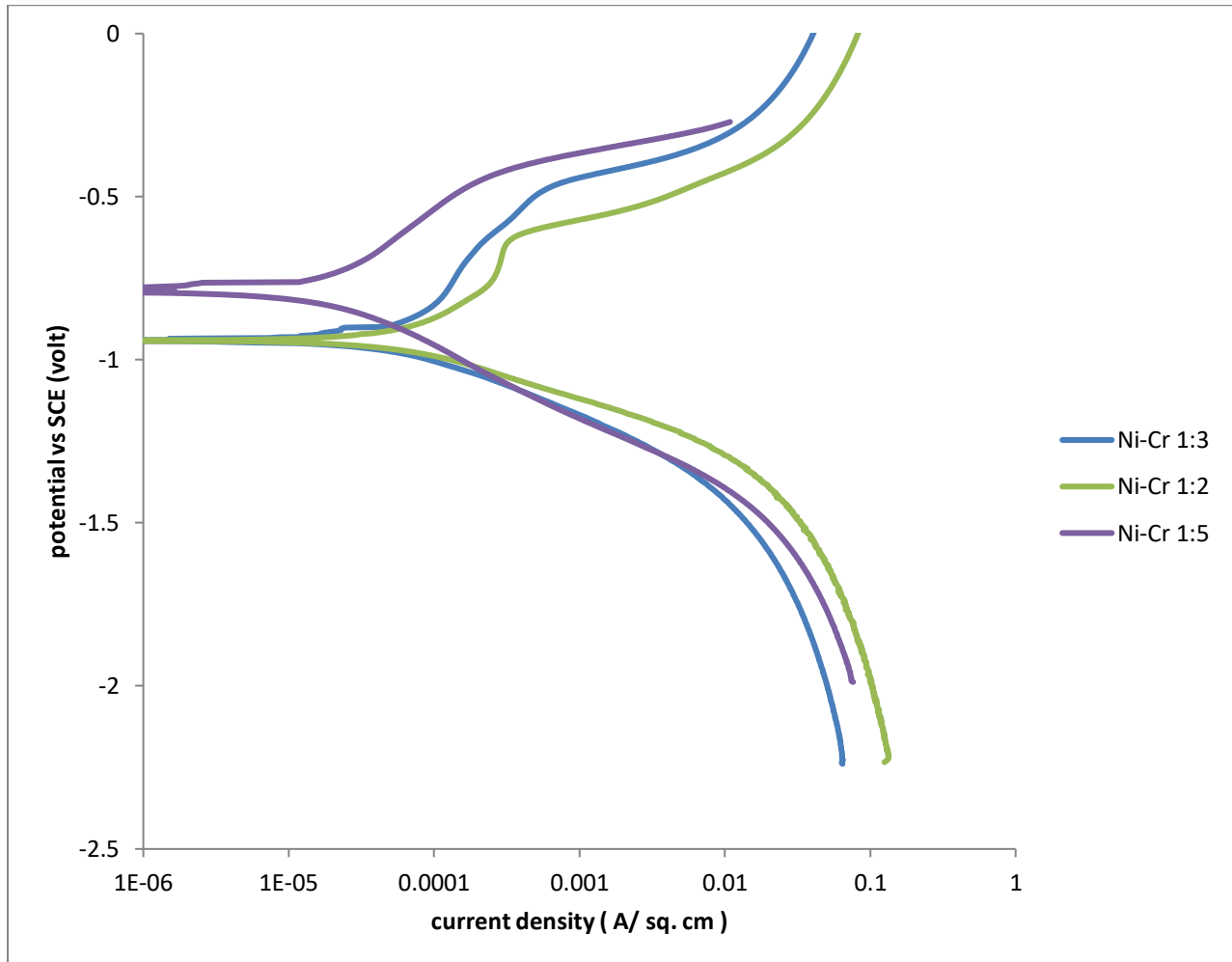


Fig 4.17a: comparison of potentiodynamic polarization of differently developed Cr-Ni coating

Fig 4.16 shows that the comparative corrosion study of differently developed Cr-Ni coated mild steel. The coatings are developed by varying the solution chemistry. It is seen that the ratio of Cr ions and Ni ions present in the solution has influence on the surface property of the developed materials. These coatings are developed keeping the current density at 300 mA/cm^2 , temperature of 45°C .

As nickel has lower deposition potential than that of chromium. So, nickel has higher tendency to be deposited. But to increase the corrosion resistance chromium is required more. To make sure that the Cr ions has deposited in large amount on the surface, the ratio is increased. As the amount of nickel ions decrease in the electrolytic solution, Cr ions will have more opportunity to be deposited. The result is also confirming this fact.

Further work on Ni-Cr coating is done with the ratio 1:5 because the corrosion rate is much lower for this type of coating. It also contains much amount of Nickel in the deposited film.

4.17b effect of various technique of electrocoating of Ni Cr (1:5)

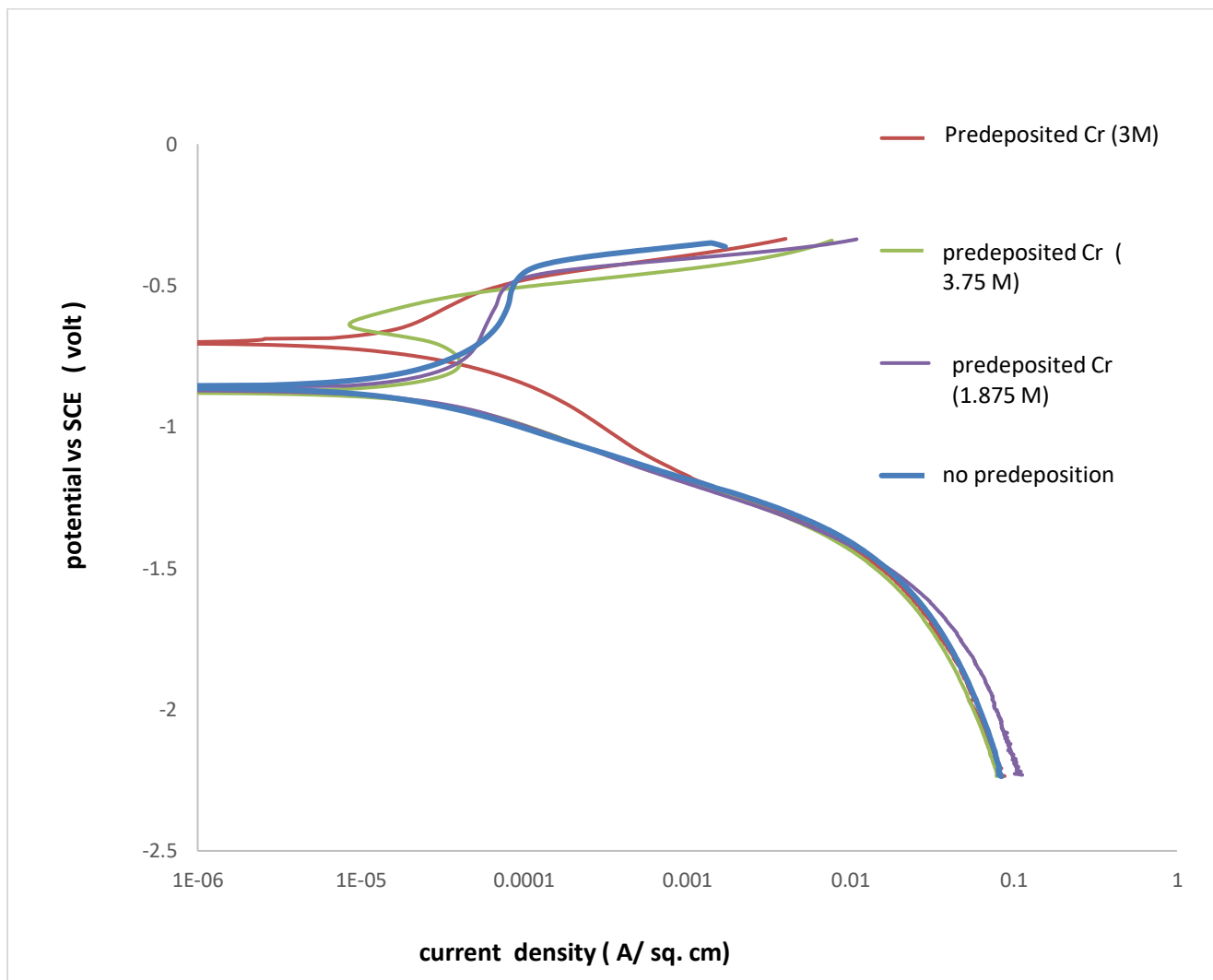


Fig 4.17b : the effect of predeposition of chromium

Fig 4.17b shows that the comparative corrosion study of differently developed Cr-Ni coated mild steel. The final ratio of chromium and nickel is fixed at 1:5. But predeposition of chromium has been used to make change on the surface property. Higher the concentration of chromium in the

predeposition, the corrosion resistance is more. A special type of coating is developed which shows the tendency of showing passivity like stainless steel. It is further discussed in the next section and compared to 304 stainless steel.

4.2 Cyclic polarization studies

The cyclic polarization curve exhibits passivity, passivity breakdown and stability of passive layer. The experiment details has been elaborately discussed in section 3.

4.21 comparison in cyclic polarization of developed chromium coating and stainless steel

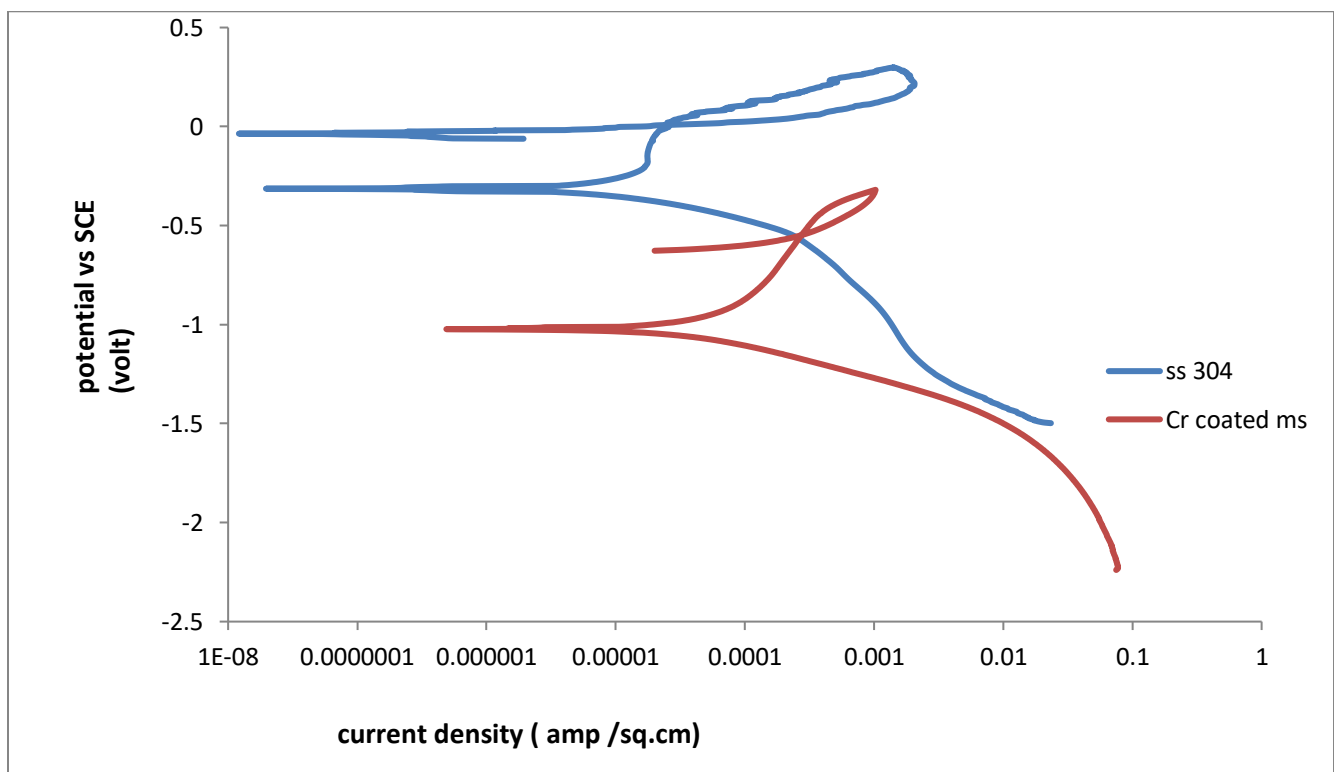


Fig 4.21 : comparative study of cyclic polarization of 304 stainless steel and best performed Cr coating

Fig 4.21 shows that the curves for stainless steel and best performed chromium coated mild steel. It is seen that the curve for the chromium coated material also shows the passivity, however passive current density is little higher than that of the stainless steel.

The re-passivation potential is indicated by the point where the reverse curves cut the passive region. The repassivation potential indicates if pit initiated can be repassivated . it is seen that this material behaves similar to the stainless steel but only at little more negative potential.

4.22 comparison of cyclic polarization of developed different ni-cr coating with stainless steel

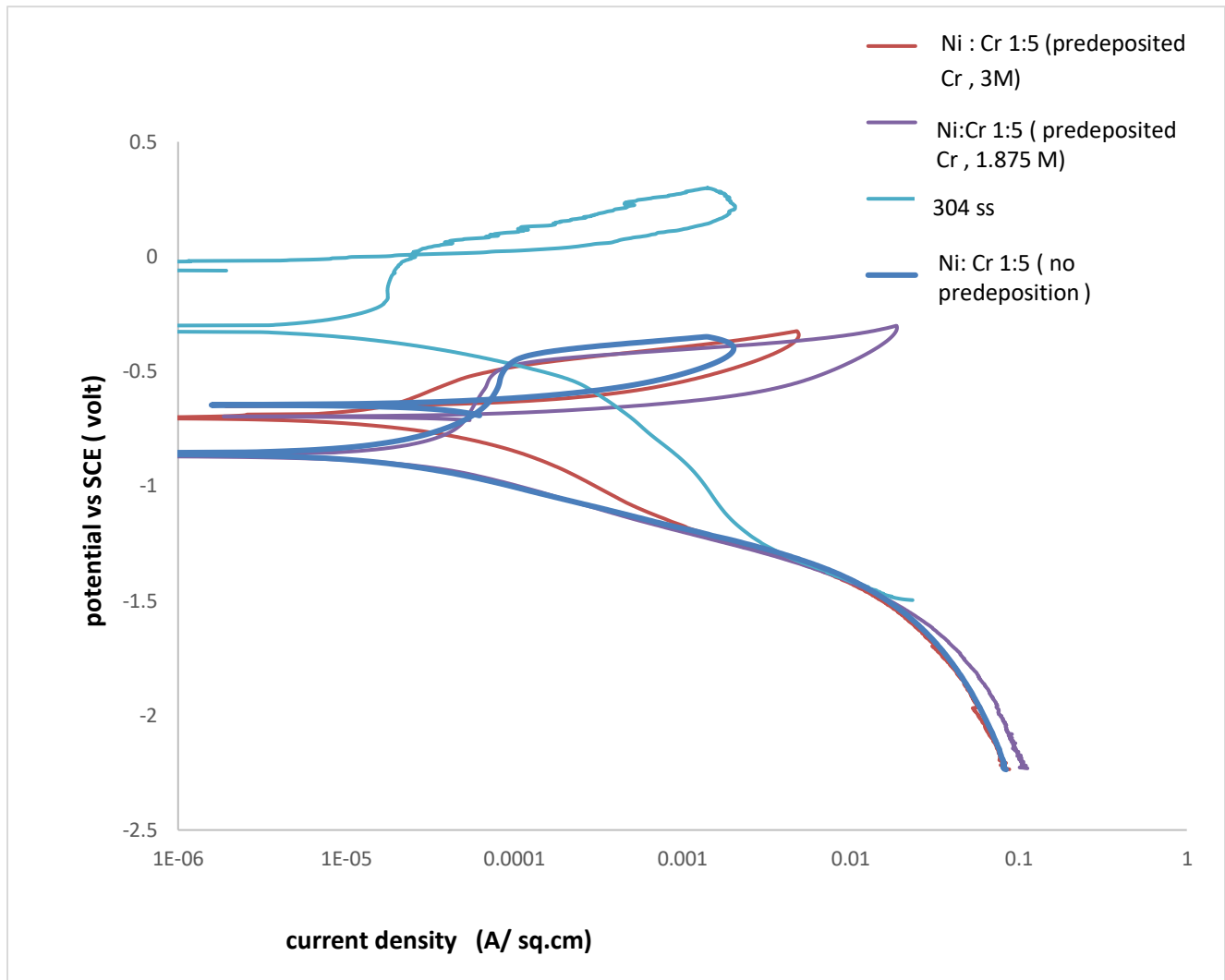


Fig 4.22 : comparative study of cyclic polarization of differently developed chromium-nickel coating and 304 stainless steel

Fig 4.22 shows that the cyclic polarization curves for stainless steel and best performed chromium-nickel coated mild steel. It is seen that the curve for the chromium-nickel coated material also shows the passivity , however passive current density is little smaller than that of the stainless steel.

4.22a comparative study of cyclic polarization

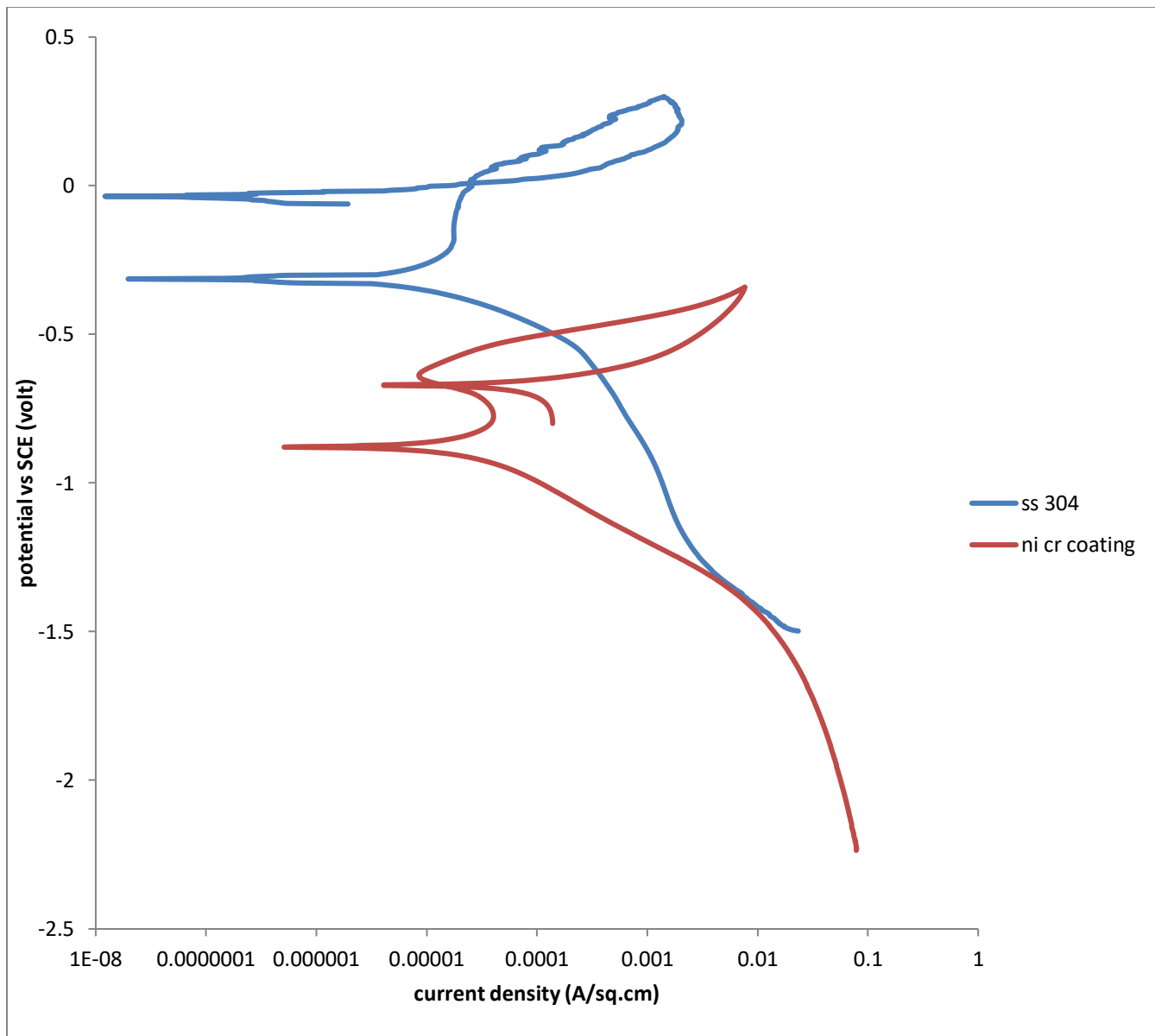


Fig 4.22a : comparative cyclic polarization study of chromium nickel coated mild steel and 304 stainless steel

Fig 4.22a shows that the cyclic polarization curves for stainless steel and one of the best performed chromium-nickel coated mild steel. It is seen that the curve for the chromium-nickel coated material also shows the passivity, however passive current density is little smaller than that of the stainless steel. It has a tendency of showing passivity like stainless steel. Though, the corrosion potential, repassivation potential, pitting potential are much lower than 304 stainless steel. A different type of curve is generated by this coating which is developed by predepositing

chromium at 3.75 M solution at 45° C, current density 300 mA/sq.cm. So, the predeposited chromium layer is so compact that it helps for self healing of the material when pitting is occurred.

4.3 Electrochemical impedance spectroscopy

The electrochemical phenomenon occurring at the metal –electrode interface can be represented by RLC circuit and is studied by eis for better understanding of fundamental aspects of electrochemical corrosion in aquas environment. In general , the interface consists of layer of positive charge and layer of negative charge which is called electrical double layer which produces a capacitance (C_{dl}) or pseudo-capacitance(Y^o) .

In addition , there are resistive load like polarization resistance (R_p) , solution resistance (R_s). There may also inductance or more capacitance due to coating. The phenomenon can be interpreted Nyquist and Bode plot which are depicted and discussed in a following section for various Cr and Ni-Cr coated mild steel.

4.31 nyquist plot for chromium coating

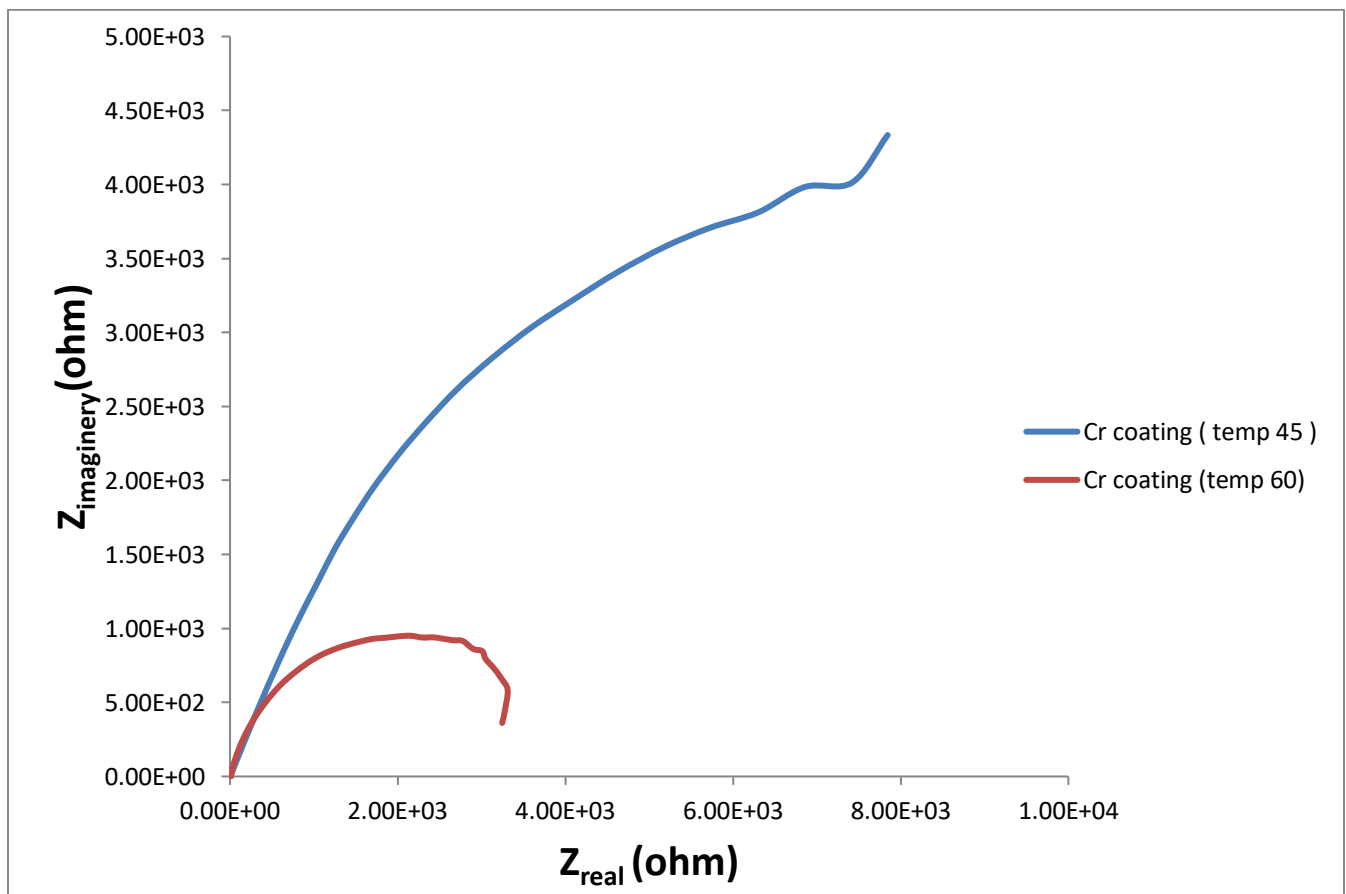


Fig 4.31 : nyquist plot of different Cr coated mild steel

Fig 4.31 shows that the comparative study of nyquist plot of developed Cr coated mild steel at current density 300 mA/cm^2 with variation in temperature. The best performing chromium coating has given the Warburg resistance. It also shows higher value of impedance while the coating developed at 60° C temperature provides lower impedance than that of the coating developed at temperature 45° C .

4.32 Bode plot for chromium coating

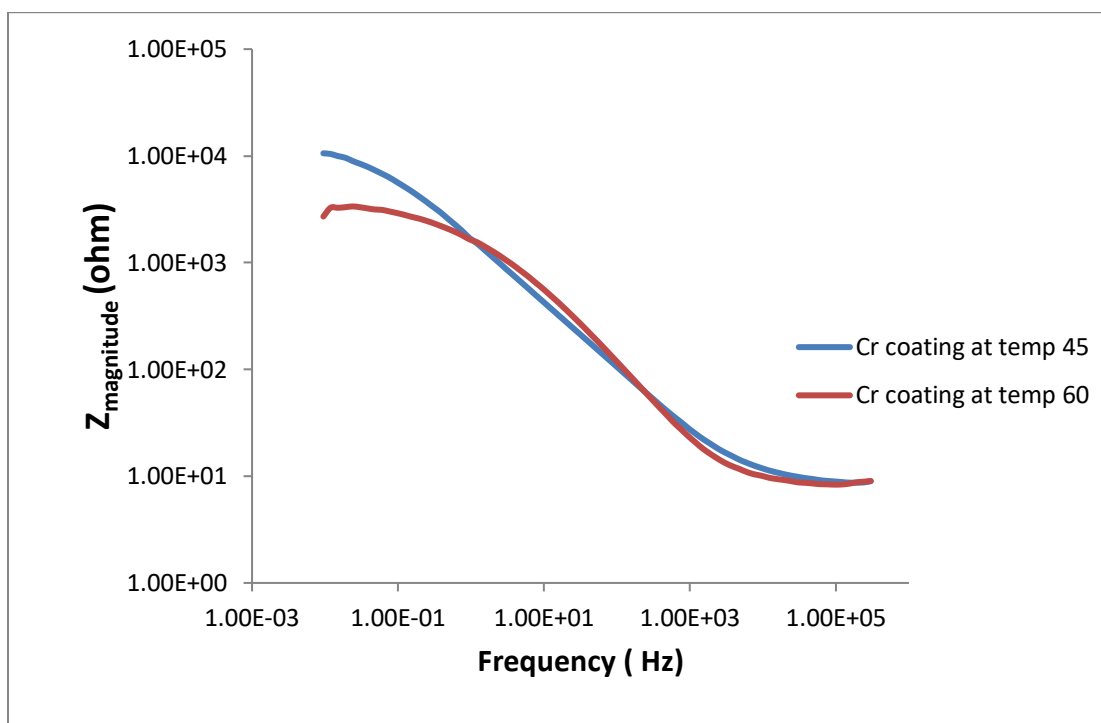


Fig 4.32a : Bode plot for chromium coating (frequency vs magnitude of Z)

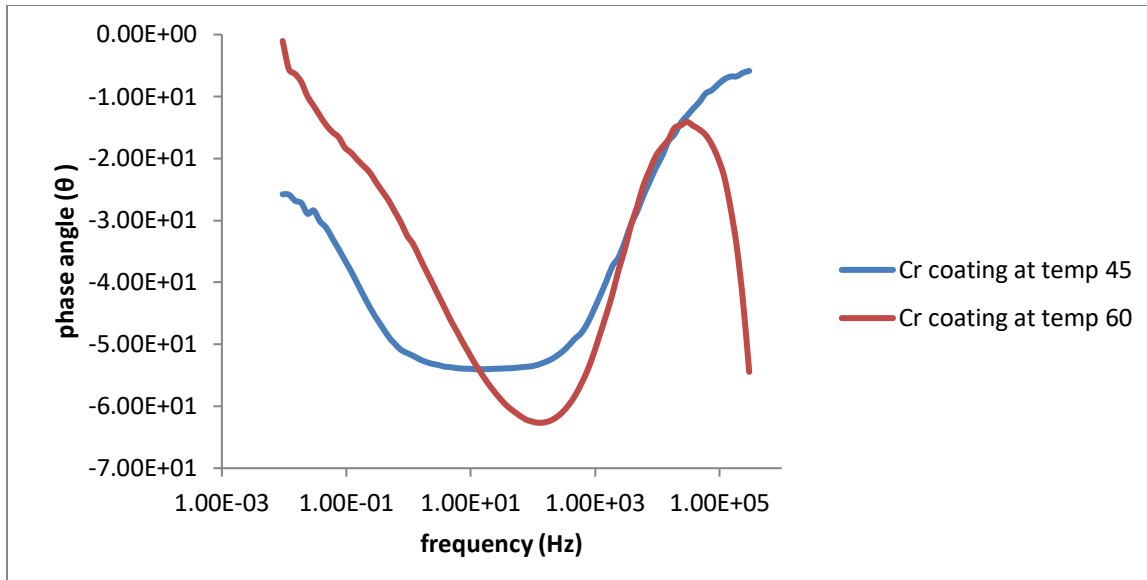


Fig 4.32b : Bode plot for chromium coating (frequency vs phase angle)

Fig 4.32a & fig 4.32b show the Bode plot for different chromium coating. Presence of capacitive load produce an angle towards -90° . If there is more than one capacitive load, the phase angle will be shifted twice. The coating developed at 60°C provides two capacitive load in it'

4.33 nyquist plot for chromium-nickel coating

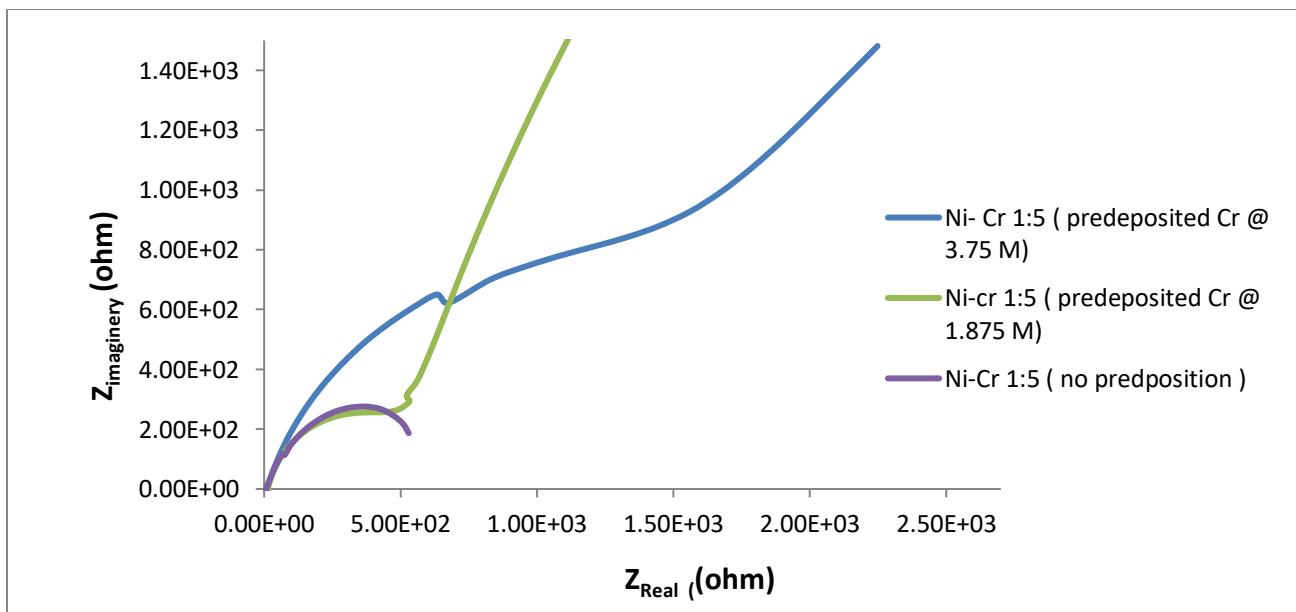


Fig 4.33 nyquist plot for nickel-chromium coating

4.34 bode plot for chromium-nickel coating

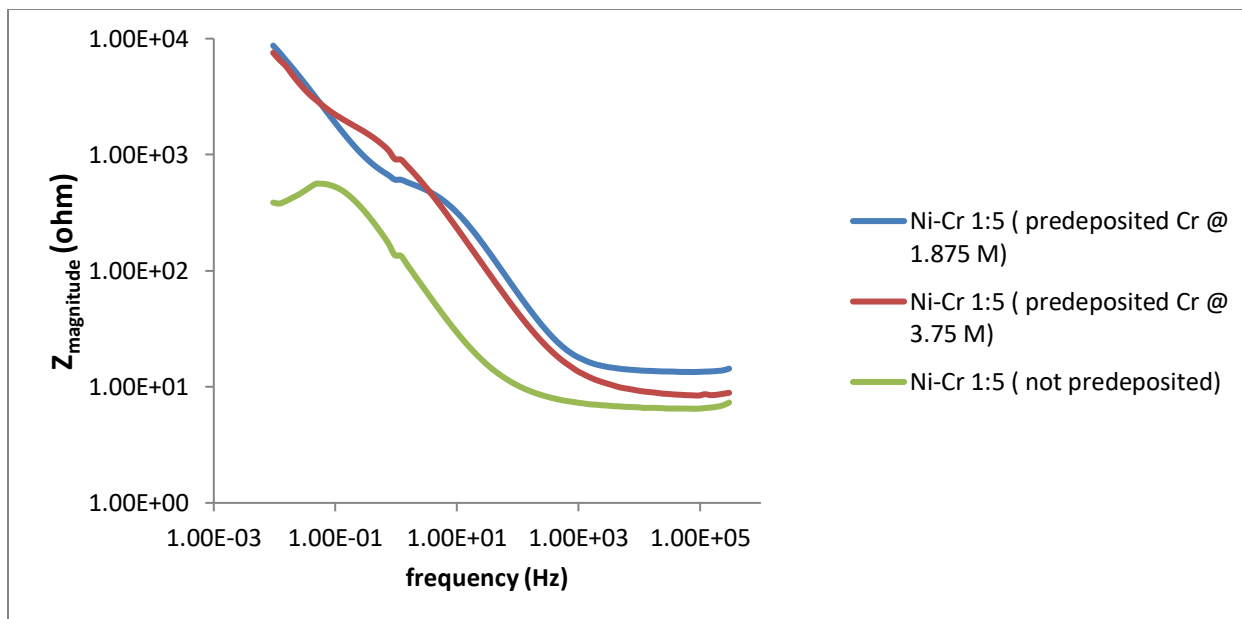


Fig 4.34a : bode plot of chromium-nickel coated mild steel (frequency vs magnitude of Z)

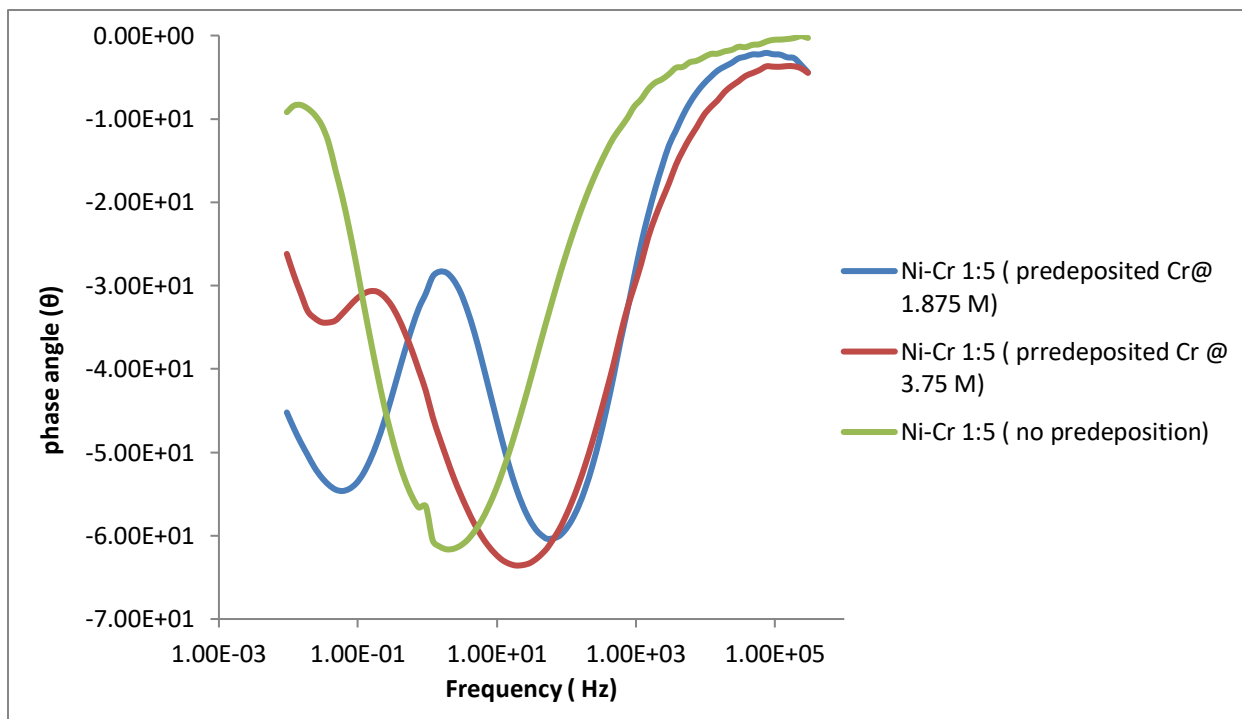


fig 4.34b : bode plot of nickel-chromium coated mild steel (Frequency vs phase angle)

fig 4.33 , fig 4.34a & fig 4.34b show the electro chemical impedance data for the chromium-nickel coated mild steel. Having obtained a good result from chromium deposition and since stainless

steel consists of two major alloys such as nickel and chromium. Nickel is postdeposited over chromium to see the effect of corrosion property. Since chromium impules passivity to the steel, it will be wise decision to deposit Chromium first , followed by post deposition of nickel or nickel and chromium both. Phase angles are shifted twice which refers to the presence of capacitive load twice in the equivalent circuit. Nyquist plot shows that the predeposited chrome coating has provided the warburg resistance.

4.35 the comparative study of electrochemical impedance informations

The model circuit is matched with EIS data by the Echem analyst software. The computed EIS data obtained from gamry framework software are tabulated in the following section:

Samples	Solution resistance (R_u) (ohm)	Polarization resistance (R_p) (ohm)	Warburg resistance (w) (ohm)	Capacitance (C_{dl}) (μF)	Equivalent circuit
Cr coated mild steel (60° C)	52.3	2525	0	4	Randle model
Cr coated mild steel (45° C)	59.1	4560	125	0.01	Warburg model
Cr-Ni coated mild steel (Cr predeposited @ 3.75M solution) 1:5	55.5	1233	150	0.07	Warburg model
Cr-Ni coated mild steel (Cr predeposited @ 1.875M solution) 1:5	50.3	597.22	170	0.075	Warburg model
Cr-Ni coated mild steel (no predeposition of Cr) 1:5	52.6	611.3	0	10	Randle model

4.4 material characterization

having synthesized a good corrosion resistance coating, it is now required to investigate the different phases and compounds of the coated material by X-ray diffraction and 3D morphology of the structures under scanning electron microscopy.

4.41 XRD analysis of chromium coating

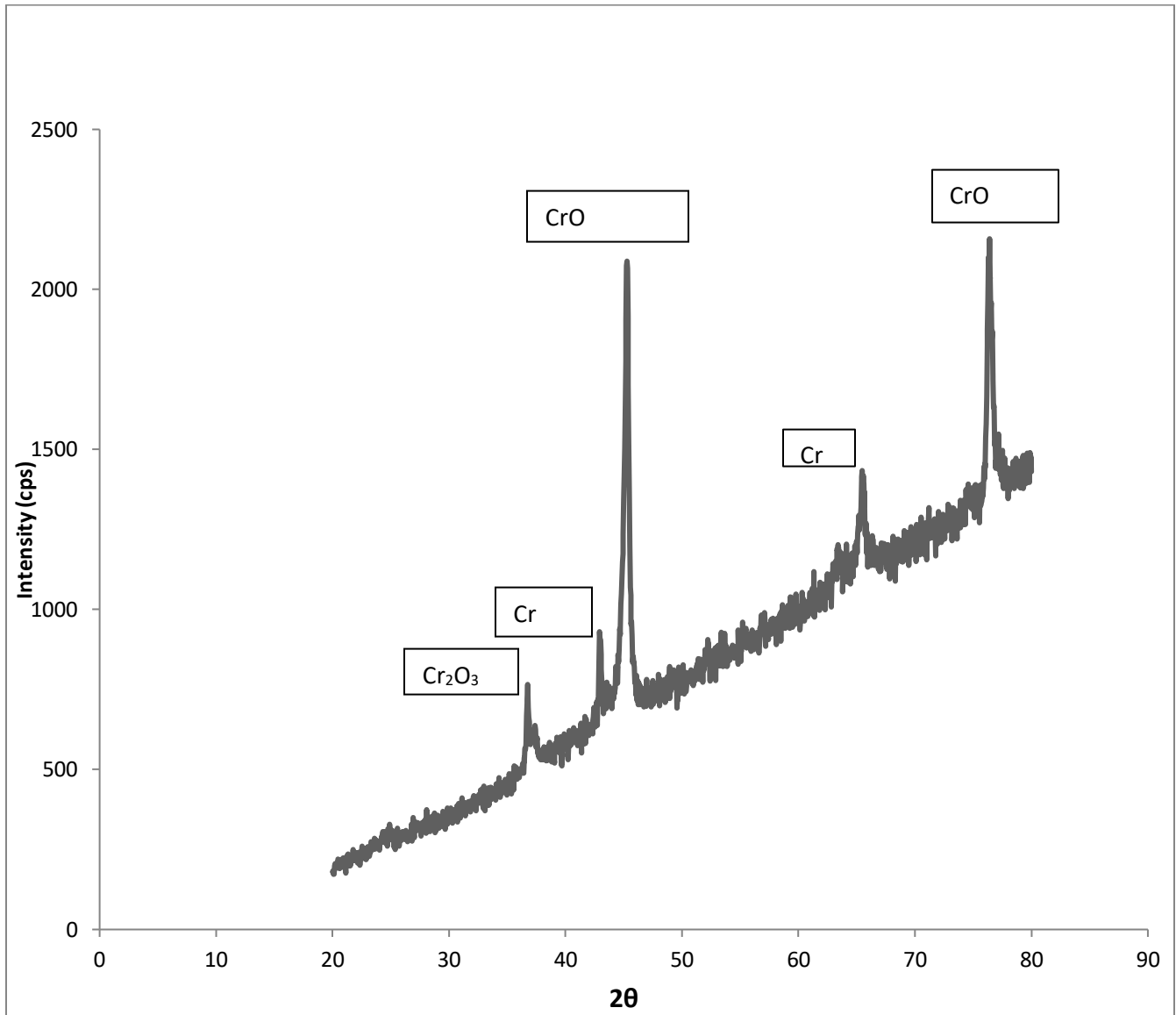


Fig 4.41 : XRD analysis of chromium coated mild steel

Fig 4.41 shows XRD analysis of chromium coated mild steel. It is found that the chromium presents in the surface tends to form oxide. This oxide layer is mainly responsible for showing passivity and better corrosion resistance property. The chromium is present in the material as chromium oxide which protects the metal from corrosive environment.

4.42 Xrd analysis of nickel-chromium coating

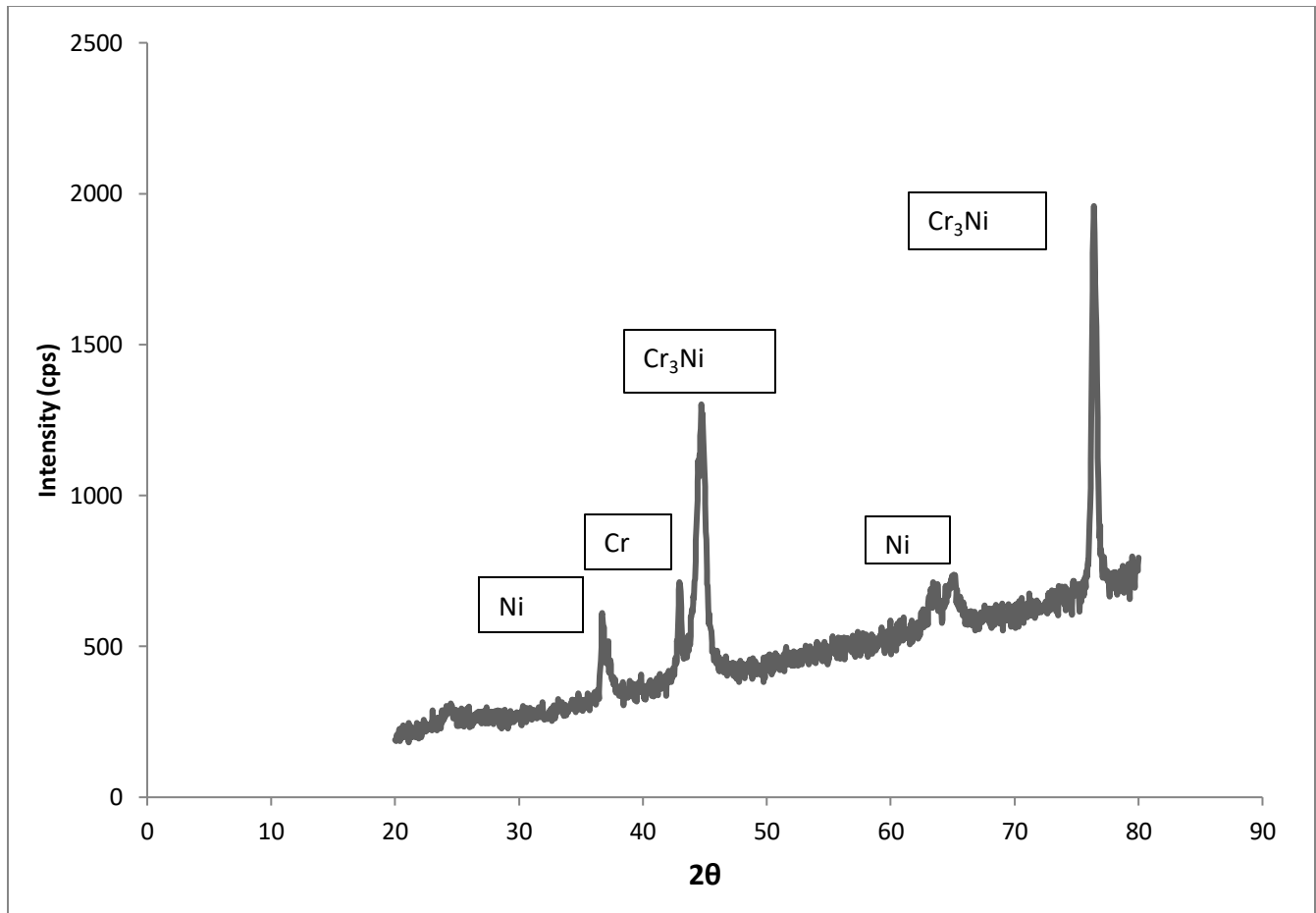


Fig 4.42 : XRD analysis of nickel-chromium coated mild steel

Fig 4.42 shows XRD analysis of nickel-chromium coated mild steel. Chromium is deposited first, then both the ions are kept in the electrolytic solution. So, both of the nickel ions and chromium ions can be deposited on the surface. but nickel has lower deposition potential which makes it easier to be deposited than the chromium ions. The xrd result also justifies the fact. On the surface, Cr₃Ni alloy is formed where nickel has more weight percentage than chromium. But chromium is also present on the surface which improves the corrosion rate of the developed material.

4.43 scanning electron microscopy of developed chromium coating :

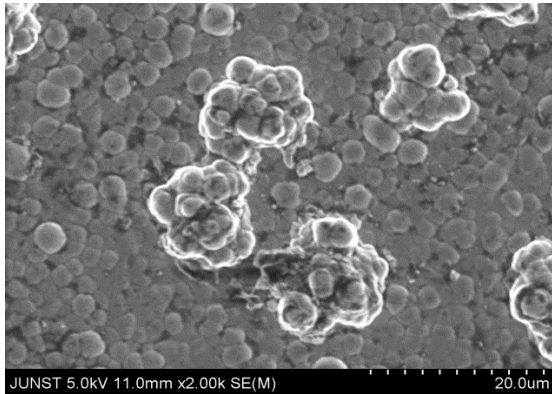


Fig 4.43a

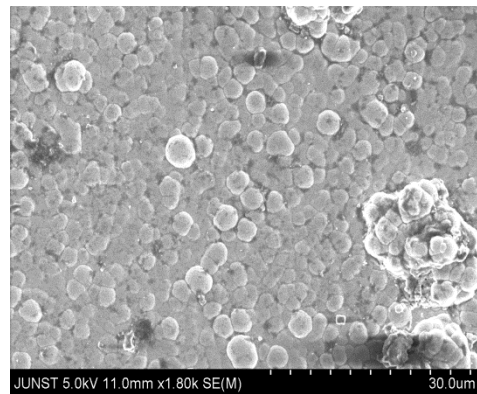


fig 4.43b

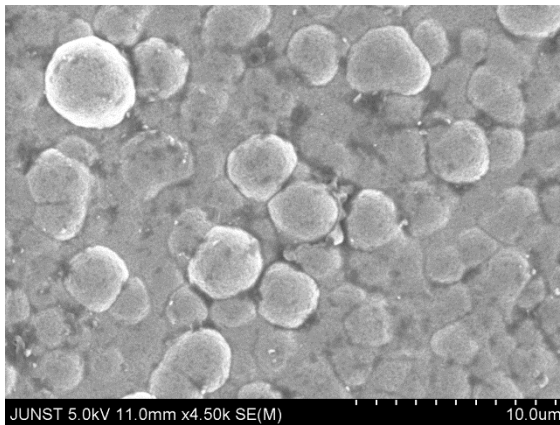


Fig 4.43c

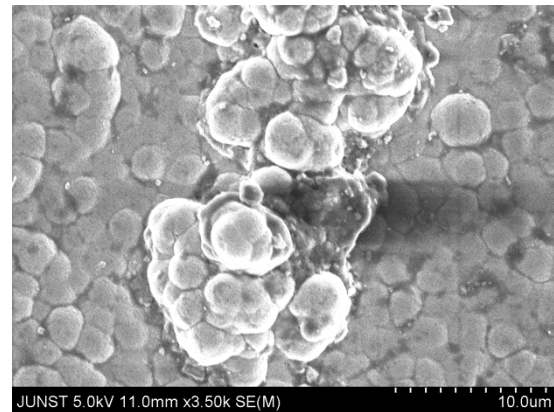


fig 4.43d

Fig 4.43a, fig 4.43b , fig 4.43c , fig 4.43d : magnified view of developed chromium electro coated mild steel

The magnified morphology of the developed chromium coating has been given in the above figures. The globular shaped chromium is present in the surface to improve the corrosion resistance. It is also seen that the surface developed by the electroplating is non-porous. Chromium is present uniformly throughout the surface. Though chromium oxide is also present in the surface discretely, uniform and compact deposition of chromium is responsible for providing passivity and corrosion resistance property.

Chapter 5 : Conclusion

5.CONCLUSION :

For the foregoing result and discussion following statements can be concluded

- 1) Low Carbon steel can be electrocoated with thin layer of chromium and nickel coating by electrodeposition process to produce a high corrosion resistance surface in aqueous chlorinated solution.
- 2) The quality of corrosion resistance coating is strongly influenced by deposition current density and to some extent on electrolyte composition.
- 3) The corrosion rate as found by potentiodynamic polarization curve decreases drastically by chromium coating and nickel coating on carbon steel compared to uncoated steel.
- 4) An optimum electrodeposition current at electrodeposition condition was achieved for both chromium coating and nickel-chromium coating that produce corrosion resistant surface.
- 5) The Electrochemical Impedance Spectroscopy study shows the polarization resistance increases with high corrosion resistant chromium or nickel coating. Nyquist plot and Bode plot follow a RLC circuit model equivalent to CPE circuit. The Electrochemical Impedance Spectroscopy result support the corrosion current obtained from potentiodynamic polarization study.
- 6) Presence of coating constituent of chromium and nickel coating are clearly found in X-Ray Diffraction studies. It also found that the chromium coating has a tendency to produce an oxide layer which can protect it from corrosion.
- 7) Scanning Electron Microscope shows different morphology of chromium coated surface along with the uncoated surface. A compact adherent passive coating was formed on the carbon steel which gave high corrosion resistant coating.
- 8) This project throws light to bring down corrosion rate of carbon steel in aqueous chlorinated environment with a minimum cost as very thin layer of nickel or chromium coating are done and maximum benefit as high corrosion resistance surface is obtained.

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