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College of Materials Engineering
Department of Metallurgical Engineering

Investigation Corrosion Behavior of Ni – TiO_2 Coating on Low Carbon Steel Substance

A Thesis

Submitted to the Department of Metallurgical Engineering
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High Diploma in Materials Engineering/ Metallurgical

By

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(B.Sc. Materials Engineering)
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بِسْمِ اللَّهِ الرَّحْمَنِ الرَّحِيمِ

﴿ وَيَسأَلُونَكَ عَنِ الرُّوحِ قُلِ الرُّوحُ مِنْ أَمْرِ رَبِّي

وَمَا أُوتِيتُم مِّن الْعِلْمِ إِلاَّ قَلِيلاً ﴾

صدق الله العليّ العظيم

(سورة الاسراء –آية ٨٥)

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Dedication

To

The One whose throne is in the sky…To the One whom we praise and thank… Allah.

To

The Messenger of Allah…Mohammed (peace and blessings of Allah beupon him and his progeny).

To

My dear father for being my first teachers.

To

My beloved mother for supporting me all the way.

To

My brothers and sisters for their constant support and encouragement.

To

To my friends with respect.

Ayat Maythem

"Acknowledgement"

In the name of Allah, the most gracious, the most merciful. First of all, great thanks to (ALLAH his MAJESTY) for enabling me to finish this study.My sincere appreciation and deepest gratitude to my supervisor Assist. Prof. Nabaa Sattar Radhi who I had the honor of being under his guidance and supervision, thanks for all the constructive suggestions, patience and continuous encouragement that are highly acknowledged through this study. Also, I wish to express my thanks to the staff of my department, Metallurgical Engineering, College Materials Engineering for their help and great facilities.

Ayat Maythem

Abstract

It is necessary to prevent corrosion and toxicity to improve the steel components and their aesthetic value that are used in our daily life , which led to a dilated interest in the electrodeposition substrates field especially the substrates of nickel (Ni) on steel.

Nickel coating was prepared by using a Watts-type bath containing 240 g/L nickel sulfate ($Ni_2SO_4 \cdot 6H_2O$), 20 g/L nickel chloride ($NiCl_2 \cdot 6H_2O$), and 20 g/L boric acid (H_3BO_3) then add a ratio of titaina (5, 10, 15) g\L to nickel electroplating solution. Micro-sized TiO_2 ceramic particles (20-30) µm were co-deposited with nickel using electrodeposition technique to develop composite coatings A nickel electrode of 99.99% purity with dimensions of (100 ×40 ×8) mm was used as anode and low carbon steel with dimensions (thickness =1mm and diameter =10 mm) as cathode (substrate) materials. The value of current density and voltage used in the coating process is (5.305A/dm^2,2V) respectively. Prior to deposition, the low carbon steel substrates were mechanically polished with silic on carbide papers of 180, 400, 600, 800, grits and put in (10% NaOH solution for 2min and then in 30% HCl solution at room temperature for 5s).

In this work, several tests were carried out, including: coating thickness, surfaces roughness, hardness, EDS, SEM and polarization tests in salt solution and tap water were carried out for coating layer.

Hardness indicate that the mechanical properties of the applied coatings with incorporated (TiO_2) reinforcement were far more superior in comparison with its own matrix as well as non (composite nickel coating).

The final results of polarization curves were carried out by Potentistatic technique for different coating layers with tap water and 3.5%NaCl a medium and find all data by computerize which shows the addition of TiO_2 extract improved the corrosion rate with (45%) than uncoating specimen, in tap water as a medium for the test performed and improved the corrosion rate with (82%) than uncoated specimen.

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Abbreviation or Symbol

Abbreviation or Symbol	***Description***	***Unit***
Wt %	Weight Percentage	
M	Metal Atom	
M^{+n}	Metal Ion	
ne^-	Numbers of Electron	
I_{corr}	Corrosion Current Density	$\mu A/cm^2$
E_{corr}	Corrosion Potential	Mv
C.R	Corrosion Rate	mpy
E.W	Equivalent Weight	g/eq.
V	Voltage	V
I	Current	A
mpy	mil/year	
HVOF	High Velocity Oxygen Fuel	

EDS	Energy Dispersive X-ray Spectroscopy	
SEM	Scanning Electron Microscopy Test	
Temp.	Temperature	C°
emf	Electromotive Force	

CHAPTER ONE

INTRODUCTION

Chapter one

Introduction

1.1 introduction

Nowadays, application of steel in product manufacturing has gained much interest because of its unique properties such as low cost, recyclability and excellent mechanical characteristics. However, low corrosion resistance of this material is the most important problem. One of the most common approaches to overcome this problem is the application of protective coatings to enhance the life span of this material.

1.1.1 Definition of Corrosion

Definition of Corrosion is the distraction or material deterioration due to its reaction by environment, this reaction may be chemical or electrochemical, which leads to change of characteristics of the metal and substantial impairments of the function of the metal, the metal ceases to be an element, and becomes a compound [1].

Physical causes that causes deterioration do not named corrosion, but it can be described as erosion, wear, or galling. Sometimes, physical deterioration accompanied with chemical attack, it can be described by the following terms: erosion- corrosion, fretting corrosion or corrosive wear [2,3].

Corrosion of metals causes many losses to the economy. Corrosion effects on the metal structures of bridges and buildings, the equipment of metallurgical and chemical plants, underground pipelines, river and sea ships and many other structures. The cost of corrosion studies has been undertaken by several countries. For example, in the United States, losses related to corrosion an amount of 100$ billion per year, that is approximately about 5% of the whole national product. Direct losses related to corrosion involve expenditures of replacing individual parts, units or plants, entire lines, and for many different preventive and protective tasks (such as the use of coatings for corrosion protection). Indirect losses emerge when equipment is corroded leads to defective products that must be rejected. About 30% of cast iron and all steel are lost due to corrosion. Part of this metal can be handling as scrap, but indeed about 10% is lost [4,5].

1.1.2 Forms of Corrosion

Classification by appearance depends on identifying forms of corrosion via visual observation (with magnification or naked eye).

1.1.2.1 General Corrosion

General corrosion is the most common form of the corrosion types and it can be uniform or nonuniform as shown in Fig. (1.1). It is described by a chemical or electrochemical reactions that occurs on the metals surfaces. The metal becomes thinner and finally cause a failure. General corrosion can be prevented or decreased by the suitable choice of material or by use of cathodic protection or corrosion inhibitor [6].

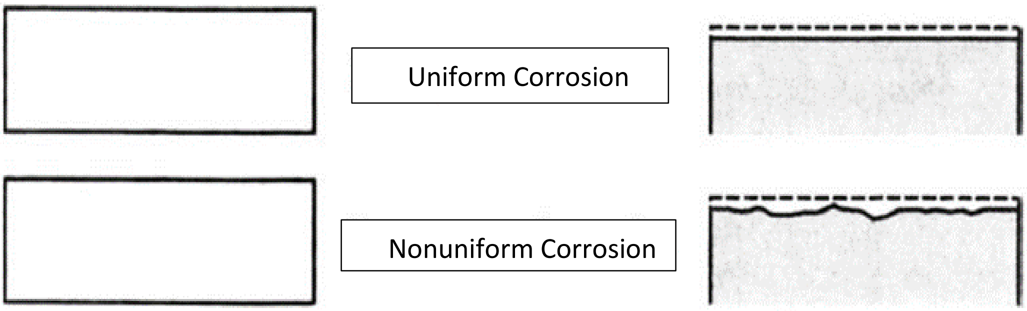


Fig. (1.1): General corrosion [6].

1.1.2.2 Localized Corrosion

Localized corrosion in pipelines and flow lines is the most-feared type of corrosion attack in practice. The attack is characterized by the formation of severely corroded regions separated with sharp steps from neighboring areas with much less attack. Localized attack develops when the steel surface is partly covered with a protective film. The attack is usually associated with high flowrates [7].

Localized corrosion is characterized by damage that occurs preferentially at discrete sites on a material surface and may result in the formation of pits, cracks and grooves. A large cathode-to-anode area ratio is generally required in order to form an intense local anode. Since this is most easily obtained in metals that are passive, then localized corrosion most commonly occurs on materials that are passive.

1.1.2.3 Pitting Corrosion

Pitting corrosion is a type of the localized corrosion which occur on the metals surface where a small area was corroded preferentially causing the formation of pits, and the biggest part of the surface still not attacked [8].Steel does not have an important passive film and the mechanism of pitting differ slightly, the anodic surface corrodes in localized area under overall easily available oxygen circumstances, with the corrosion products forming mainly at and near the cathodic regions. The operation is driven by variation in localized electrical potential and results a localized corrosion at a microscale [9].

1.1.2.4 Crevice Corrosion

Crevice corrosion is defined as a localized type of corrosion that is usually associated with a stagnant solution on the micro environmental level. These stagnant microenvironments tend to take place in shielded areas such as those formed under washers, insulation material, gaskets, surface deposits, fastener heads, disbanded coatings, threads, clamps and lap joints due to restricted oxygen diffusion into the crevice, a differential aeration cell tends to be set up between microenvironment and the external surface (bulk environment). The acidic microenvironment that is formed, together with a surface of high chloride ion concentration this is shown in the Fig. (1.2) [9].

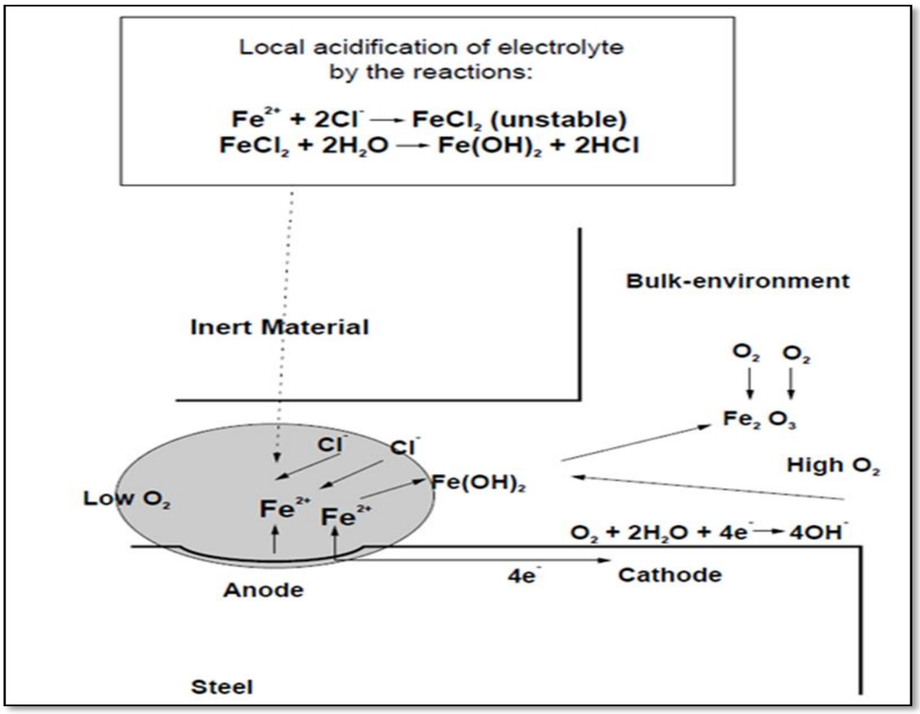


Fig (1.2) Crevice corrosion [9]

1.1.2.5 Intergranular Corrosion

Atype of localized corrosion, which occurs along the grain boundary region of the metal. This type of corrosion occurs due to the presence of a difference in the metallurgical properties that lead to different electrochemical properties of this region from other regions. So that the grain boundaries are more active to interact with the medium than the grain regions. For example, a region of welded stainless steel known as weld decay, whereby heating of the welded parts in these alloys to temperatures of 850-550°C leads to chromium depletion (due to the precipitation of chromium carbide resulting from the interaction of chromium with carbon) at the grain boundary areas and then this type of corrosion occurs when exposed to the corrosive medium, as shown in Figure (1.5). [10].

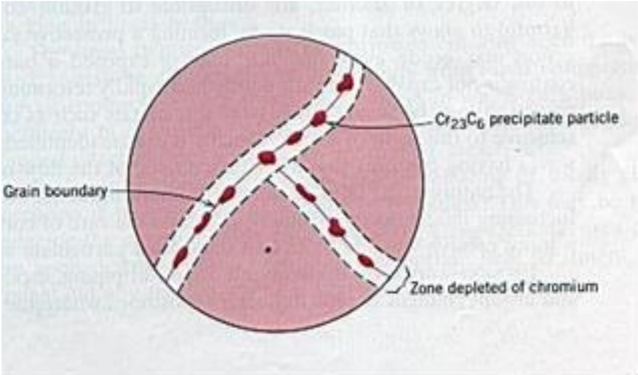


Fig. (1.5) Intergranular Corrosion[10]

1.1.2.6 Erosion Corrosion

It is a localized corrosion caused by mechanical impact with the electrochemical nature of the corrosion medium, which includes the dissolution of the metal from the surface to form dissolved ions, and these ions may form corrosion products that deviate away from the surface of the metal. [10].

1.1.2.7 Galvanic Corrosion

This type of corrosion is localized corrosion, due to the presence of two metals of different electrical voltage or different locations in the same metal that are in contact with each other, with the presence of an electrical conductive medium. In this case the rate of corrosion of one metal increases and the rate of corrosion of the other metal decreases, for to the rate of corrosion of each of them when they are individually exposed to this medium. The metal that corrodes after contact is anode and the metal that does not corrode after contact is cathode. The presence of a difference in the electrical potential between the two metals leads to the emergence of the galvanic current that causes this type of corrosion, the area of the anode and the cathode affects this type of corrosion, so it is preferable that the area of the cathode is small in relation to the area of the anode [10]

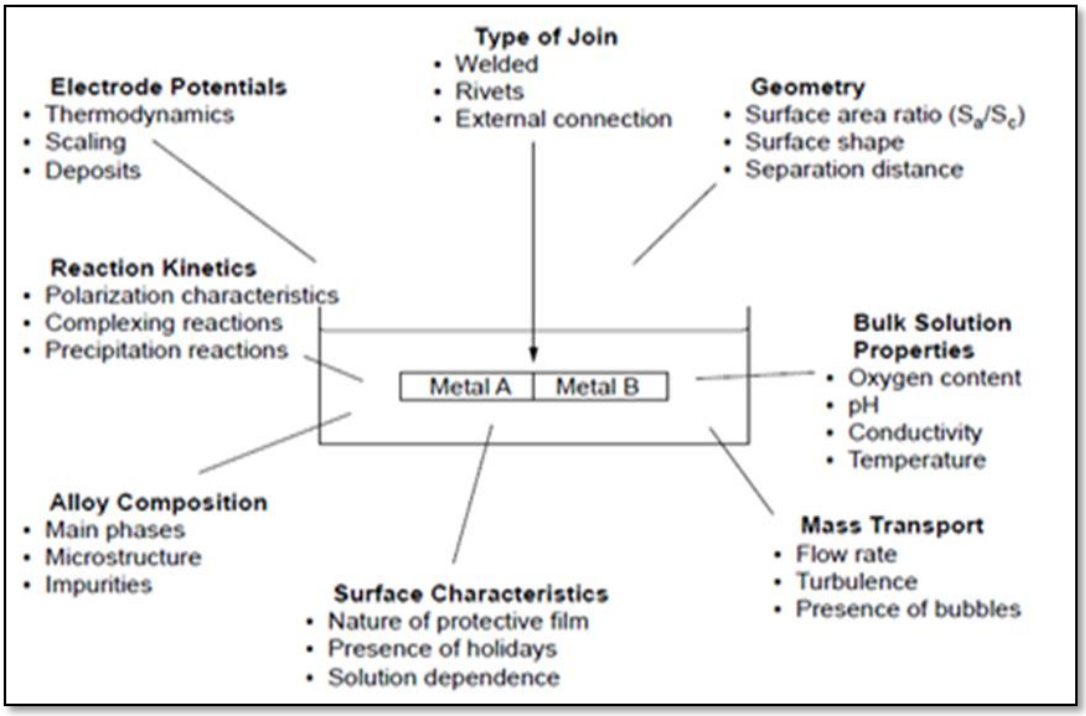


Fig. (1.4): Factors affecting galvanic corrosion [11].

1.2 Aims of the Research

The aims of this study are to protect low carbon steel by electroplating process with Watt's nickel solution and Watt's nickel solution by adding titania with (5, 10 and 15) wt% tacking in nickel solution as suspension to consideration that incorporation of nickel and titania (TiO_2) to produce composite sacrificial coatings decreases cost and enhancing corrosion resistance to tap that used in our houses.

CHAPTER TWO

THEORETICAL PART AND LITERATURE REVIEW

Chapter two

Theoretical Part and Literature Review

2.1 Corrosion Protection Methods

Corrosion problems can be solved using the following [12]:

1. Select a material which is resistant to the corrosive environment.

2. Protective coating of metal.

3. Change the service conditions, such as pressure, temperature or velocity.

4. Change environment chemistry, such as concentration, pH, impurities or aeration.

5. Add a corrosion inhibitor to the bath of coating.

6. Change the design of the system or equipment.

7. Cathodic and anodic protection.

2.1.1 Inhibitors Apply

Corrosion inhibitors are a chemical that, when available in low concentration (1 to 15,000 ppm) in a corrosive environment, retard the metal corrosion. Corrosion inhibitors are spent in electrochemical corrosion reaction. They can be solid, liquid, or gas [13].

2.1.1.1 Mechanisms of Corrosion Inhibition

There are several mechanisms that may account for the effectiveness of inhibitors. Some react with and virtually eliminate a chemically active species in the solution (such as dissolved oxygen). Other inhibitor molecules attach themselves to the corroding surface and interfere with either the oxidation or the reduction reaction, or form a very thin protective coating as shown in figure (2.1) [14].

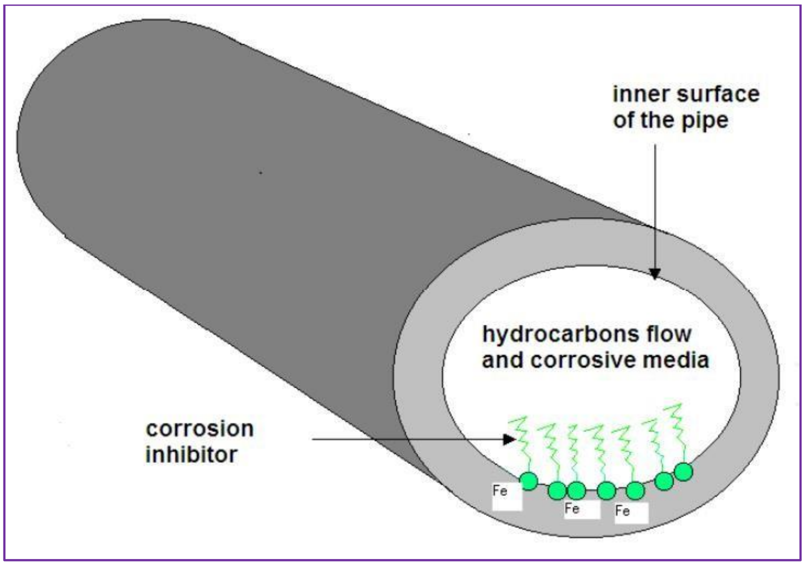


Fig. (2.1): Representation of a CI adsorbed into a metal surface [15].

2.1.2 Cathodic Protection

We can protect against corrosion by supplying the metal with electrons and forcing the metal to be a cathode. Cathodic protection can use a sacrificial anode or an impressed voltage. A sacrificial anode is attached to the material to be protected, forming an electrochemical circuit. The sacrificial anode corrodes, supplies electrons to the metal, and thereby prevents an anode reaction at the metal. The sacrificial anode, typically zinc or magnesium, is consumed and must eventually be replaced. Applications include preventing the corrosion of buried pipelines, ships, off-shore drilling platforms, and water heaters. A magnesium rod is used in many water heaters. The Mg serves as an anode and undergoes dissolution, thus protecting the steel from corroding. An impressed voltage is obtained from a direct current source connected between an auxiliary anode and the metal to be protected. Essentially, we have connected a battery so that electrons flow to the metal, causing the metal to be the cathode. The auxiliary anode, such as scrap iron, corrodes, this shown in fig. (2.2) [16]

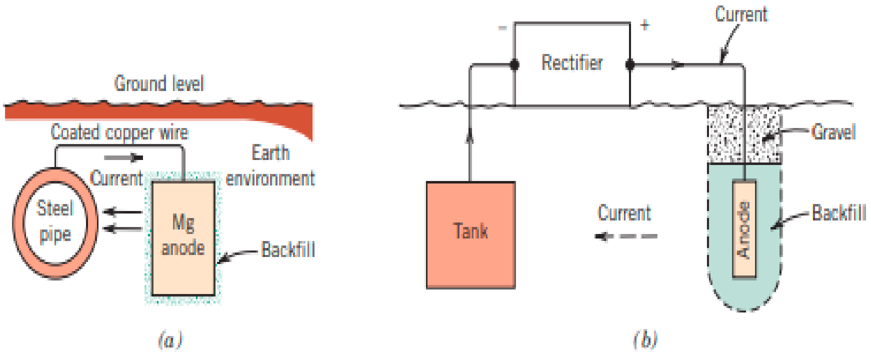


Fig. (2.2) Cathodic protection of (a) an underground pipeline using a magnesium sacrificial anode, and (b) an underground tank using an impressed current [17].

2.1.3 Anodic protection (AP)

This method is used to reduce the corrosion process and is based on the formation of a protective film of metal oxide on the surface of the metal by applying a negative potential difference that works to reduce the potential difference of these metals to the passive region of the positive polarization curve (Anodic Polarization) and this current can be obtained by Potentiostat measuring device.

This method of protection is suitable for metals and alloys that have the ability to acquire the phenomenon of passive when they are polarized anodically, such as iron, nickel, chromium and their alloys [11].

2.1.4 Protective Coating

The most effective method to prevent a metal from corrosion is the application of a layer on the surface of metal. The coating acts as a barrier between the environment and the metal. Also can acted as sacrificial anode. The recognition that one could protect a surface from environmental attack, through application of metallic, organic and inorganic coating, wherefore extending the life of the surface alone, or the entire equipment or component equipment [18].

-Metallic coatings

Metallic coatings availability enhanced corrosion resistance of metals as either sacrificial coatings or barrier coatings. This kind of coatings can be made by different techniques as electroplating, electroless, high velocity spray, hot-dip galvanizing, physical vapor deposition (PVD), chemical vapor deposition (CVD. The main application of these metallic coatings is to prevent corrosion on low alloy steels [19].

- Organic coatings

The surface of equipment is protected from environmental damage by the development of coatings, paints, and high-performance organic coatings. There are several techniques for organic coatings as acrylic paints, epoxy paints, organic zinc paints, polyurethane paints, phenolic and epoxy-phenolic coatings, fluorocarbon based coatings and silicone paints and coatings. This type is preferred because of its chemical inertness to the environment, and also has a good surface adhesion property [19,20].

- Inorganic coatings

Chemical action, with or without electrical assistance is required to produce inorganic coatings. Inorganic coatings include surface conversions, HVOF ceramic coatings, inorganic zinc silicate, flame and arc spray ceramic coating. The common surface conversions are anodizing based on oxidizing, aluminum and phosphating processes used on steels and chromate surface conversions on steel [20,21].

2.2 Metallic coating

Metallic coating provides a deposit that changes the properties features of the specimen to the core metal being used. The specimen is a composite material with a good property generally not accomplished by either core material if used alone. The coatings accomplish a corrosion-resistant deposit, and the material itself accomplish the load-bearing capability. The metal coatings, like chromium, nickel, copper, and cadmium, is usually accomplished by wet chemical processes but with problems in pollution. Some of the wet methods have changed with depositions processes and represent a good role in that coating in the future [21].

Coatings are either anodic or cathodic to the substrate. If the metal coating is less noble, in the electromotive force (emf) series it acts as anode, conversely if are more noble it acts as cathode. The environment may change from the surface of the coating to one that exists within any defects, such as scratches, cracks or corrosion pits. These defects are quite important if the coating is cathodic to the substrate. In this case, if the substrate is exposed to a corrosive environment, it will corrode rapidly. On the other hand, if the coating is anodic to the substrate, defects are less important. In this case, if the substrate becomes exposed, it will be protected by the corrosion of the coating. This is shown in Fig. (2.3). In the state of a cathodic deposition (a) the substrate is exposed to galvanic corrosion in the coating imperfection. The corrosion may be intensive because the area ratio between the anodic spot of bare substrate and the cathodic coating is very large. In the other state (b), only a cathodic reaction happens on the core metal (that is protected cathodically), while the coating is affected by an alike galvanic corrosion extended over a major area. If we need to save the core metal, low pored, good mechanical strength and constant adhesion that are more requisite for a cathodic than anodic plating [22].

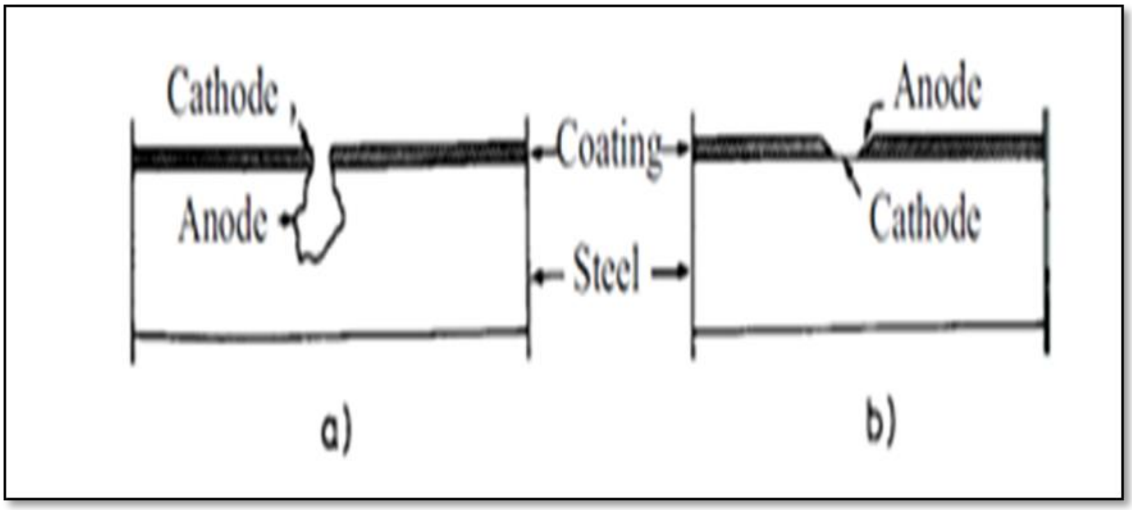


Fig. (2.3): Localized of corrosion at a defect in a metal coating on steel a) Cathodic coating, b) Anodic coating [12].

Table 2.1 Standard emf series of metals [23].

Metal-metal ion equilibrium(unit activity)	Electrode potential vs. normal hydrogen electrode at 25°C,volts
Au-Au^{+3}	+1.498
Pt-Pt^{+2}	+1.2
Pd-Pd^{+2}	+0.987
Ag-Ag^{+}	+0.799
Cu-Cu^{+2}	+0.337
H_2-H^{+}	0.000
Pb-Pb^{+2}	-0.126
Sn-Sn^{+2}	-0.136
Ni-Ni^{+2}	-0.250
Fe-Fe^{+2}	-0.440
Cr-Cr^{+3}	-0.744
Zn-Zn^{+2}	-0.763
Al-Al^{+3}	-1.662
Mg-Mg^{+2}	-2.714

Metallic coatings are used for many aims. Main aim is to get a good corrosion and wear resistance. Metallic coatings accomplish by electroplating, spraying, electroless plating, hot dipping, vacuum and vapor deposition, diffusion coating and metal cladding. The coating process for a specific application depends on several factors, including the number of parts being produced, the corrosion resistance that is required, environmental considerations, the production rate that is required, and the anticipated lifetime of the coated material. Some important plating are chromium, cadmium, nickel, zinc, and aluminum. Copper, silver, and gold are also applied in electrical devise and sometimes for specialty fastener applications [24,25 ,26].

2.2.1 Hot-Dip Coatings

In hot dipping coating, a work piece (solid metal) is put in a solution container of another metal and adherent film formed on the external layer with cooling. It is the simplest method of applying protective metal coatings to base metals but there are limitations. The melting point of the coating metal must be basically lower than that of the substrate and preferably the melting point is low enough to allow the substrate to retain the advantage of work- solidifying. There must be enough inter diffusion between the core metal and the other metal to enable a bond to combine not so much as to expend the thin coat of saving metal that is required. In experience, the most useful method for applying coatings of tin, zinc, or aluminum to steel [26,27].

2.2.2 Diffusion Coating

This process needs an initiative step then thermal processing and diffusion of the coating metal into the work piece. A traditional material known as galvannealed steel [28].

2.2.3 Thermally Sprayed Coatings

It is the generic category of material processing technique that applies consumables in the form of a finely sparative molten or semi molten droplets to make a plaiting onto the substrate kept in front of the impinging jet. The melting of the consumables may be accomplished in a number of ways, and the consumable can be introduced in to the heat source in wire or powder form. Thermal spray consumables can be metallic, ceramic or polymeric substances. Any material can be sprayed as long as it can be melted by the heat source employed and does not undergo degradation during heating [29].

2.2.4 Vacuum and Vapor Deposition

Vapor deposition mention to any operation in which materials in a vapor case are condensed over condensation, chemical reaction, or transformation to shape a tough material. These operations are made to shape plaiting to change the mechanical, electrical, thermal, corrosion-protection, optical, and wear advantage of the work piece. They are also applied to shape free-standing bodies, fibers, and films and to infiltrate fabric to shape composite materials. Vapor deposition operation usually take place in a vacuum chamber. There are two major division of vapor deposition operations: Chemical Vapor Deposition (CVD)and Physical Vapor Deposition (PVD). In PVD operations, the substrate is exposed to plasma revel. In CVD operations, thermal energy heats the gases in the chamber and motivate the plaiting reaction [21,30].

2.2.5 Electroless coating

This process is also famed as chemical coating or immersion coating. It is setup on the figuration of metal plating, making from chemical reduction of metal ions from electrolyte. The surface of the substrate must be catalytically effective and existed catalytically effective as the plating happen in a electrolyte that must hold a reducing agent. If the catalyst is a reduction product (metal), autocatalysis is guaranteed. In this state, it is thinkable to deposit a coating, in principle, of indefinite thickness. The features of electrolessplating are [24,31]:

1. Deposit with fewer bore.
2. Not require electricity power source.
3. Metallize Nonconductive materials.
4. Deposit functional layer.
5. Deposit uniform layer, until on complicated shapes.
6. Simple things for electroless plating.

The limitations of the process are as the following [24,31]:

1. Electroplating is cheaper than that electroless plating caused the

cost of the reducing agents.

2. It is less dense that cause the metal deposition ratio is bounded by

metal ion reduction in the bulk of the electrolyte.

2.3 Electrodeposition

Electrochemical deposition of metals and alloys include the reduction of metal ions from aqueous, organic, and fused-salt electrolytes. The reduction of metal ions M^+ in aqueous solution is explained by [32]

$$M^{x+}_{solusion} + Xe \rightarrow M_{lattice} \qquad (2.2)$$

It can be achieved this by means of two different operations [32]:

(1) Electrodeposition

In this process the x electrons (e) are provided by an outer electricity source. Electrodeposition is also known as electroplating “electrolytic deposition”

(2) Electroless (autocatalytic) deposition operations in this state the reducing agent is the electron source (without outer electricity source). These two operations, electrodeposition and electroless deposition, represent the electrochemical deposition.

Electrodeposition is one of the generality cost–effective and effective process of gaining composite zinc coating, with chance of dominant the deposit’s layer thickness, potential, the current regime, and room temperature operating conditions. It was showed that composite with a desired attribute may be made by using an adequate option of the electrodeposition parameters and of the particle concentration in the coating solution. It has also been showed that the particle size has a considerable action on the final properties of the composite coating [33].

The plating produced is commonly for ornamental and /or protective objective, or improving specific features of the external layer. The external layer may be conductors, like metal, or nonconductors, like plastics.

Electroplating products are applied in many manufactures, such as air space, ship, electronics, machinery, jewelry, automobile, defense, and toy manufactures [34].

The electrodeposition process, in general, consists of the dissolution of a metal from an electrode, named anode, in solution with ions of the same metal(electrolyte), the passage of a continuous electric current along with the solution and the subsequent electric discharge of the metal on an electrode surface, named cathode, in contact with the solution. The current is produced when a potential is applied between electrodes. One of the electrodes is the anode. The anode is charged positively while, the cathode, is charged negatively. The positive ions in the solution, hence, get about towards the negative electrode (the cathode) and the negative ions get about across the positive electrode (the anode), producing the electric current fig. (2.4). In the electrodes, oxidation-reduction processes are then produced. The oxidation is caused in the anode while the reduction is caused in the cathode, and these reactions lead to a change in the metal oxidation state [35].

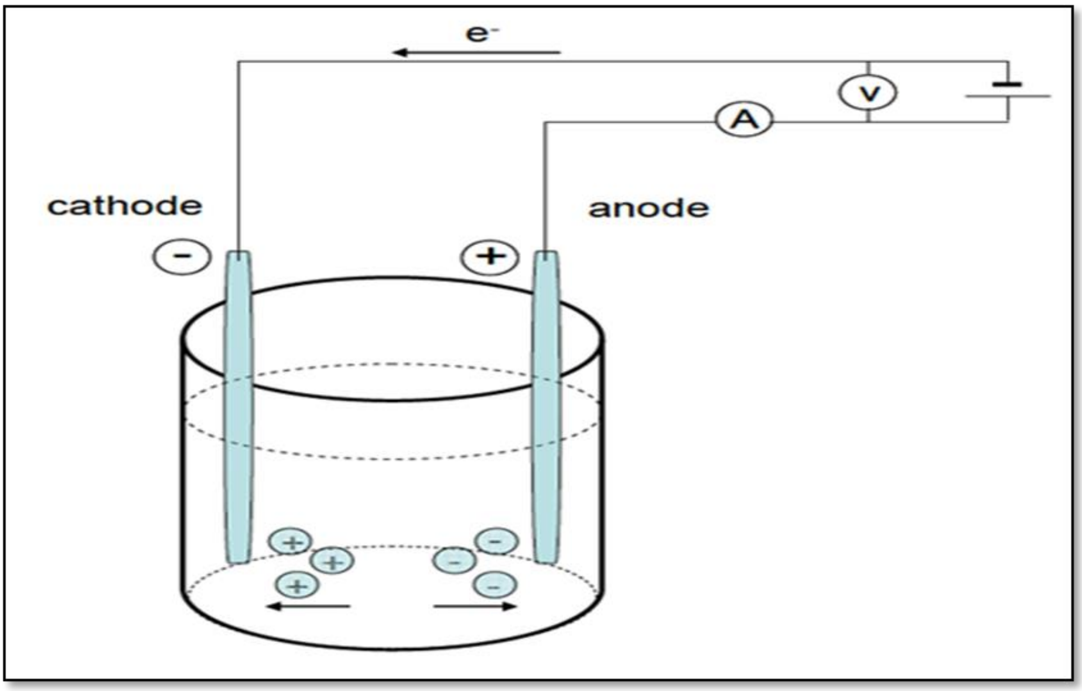


Fig. (2.4): General sketch of an electrochemical process [35].

2.3.1 Theory of Electrodeposition

The electrodeposition consists of immersing the object to be coated in a solution of the metal to be plated and passing a current between the object and another electrode. Done to get the desired electrical and corrosion resistance, reduce friction and wear or improve heat tolerance. In general, a metallic solution of the metal to be deposited is electrolyzed to have a uniform coating of the metal on the cathode. The anode is normally the pure metal with some exceptions. During the electrolysis, the anode dissolves into the electrolytic bath and metal ions from the bath solution gets deposited over the cathode as pure metal. The following reactions show the electrodeposition process [36]:

The electrolyte MA ionizes in the bath as:

$$MA(aq) \rightarrow M^{n+}\ (aq) + A^{n-(}aq) \qquad (2.3)$$

At the anode, the reactions can be carried out in two ways depending on the anode. Soluble anodes dissolve anodically into the electrolyte, whereas the reaction on insoluble anodes is generally the oxidation of water. Soluble anodes are usually used in chloride baths, and insoluble anodes are used in sulphate baths. Insoluble anodes are used to complete the electrical circuit to the solution; hence it is necessary for it to be a good conductor and to be unattacked by the bath with or without current flowing.

For soluble anodes the reaction is [36]:

$$M(s) \rightarrow M^{n+} + ne^{-} \qquad (2.4)$$

And for insoluble anodes there are two reactions depending on the pH of the solutions [37]:

$2H_2O \rightarrow O_2 + 2H^+ + 4e^-$ (acid solutions) (2.5)

$4OH^- \rightarrow O_2 + 2H_2O + 4e^-$ (basic solutions) (2.6)

At the cathode, metal ions get reduced and deposited as metal atoms:

$Mn^{n+} + ne^- \rightarrow M(s)$ (2.7)

2.3.2 Applications of Electrodeposition

Electrodeposition is used in many industrial based applications. These applications can be categorized in basically four groups [37]:

1.Decoration: A more expensive metal can be coated onto a base metal in order to improve the appearance of a base metal. This can be used for jewelry, furniture fittings etc.

2.Protection: The coating is given to a base material in order to prevent the base material from corrosion, oxidation or wear. Corrosion resistance coating includes chromium coating, cadmium coating and zinc coating.

3.Electroforming: This is used in manufacturing of moulds, dies, screens and record stampers.

4.Enhancement: Coatings with improved electrical and thermal conductivity, reflectivity and solderability etc.

2.4 Nickel electrode

Nickel is a chemical element with the symbol Ni and atomic number 28. It is a silvery-white lustrous metal [38]. Nickel belongs to the transition metals and is hard and ductile.The physical properties of nickel are listed in table (2.2).

Table (2.2): Physical properties of nickel [38]

Properties of nickel	**Numerical value**

Hardness	4.5 mhos
Melting point	1455 C°
Boiling point	2730 C°
Atomic number	28
Density at 25C°	8.908 g/cm^3
Crystal forms	FCC

Nickel plating is the electrolytic deposition of a layer of nickel on a substrate. The process involves the dissolution of one electrode (the anode) and the deposition of metallic nickel on the other electrode (the cathode). Direct current is applied between the anode (positive) and the cathode (negative). Conductivity between the electrodes is provided by an aqueous solution of nickel salts. When nickel salts are dissolved in water, nickel is present in solution as divalent, positively charged ions (Ni^{2+}). When current flows, divalent nickel ions react with two electrons ($2e^-$) and are converted to metallic nickel (Ni^0) at the cathode. The reverse occurs at the anode where metallic nickel dissolves to form divalent ions: The electrochemical reaction in its simplest form is:

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{2.8}$$

Nickel plating process can be operated for a long period of time without interruption because the nickel ions discharged at the cathode are replenished by the nickel ions formed at the anode [39]

2.5 Electrodeposition of Composite Coatings

Composite deposition is a coating protective technique which introducing homogeneously inert particles of a various material in the metal matrix; this two-phase coating improves mechanical resistance and corrosion. The enhancement of these properties depends on the combination of both metal matrix and particles. Electrodeposition of composite coatings consists of a metal or alloy matrix containing hard particles like Al_2O_3, TiO_2, SiC, WC or SiO_2 as second phases [40,41].

Nowadays, the ability to produce new composite materials with good properties by using micro and nano particles is leading to technological interests. This improvement depends mainly on the percentage and the size of the particles codeposition, also depending on the distribution of these particles in the metallic matrix [41,42].

Composite coating prepared by electrochemical co-deposition can be classified in to three types based on the analyses of the reported works [43]:

1.Coating just covered by adsorbed particles on the surface.

2.Coating containing entrapped particles.

3.Coating containing particles truly embedded in to the metal matrix.

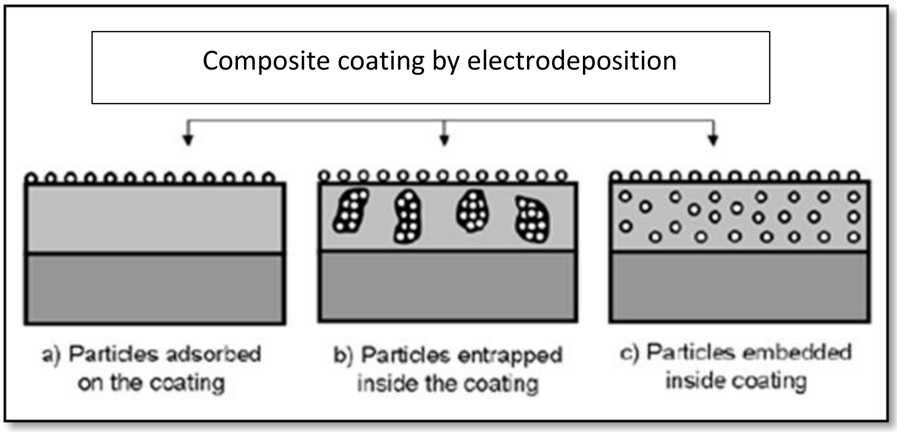


Fig. (2.5) Schematic representation of different co-deposition possibilities [43].

The (figure 2.5a) shows the first type of coating comprised of adsorbed only. The second type of coating (figure 2.5b) comprises particles, i.e. agglomerated particles inside pores. This may not be suitable for technological application as these coating is porous and may have inferior mechanical properties and corrosion performance. The third option of co-deposition as shown in (figure 2.5c), where particles are embedded well within the matrix and homogenously distributed within composite coating, is expected to have better mechanical and chemical stability of the coating. Therefore, there is a much higher probability for a potential application of such coating [43].

2.6 Literature Review

A lot of studies and researches have adopted on the coating by electroplating and corrosion properties of coated layer and wear behavior. The following are several of them:

Lung Kuo et al.,2004,[44] showed nano-ceramic particles (alumina) are readily conglomerated in traditional electrochemical electrolyte that makes composite coating Ni/Al_2O_3 difficult to prepare. The diameter of the conglomerated Al2O3 particles can be reduced by adding surfactants to the Ni bath or applying ultrasonic energy. Therefore, by using these two methods the resulting dispersion is limited. These results show when decrease in electrolyte concentration agglomerate of Al_2O_3 particles is reduced.

Gül et al. ,2009,[45] prepared Ni/Al_2O_3metal matrix composite coatings from electrolyte containing nano alumina particles by method of direct current (DC) plating to increase wear resistance and the hardness of the surface of the electrodeposited nickel .The resultes were increasing the surfactant hexadecylpyridinium bromide (HPB) content resulted in increasing of Al_2O3 volume percentage in Ni matrix providing segregation of nano-particles. The hardness values of the nano alumina reinforced electrodeposited coatings were also increased due to unique dispersion effect.

N.S.Al-Kafaja,2009,[10] Carbon steel samples were coated with (Zn-Ni) and (Zn-Ni-SiC) which the particles of silicon carbide are different particles size once microscale (73µm) and another nanoscale (70-100nm) .After electroplating, these samples were analyzed by X-ray fluorescent to confirmed all the content for each alloy. Polarization curves for (Linear polarization) were carried out by potentiostatic technique for different coatings layer and base metal for (tap water, (3%NaCl), and (3%HCl)) a medium and produce all data by computerize. The final results of this test sign that (Zn-Ni-nSiC) layer coating is more better than the base metal and two layers coating, (Zn-Ni-mSiC) and (Zn-Ni).

Chen et al. ,2010, [46] A small amount of transparent TiO_2 sol was added into the traditional electroplating Ni solution, leading to the formation of nanocrystalline Ni-TiO_2 composite coatings. These coatings have a smooth surface. The Ni nodules changed from traditional pyramid-like shape to spherical shape. The grain size of Ni was also significantly reduced to the level of 50 nm. It was found that the amorphous anatase TiO_2 nano-particles (~ 10 nm) were highly dispersed in the coating matrix. The microhardness was significantly increased from 320 HV100 of the traditional Ni coating to 430 HV100 of the novel composite coating with 3.26 wt.% TiO_2. Correspondingly, the wear resistance of the composite coating was improved by ~ 50%.

Gül , et al. , 2012,[47] investigated the effect of the concentration of the particle on the structure of Ni- SiC composite coatings produced by electrodeposition method , they show that Ni–SiC (MMCs) composites coating reinforced with particles in submicron meter on steel surfaces with high hardness and good resistance in wear therefore they used in applications that no wear is prefered such as tools and dies. The salvations were increasing the SiC particle in the electrolyte lead to increasing particle concentration of the coatings that co-deposited. Up to a maximum of 20 g/L, more increasing in the SiC particle decreased the coating particle concentration, increasing the particle content in the electrolyte lead to the lattice distortion of the metal matrix (Ni in this case), coatings wear resistance increased with SiC particle content up to 20 g/L in the electrolyte and the nano composite Ni–SiC coatings that co-deposited increase the coefficients of the friction and resistance of the wear as compared to the film of deposited Ni. This was referred to the combination of submicron size (SiC) particles in the deposit layer that increased the composite coating hardness by strengthening by refine grains and dispersion strengthening.

T Mokabber et al, (2013), [48] prepared Zn–nano-TiO_2 composite coatings were deposited on the mild steel substrate. Coatings were produced by electroplating method from sulphate bath in which Nano sized TiO2 particles were suspended. Corrosion behavior of the coatings was studied in 3·5 wt.% NaCl solutions, and their microhardness was evaluated through Vickers microhardness test. According to the results, the parameters of current density, particle concentration in the solution and temperature were optimized with respect to TiO_2 content in the composite coatings. The optimized current density, particle concentration and temperature of the bath were found to be 3 A dm^{-2}, 5 g L^{-1} and 40°C respectively. Accordingly, an increase in the amount of TiO_2 particles in the composite coatings increases the hardness of composite coatings but did not have harmful effects on corrosion resistance.

Gadhari et al , (2016), [49] The present study investigates the effect of titania particles on the micro-hardness, wear resistance, corrosion resistance and friction of electroless Ni–P–TiO_2 composite coatings deposited on mild steel substrates at different annealing temperatures. The experimental results confirmed that the amount of TiO_2 particles incorporated in the coatings increases with increase in the concentration of particles in the electroless bath. In presence of TiO_2 particles, hardness, wear resistance and corrosion resistance of the coating improve significantly. Microstructure changes and composition of the composite coating are studied with the help of scanning electron microscopy (SEM), energy dispersive X-ray analysis (EDXA) and X-ray diffraction (XRD) analysis.

In Antar et al, (2021), [50] Ni–B–TiO_2 composite coatings were elaborated it was prepared by adding TiO_2 sol in the bath solution. To achieve a systematic study, various characterization tests were carried out, including Scanning Electron Microscopy (SEM), X-Ray Diffraction (XRD), microhardness test, progressive load scratch test, reciprocating sliding test and multi-pass scratch test. The results showed that the TiO_2 structure (crystalline or amorphous) has extensively changed the microstructure of Ni–B matrix. Furthermore, it was provided superior scratch response and better wear resistance of the Ni–B deposit since it offers a compact structure.

CHAPTER THREE

EXPERIMENTAL WORK

Chapter Three

Experimental Work

3.1 Introduction

This chapter focuses on the materials and equipments that are used in this study. It also includes the description of the procedures of the coating process, beginning specimens preparation to be coated. This chapter also presents the tests for: Thickness of coating, roughness, Hardness, EDS, SEM and corrosion resistance.

3.2 Materials

The materials which are used in this study as follows:

3.2.1 Low Carbon Steel

The specimens were low carbon steel with chemical composition as present in table (3.1). The chemical analysis was performed by a spectroscopy device for metal.

The specimens that used in all the tests were prepared by using cylindrical moulds and the finals specimen have disc shape with the following dimension (thickness =1mm and diameter =10 mm) as well as the surface area for these sample are (188.495 mm^2)

Table (3.1) shows the results of this inspection of the low carbon steel.

Element	C	Si	Mn	Cr	Al	Fe
Wt.%	0.12	0.17	0.65	0.04	0.4	Rem

3.2.2 Nickel Electrode

The nickel electrode used is in the rectangular form with dimensions of (100*40*8) mm length, width and thickness respectively with high purity 99.99 %. Other materials use in this works show in the table:

Table (3.2) Other materials used in this work

Materials	Particles size (μm)	Company
TiO_2	20-30	Fluka chemical 89470
NaOH	-	Sigma-Aldrich Co.LLC
HCl	-	Sigma-Aldrich Co.LLC

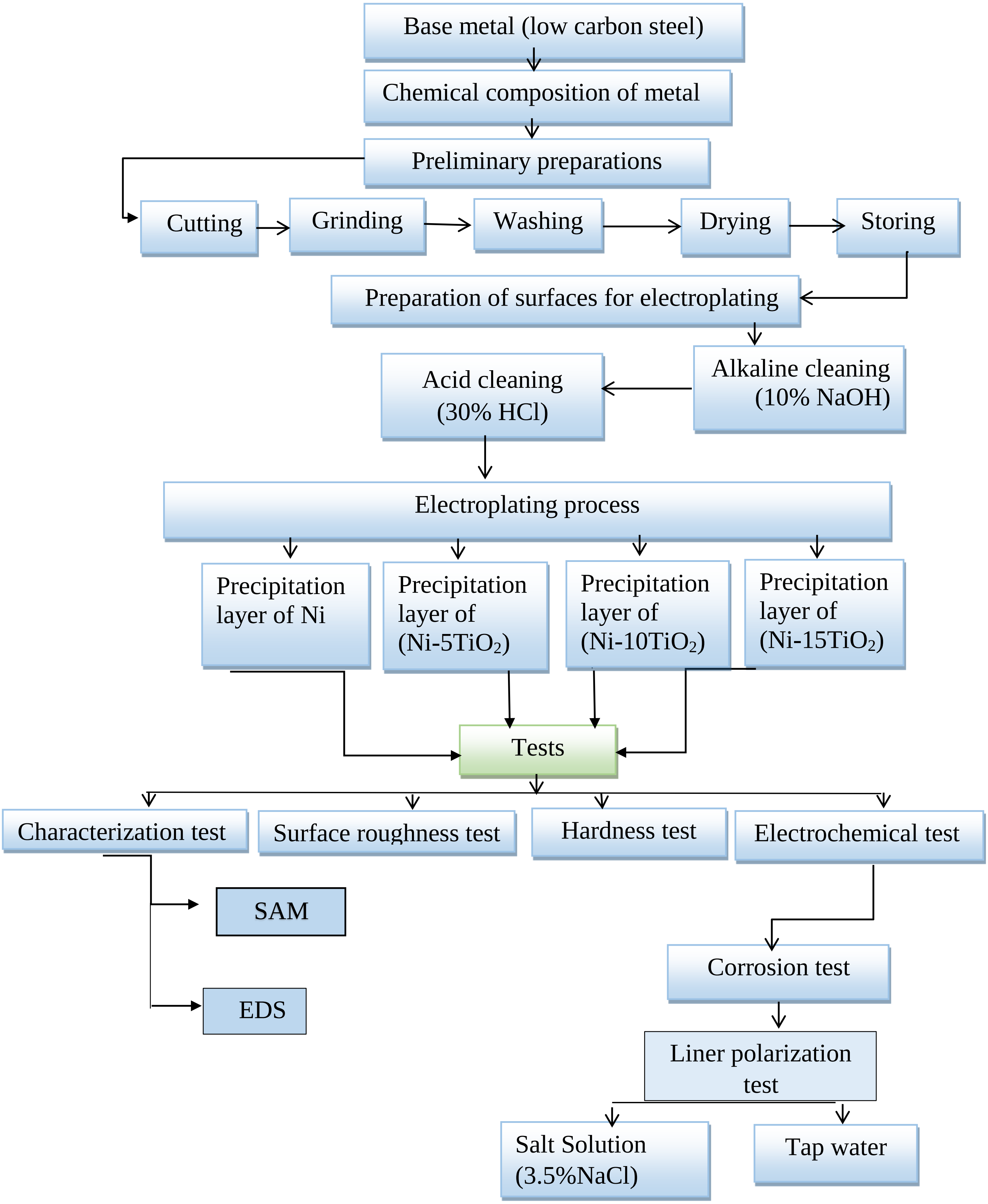

Base metal (low carbon steel)
Chemical composition of metal
Preliminary preparations
Cutting
Grinding
Washing
Drying
Storing
Preparation of surfaces for electroplating
Alkaline cleaning (10% NaOH)
Acid cleaning (30% HCl)
Electroplating process
Precipitation layer of Ni
Precipitation layer of (Ni-5TiO2)
Precipitation layer of (Ni-10TiO2)
Precipitation layer of (Ni-15TiO2)
Tests
Characterization test
Surface roughness test
Hardness test
Electrochemical test
SAM
EDS
Corrosion test
Liner polarization test
Salt Solution (3.5%NaCl)
Tap water

Fig. (3.1) : Shows the block diagram of the experimental procedure.

3.3 Surface Preparation for Plating

Surface specimen have been prepared as following:

1-All surface was fully grinding by using (Carbide paper grit silicon), that was gradually as following (180, 400, 600, 800) and this process was done by using (MP-2B grinder polisher) as shown in figure (3.2).

2-After completing every process the specimens were washed by distilled water and alcohol and then been dried by using an electrical dryer, then have been stored in desiccator.

3-The surfaces of specimens were cleaned off by alkaline and acid solutions which have been showed in the following pattern.

Fig. (3.2): Grinder polisher.

3.3.1 Alkaline Cleaning

The specimens were immersion in alkaline solutions material (10wt % NaOH) and for two minutes' period at (25°C) temperature to remove any dust and oil from the surface of the metal, after that the samples have been washed with distilled water.

3.3.2 Acid Cleaning

The treatment was carried out by acid solution (HCl) with concentrically of (30%) and with temperature of (25°C) and for five second period to remove oxides and washed it with distilled water and alcohol. The specimens were dried by using an electrical dryer thereafter the samples were weighted by an electric balance and after taking weight records of the samples, it is placed in the coating solution for electroplating process.

3.4 Equipment for Electroplating Process

Electroplating process was carried out by using beaker produce from glass has cylindrical shape and power supply which can give the current up to (0-6) A and the voltage given up to (0-20) V

Compositions of Electroplating Bath: Many experimental works are carried out to investigate the feasibility of simultaneous Watts' solution and Watts' solution with different percentage of Titania by addition (5, 10, 15) g\L. The electrolyte of watts combines nickel sulphate, nickel chloride and boric acid.

All solutions were prepared with distilled water and chemical dissolution that occur under acid conditions. Four baths were prepared for coating Watts' solution, (Watts' solution + TiO_2). The following details of all bath represent the optimum performance coating that could be obtained in this study shown show in Table (3.3).

Condition of Deposition for all specimen:
pH = 3.5
Temp. = 33 °C
Coating time = 30 min
Nickel anode = (99.9%)
Current density =5.305 A/dm^2

Voltage = 2 V

Table (3.3) components of plating solution [52].

Solution	**Chemical composition**
Ni	$NiSO_4.6H_2O$ = 240 g/L $NiCl_2.6H_2O$ = 20 g/L H_3BO_3 = 20 g/L
Ni –5TiO_2	$NiSO_4.6H_2O$=240 g/L $NiCl_2.6H_2O$ = 20 g/L H_3BO_3 = 20 g/L
Ni –10TiO_2	$NiSO_4.6H_2O$=240 g/L $NiCl_2.6H_2O$ = 20 g/L H_3BO_3 = 20 g/L
Ni –15TiO_2	$NiSO_4$.6H2O=240 g/L $NiCl_2$.6H2O = 20 g/L H_3BO_3 = 20 g/L

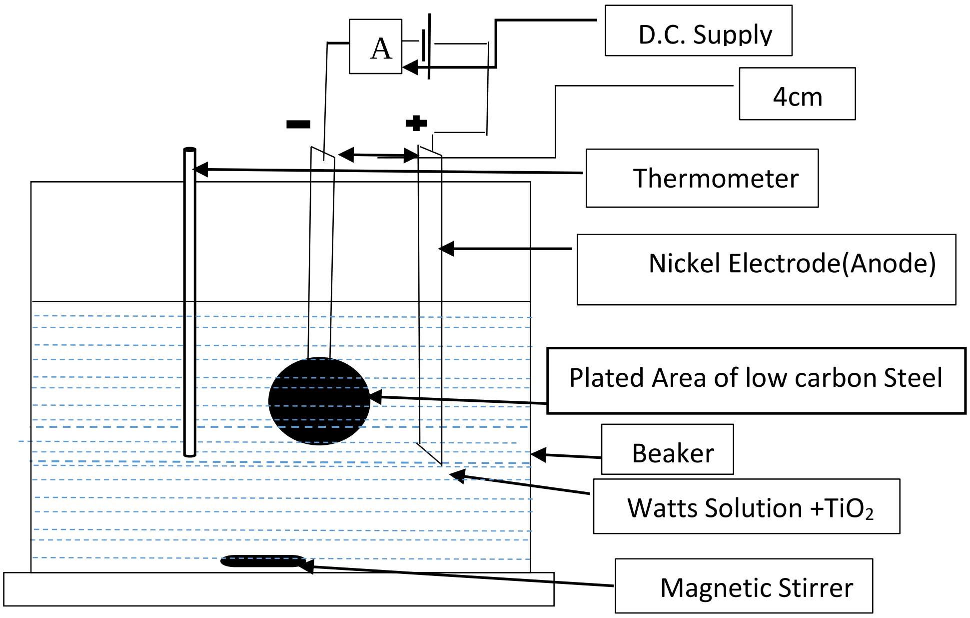


Fig. (3.3): Schematic the electrochemical cell.

3.5 Tests

The present research carried out the procedure of the upcoming tests in order to evaluate plating layers' performance.

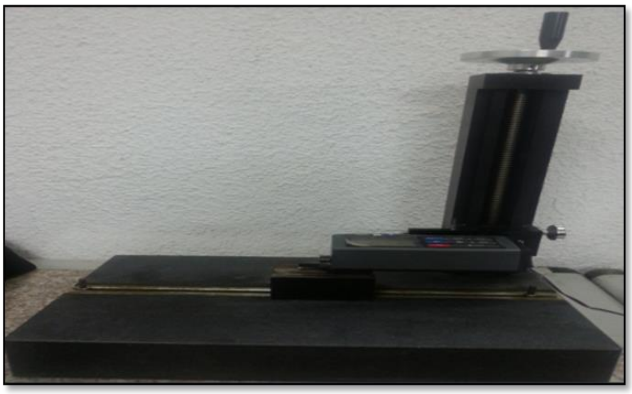
3.5.1 Measurements of Coating Thickness

The method is carried out by coating thickness gage Type (TT 260) figure (3.4) The accuracy of the device (±0.1μm). In this way measurements were taken in the three places to provide averaged sample thickness, the test was done to nickel and nickel added titania by (0.5, 1 and 1.5) wt.% coated steel specimen.

Fig. (3.4): The device of thickness measuring.

3.5.2 Surface Roughness Test

The surface roughness of nickel and nickel added titania by (5, 10 and 15) g/l coated low carbon steel specimen was measured by using the (TR-100 surface roughness tester), which is located at the University of Babylon, faculty of Material Engineering. The device passes on the specimens' surface to measure the surface roughness, the device has sensor that records the roughness of the specimen surface and takes the reading directly from the device screen. The accuracy of the device (±0.01μm).



(3.5): Surface roughness device

3.5.3 Hardness test

Vickers hardness (TH-717 Digital Vickers Hardness Tester) was measured the hardness of nickel and nickel added titania by (0.5, 1 and 1.5) wt% coated steel specimen and steel substrate without coating specimens the applied load at (200N) and holding time (10s) in College of Material Engineering / University of Babylon.

3.5.4 Scanning Electron Microscopy Test (SEM)

The morphology of the surface deposits layer on steel specimen i.e nickel and nickel added titania by (0.5, 1 and 1.5) wt% coated steel was observed by a scanning electron microscopy model (Inspect S50 FEI company), the test was done in College of Pharmacy/ University of Babylon. Figure (3.6) show the scanning electron microscopy which carried out different magnification for electroplating layer.

3.5.5 Energy dispersive X-ray spectroscopy

Energy Dispersive X-ray model (Inspect S50 FEI company), as an analytical method was used to determine the element percentage for each layer of coated specimen which nickel and nickel added titania by (0.5, 1 and 1.5) wt.% coated steel, specimen the test was done in college of pharmacy/ University of Babylon.

Fig. (3.6): The scanning electron microscopy used.

3.5.6 Corrosion test

3.5.6.1 Open Circuit Potential (O.C.P.)

The open circuit potential (O.C.P.) (also known as the equilibrium potential or open circuit voltage (OCV), is the potential at which there is no current being applied to the cell. It is simply a valuable technique that determines the potential difference between the working and reference electrodes. The O.C.P (voltage versus time) was recorded every 5 minutes for all the specimen i.e. nickel and nickel added titania by (0.5, 1 and 1.5) wt.% coated steel and low carbon steel specimens in the salt solution (3.5%) NaCl and tap water as corrosion solutions.

3.5.6.2 Liner Polarization Test

Liner polarization test was prepared according to ASTMG5-94(2011) e1. This test was done by using the Potentiostatic polarization test type (Mlab Sci-Electwchemica) in salt solution and tap water for uncoated, nickel and nickel added titania by (0.5, 1 and 1.5) wt.% coated steel specimens at 30°C. Potentiostatic polarization experiments were performed in three electrode cell containing electrolytes salt solution. The corrosion rate measurement was derived by applying the following equation[52].

Corrosion rate (mpy) = $0.1288\ i_{corr.}\ (E.W.)/A.\rho$ (3.1)

Whereas:

E. W. = equivalent weight (g/ eq.)

A = area (cm^2)

ρ =density (g/ cm^3)

0.1288 = conversion factor for metric and time.

$i_{corr.}$ = density of current (μA / cm^2).

The improvement percentage was calculated for coated specimens using the following equation[52]:

Improvement percentage = $(CR_0 - CR / CR_0) \times 100$ (3.2)

Where:

CR_0 =the rate of corrosion for master specimen (without coating).

CR =the rate of corrosion for coated specimen (with Ni or (Ni-TiO_2).

CHAPTER FOUR

RESULTS AND DISCUSSION

Chapter Four

Results and Discussion

4.1 Introduction

Experimental results have been demonstrated in this chapter which involve coating thickness, surface roughness, corrosion test results in different solutions which include (tap water and salt solution) open circuit method and other testing such as SEM, EDS, Hardness and optical microscope results.

4.2 Coating thickness:

For coating specimens, the thicknesses were (20.85, 31.15, 37.45 and 41.8) µm for Ni and Ni- TiO_2 specimens with (0.5, 1 and 1.5) wt% respectively. These results indicated that the deposit rates of the last coating layers are greatly. This can be attributed to the high diffusivity of the species caused by the presence of TiO_2. However, with the increasing amount of TiO_2 particles, the rate of thickness increased as well as is demonstrated in Table 4.1 .

Table (4.1) Coating thickness test result.

Type coating	Average (µm)
Ni coating	20.85
Ni- 5TiO_2	31.15
Ni- 10TiO_2	37.45
Ni- 15TiO_2	41.8

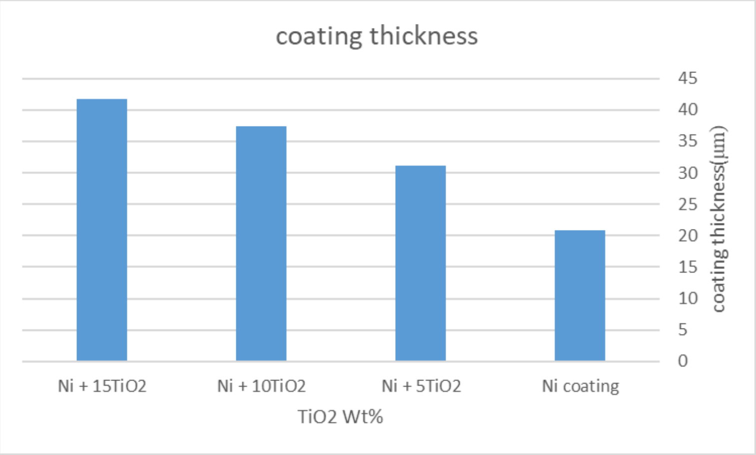


Figure (4.1) coating thickness

From table (4.1) and figure (4.1) show effect of addition percentage of titania (TiO_2) to electroplating solution of nickel which illustrated the coating thickness increase with increase of (TiO_2) percent impeded in nickel composite layer on the surface of steel specimen.

4.3 Surface roughness:

Figure (4.2) and table (4.2) show the results from the surface roughness test of the composite coating surface. Here, it notes that the surface was smoother when a concentration of 0.5 wt% TiO_2 was used and after that, the surface roughness continued to increase with an increase in the concentration of titania in the coating solution until it reached the roughest surface when the concentration was 1.5 wt% TiO_2. This according with coating thickness test the coating thickness and surface roughness increase with increase of (TiO_2) percent impeded in nickel composite layer on the surface of steel specimen.

Table (4.2) show surface roughness test result

Coating surface	Average(μm)
Base metal	0.624
Ni coating	0.975

Ni- 5TiO_2	1.133
Ni- 10TiO_2	1.925
Ni- 15TiO_2	2.330

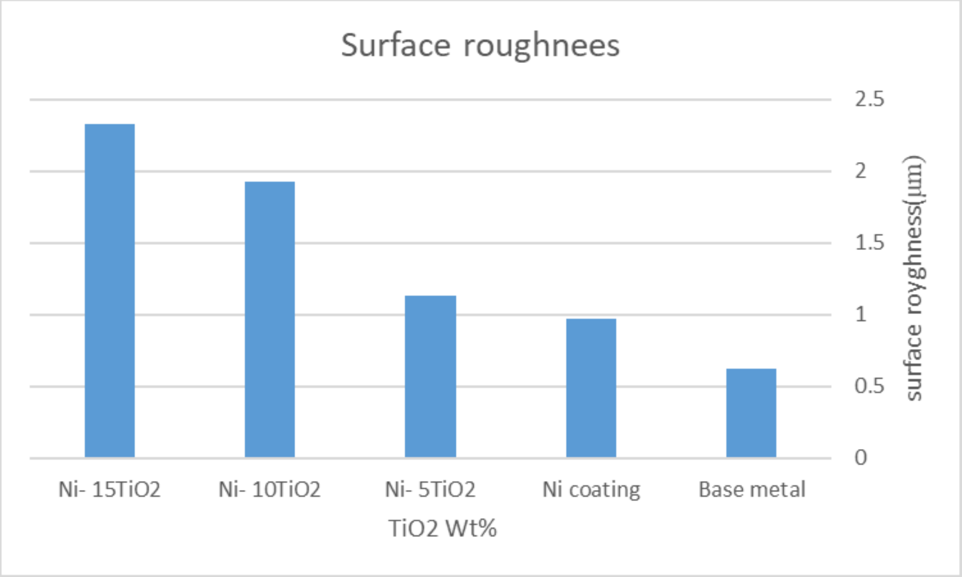


Figure (4.2) Surface roughness test result.

4.4 Hardness test

The hardness test was conducted to determine the effect of Ni and Ni-TiO_2 electrodeposited coating on the hardness values 198 HV of low carbon steel. It was also conducted to find out the effect of adding ceramic particles titania (TiO_2) with (20-30) μm particle size with different amounts to nickel solution with added percent (0.5 , 1 and 1.5) wt% on the hardness values of Ni coating and low carbon steel values. Table 4.3 shows the results of the hardness test for steel specimens and the Ni- TiO_2 layers with 0.5, 1 and 1.5 g/l TiO_2. The difference in hardness values observed between Ni- TiO_2 is due to the difference in the volume fraction of titania in each layer. The material hardness is clearly affected by the size of the particles and can be mathematically explained by the Hall-Petch relationship which states:

$$H_V = H_o + K/\sqrt{d}$$

Whereas:

H_V: Hardness of material with small grain size.

Ho: Hardness material is multi-size grain (polycrystalline grain size).

K: Constant, represents the slope of the HV hardness when drawing against and is based on the material kind.

d: Diameter of the particle.

The Hall-Petch relationship is one theory that explains why ultra-fine microstructures have higher hardness values 418 HV when compared to the coarser-grained ones with the same hardened material.

Hardness of uncoated samples are improved after coating it with nickel hard metal. Furthermore, increasing of added percent from TiO_2 (5 to 1 to 1.5) wt% could improve the hardness from (282 HV) to (341 HV) to (388 HV) and (418 HV), this results are agreement with P. Rajesh et.al, [21]. Such improvement is due to the improvement in depth morphology, distribution and increasing in TiO_2 thickness which can be clearly observed in results. Table (4.3) and figure (4.3) show for Hardness test

Table (4.3) Hardness test

Type of Coating	Average(μm)
Base metal	198
Ni	282
Ni -5TiO_2	341
Ni- 10 TiO_2	388
Ni- 15TiO_2	418

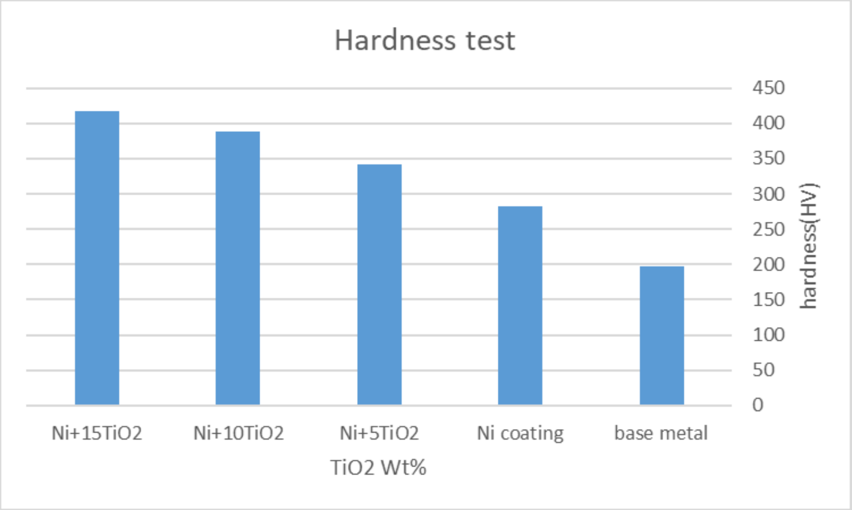
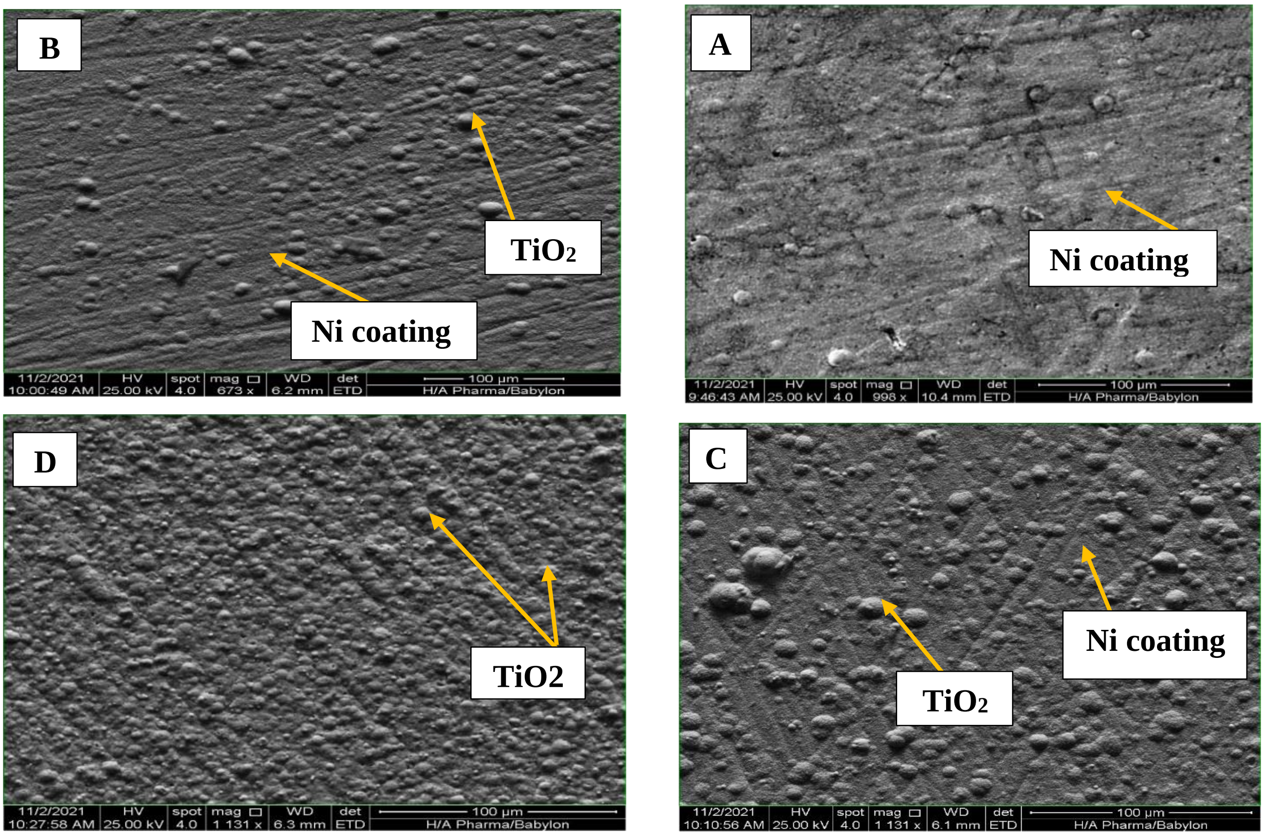


Figure (4.3) Hardness test result

4.5 Scanning Electron Microscope (SEM) results.

Figure ((4.4) A, B, C and D) demonstrated SEM microstructure of Nickel and Nickel-titania electrodeposited specimens at different amount of TiO_2 (0.5, 1 and 1.5) wt%. It is clear from the figures that the amount of TiO_2 has been progressively increased. The particles of TiO_2 are deposited in order to produce clusters which look like a heavy, aggregated composition on the base material.



Figures (4.4) SEM for Ni and Ni- TiO_2 coated specimen, A: Ni ,B: Ni-5 TiO_2, C: Ni-10 TiO_2 ,D: Ni-15 TiO_2

4.6 EDX Results

The EDX test was demonstrated to Nickel and Nickel-titania electrodeposited specimens at different amount of TiO_2 (5, 10 and 15) g/L.

The percentages of (Ni), (O) and (Ti) of composite coated layers and (Fe) for the specimens are shown in figures (4.5 (a, b, c and d)) respectively. This is expected due to the increased amount of Ti and O precipitation as the increases of added amount of TiO_2.

From figure (4.5 a) can show high percentage of Ni peak and small percentage of Fe this illustrated the Ni coated layer coat the full surface of low carbon steel

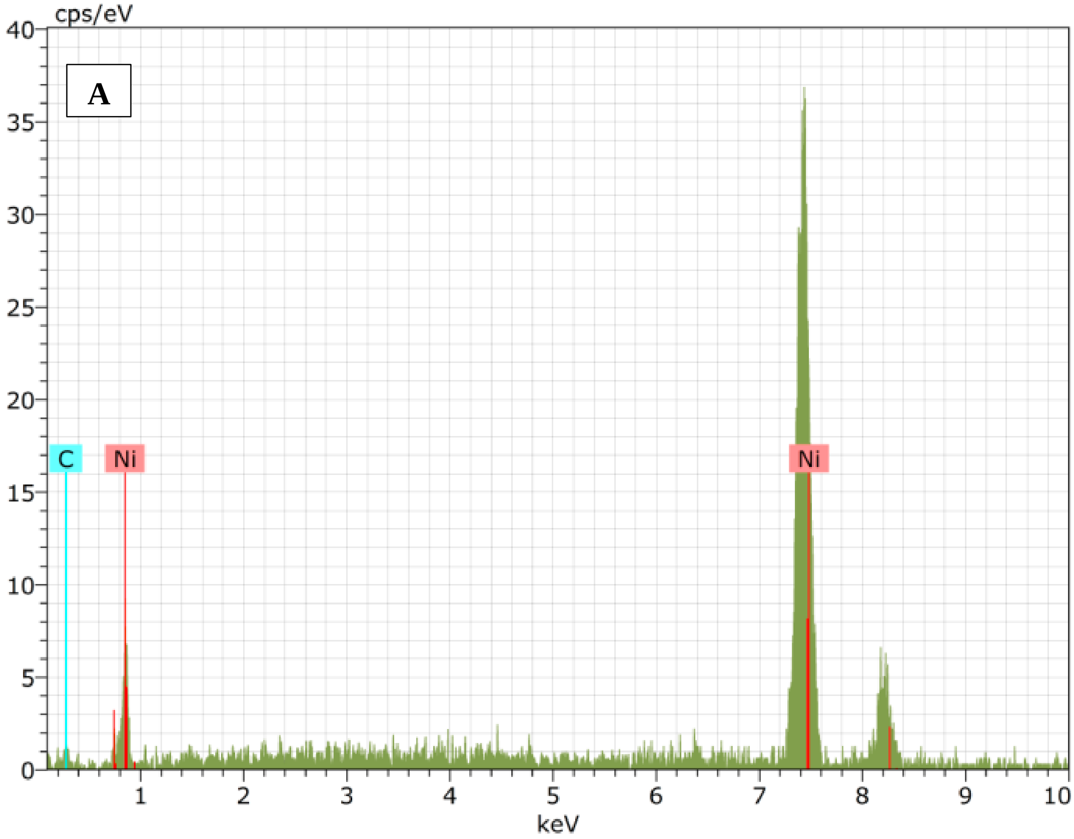


Table (4.4 A) element percentage in Ni coated specimen.

Elements	Weight percent
Ni	99.74
C	0.26

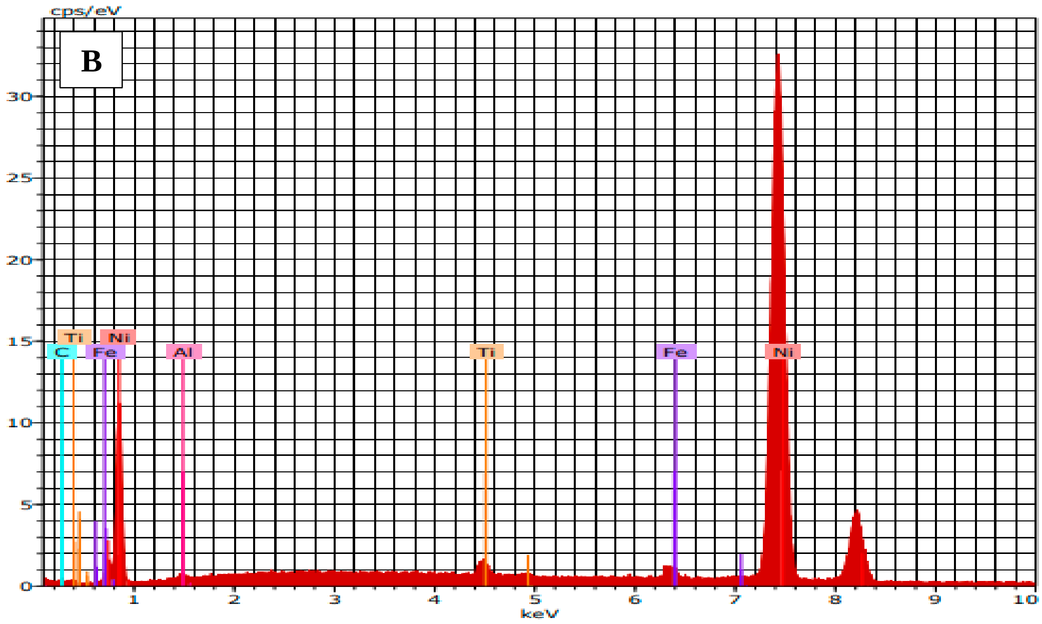


Table (4.4 B) element percentage in Ni- 5TiO_2 coated specimen

Elements	Weight percent
Ni	81.96
Fe	15.95
Ti	1.42
Al	0.4
C	0.27

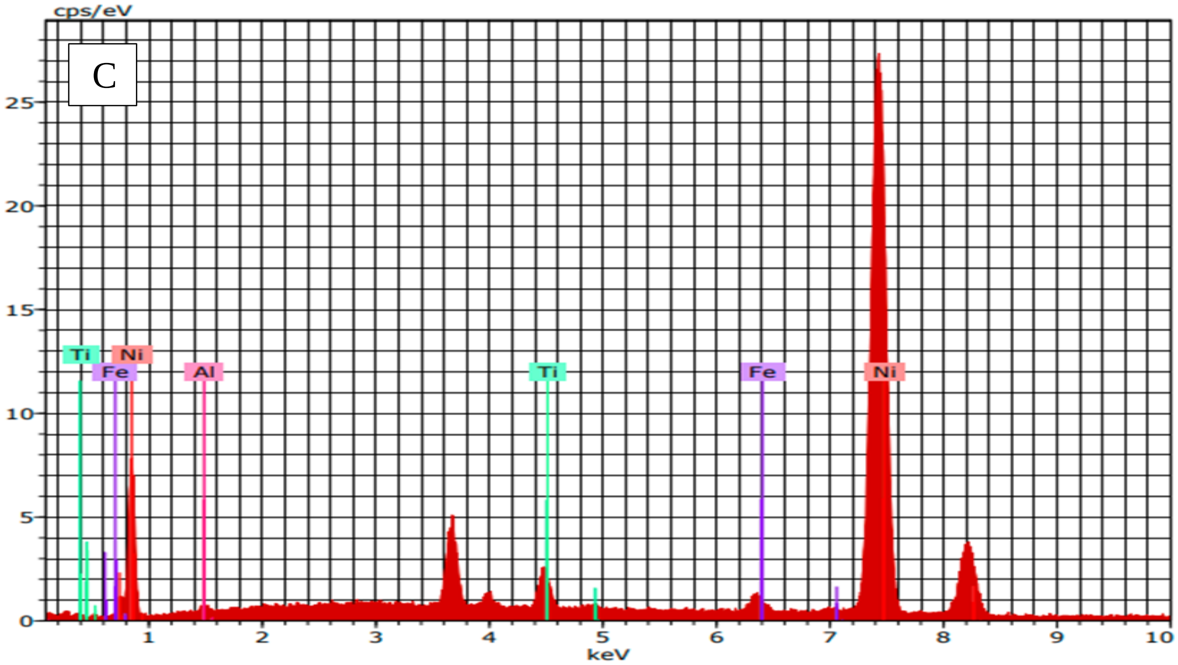
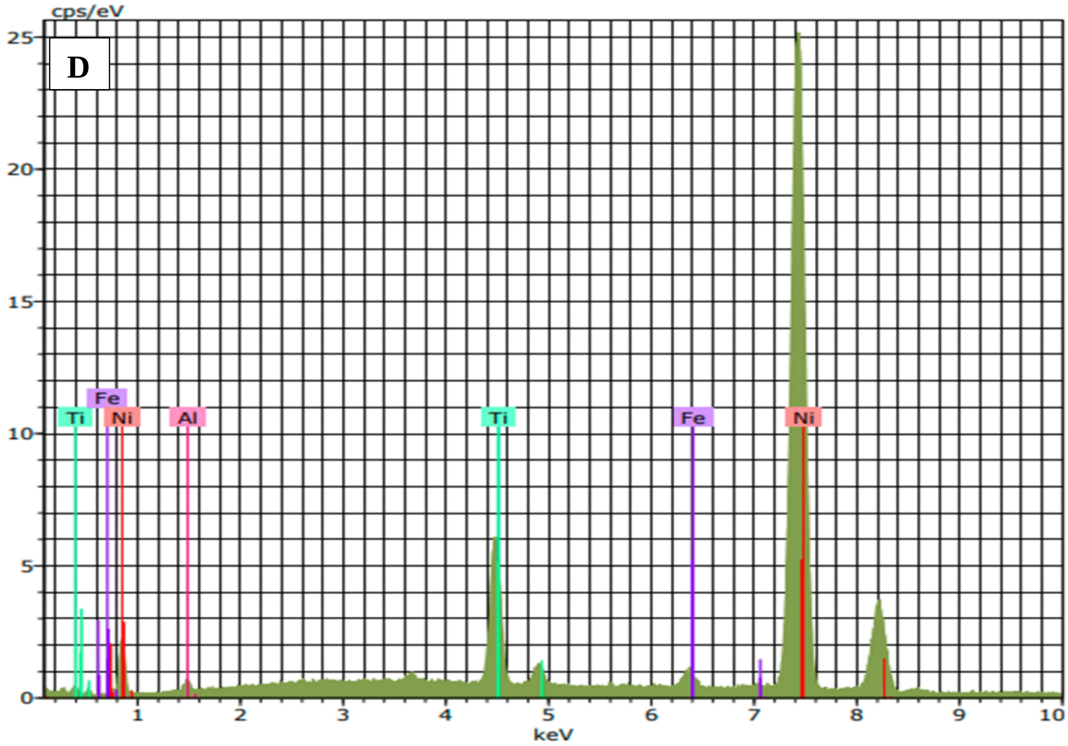


Table (4.4 C) element percentage in Ni- 10TiO_2 coated specimen.

Elements	Weight percent
Ni	80.58
Fe	18.06
Ti	0.89
Al	0.47



Figures (4.5) EDX results A: Ni, B: Ni-5 TiO_2 , C: Ni-10 TiO_2

D: Ni-15 TiO_2

Table (4.4 d) element percentage in Ni- 15TiO_2 coated specimen

Elements	Weight percent
Ni	79.09
Fe	19.31
Ti	1.1
Al	0.5

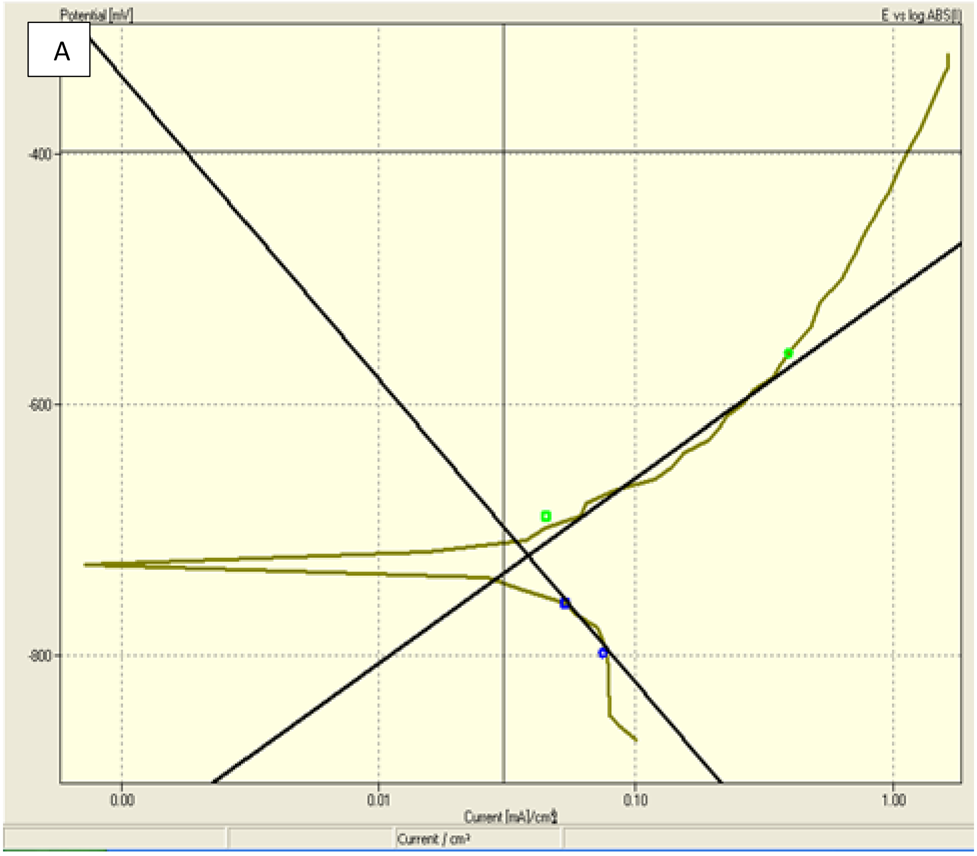
4.7 Corrosion test

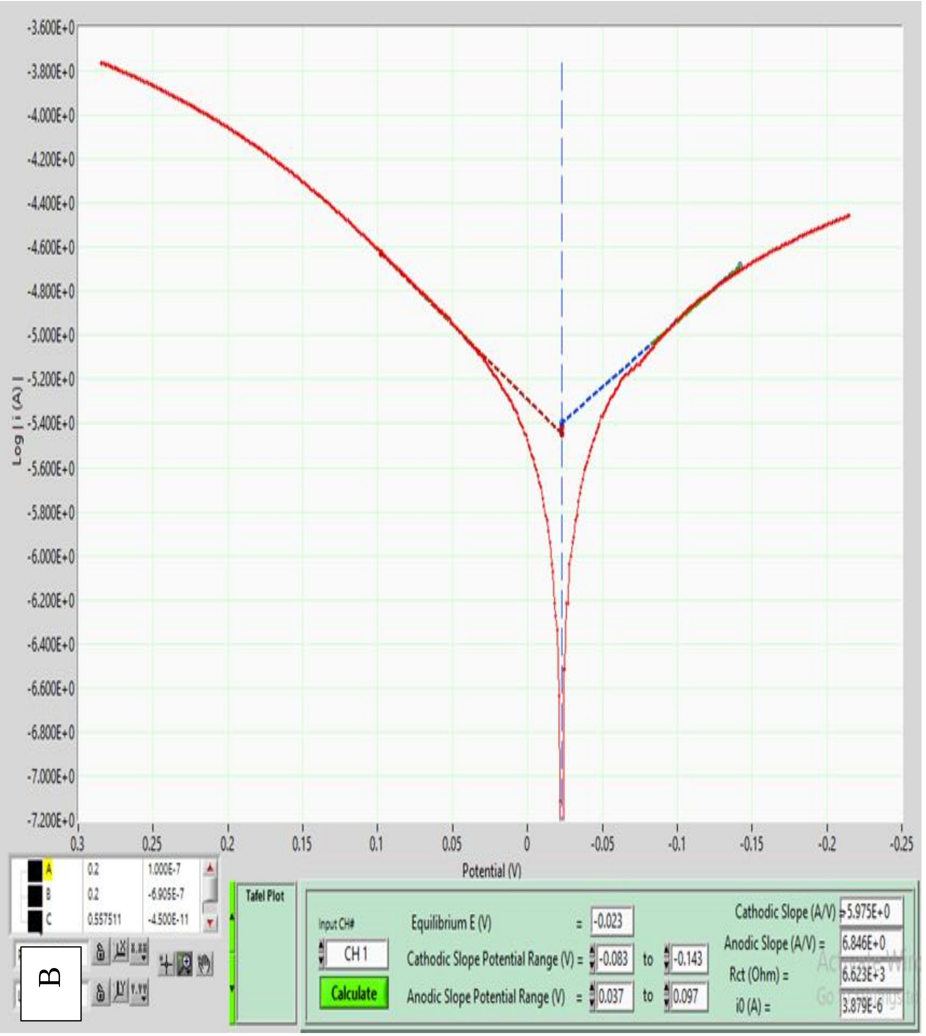
This test was done by using the Potentiostatic polarization test in salt solution 3.5%NaCl (seawater solution) and tap water for uncoated, Ni and Ni-TiO_2 coated specimens at 30 °C, with 78.539 cm^2 surface area. Corrosion parameters (corrosion potential, corrosion current, and corrosion rate), extracted from these curves, are shown in Table (4.5).

The data listed in Table (4.5) show that attrition parameters at room temperature both uncoated samples and coated samples imbedded in solution of seawater. So, the polarization curves for seawater are shown in figures (4.6 (A, B, C, D and E)). The corrosion potential of all coated specimen shows a significant shift to a positive direction and have more noble potential compared to uncoated low carbon steel specimen.

From the Table, it is clear that Ni, Ni-0.5TiO_2, Ni-1TiO_2 and Ni-1.5TiO_2 specimens have current densities and corrosion rate much lower than current densities and corrosion rate of uncoated specimen, which indicate that Ni-TiO_2 coating acts as a barrier against attack of aggressive an ion, affectively improve the corrosion resistance of low carbon steel, [52,53].

From Table (4.5) It's clear, that the samples showed the corrosion resistance of low carbon steel sample is increased after coating with Ni and Ni-TiO_2 comparison with low carbon steel uncoated sample, [54].





A	0.2	1.000E-7
B	0.2	-6.905E-7
C	0.557511	-4.500E-11

Input CH# CH 1

Equilibrium E (V) = -0.023

Cathodic Slope Potential Range (V) = -0.083 to -0.143

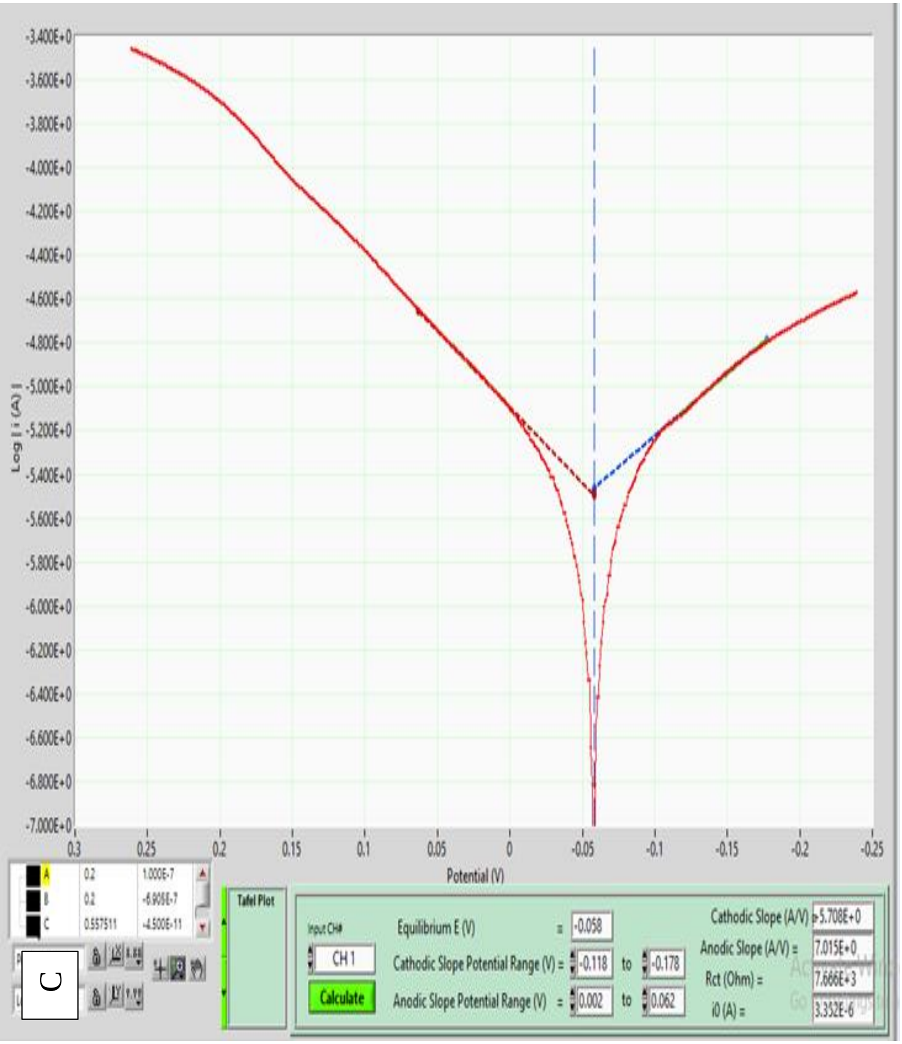
Anodic Slope Potential Range (V) = 0.037 to 0.097

Cathodic Slope (A/V) = 5.975E+0

Anodic Slope (A/V) = 6.846E+0

Rct (Ohm) = 6.623E+3

i0 (A) = 3.879E-6



A	0.2	1.000E-7
B	0.2	-6.905E-7
C	0.557511	-4.500E-11

Input CH# CH 1

Equilibrium E (V) = -0.058

Cathodic Slope Potential Range (V) = -0.118 to -0.178

Anodic Slope Potential Range (V) = 0.002 to 0.062

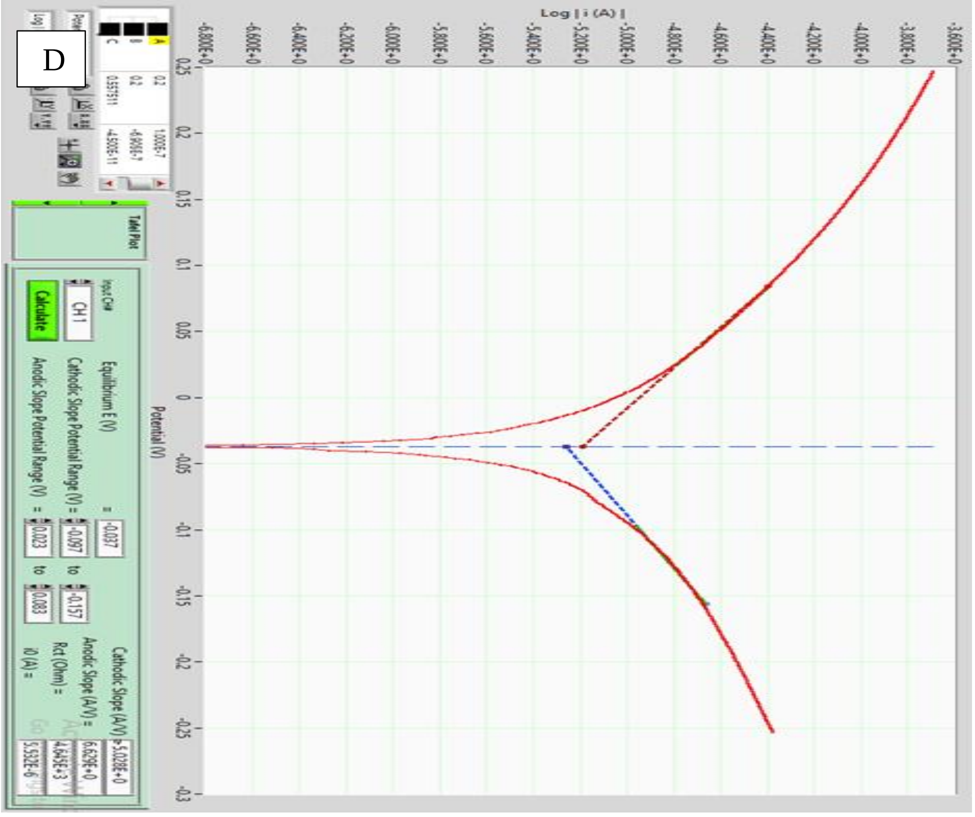
Cathodic Slope (A/V) = 5.708E+0

Anodic Slope (A/V) = 7.015E+0

Rct (Ohm) = 7.666E+3

i0 (A) = 3.352E-6

D



Input CH#: CH1

Equilibrium E (V) = -0.037

Cathodic Slope Potential Range (V) = -0.097 to -0.157

Anodic Slope Potential Range (V) = 0.023 to 0.083

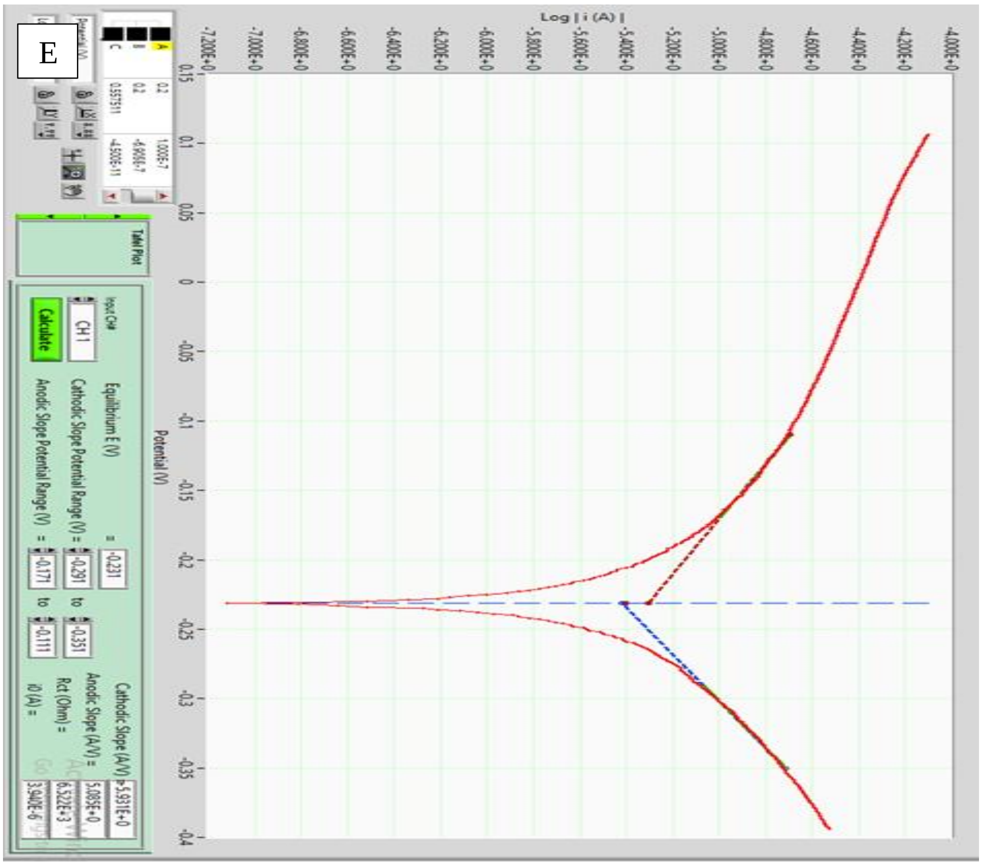
Cathodic Slope (A/V) = 5.028E+0

Anodic Slope (A/V) = 6.629E+0

Rct (Ohm) = 4.645E+3

i0 (A) = 5.532E-6

E



Input CH#: CH1

Equilibrium E (V) = -0.231

Cathodic Slope Potential Range (V) = -0.291 to -0.351

Anodic Slope Potential Range (V) = -0.171 to -0.111

Cathodic Slope (A/V) = 5.931E+0

Anodic Slope (A/V) = 5.085E+0

Rct (Ohm) = 6.522E+3

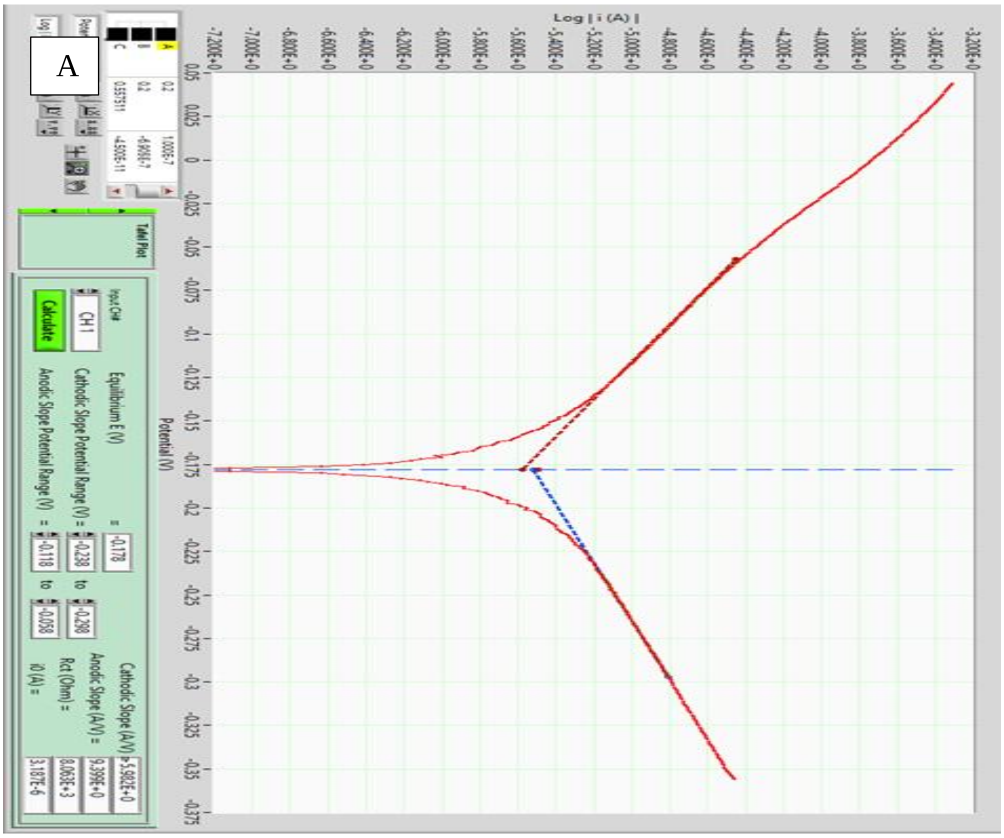
i0 (A) = 3.940E-6

Figures (4.6) Crrosion test in Tap water. (A) Base metal specimen, (B) Ni coated specimen, (C) Ni-5TiO_2 coated specimen. (D). Ni-10TiO_2 coated specimen, (E). Ni-15TiO_2 coated specimen.

Table (4.5) Corrosion rate (CR) and improvement percentage of coated specimens in Tap water.

Sample code	$I_{corr.}$ ($\mu A/cm^2$)	$E_{corr.}$ (mV)	Corrosion Rate (mpy)	Improvement Percentage%
Low carbon steel	7.047	-231	4.151	-
Ni	5.792	-179	3.160	24
Ni-5TiO_2	5.019	-137	2.739	34
Ni-10TiO_2	4.941	-58	2.659	36
Ni-15TiO_2	4.270	-23	2.280	45

Figures (4.6) and (4.7) show the polarization diagrams of all specimens and the $E_{corr.}$ (mV), I corr. ($\mu A/cm^2$). The corrosion rates (mpy) have been demonstrated in Tables (4.5) and (4.6). These results indicate a stable behavior of the Ni-TiO_2 coating layer. Along with an improvement of corrosion resistance, this TiO_2 coating is able to make changes in the surface feature in comparison with the materials without affecting the characteristics of the bulk [54, 55]. Also, the presence of TiO_2 in coatings can improve corrosion resistance of the coated specimens in tap water and salt solution [54, 56].



Input CH# CH 1

Equilibrium E (V) = -0.178

Cathodic Slope Potential Range (V) = -0.238 to -0.298

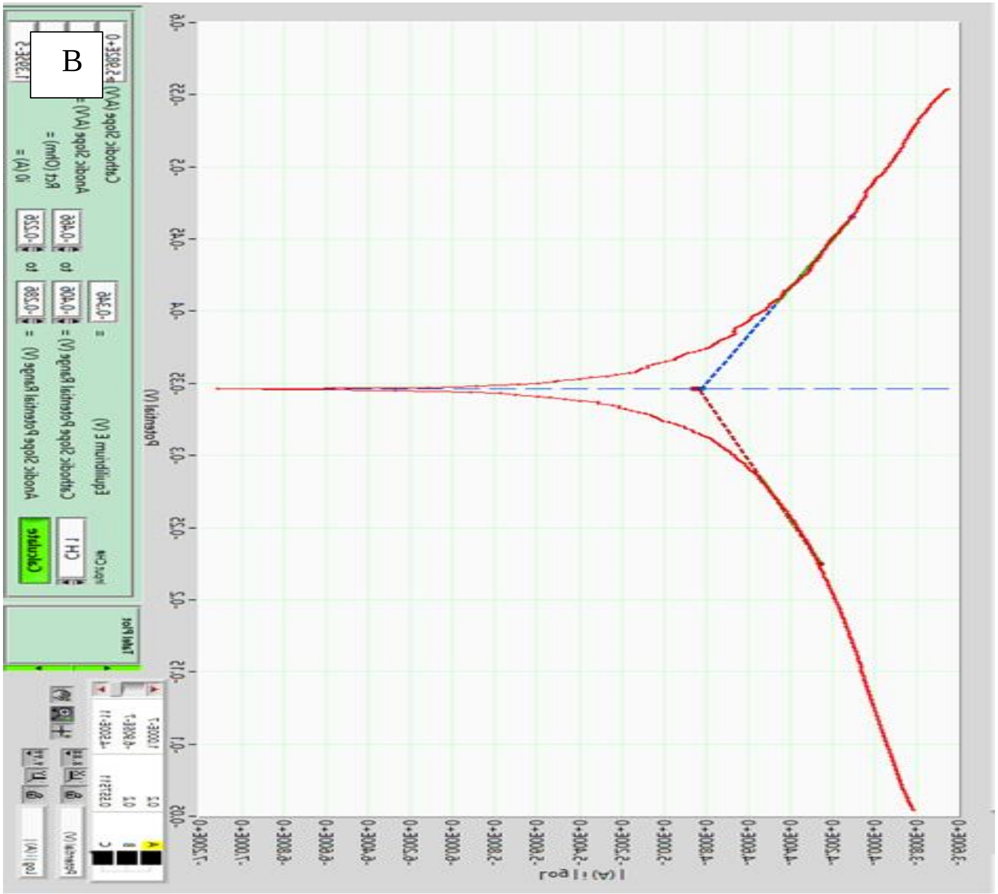
Anodic Slope Potential Range (V) = -0.118 to -0.058

Cathodic Slope (A/V) = 5.982E+0

Anodic Slope (A/V) = 9.399E+0

Rct (Ohm) = 8.063E+3

i0 (A) = 3.187E-6



Input CH# CH 1

Equilibrium E (V) = -0.346

Cathodic Slope Potential Range (V) = -0.406 to -0.466

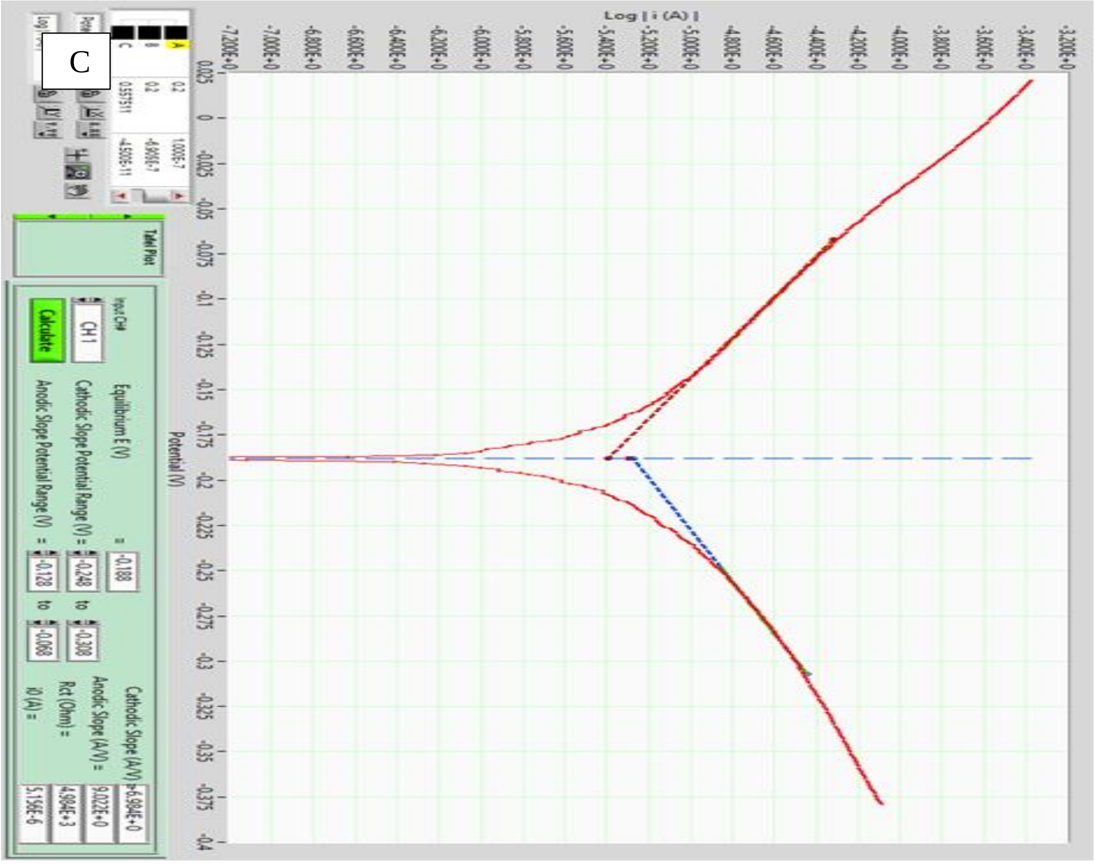
Anodic Slope Potential Range (V) = -0.286 to -0.226

Cathodic Slope (A/V) = 5.982E+0

Anodic Slope (A/V) =

Rct (Ohm) =

i0 (A) = 1.395E-5



Input CH# CH1

Equilibrium E (V) = -0.188

Cathodic Slope Potential Range (V) = -0.248 to -0.308

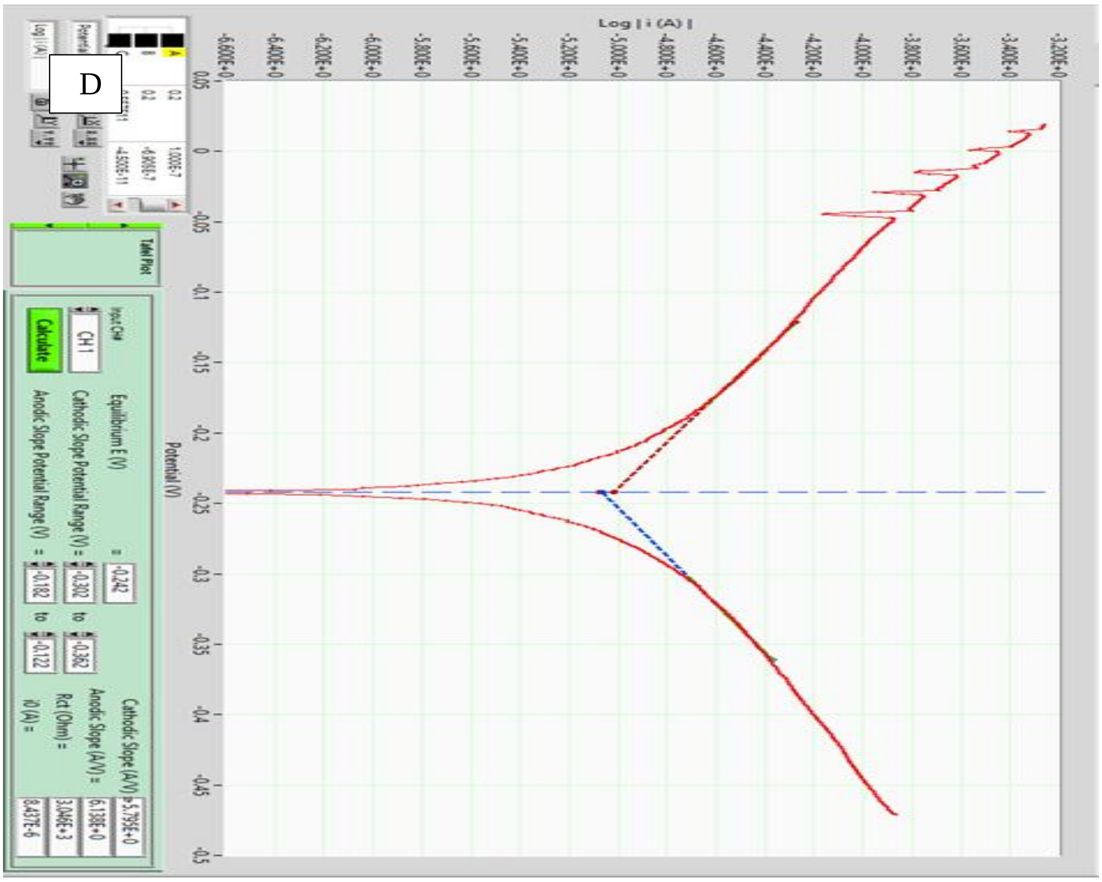
Anodic Slope Potential Range (V) = -0.128 to -0.068

Cathodic Slope (A/V) = 6.984E+0

Anodic Slope (A/V) = 9.022E+0

Rct (Ohm) = 4.984E+3

i0 (A) = 5.156E-6



Input CH# CH1

Equilibrium E (V) = -0.242

Cathodic Slope Potential Range (V) = -0.302 to -0.362

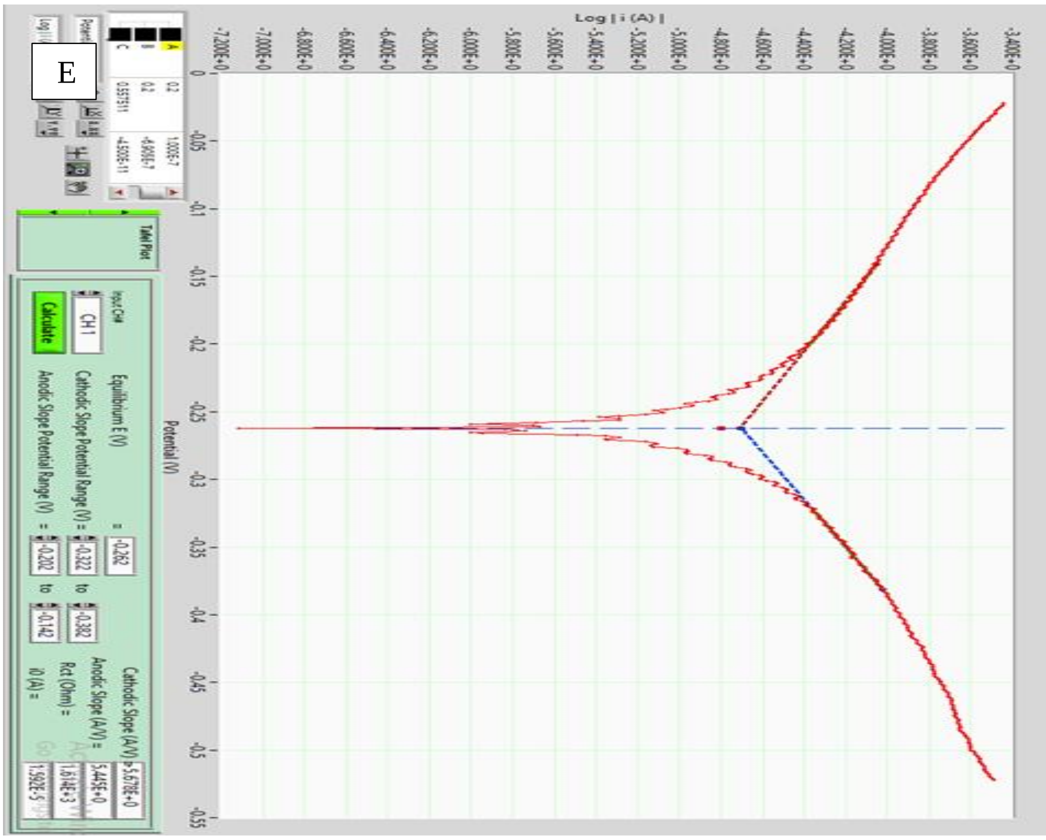
Anodic Slope Potential Range (V) = -0.182 to -0.122

Cathodic Slope (A/V) = 5.795E+0

Anodic Slope (A/V) = 6.138E+0

Rct (Ohm) = 3.046E+3

i0 (A) = 8.437E-6



Input CH# CH1

Equilibrium E (V) = -0.262

Cathodic Slope Potential Range (V) = -0.322 to -0.382

Anodic Slope Potential Range (V) = -0.202 to -0.142

Cathodic Slope (A/V) = 5.678E+0

Anodic Slope (A/V) = 5.445E+0

Rct (Ohm) = 1.614E+3

i0 (A) = 1.592E-5

Figures (4.7) Corrosion test in Salt solution(A) Base metal specimen. (B) Ni coated specimen. (C) Ni-5TiO_2 coated specimen. (D) Ni-10TiO_2 coated specimen (E) Ni-15TiO_2 coated specimen.

Table (4.6) Corrosion rate (CR) and improvement percentage of coated specimens in Salt solution.

Sample code	$i_{corr.}$ (μA/cm$_2$)	$E_{corr.}$ (mV)	Corrosion Rate (mpy)	Improvement Percentage%
Low carbon steel	20.27	-346	11.941	-
Ni	17.76	-262	9.692	19
Ni-5TiO_2	10.74	-242	5.861	51
Ni-10TiO_2	6.57	-188	3.463	71
Ni-15TiO_2	4.05	-178	2.163	82

The porosity decreases when TiO_2 particles were added. This explanation is supported by the fact that particles significantly lower both the porosity and corrosion current density. This is due to the possible filling of the pores by these fine particles. When TiO_2 particles were incorporated into the Nickel solution, the TiO_2 reduced the current density of the corrosion to the lowest value (Tables 4.5 and 4.6).

CHAPTER FIVE

CONCLUSIONS AND RECOMMENDATIONS

Chapter Five

Conclusions and Recommendations

5.1 Introduction

This chapter contains the concluding remarks, obtained from this study. It also provides recommended suggestions, which may be useful for future works.

5.2 Conclusions

In conclusion it is perhaps worthwhile to return to each of the aims set out in chapter one and briefly summarize any achievement:

1- When the percentage addition of TiO_2 increase, the properties such as coating thickness, surface roughness and hardness increased.

2-When the percentage addition of TiO_2 increase the corrosion rate improved from (24%) to (45%) in tap water and it improve form (19%) to (82%) in salt solution.

4-Thickness of coating layer (Ni-TiO_2) increase with percentage additive of titania increase.

5.3 Recommendations for Future works

It is suggested that future works in this field should be studied

1- Study the effect of addition ZrO_2 and Al_2O_3 instead TiO_2.
2- Study the effect of coating time on coating thickness.
3- Study the porosity in the coating.
4- Identifying the effective factors in the plating layer adhesion with the basic metal.

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الخلاصة:

يهدف البحث الحالي محاولة لإدخال تحسينات على خواص الفولاذ منخفض الكاربون من خلال طلاء العينات بمحلول واطس ثم أضافة دقائق من ثاني أوكسيد التيتانيوم (TiO_2) مع المحلول. وأن مادة ثاني أوكسيد التيتانيوم تمتاز بمقاومتها للتآكل في اغلب الأوساط المتعادلة والحامضية والقاعدية .

تم تحضير طلاء النيكل باستخدام محلول من نوع واطس يحتوي على (٢٤٠ غم / لتر) من كبريتات النيكل($Ni2SO4 \cdot 6H2O$) ، (٢٠ غم / لتر) كلوريد النيكل ($NiCl_2 \cdot 6H_2O$)، و(٢٠ غم / لتر) حمض البوريك (H_3BO_3) ثم أضف نسبة (٥ ، ١٠ ، ١٥) غم / لتر من ثاني أوكسيد التيتانيوم (titaina) لمحلول الطلاء الكهربائي بالنيكل. تم ترسيب جزيئات (TiO_2) صغيرة الحجم (٢٠-٣٠) مايكرومتر مع النيكل باستخدام تقنية الترسيب الكهربائي لتطوير الطلاءات المركبة. تم استخدام قطب نيكل بنسبة نقاء ٩٩,٩٩٪ بأبعاد (١٠٠ × ٤٠ × ٨) مم كأنود وكربون منخفض صلب بأبعاد (سماكة = ١ مم وقطر = ١٠ مم) ككاثود (ركيزة). قيمة كثافة التيار والجهد المستخدم في عملية الطلاء هي (٥,٣٠٥ امبير\ دسم ٢، ٢ فولط) على التوالي. قبل الترسيب، كانت ركائز الفولاذ منخفض الكربون مصقولة ميكانيكياً بأوراق كربيد السيليكون من ١٨٠، ٤٠٠، ٦٠٠، ٨٠٠، حبيبات ووضعها (محلول هيدروكسيد الصوديوم بنسبة ١٠٪ لمدة دقيقتين ثم في محلول حمض الهيدروكلوريك بنسبة ٣٠٪ عند درجة حرارة الغرفة لمدة ٥ ثوانٍ.)

في هذا العمل، تم إجراء العديد من الاختبارات، بما في ذلك: سمك الطلاء وخشونة الأسطح والصلابة واختبارات الاستقطاب في محلول الملح وماء الحنفية لطبقة الطلاء.

تشير الصلابة إلى أن الخواص الميكانيكية للطلاء المطبق مع تقوية مدمجة (TiO_2) كانت أعلى بكثير مقارنة مع العينات غير المطلية. تم أجراء اختبارات التآكل (الاستقطاب الخطي) المقاسة آلياً باستخدام تقنية (Potentistatic) لطبقات الطلاء وللمعدن الاساس وذلك في أوساط تآكليه مختلفة شملت ماء الحنفية الاعتيادي ومحلول ملحي لكلوريد الصوديوم بتركيز (٣ % NaCl) والعثور على جميع البيانات عن طريق الكمبيوتر مما يدل على أن إضافة TiO_2 أدى إلى تحسين معدل التآكل بنسبة (٤٥٪) من العينة غير المطلية.، في ماء الحنفية كوسيط لإجراء الاختبار وتحسين معدل التآكل بنسبة (٨٢٪) من العينة غير المطلية.

وزارة التعليم العالي والبحث العلمي
جامعة بابل
كلية هندسة المواد
قسم هندسة المعادن

تقصي سلوك التآكل لطلاء $Ni-TiO_2$ على سطح فولاذ منخفض الكاربون

رسالة

مقدمة إلى قسم هندسة المعادن في كلية هندسة المواد/ جامعة بابل وهي جزء من متطلبات نيل درجة الدبلوم العالي في هندسة المواد/ معادن.

من قبل

آيات ميثم حمد عبدالله

(بكالوريوس هندسة المواد)
(٢٠١٩)

بإشراف

د. نبأ ستار راضي

٢٠٢٢ م   ١٤٤٣هـ