Ministry of Higher Education and Scientific Research
University of Babylon
College of Materials Engineering
Department of Metallurgical Engineering

Investigation the corrosion behavior of composite coatings on carbon steel

This project is submitted to the University of Babylon/College of Materials Engineering Department of Metallurgical as a part of requirement for bachelor degree in

Metallurgical Engineering .

By

Reda Nayif Salman

The Supervision of

Dr: Ali Hubi Haleem

1443 A.H **2022 A.D**

بسم الله الرحمن الرحيم

رَبِّ أَوْزِعْنِي أَنْ أَشْكُرَ نِعْمَتَكَ الَّتِي أَنْعَمْتَ عَلَيَّ وَعَلَى وَالِدَيَّ وَأَنْ أَعْمَلَ صَالِحًا تَرْضَاهُ وَأَصْلِحْ لِي فِي ذُرِّيَّتِي إِنِّي تُبْتُ إِلَيْكَ وَإِنِّي مِنَ الْمُسْلِمِينَ

صدق الله العظيم

سورة الأحقاف/ اية 15

إهداء

- الى صاحب السيرة العطرة والفكر المستنير، الى من علمني أن الأعمال الكبيرة لا تتم الإ بالصبر والعزيمة والاصرار ..... فلقد كان له الفضل الأول في بلوغي التعليم العالي (والدي الحبيب) أطال الله في عمره

-الى من اعطتني من دمها وروحها وعمرها حبآ وتصميمآ ودفعآ لغد أجمل

الي من حاكت سعادتي بخيوط منسوجة من قلبها ...

الى(أمي الغالية) طيب الله ثراها

-الى من حبهم يجري في عروقي ويلهج بذكرهم فؤادي الى رياحين حياتي

(أخوتي)

-إلى أصدقاء الطرق جميعًا، الوعرة والسهلة، والمظلمة والمشرقة، أهدي هذا البحث إذ أقدم هذا الإهداء تعبيرًا عن امتناني لوجودهم في حياتي.

- الى الذين حملوا أقدس رسالة في الحياة الى الذين قدموا لنا الكثير والكثير باذلين

جهودآ كبيرة في بناء جيل الغد لتنبعث الامة من جديد الى الذين مهدوا لنا الطريق العلم والمعرفة ... الى جميع اساتذتنا الافاضل .

أهدي اليكم هذا عملي المتواضع

شكر وتقدير

أشكر الله مخلصآ أولآ وأخيرآ على نعمه الوفيرة وخيره الكثير الذي أمدني بالقوة والإرادة على تخطي الصعوبات وإكمال هذا البحث.

بداية أتوجه بجزيل شكري وأمتناني الى استاذي الفاضل (الدكتور علي هوبي) الذي منحني من وقته ومتابعتة وإرشاداتة لي مما ساعدني في تخطي وتذليل الكثير من الصعوبات التي اعترضت سبيل تقدمي خلال مسيرة بحثي هذا،

حيث كانت لآرئيه السديد وتوجيهاته الحكيمة الفضل الأول في خروج هذا البحث على ما هو عليه، جزاه الله عني كل خير والعرفان،

كذلك خالص شكري ومودتي لكل من قدم لي يد العون وكان لي نورآ في حائكات الضلام فجزاهم الله جزاء المحسنين.

APPROVAL OF THE SUPERVISOR

I certify that the numbers of this research is tagged (Investigation the corrosion behavior of composite coatings on carbon steel) It took place under my supervision in the Department of Minerals, College of Materials Engineering, which is part of the requirements for obtaining a Bachelor's degree in the Minerals Department.

Name of supervisor

Dr: Ali Hubi Haleem

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.

Composite coating was prepared by using Electro-deposition of nickel–Al2O3 composites was achieved in a characteristic watts bath on the low carbon steel. A nickel sulfamate electrolyte was used by the subsequent constituent: 300 g/l nickel sulfamate Ni (NH2SO3)2, 30 g/l boric acids, 5 g/l nickel chloride (NiCl2), 0.2 g/l sodium laurel sulfate (wetting agent), and 0.1 g/l coumarins (smoothing mediator) then add a ratio of Al2O3 (16, 24, 32) g\L to nickel electroplating solution. Micro-sized Al2O3 ceramic particles (10) μm were co-deposited with nickel using the electrodeposition technique to develop composite coatings a nickel electrode of 99.99% purity with dimensions of (100 ×80 ×2) mm was used as anode and low carbon steel as cathode (substrate) materials. The value of current density is 4.5 A/dm2 used in the coating process. Before deposition, the low carbon steel substrates were mechanically polished with silicon carbide papers of 180, 400, 600, and 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 measurements, microstructure characterization by SEM, and polarization tests in a salt solution of 3.5% NaCl to determine corrosion rate. The results of the microstructure examination showed the homogeneous distribution of aluminum oxide particles in the nickel matrix as well as a clear decrease in the corrosion rate for all added percentages of aluminum oxide and the highest decrease in the corrosion rate up to 91 when aluminum oxide was added with a percentage of 24 g/l during electroplating process.

Contents

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. In this regard various materials have been used as coating such as nickel, cadmium, synthetic and/or extracted organic compounds, modified polymers, resins and alloys.

Pure nickel coatings suffer from poor mechanical properties and the incorporation of a second hard phase during the electrodeposition process (e.g. ceramic nanoparticles) would normally permit to enhance them. Coelectrodeposition is a simple and low cost technique to produce metal matrix composite coatings that have been used widely in automotive and aerospace.

Composite coatings comprise a metal mainly (nickel, zinc ,copper, silver, cobalt and gold)or metal alloy matrix that contains a dispersed phase of nonmetallic particles that ranges from oxides (e.g. Al_2O_3, TiO_2), carbides (e.g. SiC, WC ,TiC) and (e.g. MoS_2, hexagonal BN, graphite) . Such coatings have been developed to improve material properties regarding to corrosion stability, friction protection, wear resistance, high temperature stability, self-lubrication, improved catalytic activity and electrical contacts. Nickel composite layers improve corrosion and wear resistance of steel, hence, it is used in applications that need such properties. Steel constructions could be coated with composite layers instead of pure nickel coating for its beneficial properties of extended service life control.

Coatings by microstructure are more suitable for many applications that cannot be coated with ordinary conventional coatings. This is all because of the unique properties of the micro composite materials with typical grain sizes more than 10 nm. The novel properties and various potential applications make these materials are attracting and increases the consideration from all researchers of this field. The small particles size of these materials leads to larger volume fraction of atoms in or near the grain boundaries, this lead to the superior and sometimes completely new properties as compared with the materials that came from.

Electrodeposition of nickel from acid solutions (sulphate and chloride baths), specially in the developed nations. nickel is very electronegative protection for steel substrates. It is so economical to deposit and widely supplies are high. For several years ago, the commercial available additives to the bath coating have been used, the necessity of an environmentally friendly non-commercial additives for the acid chloride bath of nickel plating has been generating increased research interest including the present investigation. The necessity to improve corrosion resistance and integrity of steel components in various manufacturing productions, industries and services facilities, now a days it add the growing interest in this field for research of electrodeposition.

1.2 Aims of the Research

The aims of this study are to protect carbon steel and improve corrosion resistance by electroplating process technology and to develop this process by tacking in to consideration that incorporation of Ni and Al_2O_3 in to modified coatings decreases cost and enhancing corrosion resistance.

Chapter two

Theoretical Part

Chapter Two

Theoretical Part and Literature Review

2.1. 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. They are reduced to metallic state by the expenditure of energy during smelting operation which involves the removal of the bulk of the combining elements. Such extracted metals are inherently unstable and show a general tendency to revert to the natural or oxidized condition by combining with the constituents of their environment. This reverse process requires no supply of energy so it occurs readily and spontaneously in order to reach a stable state, the result is seen as corrosion. 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.

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.

2.2. Forms of Corrosion

Classification of corrosion depends on one of the following factors:

1- Oxidant's nature: corrosion can be classified as "dry" or "wet". Electrolytic solution is required to have wet corrosion, whereas high-temperature gases is included by dry corrosion. Nucleation and growth phenomena of oxide layers and other compounds are the same for both kinds of corrosion.

2- Corrosion mechanism : This includes either chemical or electrochemical reactions.

3- The appearance of the corroded metal: Corrosion can be uniform or localized. The corrosion rate is the same over the entire metal surface at first case; while at the second case, only small areas are affected.

Classification by appearance depends on identifying forms of corrosion via visual observation (with magnification or naked eye). Fig.(2.1) shows many forms of wet or aqueous corrosion:

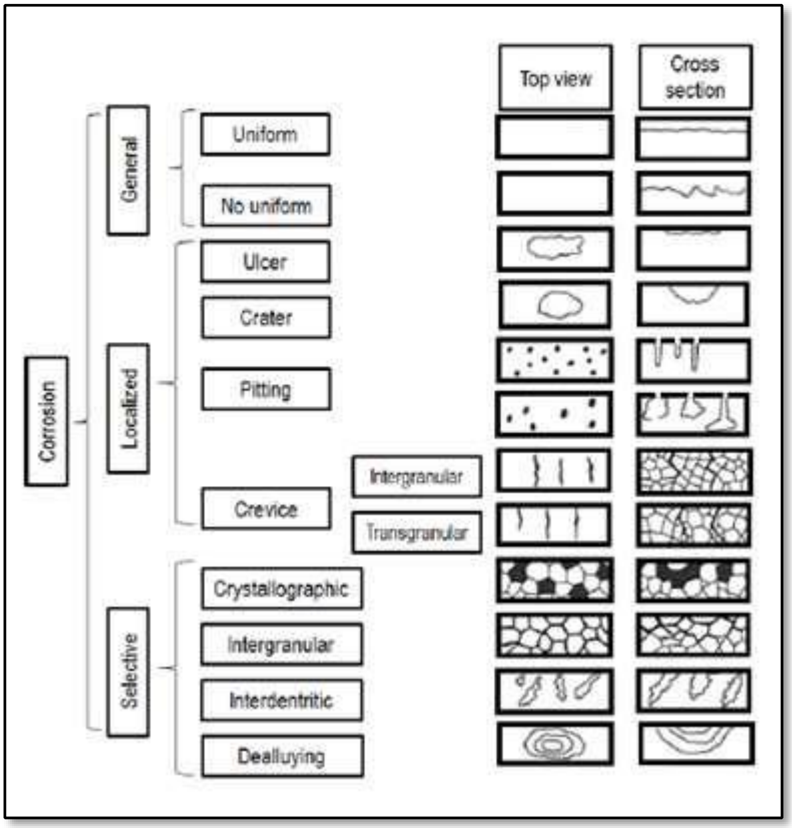


Fig.2.1: Shows different forms of aqueous corrosion.

2. 3.**Corrosion in Carbon Steels**

As per ISO 8044:2010, ‘corrosion is the physical-chemical interaction between a metal and its environment, which results in changes in the metal’s properties and which may lead to significant functional impairment of the metal, the environment, or the technical system of which they form a part’. Corrosion is seen when there is a change in the metal’s or system’s properties which can lead to an undesirable outcome. This can range simply from visual impairment to complete failure of technical systems which cause big economic damage and even present a hazard to the people.

Corrosion can be defined broadly as the destruction or deterioration of metal by direct chemical and electro-chemical reaction with its environment. Most simply stated, metallic corrosion is the reverse of electroplating. The metal being corroded forms the anode while the cathode is that being electroplated. Metallic corrosion occurs since in many environments, the majority metals are not inherently stable and tend to revert to some more stable combination of which the metallic ores as found in nature are familiar examples

Carbon steel is the most widely used engineering material. It has relatively limited corrosion resistance. The cost of corrosion of carbon steel to the total economy is very high. Since the carbon steels represent the largest single class of alloys in use, both in terms of tonnage and total cost, the corrosion of carbon steels is a problem of enormous practical importance. In carbon steel, the typical corrosion process can be regarded as the thermodynamically favored reverse reaction of the metal-winning (extraction) process as shown in Fig 2.2.

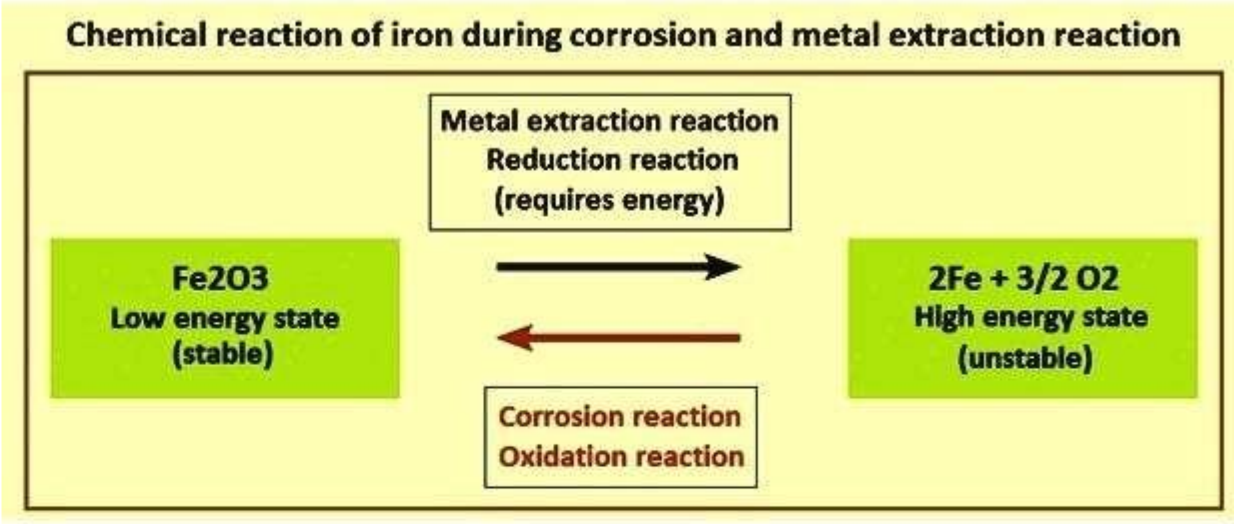


Fig 2.2 Chemical reaction of iron during corrosion and metal extraction reaction

Carbon steel (which include mild steels) is by its nature has limited alloy content, usually less than 2 % by weight for the total of all additions. Unfortunately, these levels of addition do not generally produce any remarkable changes in general corrosion behaviour. One possible exception to this statement is the weathering steels, in which small additions of copper, chromium, nickel, and / or phosphorus produce significant reductions in corrosion rate in certain environments. At the levels of various elements in which they are present in the carbon steel, the elements have no significant effect on corrosion rate in the atmosphere, neutral waters, or soils. Only in the case of acid attack, an effect observed. In this case, the presence of phosphorus and sulphur markedly increase the rate of attack. Indeed, in acid systems, the pure irons appear to show the best resistance to attack.

Corrosion reactions take place when conditions are thermodynamically in favor of the chemical reactions. When this happens, then potential other factors drive the speed of the reaction (kinetics of the reaction). The rate of corrosion is highly dependent on the environment, in which the carbon steels are used. In solving a particular corrosion problem, a dramatic change in attack rate can often be attained by altering the corrosive environment. Since corrosion is such a multifaceted phenomenon, it is generally useful to attempt to categorize the various types based upon the environmental basis, such as atmospheric corrosion, aqueous corrosion, corrosion in soils, concrete, and boilers etc.

2. 4.Types of corrosion reactions

There is a distinction between the types of corrosion which normally describes the interaction between the metal and the environment, and forms of corrosion which describes the phenomenological appearance.

Chemical reaction – It is a typical chemical corrosion reaction which occurs at high temperatures, where the metal reacts with hot gases and forms an oxide layer.

Metallo-physical reaction – The example of the Metallo -physical reaction is the embrittlement caused by hydrogen which diffuses into the metal, possibly leading to failure of a component. Embrittlement can be the result of a careless manufacturing process. It can also be initiated by corrosion processes (metal dissolution) such as corrosion-induced hydrogen assisted cracking.

<u>Electro-chemical reaction</u> – It is the most common type of corrosion reaction. The reaction implies an electrical exchange by way of electrons in the metal and ions in a conducting electrolyte, such as a water film on its surface.

The overall reaction can be separated in two partial reactions namely (i) metal dissolution, also known as oxidation or anodic reaction (Fe = Fe2+ + 2 e-), and (ii) reduction or cathodic reaction, a reaction mainly involving the oxygen present in the air with water (O2 + 2 H2O + 4 e- = 4 OH). These two partial reactions can take place on the metal surface in a fairly homogenous distribution leading to uniform attack or can occur locally and separately, leading to localized forms of corrosion such as pitting corrosion.

The mechanism and the electrochemical nature of the corrosion reaction define the necessary requirements for corrosion to take place (Fig 2.5.). These requirements are (i) a conducting metal, (ii) an electrolyte (a thin moisture film on the surface is already sufficient), and (iii) oxygen for the cathodic reaction.

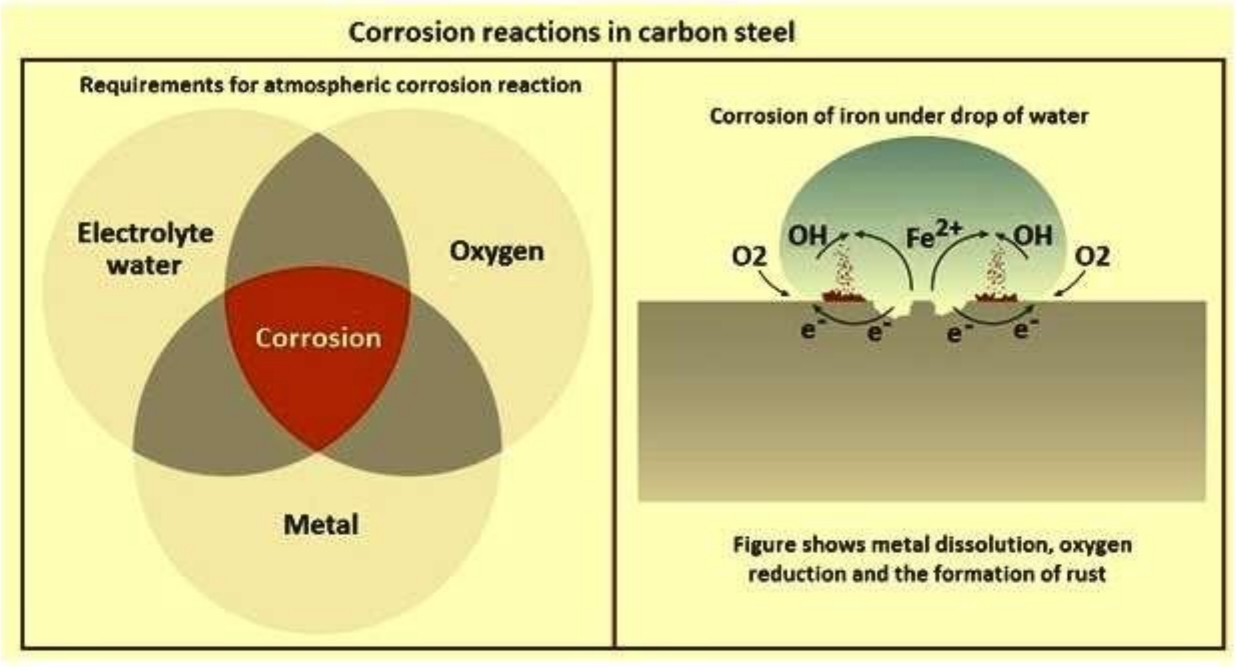


Fig 2.3. Corrosion reactions in carbon steel

Fig 2.3 also shows the basic corrosion mechanism of iron under a drop of water. Both iron dissolution and oxygen reduction reactions take place with slight separation on the surface, and their products (Fe ions and OH ions) react in the water drop to form red rust (corrosion product). The simple model of the corrosion reaction of Fig 2.4. explains many forms of corrosion and also to deduct measures to reduce corrosion. By preventing or slowing down one of the partial reactions, the overall corrosion rate can be reduced.

2.5.Forms of corrosion

There are six main forms of corrosion (Fig 2.4). These are (i) uniform corrosion / shallow pitting corrosion, (ii) pitting corrosion, (iii) environmental induced cracking, (iv) crevice corrosion, (v) inter-crystalline (inter-granular) corrosion, and (vi) galvanic corrosion.

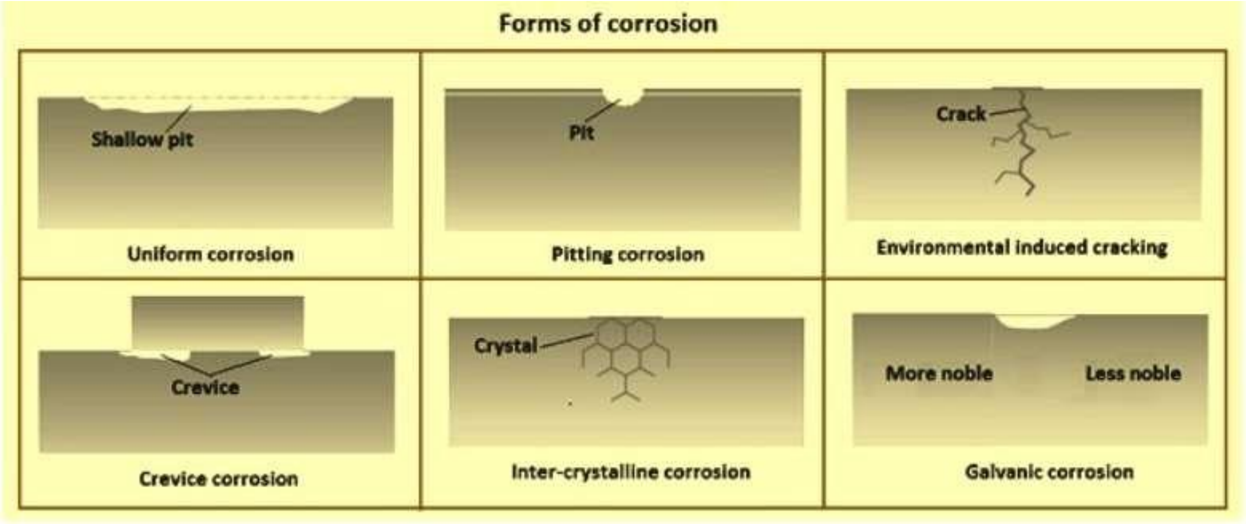


Fig 2.4. Forms of corrosion

2.5.1 Uniform corrosion/ shallow pitting corrosion – Uniform

corrosion is a form of corrosion where the surface is removed almost evenly. The partial reactions (metal dissolution and oxygen reduction) are statistically distributed over the surface, leading to more or less homogenous dissolution of the metal and uniform formation of corrosion products (e.g. red rust on carbon steel). The extent of this form of corrosion can normally

be well estimated on the basis of previous experience. The rate of corrosion is normally given in micrometers per year. Using these average values, it is possible to calculate the life expectancy of a component, and thus to enhance its life expectancy by increasing its thickness.Uniform corrosion takes place on unprotected carbon steel and on zinc-coated steel under atmospheric conditions. In reality, purely homogenous corrosion attack is unlikely to take place. There are always areas, especially on complex steel parts, which corrode faster than others leading to a more or less rough surface with an irregular covering of corrosion products.

2.5.2 Pitting corrosion – Pitting corrosion is a localized form of corrosion which leads to the creation of small holes or pits in the steel. This form of corrosion is mainly found on passive metals mainly which owe their corrosion resistance to a thin oxide layer on the surface with a thickness of only a few nanometers. The corrosion initiating process starts with a local break-down of the passive layer. Local corrosive attack can be initiated on steels, for example, by chloride ions. Pitting corrosion can be quite problematic. Whereas uniform corrosion can be seen clearly on the surface, pitting corrosion often appears only as small pinholes on the surface. The amount of material removed below the pinholes is generally unknown, as hidden cavities can form, making pitting corrosion more difficult to detect and predict. Technically, there is no reasonable way to control pitting corrosion. This form of corrosion must be excluded right from the start through design considerations and use of the right material.

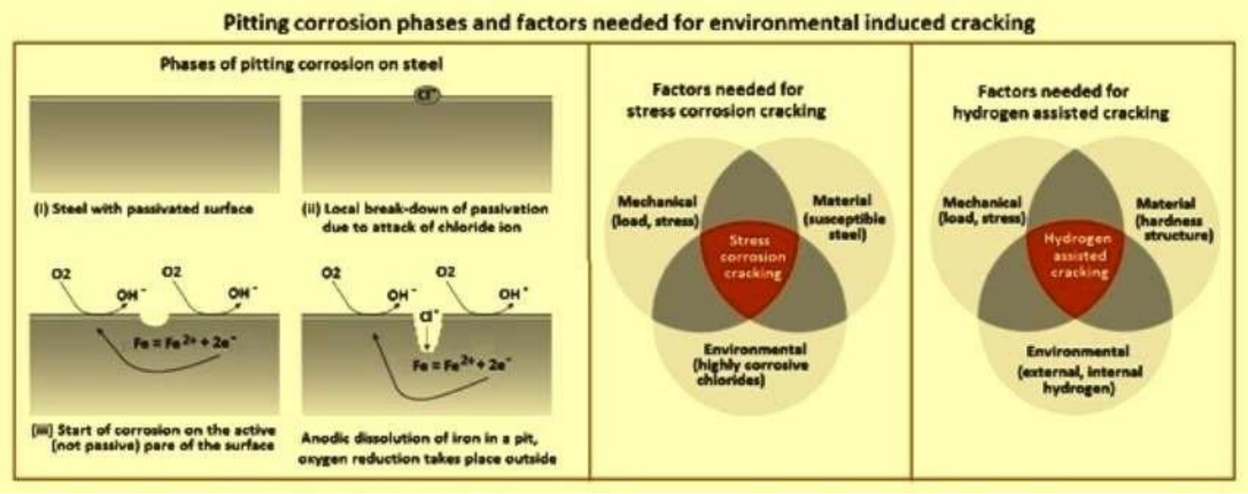


Fig 2.5. Pitting corrosion phases and factors needed for environmental induced cracking

2.5.3. Environmental induced cracking – There are two types of environmental induced cracking. These are (i) stress corrosion cracking, and (ii) hydrogen-assisted cracking (Fig 2.5).

2.5.4. Stress corrosion cracking is a combined mechanical and electrochemical corrosion process which results in cracking of certain materials. It can lead to unexpected sudden brittle failure of normally ductile metals subjected to stress levels well below their yield strength. Internal stresses in a material can be sufficient to initiate an attack of stress corrosion cracking.

2.5.5. Stress corrosion cracking is not simply an overlapping of corrosion and mechanical stresses, but can be understood as an auto-catalytic, selfaccelerating process leading to high metal dissolution rates (anodic reaction). Initially, a small pit is formed and develops into a crack due to the applied or residual stress in the material. The crack formation opens up a new active (non-passive) metal surface, which again corrodes very easily. This leads to further crack propagation and again to the exposure of new highly active metal surfaces in the crack. Metal dissolution in the

crack advances rapidly until mechanical failure occurs. Stress corrosion cracking is a highly specific form of corrosion which occurs only when the following three different requirements are fulfilled at the same time (Fig 4) namely (i) mechanical (load, stress), (ii) material (susceptible alloy, e.g. steel), and (iii) environment (highly corrosive, chlorides). It is well known that certain grades of steel can suffer stress corrosion cracking in harsh environments such as indoor swimming pools. In most of these cases, corrosion is initiated by chlorides attacking the passive layer.

2.5.6. Hydrogen-assisted cracking is caused by the diffusion of hydrogen atoms into the steel. The presence of hydrogen in the lattice weakens the mechanical integrity of the metal and leads to crack growth and brittle fracture at stress levels below the yield strength. Like stress corrosion cracking, it can lead to sudden failure of steel parts without any detectable warning signs. In common applications, hydrogen damage is usually only relevant for high-strength steel with a tensile strength of around 1 MPa or higher.As for the stress corrosion cracking, three different conditions (Fig 4) are to be present at the same time. These are (i) mechanical (load, stress), (ii) material (hardness structure), (iii) environmental (external hydrogen, internal hydrogen).

The source of hydrogen can be the production process such as steelmaking, pickling and electro-galvanizing (primary hydrogen). A secondary source can be the hydrogen formed during a corrosion process. During the corrosion process, hydrogen is formed and diffuses into the material. This hydrogen intake leads to a decrease in the toughness or ductility of the steel.

2.5.7. Crevice corrosion – Crevice corrosion refers to corrosion occurring in cracks or crevices formed between the two surfaces (made from the same metal, different metals or even a metal and a non-metal). This type of corrosion is initiated by the restricted entrance of oxygen from the air by diffusion into the crevice area leading to different concentrations of dissolved oxygen in the common electrolyte (the so-called aeration cell). Again, the two partial reactions take place on different parts of the surface. Oxygen reduction takes place in the outer areas with higher oxygen concentrations easily accessible by the surrounding air, whereas the anodic metal dissolution occurs in the crevice area resulting in localized attack (e.g. pitting). It can also occur under washers or gaskets, when the entry of water underneath is not prevented.

2.5.8. There are lower and upper limits to the size of a crevice in which corrosion can be induced. If the crevice is too tight, no electrolyte for corrosion is introduced. If the crevice is too wide to reduce oxygen entrance, the aeration cell and consequently different concentrations of oxygen cannot develop. However, the critical crevice width depends on several factors such as the type of steels involved, the corroding environment and wet / dry cycles.

2.5.9. Inter-crystalline (inter-granular) corrosion – Inter-crystalline corrosion is a special form of localized corrosion, where the corrosive attack takes place in a quite narrow path preferentially along the grain boundaries in the metal structure. The most common effect of this form of corrosion is a rapid mechanical disintegration (loss of ductility) of the material. Normally it can be prevented by using the right material and the production process. A well-known example is the so called sensitization of stainless steel. When certain grades of this material are kept at a temperature within the range of 500 deg C to 800 deg C for a considerable time, e.g. during a welding process, chromium-rich carbides are formed, resulting in chromium depletion at the grain boundaries. Consequently, the grain boundaries possess a lower degree of corrosion resistance than the residual material, leading to localized corrosive attack.

2.5.10. Galvanic (contact) corrosion – Galvanic corrosion refers to corrosion damage where two dissimilar metals have an electrically conducting connection and are in contact with a common corrosive electrolyte. In the electro-chemical model of corrosion, one of the two partial reactions (anodic metal dissolution and cathodic oxygen reduction) takes place almost exclusively on one metal. Normally, the less noble metal is dissolved (anodic metal dissolution), whereas the more noble part is not attacked by corrosion (serves only as the cathode for oxygen reduction). Where galvanic corrosion takes place, the rate of corrosion of the less noble metal is higher than it is in a free corroding environment without contact to another metal.Using thermodynamic data and taking common experience gained in typical applications into account, it is possible to predict which material combinations are affected by galvanic corrosion. A positive example of the galvanic corrosion phenomenon is the way zinc protects carbon steels and low-alloyed steels. Zinc is the less noble metal which actively protects steel by being corroded itself

2.5.11. Atmospheric corrosion of carbon steel

The corrosion of carbon steel in the atmosphere and in many aqueous environments is best understood from a film formation and breakdown standpoint. It is an inescapable fact that iron in the presence of oxygen and / or water is thermodynamically unstable with respect to its oxides. Thus, the question is never whether the steel is going to corrode, but rather at what rate. In the absence of film formation and with a constant environment, one is to expect the oxidation rate to be constant. On the other hand, if the corrosion product film which forms isolates the steel from the corrosive environment, then a zero corrosion rate is expected after the initial film formation period. A tightly adherent film which permits only diffusion transfer of the reactants is characterized by a corrosion rate which decreases with the square root of the exposure time. Since the above idealizations are rarely encountered in the corrosion of carbon steels, it is obvious that other factors which tend to disrupt stable film formation are operative. These factors can be external, such as erosion by wind or rain, or they can be internal to the film itself, such as stresses caused by the different specific volumes of metal and oxide.The corrosion of iron in the atmosphere proceeds by the formation of hydrated oxides. The half-cell reactions can be expressed by the equations (i) $1/2O_2 + H_2O + 2e = 2(OH)-$ (cathodic), and (ii) $Fe = (Fe)^{2+} + 2e$ (anodic). Further reactions can then occur, such as (i) $(Fe)^{2+} + 2(OH)- = Fe(OH)_2$, and (ii) $2Fe(OH)_2 + H_2O + 1/2O_2 = 2Fe(OH)_3$.

The hydrated oxides can lose water during dry periods and revert to the anhydrous ferrous and ferric oxides. In addition, a layer of magnetite (Fe3O4) or FeO·Fe2O3 often forms between the layers of iron oxide (FeO) and hematite (Fe2O3). Actually, the various oxides and hydroxides of iron form a rather complicated system of compounds. The compound FeOOH has been found to exist in three different crystal forms plus an amorphous form. The occurrence of the various oxide types is dependent on pH, availability of oxygen, various atmospheric pollutants, and the composition of the carbon steel, as in weathering steels containing copper and phosphorus. The actual nature of the corrosion film is important since FeO and FeOOH seem to be more adherent than Fe3O4 and Fe2O3, and hence more likely to slow the corrosive attack, but the higher oxides and oxy-hydroxides are more prone to spallation.

Since there is a substantial variation in the corrosion rates of carbon steels in different atmospheric environments (rural, urban, industrial, and marine etc.), it is only logical to determine which of the factors that contribute to these differences. Although the prediction of corrosivity is not possible, it appears that humidity, temperature, and the levels of chloride, sulphate, and probably other atmospheric pollutants present each exert an influence on the corrosion rate of carbon steels.

2.6. Effects of humidity and atmospheric pollutants

Since atmospheric corrosion is an electrolytic process, the presence of an electrolyte is needed. This does not mean that the steel surface is to be awash with water. In fact, a very thin absorbed film of water is all that is needed. During an actual exposure, the steel spends some portion of the time awash with water because of rain or splashing and a portion of the time covered with a thin adsorbed water film. The portion of time spent covered with the thin water film depends quite strongly or relative humidity at the exposure locations. Various studies have shown that time of wetness, although an important factor cannot be considered in isolation when estimating corrosion rates. An example of this fact is shown in Fig 5, in which the weight gain of iron is plotted as a function of relative humidity for an exposure of 55 days in an atmosphere containing 0.01 % sulphur dioxide. In the lower right-hand corner of Fig 5 is the measured corrosion rate for iron exposed for the same time in a sulphur dioxide free environment at 99 % relative humidity.

Another feature of interest is the apparent existence of a critical humidity level below which the corrosion rate is small. The critical humidity in a sulphur dioxide containing environment is around 60 %. This behaviour contrasts with that of steel in contact with particles of sea salt, as shown in Fig 2.5. In Fig 2.6, the corrosion rate shows a steady increase with increasing humidity. Although there is a scarcity of data, it seems reasonable that oxides of nitrogen in the environment also show an accelerating effect on the corrosion of carbon steel. Indeed, any gaseous atmospheric constituent capable of strong electrolytic activity is to be suspected as being capable of increasing the corrosion rate of carbon steel. In short, it can be seen that there is an accelerating effect of chloride ions on the atmospheric corrosion,

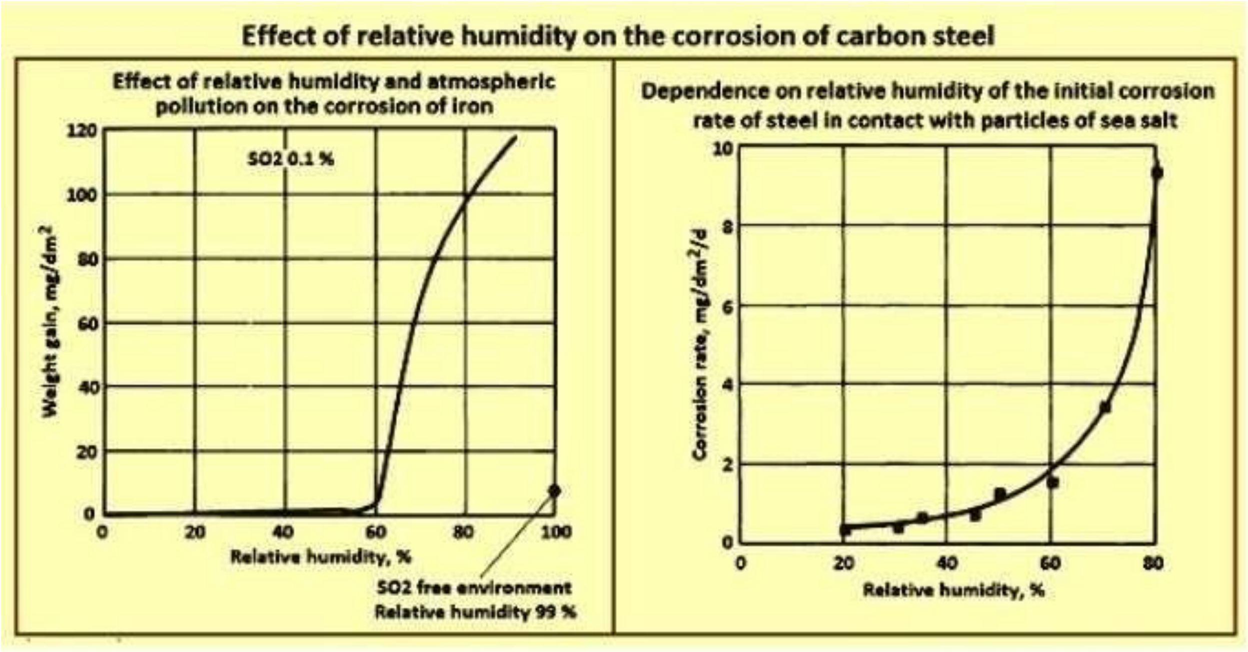


Fig 2.6 Effect of relative humidity on the corrosion of C steels

2.7.Corrosion protection of carbon steels

Corrosion protection (Fig.2. 7) is often a necessary consideration in selecting carbon steel for a given structural application. Corrosion can reduce the loadcarrying capacity of a component either by generally reducing its size (cross section) or by pitting, which not only reduces the effective cross section in the pitted region but also introduces stress raisers which can initiate cracks. Obviously, any measure which reduces or eliminates corrosion extends the life of a component and increases its reliability. The economics, environmental conditions, degree of protection needed for the projected life of the part, consequences of unexpected service failure, and importance of appearance are the main factors which determine not only whether a steel part needs to be protected against corrosion but also the most effective and economic method of achieving that protection.

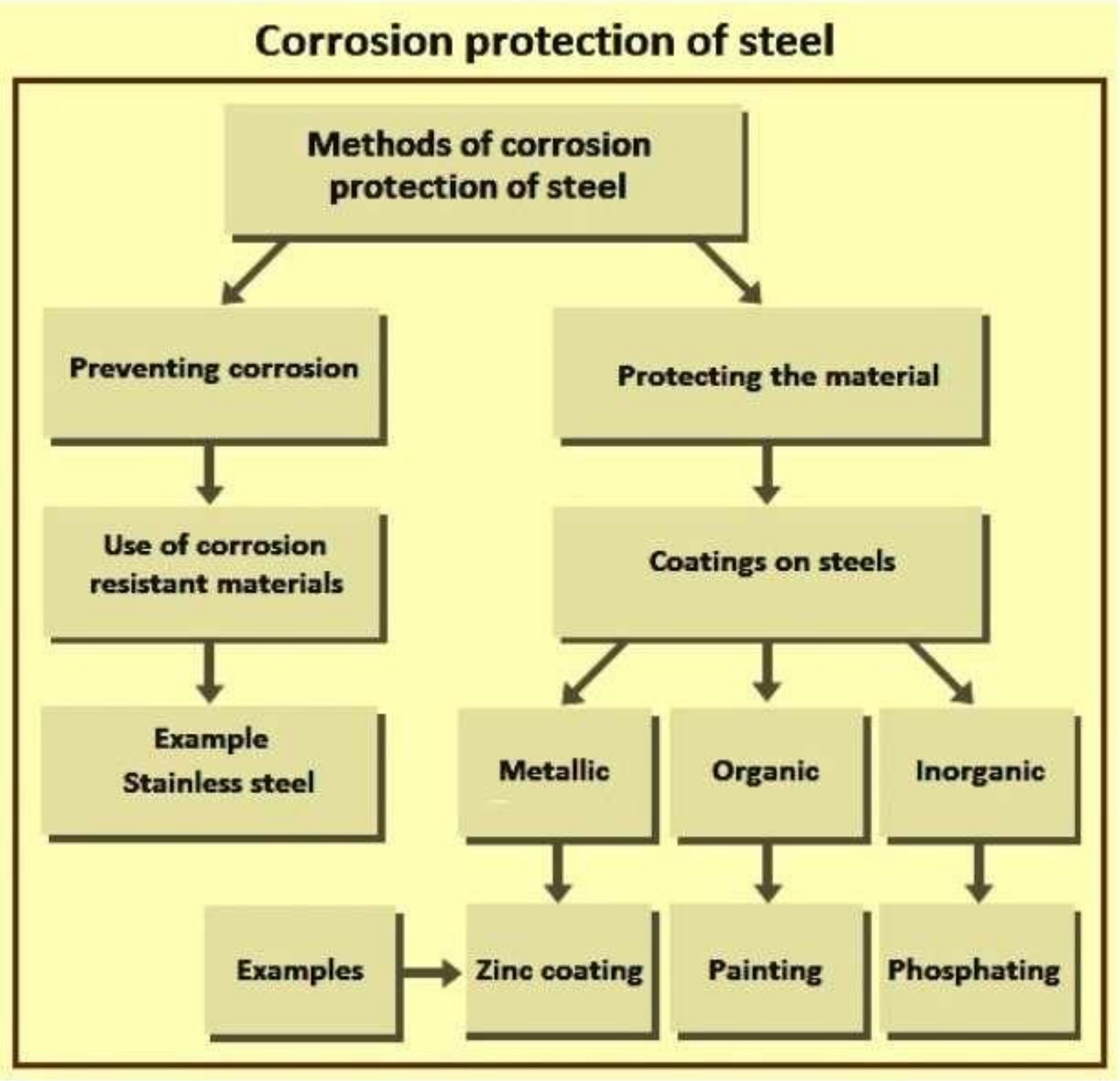


Fig 2.7 Corrosion protection of steel

There are two methods of minimizing the corrosion of steels. The first is to separate the reacting phases, and the second is to reduce the reactivity of the reacting phases. The separation of the reacting phases can be accomplished by metallic, inorganic or organic coatings, and film-forming inhibitors. Reactivity can be reduced by alloying, anodic or cathodic protection, and chemical treatment of the environment. Some methods of protection combine two or more forms.

In most environments, the corrosion rate of carbon steel is typically around 20 micrometers per year in a rural outdoor atmosphere and rising to more than 100 micrometers per year in coastal environments. It is normally too high for a satisfactory application. The product design does not generally account for a base material loss. Hence, cost-efficient corrosion protection solutions are necessary for carbon steel. In alkaline surroundings, however, steel normally remain stable. This explains why, for example, reinforcement bars made of carbon steel are already very well protected against corrosion in the alkaline environment of the surrounding concrete.

2.8 .Coating protection of carbon steel

Several types of coatings are applied to enhance the corrosion resistance of carbon steels. Coating practices range from oiling for low-cost, temporary protection to vapour deposition for long-term corrosion, heat, and wear resistance. For economic reasons, the desired degree of protection is to be determined before a coating is selected.

Effective temporary protection during shipment or storage can be obtained by coating the carbon steel with mineral oil, solvents combined with inhibitors, emulsions of petroleum-based coatings, or waxes. These types of coatings are applied after acid pickling or between coating sequences. These coatings are not expected to provide long-term corrosion protection.

Surface preparation is important for all coating processes. Any oxide on the steel surface is to be removed by pickling or blasting. Degreasing is necessary after oxide removal or when the steel has been given a temporary coating, and it can be accomplished by several means. Ideally, the first step in the coating process is to be started immediately after cleaning.

2.9. Coating processes

These are used to apply coatings of zinc, aluminum, lead, tin, and some alloys of these metals to carbon steels. The hot-dip process consists of immersing the steel in a molten bath of the coating metal.

2.9.1. Zinc coating or galvanizing is a good choice for the corrosion protection of carbon steel. Several suitable processes are available for the application of zinc coatings on steel. The corrosion rate of zinc is more than ten times lower than that of steel, at around 0.5 micrometers per year in rural/urban atmospheres and rising to up to around 5 micrometers per year in coastal environments. The low corrosion rates are the result of the formation of stable layers of corrosion products containing carbonates (from CO2 in the air) and chlorides (if they are present in the atmosphere). Conditions where the formation of such insoluble corrosion products is not possible leads to much higher corrosion rates, limit the suitability of zinc as a protective coating. These include permanently wet conditions or exposure to high concentrations of industrial pollutants such as sulphur dioxide. In these environments, soluble corrosion products are formed preferentially and they can be washed off by rainfall. In addition to decreased corrosion rates, zinc also provides cathodic or sacrificial protection to the underlying steel. Where scratching, chipping or any other damage to the zinc coating exposes the steel, a special form of galvanic corrosion takes place. Zinc, being a less noble metal than steel, corrodes preferentially, thereby helping to keep the exposed steel surface protected.

Zinc coatings are consumed quite homogeneously during atmospheric corrosion. Accordingly, in a given application, doubling of the coating thickness normally also doubles the time until the zinc is consumed and red rust on the steel substrate occurs. Zinc is not stable in alkaline environments and is readily attacked in solutions with a pH-value of 10 or higher.

The method of zinc coatings are electro galvanizing, hot dip galvanizing, and Sherardizing. Sherardizing is a method of zinc coating utilizing a thermal diffusion process.

2.9.2. Aluminum hot-dip coatings (aluminizing) provide carbon steels with resistance to both corrosion and heat. In many environments, aluminum protects steel galvanically in much same way as zinc. Zinc-aluminum and aluminum-zinc alloys are also applied to steel by hot dipping. Heating aluminized steel results in the formation of an iron-aluminum inter-metallic compound which resists oxidation at temperatures upto around 800 deg C. Aluminized steel is often used where heat resistance is needed, for example, in automotive exhaust systems.

Hot-dip tin coatings provide a decorative and non-toxic barrier coating. Tin does not galvanically protect the steel substrate. For this reason, lacquers or other organic coatings are often used to fill pores in the tin coating and provide enhanced barrier protection.

Hot-dip lead coatings are sometimes used on steel which is exposed to sulphuric acid fumes or other aggressive chemical environments. Terne plate, a lead-tin alloy coating, gives more protection than pure lead coatings and is solderable.

Electroplated coatings are applied to steel for corrosion resistance, appearance, solderability, or other special requirements. A wide variety of materials are electroplated on steel, including zinc, aluminum, chromium, copper, cadmium, tin, and nickel. Multi-layer coatings can also be applied by electroplating. An example is the copper-nickel-chromium plating system used for bright automotive trim.

2.9.3.Clad metals – Carbon steels can be bonded to more corrosion-resistant materials, such as copper and stainless steels, by cold roll bonding, hot roll bonding, hot pressing, explosion bonding, and extrusion bonding. The resulting lamellar composite material has specific properties not obtainable in a single material.

2.9.4..Thermal spray coatings – These coatings provide effective long-term corrosion protection for steels in a wide range of corrosive environments. They are applied by one of several processes, including wire flame spraying, powder flame spraying, and electric arc spraying. Zinc, aluminum, and zinc-aluminum alloys are the most common coating materials applied by thermal spray techniques. Austenitic stainless steels, aluminum bronzes, and MCrAlY (where M = Co, Ni or Co/Ni) coating materials have also been used for specific applications. For maximum corrosion resistance, thermal sprayed coatings are sealed with an organic top coat. Thermal spray coatings are frequently used for corrosion protection in marine applications.

2.9.5.Vapour-deposited coatings – These are sometimes used for the protection of carbon steel, although the cost of such coatings can be very high. In vapour deposition, whether it is physical vapour deposition or chemical vapour deposition, the coating material is transported to the substrate in the form of individual atoms or molecules. A wide range of coating materials can be applied by vapour deposition. If applied to a sufficient thickness, the coating is essentially pore-free and dense, thus providing excellent barrier protection. A well-known application for vapour-deposited coatings on steel is ion vapour deposited aluminum coatings on steel aircraft and aerospace components.

2.9.6. Phosphate or chromate conversion coatings – These are used to enhance the corrosion resistance of steels. By themselves, they provide slightly better corrosion resistance than bare steel. More often, they are used in conjunction with another coating system. Conversion coatings are applied after hot-dip galvanizing and provide good corrosion protection when top coated with an organic coating system.

In the phosphating, steel is dipped into an acidic solution containing metal (Zn, Fe) phosphate salts. The solution reacts with the steel surface forming a microcrystalline layer of phosphates on the surface. This results in a rough surface with excellent oil-retaining properties.

2.9.7.Organic coatings – These coating consists of paints, which are used more often for corrosion protection of steels than any other type of coating. Properly applied, the paints provide excellent protection at a relatively low cost. A wide variety of coating materials and application methods are available for the applications of the paints.

2.9.8.Ceramic coatings – Ceramic coatings used to protect steel include silicate cements and porcelain enamels. Monolithic cement linings provide good resistance to chemicals and thermal insulation. They can be applied by casting or spraying. Porcelain enamels are glass coatings which are fused onto the steel surface at or above 425 deg C to provide a glassy coating with good corrosion resistance and high hardness. The composition of the enamel can be varied to provide desired properties, such as improved resistance to alkalis.

2.9.10. Other nonmetallic materials coatings – These coatings are sometimes used as coatings or linings for steel in corrosion applications. These include rubbers (both natural and synthetic) and other elastomers and such plastic materials as epoxies, phenolics, and vinyls. A wide variety of properties and resistances to specific environments are available. Rubber linings have been used for many years in steel storage tanks for hydrochloric acid and sulphuric acid. Plastic linings are employed for plating tanks and similar applications.

2.9.11. Multi-layer coatings – When the corrosion protection provided by the metallic coating is not sufficient, then the steel can be further protected by additional coatings, mainly organic paint with or without metallic flakes. An example of this is the multi-layer coating on fasteners consisting of an electroplated Zn alloy coating with an additional organic top coat.

2.10 Carbon steel

Carbon steel is an iron-carbon alloy, which contains up to 2.1 wt.% carbon. For carbon steels, there is no minimum specified content of other alloying elements, however, they often contain manganese. The maximum manganese, silicon and copper content should be less than 1.65 wt.%, 0.6 wt.% and 0.6 wt.%, respectively.

2.10.1 Types of carbon steel and their properties

Carbon steel can be classified into three categories according to its carbon content: low-carbon steel (or mild-carbon steel), medium-carbon steel and high-carbon steel. Their carbon content, microstructure and properties compare as follows:

Carbon content (wt.%)	Microstructure	Properties	Examples	
Low-carbon steel	< 0.25	Ferrite, pearlite	Low hardness and cost. High ductility, toughness, machinability and weldability	AISI 304, ASTM A815, AISI 316L
Medium-carbon steel	0.25 – 0.60	Martensite	Low hardenability, medium strength, ductility and toughness	AISI 409, ASTM A29, SCM435
Highcarbon steel	0.60 – 1.25	Pearlite	High hardness, strength, low ductility	AISI 440C, EN 10088-3

2.10.2. Low-carbon steel

Low-carbon steel is the most widely used form of carbon steel. These steels usually have a carbon content of less than 0.25 wt.%. They cannot be hardened by heat treatment (to form martensite) so this is usually achieved by cold work.

Carbon steels are usually relatively soft and have low strength. They do, however, have high ductility, making them excellent for machining, welding and low cost.

High-strength, low-alloy steels (HSLA) are also often classified as lowcarbon steels, however, also contain other elements such as copper, nickel, vanadium and molybdenum. Combined, these comprise up to 10 wt.% of the steel content. High-strength, low-alloy steels, as the name suggests, have higher strengths, which is achieved by heat treatment. They also retain ductility, making them easily formable and machinable. HSLA are more resistant to corrosion than plain low-carbon steels.

2.10.3. Medium-carbon steel

Medium-carbon steel has a carbon content of 0.25 – 0.60 wt.% and a manganese content of 0.60 – 1.65 wt.%. The mechanical properties of this steel are improved via heat treatment involving austenitising followed by quenching and tempering, giving them a martensitic microstructure.

Heat treatment can only be performed on very thin sections, however, additional alloying elements, such as chromium, molybdenum and nickel, can be added to improve the steels ability to be heat treated and, thus, hardened.

Hardened medium-carbon steels have greater strength than low-carbon steels, however, this comes at the expense of ductility and toughness.

2.10.11. High-carbon steel

High-carbon steel has a carbon content of 0.60– 1.25 wt.% and a manganese content of 0.30 – 0.90 wt.%. It has the highest hardness and toughness of the carbon steels and the lowest ductility. High-carbon steels are very wear-resistant as a result of the fact that they are almost always hardened and tempered.

Tool steels and die steels are types of high-carbon steels, which contain additional alloying elements including chromium, vanadium, molybdenum and tungsten. The addition of these elements results in the very hard wear-resistant steel, which is a result of the formation of carbide compounds such as tungsten carbide (WC).

2.11. Production and processing

Carbon steel can be produced from recycled steel, virgin steel or a combination of both. Virgin steel is made by combining iron ore, coke (produced by heating coal in the absence of air) and lime in a blast furnace at around 1650 °C. The molten iron extracted from the iron ore is enriched with carbon from the burning coke. The remaining impurities combine with the lime to form slag, which floats on top of the molten metal where it can be extracted.

The resulting molten steel contains roughly 4 wt.% carbon. This carbon content is then reduced to the desired amount in a process called decarburisation. This is achieved by passing oxygen through the melt, which oxidises the carbon in the steel, producing carbon monoxide and carbon dioxide.

2.12. Examples & Applications

2.12.1. Low-carbon steel

Low carbon steels are often used in automobile body components, structural shapes (I-beams, channel and angle iron), pipes, construction and bridge components, and food cans.

2.12.2.Medium-carbon steel

As a result of their high strength, resistance to wear and toughness, mediumcarbon steels are often used for railway tracks, train wheels, crankshafts, and gears and machinery parts requiring this combination of properties.

2.12.3. High-carbon steel

Due to their high wear-resistance and hardness, high-carbon steels are used in cutting tools, springs high strength wire and dies.

2.13. Comparison of properties and applications of different grades

Examples, properties, and applications of the various carbon steels are compared in the following table.

Type	**AISI/ASTM name**	**Carbon content (wt.%)**	**Tensile strength (MPa)**	**Yield strength (MPa)**	**Ductility (% elongation in 50 mm)**	**Applications**
Low	1010	0.10	325	180	28	Automobile panels, nails, wire
Low	1020	0.20	380	205	25	Pipes, structural steel, sheet steel
Low	A36	0.29	400	220	23	Structural

Low	A516 Grade 70	0.31	485	260	21	Low-temperature pressure vessels
Medium	1030	0.27 – 0.34	460	325	12	Machinery parts, gears, shifts, axles, bolts
Medium	1040	0.37 – 0.44	620	415	25	Crankshafts, couplings, cold headed parts.
High	1080	0.75 – 0.88	924	440	12	Music wire
High	1095	0.90 – 1.04	665	380	10	Springs, cutting tools

Chapter Three

Experimental Work

Chapter Three
Experimental Work

3.1 Introduction

This chapter focuses on the materials and equipment's that are used in this study. It also includes the description of the procedures of the coating process, beginning with specimen's preparation to be coated. This chapter also presents the tests for: corrosion, wear, roughness, XRD, SEM and optical microscopy. Figure (3.2) shows the block diagram of the experimental procedures.

3.2 Materials

The materials which are used in this study as follows:

3.2.1 Low Carbon Steel

Spectrometer inspection has been performed on the selected alloy in order to give certainty to the elements content and obtain the full chemical composition of the alloy. This inspection has been performed in General Company of AL Askandriya for Mechanical Industries by using a computerized spectrometer. This inspection is accomplished by put a metal specimen with dimensions of (100,80,2) mm length, width and thickness respectively in the inspection chamber, then the application of electric spark will lead to the chemical reaction on the metal surface and from the obtained spectrum of each element the linked computer can identify the percentage of each element through the reverse signals, which are reversed from the photo cells of each elements in the equipment and so the list of element content will be given in the monitor of communicated computer. Table3.1 shows the Chemical composition of the used specimen.

Table 3.1: Chemical composition of the used specimen.

Element	**Mn**	**Si**	**C**	**Cr**	**Fe**
Wt %	**0.54**	**0.15**	**0.13**	**0.06**	**Balance**

3.2.2 Nickel Electrode

The Nickel used is in the rectangular form with dimensions of (100, 80, 2) mm length, width and thickness respectively with high purity 99.99 %wt.

3.2.3 Powders

1- The powders which were used to coat the carbon steel is:

-Alumina

The type of alumina used in this work was α-Al_2O_3 which has a melting point 2000ºC and particle size 80 nm with white color. Figure 3.1 shows the X-ray diffraction pattern of Al_2O_3.

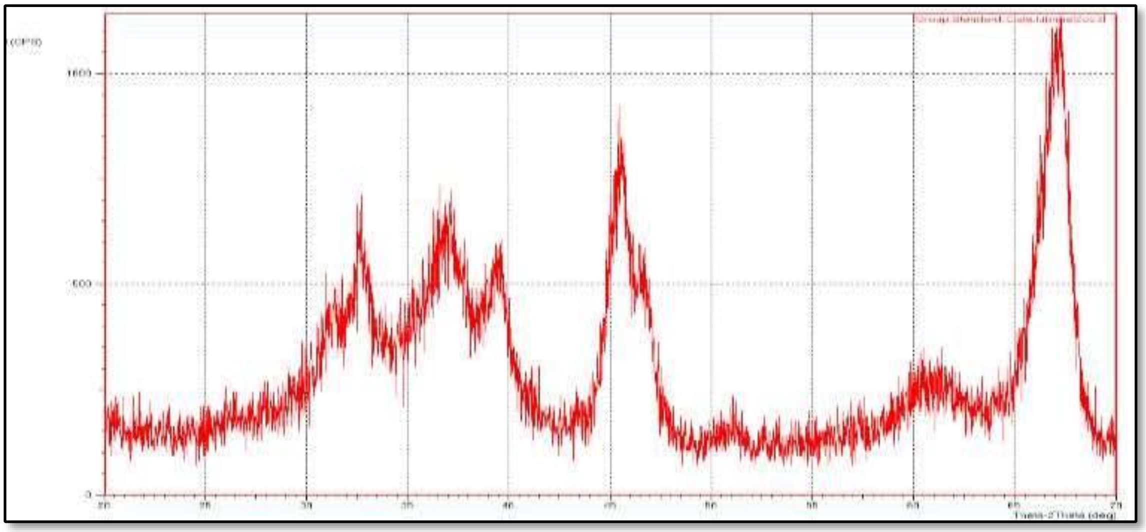


Fig. 3.1: The pattern of XRD for α-Al_2O_3.

Table 3.2: Illustrate chemical materials used in preparing electroplating solutions.

material	**Formula**	**Purity %**	**Origin**
nickel sulfamate	$Ni(NH_2SO_3)_2$	99.9	Sigma-Aldrich Co.LLC.
Boric acid	H_3BO_3	99.77	Floka
nickel chloride	$NiCl_2$	99.57	Sigma-Aldrich Co.LLC
Alumina powder	Al_2O_3	99.67%	BDH Chemicals Ltd., Poole England.

3.2.4 Sodium Hydroxide (NaOH)

It is a solved and chemical cleaning material from company (Sigma-Aldrich Co.LLC.) which is used to clean the specimen from dust and oil before coating with concentration (10 wt.%).

3.2.5 Hydrochloric Acid (HCl)

It is a solved and chemical cleaning material from company (Sigma-Aldrich Co.LLC.) which is used to clean the specimen from greases and impurities before coating with concentration (30%).

3.2.6 Emery Paper

Emery paper no. (220, 240, 400, 600, 800, 1000, and 1200) which is used to prepare the specimen for plating.

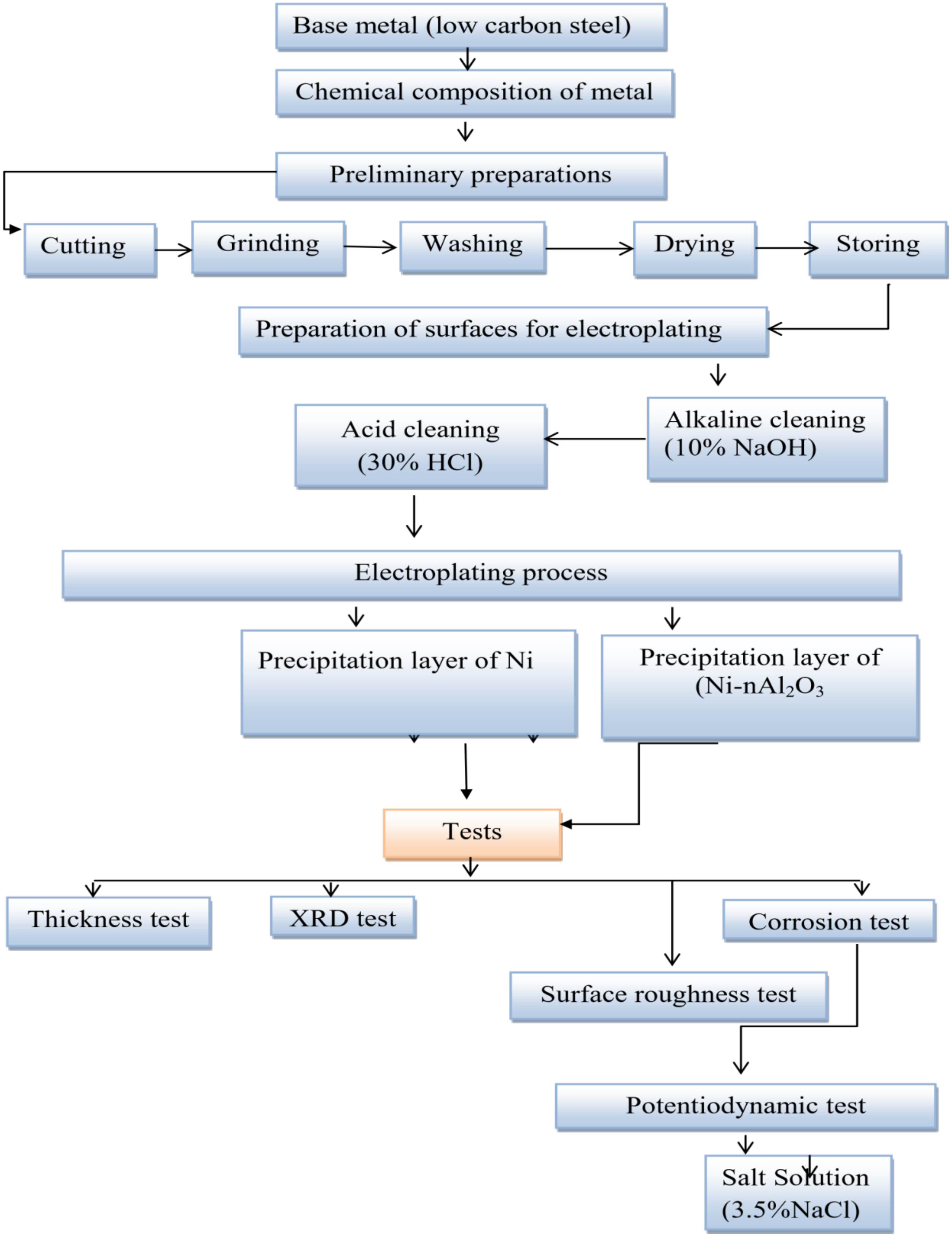


Fig. (3.2): Shows the block diagram of the experimental procedure.

3.3 Surface Preparation for Plating

Surface specimens have been prepared as following:

1-All surface was fully grinding by using (Carbide paper grit silicon), that was gradually as following (220, 240, 400, 600, 800, 1000, 1200) and this process was done by using (MP-2B grinder polisher) as shown in Fig. (3.3).

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

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

Fig.(3.3): Shows grinder polisher

3.3.1 Alkaline Cleaning

The specimens were immersion in alkaline solutions material (10wt % NaOH) and for two minutes period at (75ºC) temperature by stirring the solutions at (2000) r.p.m. 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 (20-25 °C) and for two minutes 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 a sensitive electrical scale German type (Sartorius Bp 3015 g,d=0.1mg) and after taking weight records of the samples and measuring the dimension they were placed in glass storage (desiccator) which contains particles of silca gel for absorbing wetness to protect the specimens from corrosion.

3.4 Equipment for Electroplating Process

3.4.1 The Device Used In Plating Process

The electroplating process was carried out by plating device which contains numerous of baths which are parallel rectangles baths with dimension of (29x21x18) cm length, width and height respectively and made by polyethylene which can be found in the college of materials engineering laboratories at Babylon University. The device contains an electrical heater and every bath is equipped with thermostat to determine the dissolving's temperature, processing the dissolving material by using magnetic stirrer which is fixed in the device holder. Figure (3.3) shows the electrochemical cell used in this work

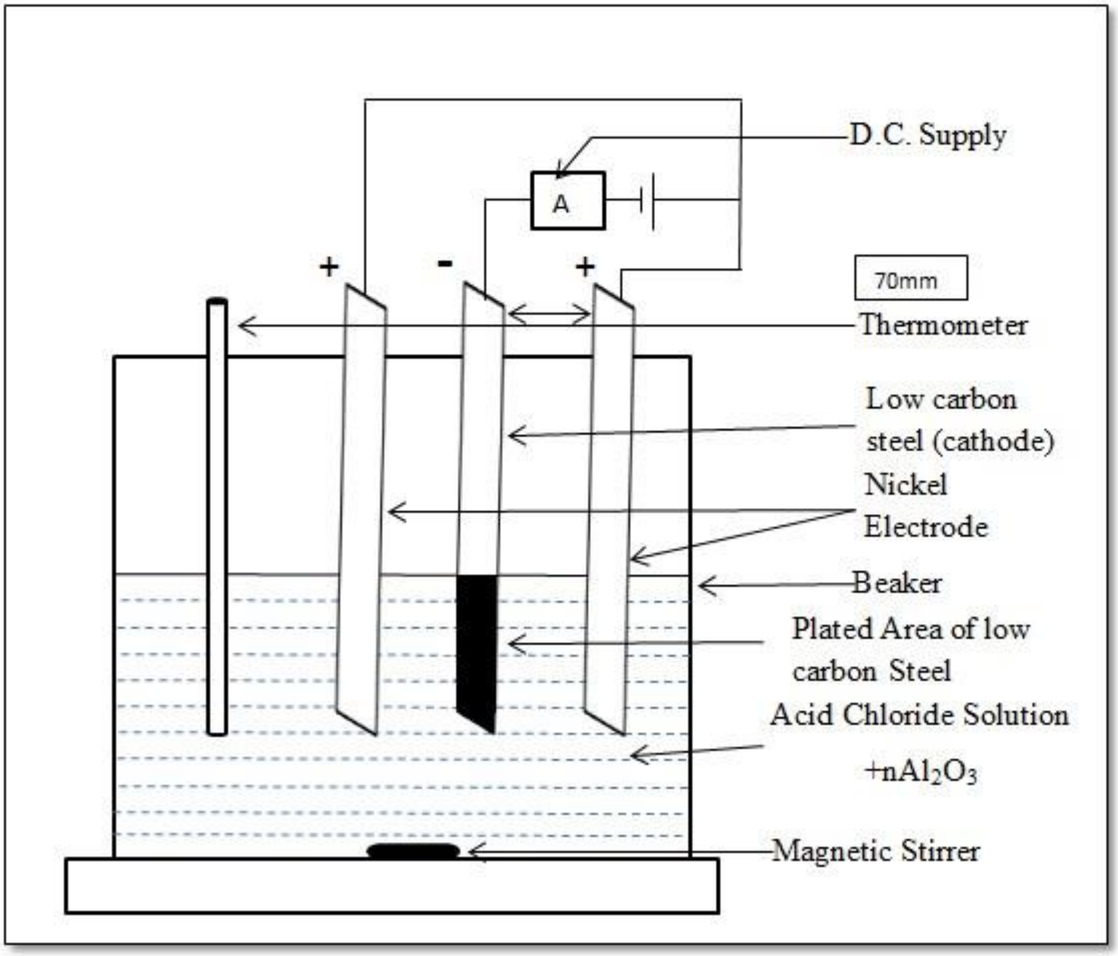


Fig. (3.3): Schematic the used electrochemical cell.

The device contains a power supply with density of (0-6) A, as for the given voltages range (0-20) V. DC supplier was attached with the steel specimen to the negative side, while the positive side was connected with Ni electrodes by a wire.

The distance between the positive electrode and the negative electrode is (70mm). PH is measured by using the device (PH/TDs meter).

3.4.2 Compositions of Electroplating Bath

Many experimental works are carried out to investigate the feasibility of simultaneous Ni, (Ni-n Al_2O_3) by electroplating process to reach demand percentage for the layer coated.

All solutions were prepared with distilled water and chemical dissolution that occur under acid conditions.

Electro-deposition of nickel–Al_2O_3 composites was achieved in a characteristic watts bath on the low carbon steel. A nickel sulfamate electrolyte was used by the subsequent constituent: 300 g/l nickel sulfamate Ni $(NH_2SO_3)_2$, 30 g/l boric acid, 5 g/l nickel chloride ($NiCl_2$), 0.2 g/l sodium laurel sulfate (wetting agent), and 0.1 g/l coumarin (smoothing mediator). Completely of the bath constituents were varied in one liter of distilled water. The bath constituent is like to that of Guglielmi and extra lucrative plating bath. It was originate that extreme quantities of the surfactant (coumarin) could reason effervescing of the plating bath as Al_2O_3 particulates were supplemented and, consequently, least amounts of preserving were added.

Afterward the plating bath was performed, Al_2O_3 powder was supplemented. Powders were co-deposited in the nickel matrix to transport for nickel - Al_2O_3 composite coating. Aluminum oxide powder got from BDH Chemicals Ltd., Poole England, great purity, 10 µm max. size are added in amounts 8, 16, and 24 g/liter.

3.4.3 Electroplating Process

The electroplating process was tested by placing the solutions in plating bath (after measuring its pH) and fixing the positive electrodes and preferred plating samples materials. The bath was prepared with its current density and the required voltages at the required temperature for plating process in order to avoid changes in concentricity of the achieved solution causes by evaporation losses the addition of ratio (2-5%) volume of the solution during one day of work for the purpose of ensuring continually of the plating process with its average. The time period of placing the samples in plating bath and current density is what determines the thickness of the plating layer. After the required period process of deposition, certain thickness of the plating from the metal is done. The specimens are extracted out of the plating bath washed with distilled water , alcohol and dried with hot air current thereafter weight measurement are taken and then stored samples in glass desiccator to get rid of the wetness which causes corrosion.

The work piece was located straight in the bath at one cm underneath the level of solution and fixed steeply in the motivated tributary of the electrodeposition bath.

The bath was retained at 50 ℃ and PH ≅ 4.0. It was originate that deposition current density nearly 4.5 amps / dm^2 gave the greatest outcomes, and this current density was stable for all coatings in this research. To summary Table 3.3 illustrates the main experiments parameters for characteristic coating deposition.

Table 3.3: Main Dispensation Limitations for a characteristic electro chemical co deposition coating

Coating Bath	Nickel Sulfamate
The particulate size~	25 µm max.
Particulate filling (Al_2O_3)	16,24, and 32 g/l
Temperature	50 °C
PH	4.0 – 4.1
Current Density	4.5 A/dm^2
Moving Speed	400 rpm

Coating Time	3 hrs.

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

For this work, the measurement was done by two ways:

-The first method is carried out by coating thickness gage Type (TT 260) used eddy current method figure(3.5) ,The accuracy of the device (0.1μm±) . In this way measurements were taken in the three places to provide averaged sample thickness.

Fig. (3.5): Shows the device of thickness measuring.

-The second method depends on optical microscope.

In the present research the measurement of coating thickness was almost (1224μm).

3.5.2 X-Ray Diffraction Test

The coatings were examined for the identification of the crystalline phase. The phase composition of coating was identified with X-ray generator with copper Kα radiation ($\lambda = 1.5406$ A^o) and a nickel filter. The diffractometer scanning speed was adjusted to 6^o per minute and the range of the diffraction angle (2θ^o) was (20^o-80^o) and step time 0.6 sec. The image plate XRD system worked with (target: Cu) radiation operating at 40.0 KV and 30mA. Figure (3.6) shows the x-ray machine used was a SHIMADZU LabX XRD-6000, Japan.

Figure (3.6): Shows x-ray machine used (SHIMADZU Lab XRD-6000).

3.5.3 Energy Dispersive X-Ray (EDX)

Fig. (3.7) showed Energy Dispersive X-ray model (Inspect S50 FEI company), as an analytical method was used to determine the concentrations for layer coating Ni-n -Al_2O_3.

Fig.(3.7): Shows energy dispersive x-ray.

3.5.4 Scanning Electron Microscopy Test (SEM)

The morphology of surface deposits was observed by a scanning electron microscopy model (Inspect S50 FEI Company). Fig. (3.8) shows the scanning electron microscopy which carried out different magnification for electroplating layer.

Fig. (3.8): Shows the scanning electron microscopy used.

3.5.5 Micro Structure Test

This test has been accomplished on cross section of specimens, grinding steps which were performed with different silicon carbide paper ranging from 220 to 1200 grid. The polishing was carried out by polishing cloths using diamond past. These specimens were then cleaned with water and alcohol and dried, micro structure of specimens was observed with magnification rag of 40X. An optical microscope is used to examine the surface of the coating. It is also equipped with a camera to obtain image.

Test was carried out for three specimens which are Ni, (Ni-n Al_2O_3). Figure (3.9) shows the optical microscope.

Fig.(3.9): Optical microscope machine.

3.5.6 Electrochemical Tests

Electrochemical tests were used in this work to determine corrosion parameters which involved E_{corr}, i_{corr} and corrosion rate, by using Tafel Extrapolation Technique.

3.5.6.1 Electrolytic Solution

The electrolyte employed in this investigation was sodium chloride (3.5%NaCl).

3.5.6.2 Polarization Curves

Electrochemical corrosion cell was constructed according to American Society for Testing and Materials (ASTM G5) as shown in figure(3.10). It is composed of spherical glass which has necks to fit cell electrode, working electrode (steel), and saturated calomel electrode (SCE) has potential of (241 mV) as a reference electrode to measure electrode potential connected to the cell by a salt bridge and a luggin-habber capillary. It is kept in such a way that the working electrode and it tip remained at a distance of about 2 mm to avoid ohmic drop. The temperature of corrosion test was 25°C. Platinum electrode (counter electrode) was used for conducting polarization experiment. Also a neck for inlet gas was provided.

Polarization experiments were performed in Winking M Lab 200. The polarization curves were plotted. Both corrosion current density (i_{corr}) and corrosion potential were calculated by Tafel Extrapolation Technique. The electrochemical system used shown in Fig. (3.10).

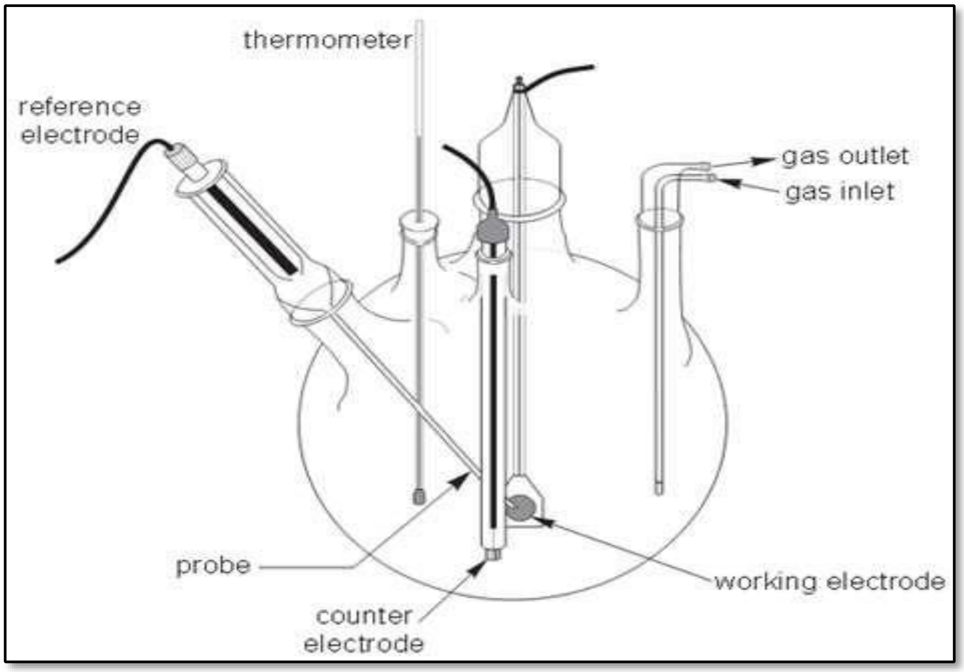


Figure (3.10): Schematic electrochemical cell.

The polarization curves were measured potentiostatcally at a scan rate 0.4 mV/s from an open circuit potential of (200 mV) below the open circuit potential and the scan was continued up to (200 mV) above the open circuit potential**.**

Corrosion rate measurement is obtained by using the following equation:

$$\text{Corrosion Rate (mpy)} = \frac{0.13 i_{coor} \, (E.W.)}{A.\rho} \quad \text{-------------} \ (3.1)$$

where:

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

A = area (cm^2).

ρ = density (g/cm^3).

0.13 = metric and time conversion factor. icorr

= current density ($\mu A/cm^2$).

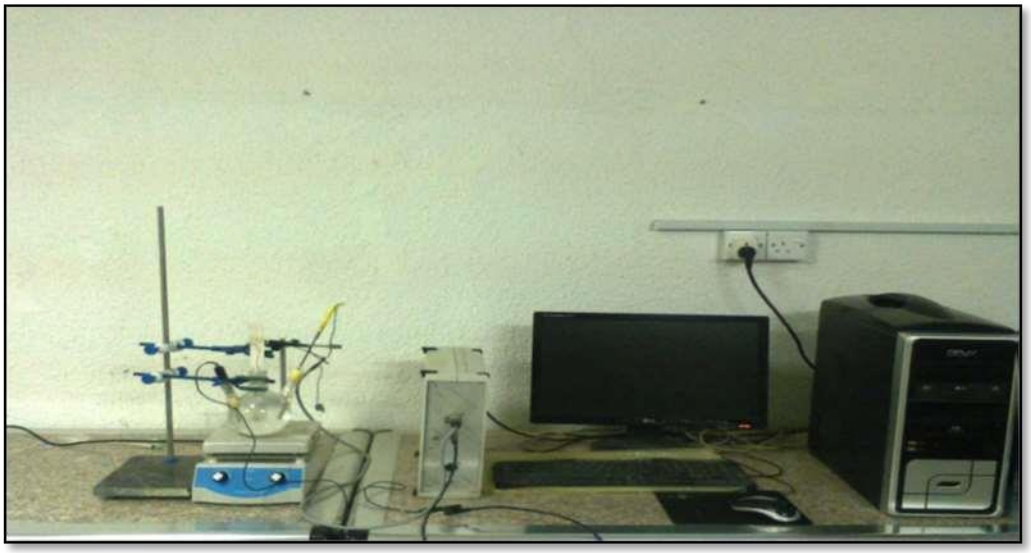


Fig. (3.11): Shows the electrochemical system.

Chapter Four
Results and Discussion

Chapter Four

Results and Discussion

4.1 Introduction

Experimental results have been demonstrated in this chapter which involve XRD, corrosion test results in 3.5 wt. NaCl solutions, linear polarization method, mechanical properties .

4.2 X-ray Analysis

Composite Ni–Al_2O_3 coatings that are produced by the method of electroplating were examined by XRD, as presented in Figs. (4.1). XRD analyses showed that the particles of Al_2O_3 did not react with the Ni. In this situation, particles of alumina (Al_2O_3) were distributed in Ni coating homogenously. Also it should take the consideration that the particle content is not the only factor which has obvious effect on the mechanical properties such as hardness.

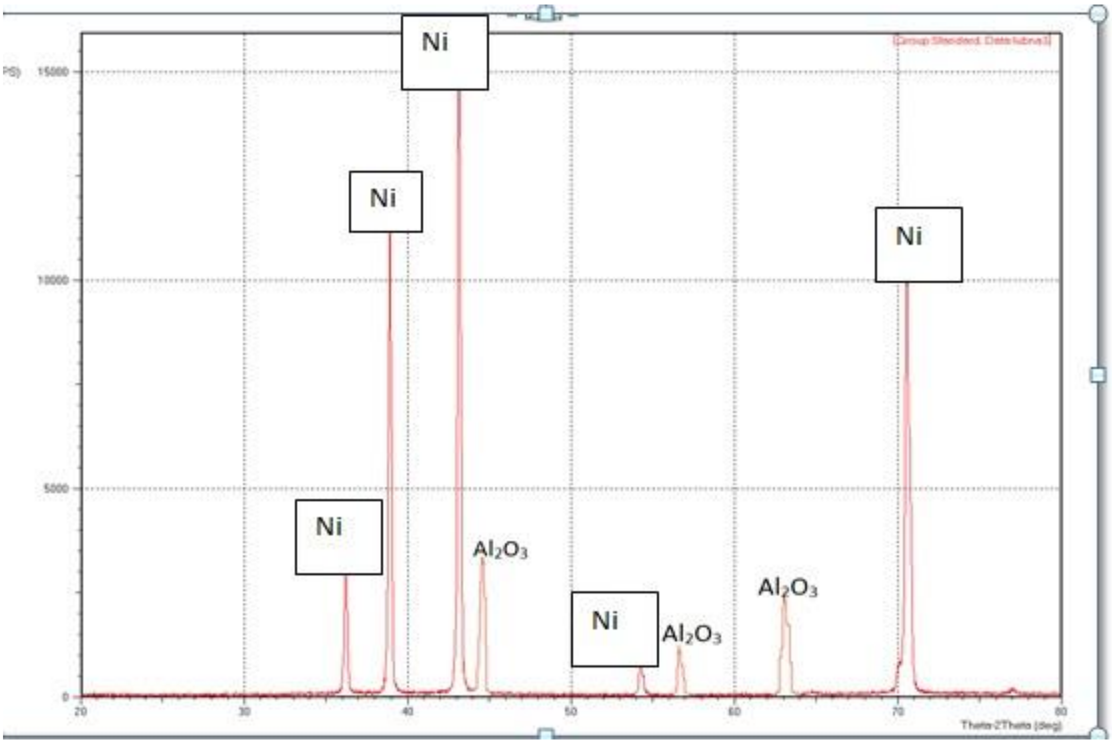


Fig.(4.1): XRD patterns of Ni – 32 g/l Al_2O_3

composite samples.

4.3 Microstructural Examination

Figures (4.2) show the SEM micrographs of the surface coating at different magnification. It is obviously shown in SEM images of the alumina reinforced nickel composite coatings. As shown from the micrographs that there are large agglomerations of alumina particles. The increase in agglomerations of fine particles alumina results from the lowest particle size. The SEM study that was performed on the agglomerates reveals that they are composed of the ceramic particles. It shows that the crystals that did not apparently define in shape with some coarse but tightly packed. The surface crystals feature was not particularly smooth. This notice shows that nickel – electroplating of metals in the solution of acid chloride without any additives may not be resist the corrosion strongly. The little course structure might be as a result of the absence of leveling agents in the acid solution. The presence of this type of nickel plating will of course depend on the conditions under which the experiments are carried out. The amorphous crystal structure of the plated sample surface that observe could be as a result of the acid solution poor throwing power.

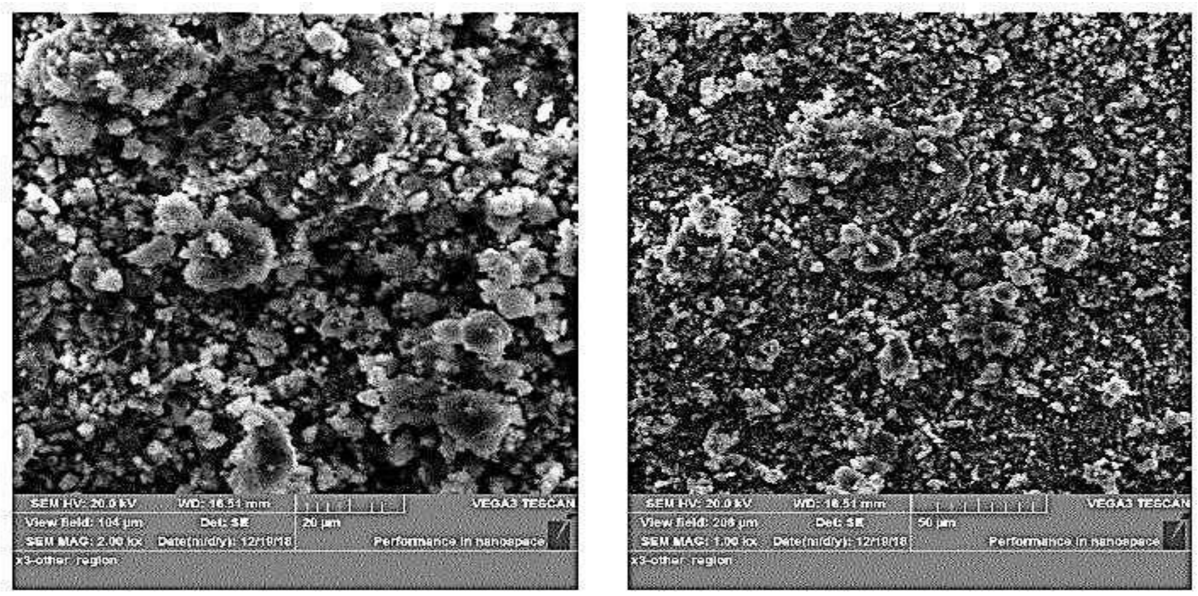


Fig.(4.2): SEM of Ni-32 g/l Al_2O_3 coating at different magnification.

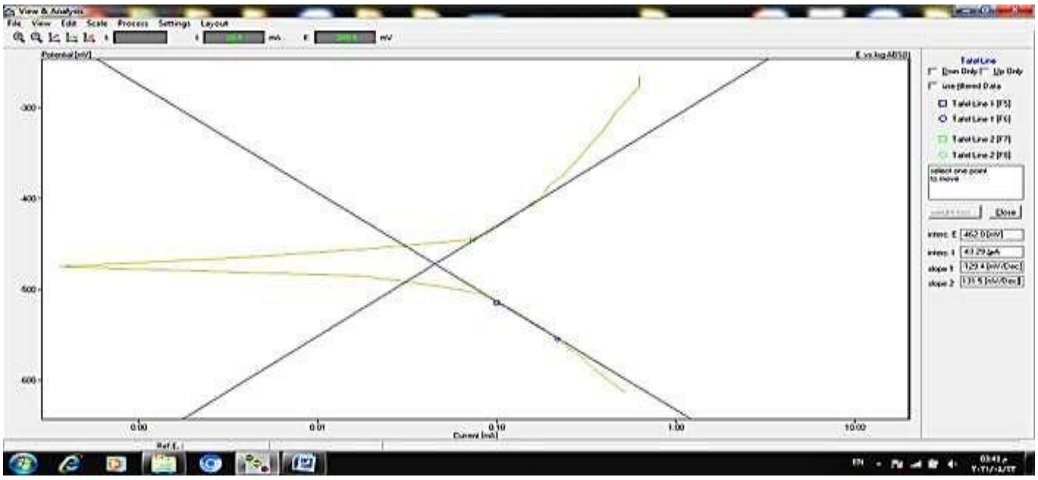
4.4 Coating Thickness

Average coating thickness has been measured by computerized optical microscope at magnification 40X. The measured thickness of the coating is not the same for samples, where Ni coating has the smallest thickness of 16 µm while the largest thickness is for (Ni- nAl_2O_3) coating of 21 µm that may be due to the particle size of the samples where for Al_2O_3 is 10 µm.

4.5 Corrosion Behavior

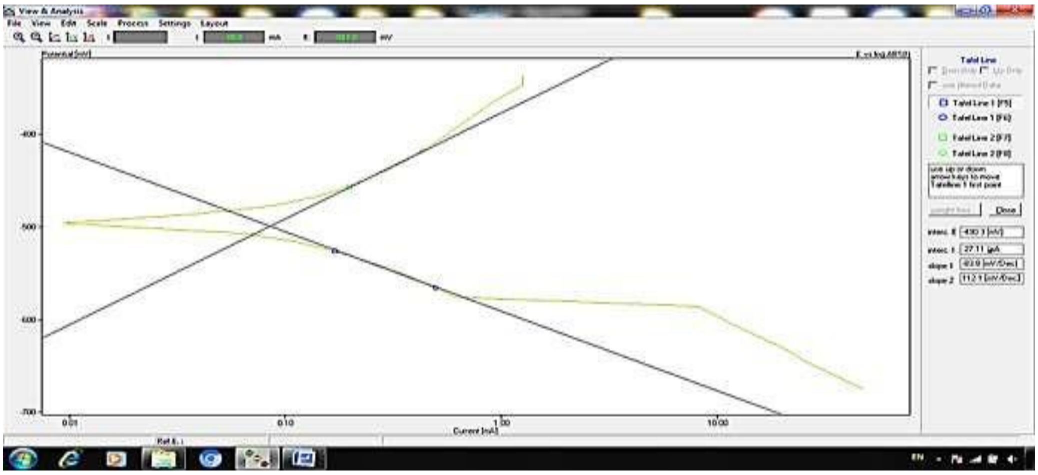
The corrosion behavior of coating was analyzed by studies of the polarization and the curves of the polarization are shown in figure (4.3) at 3.5 wt. NaCl. When compared the Ni coating with(Ni-Al_2O_3). In case of coated specimens, the corrosion potential of coating samples shifts towards more positive direction, improving corrosion resistance of the coating. The current density of the corrosion is an important parameter that used to evaluate the corrosion reaction kinetic. The difference between polarization curves is mainly due to corrosion current density and it indicates that corrosion reactions takes place continuously at the interface and the coating bonding state at the substrate keeps changing during the corrosion test.

The composite coating were used for decreasing the corrosion rate and providing good protection to alloy substrate from corrosion. As results efficiency increasing for all samples with comparison of carbon steel. Fig (4.3) were illustrated the polarization curves for carbon steel with and without composite coating using (16,24,and 32g/l) Al_2O_3 particulates.



intersc. E 462.0 [mV]
intersc. I 43.29 µA
slope 1 129.4 [mV/Dec]
slope 2 131.5 [mV/Dec]

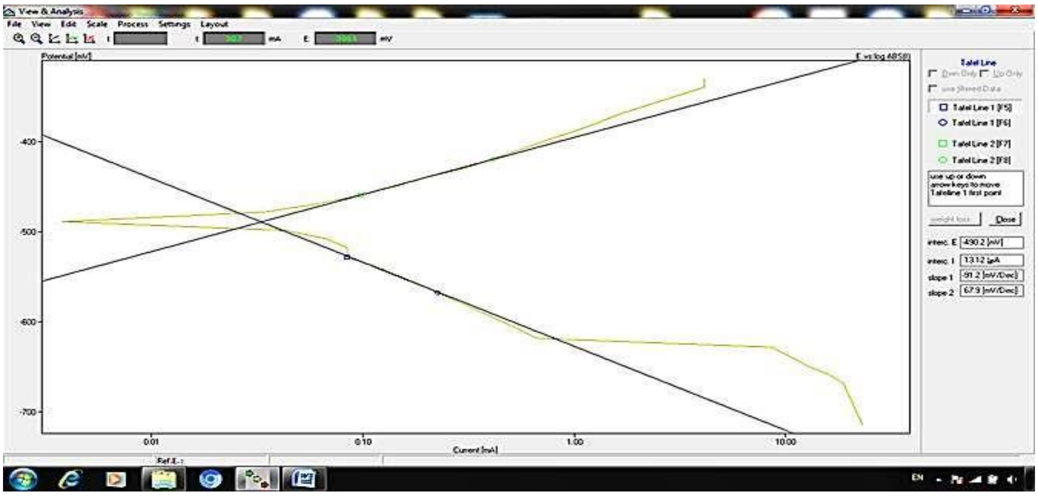
A- Carbon steel without coating



use up or down arrow keys to move Tafelline 1 first point

interc. E -430.1 [mV]
interc. I 27.11 µA
slope 1 -83.0 [mV/Dec]
slope 2 112.1 [mV/Dec]

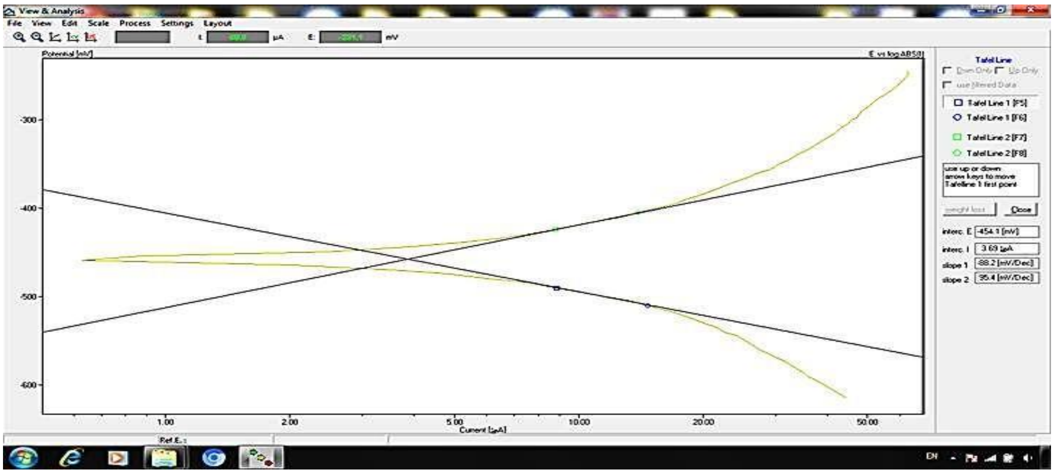
B:Carbon steel with Ni electro plating coating



use up or down arrow keys to move Tafelline 1 first point

interc. E -490.2 [mV]
interc. I 13.12 µA
slope 1 -91.2 [mV/Dec]
slope 2 67.9 [mV/Dec]

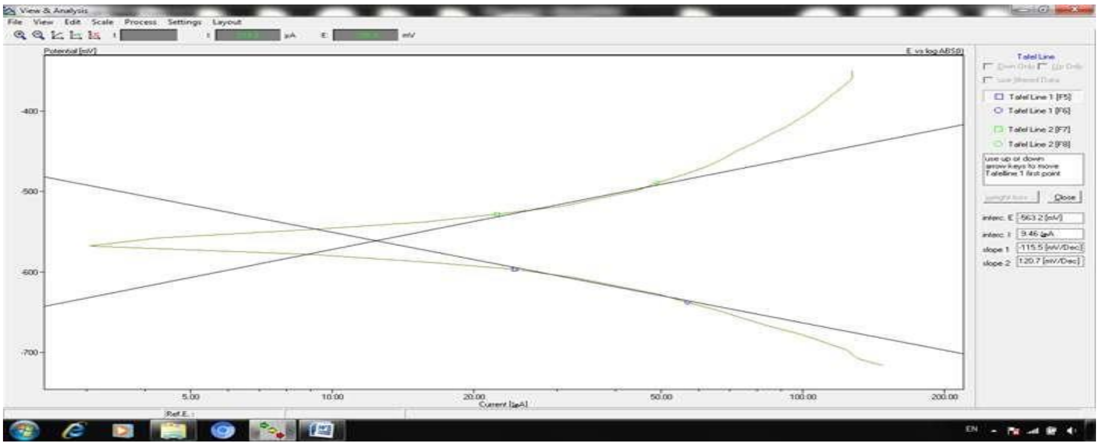
C- Carbon steel with Ni $–Al_2O_3$ composite coating (16 g/L)



use up or down arrow keys to move Tafelline 1 first point

interc. E -454.1 [mV]
interc. I 3.69 µA
slope 1 -88.2 [mV/Dec]
slope 2 95.4 [mV/Dec]

D- Carbon steel with Ni $–Al_2O_3$ composite coating (24 g/L)



use up or down arrow keys to move Tafelline 1 first point

intec. E -563.2 [mV]
intec. I 9.46 µA
slope 1 -115.5 [mV/Dec]
slope 2 120.7 [mV/Dec]

E- Carbon steel with Ni –Al_2O_3 composite coating (32 g/L)

Fig (4. 3) Polarization curve for carbon Steel in 3.5% NaCl with and without composite coating (0, 16, 24, and 32g/L) samples

The outcomes of the electro-chemical test for nickel –Al_2O_3 composite coating are exposed in Table 4.1 that mention corrosion potential, corrosion current, and corrosion rate. It is detected that by cumulative aluminum oxide particulates in the coating , corrosion rate is decreased and the potential is shifted to more active regions. The corrosion current density (*icorrosion*) and the corrosion potential (*E corrosion*) considered from the intersection of the Cathodic and anodic Tafel curves by consuming the extra polarization technique which is shortened in Table (4.1). It could be noticed that there is an important shift toward lower current densities of the polarization curves for specimens with different aluminum oxide particulates amount in the coating solution. For example carbon steel corrosion current density is around 42.31**(A/cm^2)** while for Ni electroplating 29.32 **(A/cm^2) , for** 16% Al_2O_3 is about 15.81 **(A/cm^2)** and for 24% Al_2O_3 is about 5.98 **(A/cm^2)** and for 32% Al_2O_3 is about 10 **(A/cm^2)**. Further, it can be seen the most improvement percentage is 91% when the concentration of aluminum particulates in coating solution is 24 g/liter. These outcomes specify stability behavior of nickel- Al_2O_3 coating layer. This layer is able to change the surface properties of carbon steel without affecting the base alloy.

Table 4.1: Corrosion potential(Ecorr.), Corr. Current density(μA/ cm^2), and corrosion rate(mpy) for carbon steel with and without coatings in . 3.5%NaCl

Parameters	**Concentration v/v%**	***i*corr (A/cm^2)**	**Ecorr (mV)**	**Corrosion Rate (mm/y)**	**IE%**
Alloy in 3.5% NaCl solution with composite coating	Base	42.31	462.0	0.4329	----
	Ni electroplating	29.32	490.3	0.2711	37%
	16 g/L	15.18	490.2	0.1312	70%
	24 g/L	5.98	454.1	0.0369	91%
	32 g/L	10.4	563.2	0.0946	78%

Then since the aluminum oxide particulates are so vigorous consequently aluminum oxide created simply round the particulates and render them unbiased. Hence , they act as unbiased particulates in corrosive ambient and distribute homogeneously in the coating.

4.6 Surface Roughness Test

It is obvious from Table(4.2) that the addition of micro particles Al_2O_3 did not affect the surface roughness of Ni coating. Surface roughness can effect a components chemical and physical stability. Surface that have to stand up to hostile environments(temperature, humidity, or hostile chemicals) must be as smooth as possible in order to present the minimum surface area for attack, and to have as few defects or weak spots as possible. Excess surface roughness can lead to unacceptably high levels of frictional heating, causing damage and even failure.

Table(4.2) Surface roughness results

Type of Coating	Surface Roughness Results(µm)	Average(µm)
Ni	0.83	0.83
	0.84	
	0.82	
Ni-16 g/lAl_2O_3	0.83	0.84
Ni-24 g/lAl2O3	0.85	
Ni-32 g/lAl_2O_3	0.84	

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 Al_2O_3 increase, the properties such as coating thickness, and surface roughness increased.

2- When the percentage addition of Al_2O_3 increase the corrosion rate decreased from (37%) to (91%) in salt solution.

4- Thickness of coating layer (Ni- Al_2O_3) increase with percentage additive of alumina 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 TiO_2 and ZrO_2 instead Al_2O_3

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.

REFERENCE

Reference

[1] M.G.Fontana, *"**Corrosion Engineering**"*,3rd ed.,McGraw-Hill,1986.

[2] Mohammed Abdul Mahdi Hussein*,*" ***Development of Electroplating Zn-Ni Base System for Aerospace Industries***", Ph.D., thesis ,Department of Materials Engineering University of Babylon, 2007.

[3] R. Winston Revie and Herbert H. Uhlig, *"**corrosion and corrosion control,**"* 4rdedition , John Wiley & Sons, Inc. , 2008.

[4] Wilhelmus Maria Bos," ***Prediction of coating durability - Early detection using electrochemical methods,***" Gildeprint drukkerijen B.V.,Enschede, The Netherlands,2008.

[5] Ahmed Fadhil Hamza Al-Gibouri " ***Protect of Carbon Steel, Aluminum And Copper Against Corrosion By Using New Organic inhibitors*** " A Thesis of the Master Materials Engineering, 2007**.**

[6] Sastri V. S**.**," ***Green corrosion inhibitors: theory and practice.*** " Vol.

10. John Wiley & Sons, (2012).

[7] Dugstad A., Lunde L., and Nesic S., *"**Control of internal corrosion in multi-phase oil and gas pipelines.**"* In Proceedings of the conference Prevention of Pipeline Corrosion, Gulf Publishing Co. (1994).

[8] Ahmad Z. *"**Principles of corrosion engineering and corrosion control**"* handbook Published in the Butterworth-Heinemann/IChemE Series, (2006).

[9] Revie R. W., *"**Oil and gas pipelines: Integrity and safety handbook.**"*

John Wiley & Sons, (2015).

[10] Nabaa Sattar AL-Kafaji '' ***Study the characteristic of metal-ceramic coating for low carbon steel*** '' A Thesis of the Master Materials Engineering, 2009.

[11] P. A. Schweitzer, P. E *"**Metallic Materials Physical, Mechanical, and Corrosion Properties**"* Marcel Dekker, Inc,2003.

[12] S.A.Bradford, *" **corrosion control,**"* 2rd editio ,2001.

[13] Groysman, A**.,** ***"Corrosion in systems for storage and transportation of petroleum products and biofuels: identification, monitoring and solutions"***. Springer Science & Business Media, (2014).

[14] Callister, William D. ***"Fundamentals of materials science and engineering: an interactive e-text."***, John Wiley & Sons, Inc., (2001).

[15] Aliofkhazraei M., ***"Developments in Corrosion Protection."*** handbook, Publisher: InTech, (2014).

[16] Askeland, D.R., Fulay, P.P. and Wright, W.J. ***''The science and engineering of materials''*** 6th edition., 2010. Cengage Learning Inc.

[17] Callister, William D. ***" Materials science and engineering: an introduction."***, John Wiley & Sons, Inc., 7 th edition PP.650,2007.

[18] P. R. Roberge ***,"Corrosion Engineering Principles and Practice,"*** McGraw-Hill Companies, Inc.2008.

[19] B. D. Craig, R. A. Lane and D. H. Rose ***,"Corrosion Preventionand Control,"*** Alion Science and Technology, September,2006.

[20] A. Groysman, ***"Corrosion for Everybody,"*** Springer Science &Business Media, P.36,PP.143, 2009.

[21] P. R. Roberge***," Handbook of Corrosion Engineering,"*** McGraw-Hill Companies,P.1129, 2000.

[22] E. Bardal," Engineering Materials and Processes***," Springer-VerlagLondon Limited, 2004.***

[23] M.G.Fontana, ***"Corrosion Engineering"***,3rd ed.,McGraw-Hill,1986.

[24] P.A.Schweitzer ***"Corrosion Engineering HandBook"*** 2nd edition, Taylor and Francis Group,LLC,2007.

[25] M. Paunovic and M.Schlesinger ***,"Fundamentals of electrochemical deposition,"***2nd edition John Wiley & Sons, Inc. ,2006.

[26] Souza, M. E. Pires, Ariza, Edith , Ballester, Margarita , Rocha, L. Augusto, Freire, Célia M. A***.,"Comparative behaviour in terms of wear and corrosion resistance of galvanized and zinc-iron coated steels"*** Revista Matéria, Vol. 12, No. 4, PP. 618 – 623, 2007.

[27] R. A. Higgins***," Engineering Metallurgy,"*** 6th edition 1993 .

[28] A.H. Haleem, *" **Improvement of Inconel 600 Oxidation Properties by Aluminizing-Chromizing,**"* Ph.D., thesis, Department of Production Engineering and Metallurgy University of Technology,2006.

[29] L. S. Faiq ***,"Improvement of Mechanical Properties and Corrosion Behavior of Drilling Equipments Columns by Ceramic Coatings ,"***MSc. A thesis, Department of Materials Engineering, University of technology,2013.

[30] J. R. Davis**, *"Corrosion: Understanding the Basics,"*** ASM International, 2000.

[31] Ray Taheri**,*" Evaluation of Electroless Nickel-Phosphorus (EN) Coatings,"*** Ph.D. A thesis Department of Mechanical Engineering University of Saskatchewan,2003.