A STUDY OF THE CONVENTIONAL CO-DEPOSITION OF Ni-Co COATINGS TO IMPROVE THE CORROSION RESISTANCE OF STEEL

A THESIS SUBMITTED TO THE GRADUATE SCHOOL OF APPLIED SCIENCES

OF

NEAR EAST UNIVERSITY

By

ISMAIEL MOHAMED A A OMINEM

In Partial Fulfillment of the Requirements for

the Degree of Master of Science

in

Mechanical Engineering

NICOSIA, 2017

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Approval of Director of Graduate School of Applied Sciences

Prof. Dr. Nadire Çavuş

We certify this thesis is satisfactory for the award of the degree of Masters of Science in Mechanical Engineering

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I hereby declare that all information in this document has been obtained and presented in accordance with academic rules and ethical conduct. I also declare that, as required by these rules and conduct, I have fully cited and referenced all material and results that are not original to this work.

Ismaiel Mohamed A A, Ominem

Signature:

Date:

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ABSTRACT

Surface coating is a common method used for improving the corrosion resistance properties of low carbon steel in a wide range of aggressive environments including marine environment. In the present work, two plating baths were prepared to deposit nickel and nickel-cobalt layer on AISI 1021 low carbon steel. Solution composition and operating condition of Watt's plating bath was followed to conduct this experiment. Moreover, the properties of deposited film was investigated by electrochemical measurements (open circuit potential) to compare the improvement in corrosion resistance.

The metal deposition parameters used in the preparation of functional nickel and nickel-cobalt plating experiments included temperature, current density, time, and type of anode material. Microstructure with morphology for electrodeposition had been investigated using SEM and X-ray diffraction analysis. The electrochemical properties of nickel-cobalt alloy coating were tested in a 3% NaCl solution using the open circuit potential measurement. Test results showed that the deposited coating layers are crack-free and exhibited excellent adhesion on the steel substrate. It was found that the current density had a major influence on the rate of coating deposition with 30 mA/cm^2 as the optimum level. It can be deduced from the corrosion behavior diagrams that the deposited nickel-cobalt coating can improve the corrosion resistance of a steel substrate in the marine environment.

Keywords: Deposition; corrosion resistance; current density; pH; steel substrate; open circuit potential; marine environment

ÖZET

Düşük karbonlu çeliklerde deniz ortamı gibi agresif ortamlara karşı paslanma direncinin yükseltilmesinde yüzey kaplamaları yaygın olarak kullanılan bir yöntemdir. Bu çalışmada, karbon çelik numunelerin yüzeyi Watt's banyosunda elektrokaplama yöntemi kullanılarak nikel ve nikel-kobalt ile kaplanmıştır. Kaplamaların kalitesi fiziksel ve elektrokimyasal ölçümlerle değerlendirilmiştir.

Çelik numunelerin yüzeyleri nikel ve nikel-kobalt ile kaplanırken sıcaklık, zaman, akım yoğunluğu ve anod malzemesinin etkileri irdelenmiştir. Elde edilen kaplamaların içyapı ve morfolojileri SEM (Taramalı Elektron Mikrokobu) ve XRD (X-Işınları Kırılma Yöntemi) cihazlarında incelenmiştir. Ayrıca, nikel-kobalt kaplamaların elekrokimyasal özellikleri % 3 NaCl çözeltisinde açık hücre potansiyel ölçümleri ile değerlendirilmiştir. Yüzey kaplamalarının çatlak içermediği ve çelik yüzeyine mükemmel biçimde yapışmış olduğu tespit edilmiştir. Akım yoğunluğunun kaplama hızı üzerinde büyük etkisinin olduğu ve optimum değerinin 30 mA/cm2 dolayında bulunduğu görülmüştür. Korozyon akış çizgesi diyagramları incelendiğinde nikel-kobalt kaplamanın deniz ortamında çelik yüzeyinin paslanma direncini önemli ölçüde arttıracağı anlaşılmıştır.

Anahtar Kelimeler: Çökeltme; korozyon direnci; akım yoğunluğu; pH; çelik alt tabaka; açık devre potansiyeli; deniz ortamı

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ACRONYMS AND ABBREVIATIONS

Ni-Co:	Nickel-cobalt
Emf:	Electromotive force series
SEM:	Scanning electron microscope
XRD:	X-ray diffraction
pH:	Hydrogen ion concentration
DC:	Direct current
EIS:	Electrochemical impedance spectroscopy
LPR:	Linear polarization resistance
OCP:	Open circuit potential
HSLA:	High strength low alloy
IL:	Ionic liquid
Redox:	Reduction oxide reactions
CV:	Cyclic voltammetry
FCC:	Face cubic center
HCP:	Hexagonal Close Packed
EDS:	Energy dispersive spectroscopy
Rpm:	Revelation per minute
RC:	Reversing current
PC:	Pulsating current
AC:	Alternating current
PO:	Pulsating Over-potential

EPCR:	electrodeposition at periodically current rate
XRF:	X-ray fluorescence
CRT:	cathode ray tube television
M:	Molarity
CE:	Counter electrode
SCE:	Saturated calomel electrode
RE:	Reference electrode
WE:	Working electrode

CHAPTER 1
INTRODUCTION

1.1 Overview of Ni-Co Alloy Coating

Electrodeposition can be defined as a treatment that modifies the metal surface, without changing its bulk properties in order to improve the appearance of the surface, increase the corrosion, wear and abrasion resistance (Popov, 2002). In most engineering applications, it is the functional properties that are of interest for improvement and development. For instance, it is very important to raise the surface hardness of a metal or alloy in order to improve its wear resistance. On the other hand, in chemical and petrochemical processes, the corrosion resistance is the most important property. Wear and corrosion exist as some important phenomena of energy and material losses in mechanical and chemical processes. For the previous reasons, electrodeposition of alloy coatings is widely used in the field of surface engineering in order to fulfill the continued demand for increasing the surface quality of both decorative and functional coatings (Kharmachi, 2015).

In contrast with other technique such as sputtering and chemical vapor deposition, electroplating offers a more versatile technique for producing single or multi-layer coatings especially due to its low cost. Electrodeposition of metallic coatings such as Ni-Co alloys on steel surfaces is widely used surface treatment method because it is easy, simple, and economic method. This method can also be used at ordinary conditions of temperature and pressure. Nickel and Ni-Co alloy coatings are most attractive due to their low porosity content and high corrosion resistance. However, Future improvement in these properties is still considered necessary for special purpose applications. Over the years, electroplated nickel-cobalt alloys have been found mainly because of their unique physical and chemical properties and wide range of applications. It has got much attention when it was observed to be the most important potential candidates to be a substitute of toxic hexa-valent chromium electroplating (Hyie, 2016).

Carbon steel is a common engineering material. It is readily corroded in a wide range of environments. For this reason, many corrosion control strategies have been developed to reduce the corrosion rate of this material. Coating of metallic surface by electro-deposition is one way to reduce the corrosion damage and improve the surface properties. Corrosion in general form is the destructive chemical or electrochemical reaction or loss in material properties when the materials are in contact with their environment. Since corrosion happens through electrochemical reactions, it's possible to apply electrochemical technique in order to study the corrosion process. In this research work a small test sample, approximately a few square centimeters of surface area, used to model low carbon steel metal in corrosive system. Test sample immersed in 3% NaCl solution. Another two electrodes called reference electrode and counter electrode were also immersed in this solution and all these electrodes were linked with device named potentistate. The potentiostat permits changing the potential of the metal sample in a controlled manner and measures the current that flows as a function of applied potential.

However, there is still lack of data on corrosion and wear resistance properties of these surface treatment method. Therefore, investigation of the conventional co-deposition of Ni-Co alloys on carbon steel substrate has been explored and the corrosion performance of the deposited layer has been evaluated by electrochemical corrosion test methods.

1.2 Problem Statement

Corrosion frequently leads to failure of the metal parts in service or makes parts susceptible to failure by some other mechanism. The electrochemical nature of corrosion can be clearly seen when zinc placed in acidic environment like hydrochloric acid, rapid reaction occurs. Moreover, since the environment can't be changed, the change in surface treatment are generally required.

Zinc coating provides good corrosion resistance because it lies at the end of electrochemical series and it offers cathodic protection to the steel component. If the coating scratches or failed zinc layer supplies electrons to steel and it works as a sacrificial anode. Because of this is that zinc corroded and steel will be protected. However, zinc coating doesn’t perform well in acidic environment in addition its wear resistance is too low. Nickel coatings can overcome of these difficulties if the coating layer covers all steel surface and minimize the porosity of coating. When nickel coating scratches or failed, corrosion rate increased rapidly because steel now becomes sacrificial anode instead of nickel coating. To avoid this, the parameters which has a high effect to minimize the porosity of coating were chosen to study and investigate.

1.3 Aim of the Thesis

The purpose of this work is to investigate the optimum conditions for the conventional Co-deposition of nickel-cobalt electro deposition on carbon steel surfaces. Secondly, the performance of coated low carbon steel in marine environment is to be evaluated by electrochemical corrosion testing.

1.4 Limitations of the Study

This thesis is expected to be successful in addressing the objectives of the study. An in-depth research will be conducted to keep up with the development in the field of electrometallurgy. Naturally, there are some limitation to this study. First, the parameters studied are limited as it covered only four major parameters. Furthermore, in usual practice, electrodeposited layers are followed by heat treatment for the purpose of improving hardness which is not conducted here. Finally, other electrochemical measurements such as potentio-dynamic and linear polarization resistance are not performed the current work.

1.5 Thesis Overview

Chapter 2: The chapter is a brief summary of the studies those reported on the parameters that affect the electroplating of nickel and nickel-cobalt alloy on steel substrates which were based on the experimental analysis.

Chapter 3: In this chapter includes definitions, concepts, principles, necessary data and theories that related to electrodeposition process and nickel plating was presented.

Chapter 4: This chapter presents the material and the method used in this research. It includes the details of the design and construction of electroplating cell used for the purpose of the current investigation.

Chapter 5: The results for two types of electrodeposition bath that have been tried are presented. The first type of bath is for nickel coating deposition whereas second is designed to deposit Ni-Co electrodeposition.

Chapter 6: The last chapter, includes conclusion and recommendations for future work that may be carried out.

CHAPTER 2
PREVIOUS WORK

2.1 Effect of Operating Parameters on Nickel Electrodeposition

Ker Kerr et al. (1997) mentioned in their work that the techniques employed by electrochemical for measuring of the porosity of electroless deposits of nickel (1 to 24 µm) acts on steel through hypophosphite baths was taken in consideration. By the use of Tafel extrapolation the rate of corrosion of the coated sample submerged in 0.125 M H_2SO_4 at 22ºC was examined and the results showed that there was a decrease in corrosion rate when the porosity decreased. The deposit porosity was indicated through the analysis which was conducted on the anodic polarization curves and on the data of current-time. Another testing which had also taken place was the examination of the samples which were tested already, they consisted of different deposit thickness and of a non-porous coating, this experimentation was conducted by galvanic coupling. As the experiments were conducted the porosity had decreased for the thicker deposits but the shape of the porosity and the thickness curve of the coating curve had shown similar results for all different methods applied for the experimentation.

Sriv Manuscript prepared by Srivastava et al. (2006) emphasized on how fluctuation takes place in microstructure and the decomposition actions of electrodeposited nickel as in comparison to the addition of cobalt. In order illustrate the coatings of alloy various different analysis were conducted which were carried out by two different microscopes, one of them was electron and the other optical, and also the other analysis was of energy dispersive X-ray. Through the analysis it was found that the alloy co-deposition was irregular. The measurements of cross-section microharness showed that the maximum level of hardness of cobalt reached at 50 wt.% and after reaching this level it had started to decrease when the cobalt was increased. An attempt to see the relationship between microstructure and microhardness was done. Through the increase of cobalt, optical micrographs were able to point out the change in microstructure from mixed columnar-fibrous to lamellar and also to the fibrous. Through the use of X-ray diffraction (XRD) experiments revealed that the structure of the crystal was cubic for the cobalt within the range of 0 wt.% - 50 wt.%. As the amount of cobalt was increased to 70 wt.% there was a change in the crystal structure which showed that the structure was changed to a hexagonal structure. Along with the change in the structure of the crystal when cobalt was increased, another change was observed which was of the preferred orientation. In order to study the corrosion behavior of Ni-Co alloys, two different studies were made which were: electrochemical impedance and potentiodynamic polarization. In order to quantify the physical behavior of the corrosion the use of equivalent circuit was made. As the studies were carried out, the results showed a difference in corrosion resistance among Ni-20% Co alloy and Ni-Co alloy. The Ni-20% Co alloy had shown a greater resistance than Ni-Co alloy. And, for carrying out the tests both types of alloys for the deposition, both were applied with coatings of plain cobalt and plain nickel.

Kale Kilit's operational considerations for the brightening and carrying agents were provided by a study carried out by Gezerman and Corbachioglu (2010). The study also investigated the changes in the coloring of plating of the original bath when Fe2+ was applied to the nickel plated baths. It was used as an agent for brightening and for the analysis of the color, and these were checked under spectrophotometer at 350 nm, with the light coolness at 6500K and D65 (Average North Sky Daylight) light. In order to reach the desired color, Fe^{2+} agent was applied without having any sort of problems or interfering from dye after the nickel plating was applied by electrolysis. Through the analysis carried out on nickel plating bath, number of tests were carried out of which brittle test is one of tests. Brittle test was used for obtaining number of ideas regarding how accurate were the choices which were made for the given standards.

Sadi It was observed by Güler et al. that in order to reduce the friction the use of nickel composites which had co-deposited insoluble and solid lubricant particles was done. Hydrogen evolution reaction (HER) is known to contend with nickel deposition. Fractional factorial design was also taken into consideration in studying the impact which the parameters and the interaction effects on the pean current density of hydrogen evolution reaction during the electrodeposition of NI and Ni-MoS2 composite coatings. In the study the parameters that were studied used the following properties for carrying out the tests:

- MoS_2 particle concentration (0-30 g/l)
- Temperature (30-50ºC)
- pH (2-4) and

Two surfactants

- Ammoniumlignosulfonate (ALS) and
- Depramin-C (DC) (0-1 g/l)

Potentiostat had been used in order to assist with electrodeposition processes which were passed out from a typical Watts bath that had contained the leveler, an agent for wetting, and also a brightener. In order to make the peaks noticeable on the linear sweep voltamograms, the peak current densities had to be extended to a greater value. Following are the changes which were made in order to make it noticeable: 20 mV/s to 100 mV/s over the range of 0 to 2.5 V. Hydrogen evolution reaction's peak current densities for each of the experiments carried out were determined through the use of fractional factorial design for the processing of two surfactants which were ALS and DC. It was observed that peak current density of Hydrogen evolution reaction had decreased irrespective of the surfactant which had been used when MoS_2 was added, the pH value was increased and the temperature was decreased. At the same time, it was observed that the peak current density was increased with the use of surfactants.

In the study "Effect of electrodeposition parameters on the current density of hydrogen evolution reaction in Ni and Ni-MoS2 composite coatings" conducted with the use of pulsed composite electrodeposition and interdiffusion treatment on a low carbon steel, Chen and Zhao (2013) had produced the Ni-Al composite coating. For the production of the Ni-Al coatings, continuous Ni-rich phase was used and within the Ni-rich phase discrete Al-rich particles were enclosed. One of the most important and positive point of the coating was that it did not have any cracks and the bond between the coating and steel is very strong. Following are the parameters for the optimized processing of composite electrodeposition: duty cycle, 2; pulse frequency, 800 Hz; and current density, 3 A/dm^2. Coating can have an improved resistance towards corrosion of A3 steel in the aquatic environment and depending on how thick the coating is it can be improved, most suitable thickness which was observed was 100~150 μm, this was indicated by the polarization curve and the EIS.

Nigam et al. (2015) carried out their study to check “the pulse current electro-deposition technique to deposit nickel on a high strength low alloy (HSLA) steel substrate.” In order to confirm the nickel coating XRD and EDAX were conducted and to check the features of the coating SEM and optical microscopy was implemented. For checking the behavior of nickel coating electrochemical polarization was conducted, and through the results of polarization curves it was indicated that the current density which had been applied during pulse electro-deposition had played an important part on features of the coating of nickel.

2.2 Co-deposition of Nickel-Cobalt Alloy

A research was carried out by Yand and Deng (2011) on the electrodeposition of Ni-Co alloy foils on titanium substrate in an acid chloride-sulphate bath. In those tests impact of electrodeposition parameters were checked, and these parameters consisted of the temperate, pH level, sacchrain concentration, cobalt sulphate, and current density on the efficiency and the composition were analyzed in full detail. Through the SEM and XRD, microstructure and the morphology of the deposits were checked. As the tests were conducted, the analysis showed that the best parameters which should be applied were temperature 40-50°C, pH 2-3, saccharin 2-3 g/l, cobalt sulphate 20 g/l and current density 3-4 A/dm^2. Irregular Ni-Co co-deposition was observed through the deposits were analyzed through chemical analysis by the help of EDS. As the SEM test was applied, it revealed the presence of the Ni-Co alloy deposits which were compact and smooth, but there was presence of hydroxide particles towards the surface. “The crystallographic structures of Ni-Co alloy foils were the FCC Ni solid solution.” FCC Ni solid solution was based on the crystallographic structures of Ni-Co alloy foils. No-Co Alloy foils with the properties of 17.3 - 37.2 wt% and thickness of 20 - 45 μm had bright with a low remaining stress and a strong toughness.

A study carried by Srivastava et. al. (2012) on the comparison of structure and properties of three substances which included cobalt, nickel and nickel-cobalt alloy coatings that were attained from ionic liquid (IL) which were acquired from aqueous electrolyte. A cheap and non-toxic ionic liquid was known as choline chloride was chosen for the electrodeposition. As the results came out, it was observed that the coatings which were acquired from aqueous electrolyte had lower micro-hardness when compared to the ones acquired from iconic liquid. Along with that, the surface morphology of both substances appeared different. When observed through the X-ray diffraction, it was seen that the coatings which consisted of rich nickel had face centered cubic crystal structure, on the other hand, the coatings which consisted of cobalt had formed hexagonal structure which was closely packed together. As the comparison which observed the behavior of corrosion of coatings was conducted, it was seen that Ni coated sample had a greater resistance towards the corrosion regardless of the amount of adopted electrolyte.

An investigation of nickel and cobalt on the austenitic stainless steel (AISI 304) was studied by Silva et al. (2012). They studied the co-deposition of both (nickel and cobalt) on AISI 304 by applying a square waveform current in the cathodic part. This procedure had allowed for the creation of a fully developed, stable and open porous 3D dendritic structure, this structure could be used for the redox super capacitor as an electrode. Investigation carried out by Silva et al. (2012) had also pointed out the impacts of applied current density on the mass, chemical composition and morphology of Ni-Co films and as well as the resulting three-dimensional porous dendritic structure. Studies on morphology and physicochemical were done by SEM, EDS and XRD. Cuclic voltammetry (CV) was used on the materials to check their electrochemical behavior. The analyzed results of the study had pointed out the mechanisms which were involved in the process of co-electrodepostion, how the film composition is tailored through the lower limit current density and also its activity of electrochemical.

Corrosion resistance of Ni-Co alloy and Ni-Co/SiC was investigated by a study carried out by Bakhit et al. (2014). This study was carried out to study how these two coatings resisted to the corrosion in a modified Watts bath by the use of SCD technique. This technique was assessed by potentiodynamic polarization measurements which were using in 3.5% NaC1 solution and was observed as a function of deposition conditions. SEM and XRD were used to illustrate the chemical, phase and morphology compositions of the coatings. By the increase in the concentration of cobalt in electrolyte, it had been detected that Ni-Co alloy coating which contained cobalt had increased. By having to keep deposition current density at 3 A/dm^2 and particle concentration at 5 g/1, SiC nanoparticles at its highest percentage (8.1 vol.%) in Ni-Co/SiC nanocomposite coating had been achieved. SiC nano-particles were uniformly distribute throughout the nanocomposite coating which was analyzed through EDS and SEM. Through the help of potentiodynamic polarization testing, it was observed that the resistance of No-Co alloy coatings had been varied as a function of cobalt content, and along with this, it was observed that corrosion resistance of Ni-Co alloy coating was lower than that of Ni-Co/SiC coating.

A study was conducted by Hagarová et al. (2015) carried out a study on the "Ni-Co alloy coatings deposited to copper substrate electrochemically from a sulphate bath" which was based on experiments. Study revealed that if, the concentration level of cobalt sulphate was increased in the electrolyte 20 $g.l^{-1}$ to 45 $g.l^{-1}$, as its outcome there would be a steady increase in the content level of cobalt in the alloy coating 31.8 wt% Co up to 49.2 wt% Co. Different current densities were applied to the Ni-Co alloy coatings. 90 to 98.5% was the range at which current efficiency was attained, and here it the increase in the current density had led to decrease in the current efficiency. Current density and Co content had significantly impacted the size of grains and morphology of the alloy coatings. Finger gain structure was achieved by having to increase the Co content. The highest value of hardness which was 556.3 HV 0.1 had the coating with 42.6% and the concentration at this point was of 30 $g.l^{-1}$ $CoSO_4$ in sulphate bath.

The work of Khamachi and Berço (2015) examined the deposition of Ni-Co alloy with different nickel concentration that was deposited upon carbon steel substrate. Co-deposition phenomenon of Ni-Co coating was characterized as irregular behavior. Scanning electron microscope (SEM) and X-ray diffraction (XRD) were used to investigate the microstructure and morphology of deposited layer. The SEM micrographs showed granular crystals and smooth surface morphology, the combination of FCC and HCP structure were described by using XRD patterns that highly depend on cobalt content in deposition film. Electrochemical measurements such as potentiodynamic polarization and electrochemical impedance spectroscopy (EIS) were performed in 3% NaCl solution to evaluate the electrochemical properties of Ni-Co alloy deposited film. A good corrosion resistance was obtained with high nickel contents.

Pérez-Alonso et al. (2015) through experimentation was able to produce nickel-cobalt by the use of electroless-plating deposition from two solutions CoSO4 and NiSO4, it was based on electrodes that had different ratios of Ni-Co. Linear Seep Voltammetry was used to perform the electrodes for OER and HER reactions. The electrodes which had shown the lowest over-potential for HER contained only Ni-ELP. And, the Ni-Co electrode which contained 30% Co concentrations had exhibited for OER the lowest over-potential. Two electrodes were used to carry out the test for durability. 2.2 V was the result of having electrolytic cell at 0.3 A.cm^{-2}, by making use of No-ELP for HER and Ni70Co30-ELP for OER. Features of the electrodes which were used by SEM/EDS had revealed that there was stability in the electrodes after the H2) alkaline electrolysis for 70 h. After all the experimentation had been conducted, it was concluded that electroless-plating was successful and is a good way to produce stable nickel electrodes for alkaline water electrolysis.

In their work Shetty and Hegde (2016) showed that if, ultrasound effect was applied parallel with the electrodeposition process, it could result in stability of Ni-Co alloy coatings. By applying the ultrasound effect of the known power density it can assist to bring out the modulation in a mass transfer process at cathode. There has been development of Ni-Co alloy coatings with the significant change in the phase structure, the compostion and as well as the surface morphology, through the ultrasound effect of various power densities. By the use of electrochemical methods, Corrosion performances of ultrasound-assisted No-Co alloy coatings were measured. The data acquired had shown that sonolectrodeposited coatings of No-Co alloy developed at power density and current density of 4.0 Adm^{-2} and 1.2 Wcm^{-2}(represented as (Ni-Co) 4.0/1.2) had higher resistance about 3 times compared to its conventional coating which if deposited at 4.0 Adm^{-2} (Ni-Co), by using the same bath. Because of the changes in the limiting c.d. (IL), there was a connection between the increase of Co content in the alloy and the corrosion protection efficiency. In the study it was discussed through the tests performed by the usage of SEM, EDS, and XRD that enhanced corrosion resistance of sonoelectrodeposited Ni-Co alloy coatings exists.

CHAPTER 3
LITRETURE REVIEW

3.1 The Process of Electrolysis

Electrodeposition process basically involves passing electric current through two electrodes that immersed in the conducted electrolyte, positively charged electrode called anode and negatively charged electrode called cathode. When electric potential applied between anode and cathode, the charges ions in electrolyte will migrate towards opposite charge electrode. In nickel electroplating process, the positively charged ions Ni^{++} discharged at cathode ,which is steel substrate in this case, depositing nickel on the steel surface as shown below in figure 3.1 (Nickel Institute, 2014).

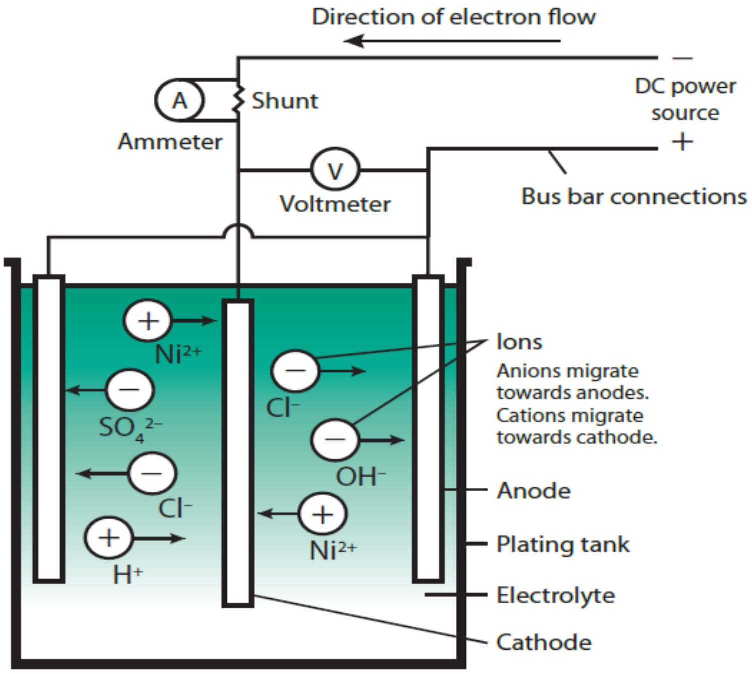


Figure 3.1: Basic electrical circuit for electroplating (Nickel Institute, 2014)

3.1.1 Anode

In the electrochemistry, oxidation takes place and has the positive polarity contact in an electrolytic cell. It is in the anode, where anions which are the negative ions have chemical reaction by the electrical potential and produce electrons (oxidation), which then move up into the driving circuit.

Nickel anodes in electroplating have various functions, out of those the main functions are as follow:

- It acts as a conductor for the electric current, it drives the current to electrolyte.
- It replaces the nickel ions which are discharged at the cathode.
- It distributes the current in a uniform manner over the surface of cathode (Nickel Institute, 2014).

3.1.2 Cathode

In electrochemistry, negative polarity is applied to the drive cell in the cathode. Hydrogen has, or pure metal cause the reduction in the cathode from metal ions. Depending on operations of the device, there can be either negative or positive cathode polarity in respect to anode (Nickel Institute, 2014).

3.1.3 Faraday's law

Faraday showed that the quantity of metal placed at the cathode and the quantity dissolved at the anode are directly corresponding to the current and time and could be calculated through the following expression:

$$m = 1.095 * a * I * t \tag{3.1}$$

Where, m represents the amount of metal placed at the cathode or dissolved at the anode which is measured in grams, I represents amount of current flow through plating cell in amperes, t represents time of the current in hours, and a represents the ratio of current efficiency. The proportionality constant (1.095) in grams per ampere hour equals M/nF, where M is the atomic weight of nickel (58.69), n is the number of electrons in the electrochemical reaction, and F is Faraday’s constant, equal to 26.799 Ampere-hour (more commonly given as 96,500 C), (Di Bari, 2000).

3.1.4 Rate of deposition

According to Faraday, quantity of electricity which is required to deposit 1 gram equivalent of metal is a constant and holds the value of 96,500 coulombs (known as ampere-seconds or 26.799 ampere-hours. There is a way of calculating the amount of nickel dissolved or the weight of the nickel deposited at the cathode by having to apply this relationship:

$$W = 1.095\ It \tag{3.2}$$

The amount of nickel dissolved or deposited at the anode or cathode in grams is represented by W, the flow of the current which flows through the tank is represented by I in amperes and the time which the current flows in hours is represented by t (Nickel Institute, 2014).

3.1.5 Current efficiency

Mostly hydrogen evolution is happened in metal deposition. By doing this the metal is deposited but doing so only a part I_{Me}, is used of the total current, I, through the cell. The efficiency of the current is able to indicate the amount of total current which is used for the deposition of the metal. In the electrodeposition process it is considered as a very important parameter (Nickel Institute, 2014).

$$\eta_I = \frac{I_{Me}}{I} \tag{3.3}$$

3.1.6 Electrodeposition at a periodically changing rate

For a far long period of time it has been known that the usage of a periodically changing current in the metal electrodeposition practice results in great improvements in the quality of electrodeposits. There are three types of variations of current which are useful: pulsating current (PC), reversing current (RC) and sinusoidal, which are for alternating the current superimposed on a direct current (AC). In the recent times, there seems to increased discussion on the positive impacts of pulsating overpoteinal (PC). Though it is this type of electrodeposition at a periodically changing rate (EPCR) is very important if look from the theoretical side and has to offer a number of possibilities for experimentation, yet it is still not made use of as frequently in the practice of metal electrodeposition (Popov, 2002).

3.1.6.1 Reversing current

Figure 3.2 illustrates the reversing of the current. It is presented by the current density of cathodes and anodes, at the same time is also presented by the time of the flow of current in the direction of cathodes and anodes and as well as the direction of it.

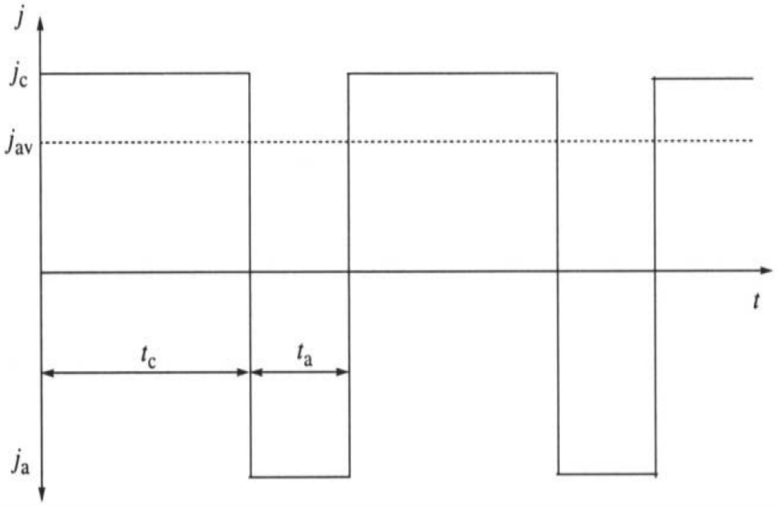


Figure 3.2: Wave form of a reversing current cycle (Popov, 2002)

3.1.6.2 Pulsating current

The pulsating current comprises of a replication of square pulses. Figure 3.3 shows how it is similar to the RC in shape expect that anodic component is absent.

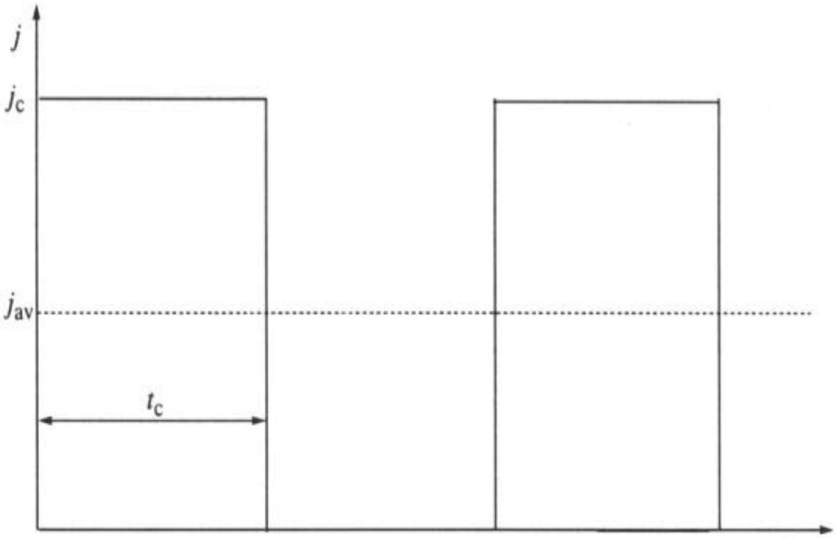


Figure 3.3: Waveform of pulsating current cycle (Popov, 2002)

3.1.6.3 Alternating current superimposed on direct current

Figure 3.4 represents the sinusoidal AC superimposed on a direct cathodic current (DC).

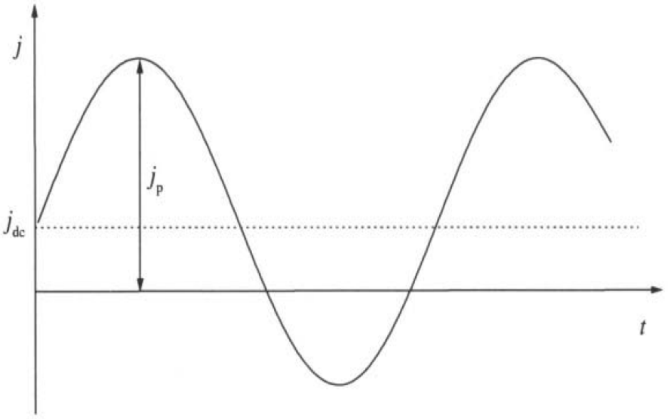


Figure 3.4: The shape of sinusoidal alternating current (Popov, 2002)

3.1.6.4 Pulsating over potential

There is a repetition of over-potential pulse of various shapes in the pulsating over-potential. The square-wave PO is defined in the same manner as the PC except for that the over-potential pulsates between value of amplitude and zero in place of density of the current. EPCR consists of a range of waveforms of current and over-potential but the ones mentioned above are the most important ones (Popov, 2002).

3.2 Chemistry of Ni-Plating Solutions

Today in the world, electroplated nickel is being used commercially over 150,000 tons. This huge number of shows the importance it holds and how useful it is. Electroplating has number of features out which one is that if the composition of the electrolyte and the conditions of its operations are modified, it allows to customize the shape and properties of the nickel depending on what it is to be used for (Nickel Institute, 2014).

3.2.1 Surface preparation

The metal coating characterizes metal electrodeposit which distinguishes the properties of the surface from properties of a basic metal and from the ones which are electrodeposited. It should hold the adhesive property which is not porous and deprived of any internal stresses. The adhesiveness depends on how the substrate was prepared for electrodeposition, which should result in a clean surface and is ready to accept a satisfactory deposit. If the surface is not prepared correctly, it can cause the coating to peel off which makes is useless. Another situation which can cause the peeling or crashing of the deposit is internal stresses, and this is resulted when different materials in the lattice do not corporate with each other. And if the such problems do not exist in the electrodeposited metal's lattice than the mechanical characteristics of the electrodeposit are basically the similar to the characteristics of the metal which is produced thermally. And if the deposit consists of porous than it is not possible to completely transform the characteristics of the surface of basic metal to the characteristics of electrodeposited (Popov, 2002) .

3.2.2 Watt's plating bath

Prof. Oliver P. Watts was the developer of the "Watts" formulation and nickel plating solutions for the decorative and functional plating were mostly are based on his formulation. This formulation is the combination of nickel chloride, boric acid and nickel sulphate. Table 3.1 shows a typical formulation together with operating parameters (Nickel Institute, 2014).

Table 3.1: The Watt's bath chemical composition and operating conditions

Nickel Sulphate ($NiSO_4.6\ H_2O$)	240 - 300 g L^{-1}
Nickel Chloride ($NiCl_2.6\ H_2O$)	30 - 90 g L^{-1}
Boric Acid (H_3BO_3)	30 - 45 g L^{-1}
Temperature	40 - 60 °C
PH	3.5 - 4.5
Cathode Current Density	2 - 7 A dm^{-2}

3.2.3 Function of ingredients

Nickel ions are mainly extracted from nickel sulphate with having nickel chloride as a contributing source. There are two main functions of nickel chloride: it significantly increases the conductivity of the solution which results in reduction of the required voltage and it is very important in the procurement of suitable dissolution of nickel anodes.

Function which controls the pH of a solution is boric acid that acts as a buffer. In order to adjust the pH of a solution, sulphuric acid is added regularly. Boric acid is used for limiting the effect on pH which results from the discharge of hydrogen ions, hence simplifying pH control. The operating mechanism of boric acid is very complicated, but mostly it exists in a mix solution of borate ions and non-ionized boric acid. The limiting of pH is change through boric acid takes place when the hydrogen is released, some of the boric acid will ionize which will result in replacement of hydrogen ions which were lost and at the same time when this action takes place formation of borate ions takes place. To adjust level of pH the acid is added, at this point the borate ions associate with the hydrogen ions in order to reform the boric acid. Therefore, the only time when boric acid is lost is through the drag out or through losses of other solutions (Nickel Institute, 2014).

3.2.4 Bright nickel plating

The solution of nickel electroplating known as the modem bright employs mixtures of additives which are cautiously formulated that produce bright deposits. These deposits have great scratch-filling and leveling characteristics, fair ductility, and most important of all the internal stress is low. The modern processes today are able to produce bright deposits in areas where the current density is low, it permits the use of high average current densities and the temperatures of the bath, they have low sensitivity to the metallic pollutants compared to the solutions from the past, they also offer non-step purification of the plating solution through filtering the by activated carbon, and they also price breakdown products which are also removable through the activated carbon and do not have an overreaction to the anode. Watts nickel and the bright nickel electroplating both have same compositions (see Table 3.1).

Bright nickel electroplating additives can be put into three different categories which are carriers, auxiliary brighteners and brighteners.

Only carries will be explained because its most common additives, carries are the organic compounds which are mostly with a scent and contain sulphur. Example of the compounds are as follow: Benzene sulphonic acid, p-toluene suphonamide, 1,3,6-naphthalene sulphonic acid, allyl suphonic acid and saccharin. Brighteners produce a number of excellent deposits which have a good leveling and ductility characteristics over a range of broad current density. Compounds which are produced through the brighteners include o-sulpho benzaldehyde, formaldehyde chloral hydrate, allyl sulphonic acid, 4-diol, 2 butyne-1, thiourea coumarin and number of other compounds (Nickel Institute, 2014).

3.2.5 The porosity of nickel electrodepositions

The porosity is one of the most vital characteristics of an excellent adherent and one which stresses less metal coating. The porosity of coating could be decreased to minimum value with increasing the deposition time as well as current density as shown in figure 3.5.

3.2.6 Deposition with minimum porosity

The porosity of the deposits of metal are depended on how thick is the thin surface film formed and the distribution of the current density on the micro-profile and the macro-profile.

The fundamental qualities of plating baths which create great deposits ought to be:

- Conducting electrolyte which makes a low as possible ohmic resistance of solution.
- The use of different kinds of additives, the synergetic effects of which improve the deposition conditions in the way described in the previous section.

There are likewise some different added substances which are utilized sometimes for various reasons or activators of anode dissolution.

In the electroplating process, the current regimes hold a great importance. One of the current regimes which is considered the simplest one contains a small pulse which is of large current density followed by a lengthy deposition. From this process nucleation takes place under much more appropriate conditions than the ones which exist at the time of deposition of a low current density, and this permits a far less coarse deposits to be during the lengthy electrodeposition process. The plating process can also be improved through the regimes which consist of the periodic repetition of different over-potential and current waves. Although the fundamentals of electroplating being very simple, the overall process is too complicated and consists of a large number of sequences (Popov, 2002).

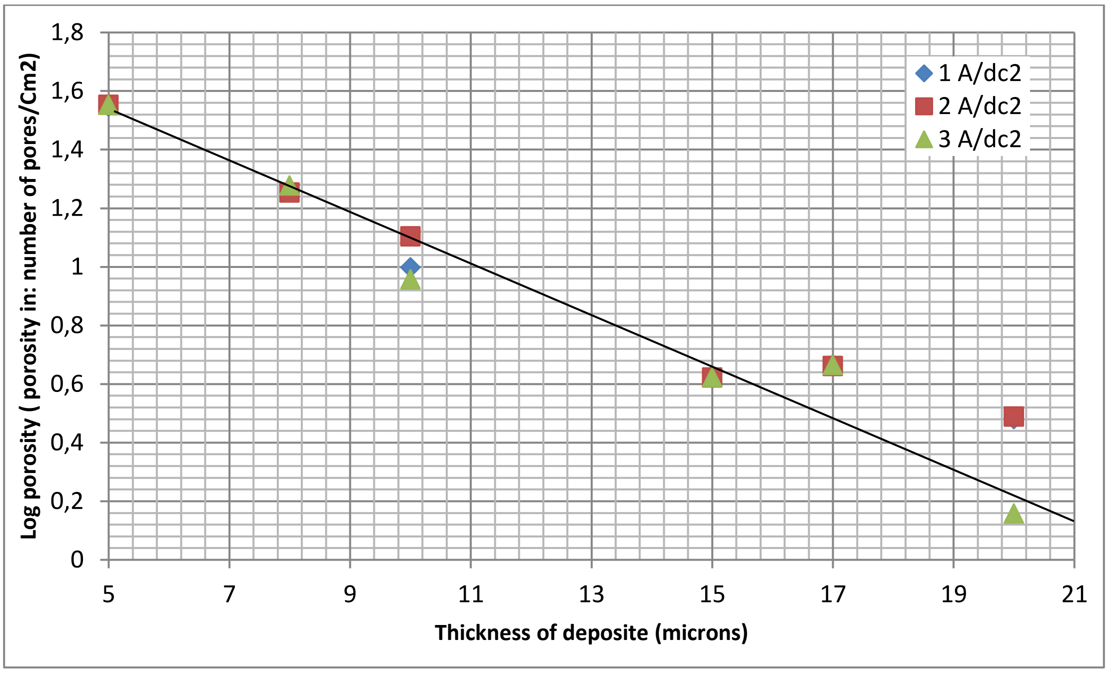


Figure 3.5: Relationship between porosity and thickness of metal deposit (Popov, 2002)

Zinc coating provides excellent corrosion resistance because it offers cathodic protection when protection film is failed because it lies at the anodic end of the emf series. Zinc layer can supply electrons to steel and performed as sacrificial anode for this reason any corrosion of zinc coating will proceed extremely slow rate because the ratio of the anode to cathode surface area. Also, zinc coating can be considered less expensive when it compared to other metallic coating.

However, one of the main disadvantage of zinc coating is not very resistant to wear phenomena specially at high temperature, zinc is even easier to dissolve in acid than iron is. Although zinc plated surfaces have smooth and metallic look, the nickel appearance still is much better than zinc.

In spite the nickel plated surfaces offers only barrier layer protection and once its scratcher through or have pores, it actually accelerates corrosion rate. Nickel plating also applied to improve hardness and magnetic properties beside heat resistance which aren't available in zinc plating.

3.3 Nickel Plating Cell

3.3.1 Electrodeposition

As electrodeposition is the main focus of this study, it is defined as "a treatment that modifies the surface of a metal or occasionally a non-metal, without changing its bulk properties, in order to improve the appearance of a surface, to increase the corrosion and abrasion resistivity." Previously, the main aim of electrodeposition was the improvement of the appearance but now the aim has been moved on to characteristics of surface change from those of substrate material to the ones which are of electroplated metal. The surface characteristics can be changed by the coating, it can be done only if the coating is without any porous, compact, and is a good adherent. Objects which are made of metal today are mostly electroplated, but electrodeposition technology is used mostly when it comes to the electronic components. Molten salts, aqueous and non-aqueous solutions are used in order to perform electroplating process but it depends on the type of electrodeposited metal, out of the three solutions aqueous solutions are the mostly used ones (Popov, 2002).

3.3.2 Electrodeposition at constant current (conventional plating)

Fr In electrolytic conductor ions transport the charge but in the metallic conductors it is free electrons. There must be an electrical contact both from and to the electrolyte which is done by metallic and this is performed when an electrolytic conductor is to be included in an electrochemical circuit. If a metallic conductor was to be submerged in an electrolyte solution it becomes an electrode, and if there were two electrodes which are connected electrolytically they symbolize an electrochemical cell. Figure 3.6 shows the simplest electrochemical circuit.

Figure 3.6 which shows the steady flow of current can be sustained if, a change in the charge carrier is made at the interface of metal-electrolyte which can be done through a transformation done chemically that includes the transfer of electrons across the interface through electrochemical reaction. By having to perform this process it creates a bridge between the current of ions which are in the electrolytic part and the current of electrons in the metallic part of the electrochemical circuit (Popov, 2002).

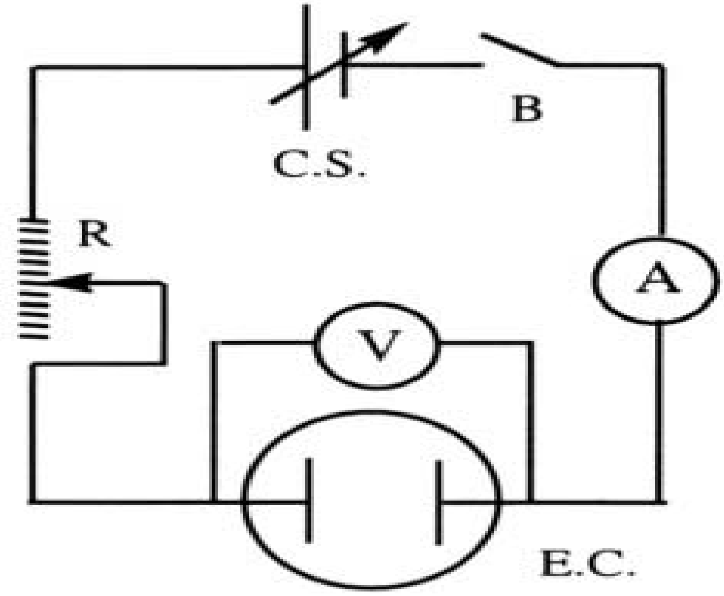


Figure 3.6: An electrochemical circuit. C.S: current source, R: ohmic resistance, V: voltmeter, A: ampermeter, E.C: electrochemical cell, B: circuit breaker (Popov, 2002)

3.3.3 Possible electrochemical reactions

There can be occurrence of electron transfer reaction which takes place at the metal-electrolyte if metal ions which are present in the solution are the same as the ones in the electrode metal lattice, or if there is presence of the same substance in the electrolyte in two oxidation states, and this causes a potential difference. This interface behaves in a manner which is similar to of an electrical circuit that consists of a capacitor and a resistor in parallel. There is a transfer of electrons till a dynamic equilibrium is reached. When there are metal electrodes, this process may take place with the dissolution of the metal electrodes or with the deposition of ions from solution onto the metal electrodes, but it depends on the system applied (Popov, 2002).

3.3.4 Types of Ni-anodes

In order to carry out the Ni deposition process, there are various requirements which are to be fulfilled, the anodes should have an appropriate size, shape and as well as the composition, and it must be positioned in a way in which it will its position will distribute the current uniformly. An example of a good placement of anodes would be when they are installed in a manner in which they are closely spaced along to the anode bar and are located just opposite to the plating racks. Installing the anodes shorter than the racks is one of the recommended ways through with the excessive current to the bottom of the racks can be avoided. Also, if the current flow to the edges of the racks is to be avoided, it can be done by positing the anodes from a good distance from the edges. And, at the same time the parts should be placed in the middle and by having to place them closer to the anodes.

It is important that at all times there should be electrical contact with the anodes. As nickel anode has a higher percentage of purity up to 99.95, it is recommended to make use of anodes which consists of nickel metal, it is because it helps to replenish the nickel ions and also to simplify the solution control. Besides from the high purity level, there is availability of activated grade, which has a small amount of sulphur in it but it decreases the potential of the anode (Nickel Institute, 2014).

3.3.5 Titanium anode baskets

Titanium is used for the fabrication of nickel plated anode baskets, and this has great characteristics for strength and lightness. This can be found in shape of rods, mesh and sheets. The use of titanium is very helpful for anode basket, without having to as an anode itself it is able to conduct the electrical current to nickel metal. And this is because of the protective oxide film which develops when the electrolysis process takes place.

3.3.6 Power consumption

One of the advantages of pure forms of primary nickel is that it can operate without having to clean it on regular bases. Corrosion of titanium anode baskets can take place due to the size and the shape of pure nickel pieces which impacts the power consumption. As compared with the larger pieces of pure nickel the smaller ones do not require a large power demand which means they have the lowest risk to titanium baskets.

3.3.7 Insoluble anode

There is a use of insoluble anodes instead of nickel anodes, it is done when the nickel anodes cannot be used in a certain condition. Insoluble anodes are produced through the use of platinized, titanium, even though graphite can be used as well as an inactive conductive material. The pH level of the solution which is in the anodes will decrease because of the separation of hydrogen ions from the oxidation of water the surface of the anode. And, oxygen and / or chlorine might be released at the same time (Nickel Institute, 2014).

3.4 Application of Nickel Coatings

3.4.1 Decorative nickel plating

Today nickel plating is used in a lot of decorative applications. Some of the components which include nickel plating are cycle and marine industries, household appliances, automotive and other consumer related products. The main purpose for applying decorative plating to these items is to increase the decorative appeal of these products.

3.4.2 Functional nickel coating

In engineering, the functional characteristics maintain the interest and they are used for the development and for improvements. For example, in order to develop the wear resistance it is vital that the surface hardness of a metal is increased. If, looked in the chemical and petrochemical process, the most important characteristic is the corrosion resistance. Both the corrosion and wear are present in some of the most important phenomena of energy and material losses in chemical and mechanical processes.

For the modification or improvement of resistance in corrosion, hardness, wear, magnetic, adhesion and number of other characteristics the use of electrodeposited nickel coating is made. And, doing so the appearance of the coating should be taken into consideration because it is important, and the surface which is plated must be free of any defects.

There are number of things which should be looked up when nickel coating is being applied. It includes the drying cylinders or rolls, oil field valves, hydraulic rams, automotive cylinder lingers and drive shafts. Other uses of nickel are of plating the coins, jewelry and electric circuit boards (Nickel institute, 2014).

3.5 Testing of Nickel Electrodeposition

3.5.1 Appearance and surface quality

Nickel deposits on steel exhibit good corrosion resistance in a wide range of environments in the absence of pores or defects in coating. But since nickel is more noble than ferrous substrates, sever corrosion can result at the base of any through-pores due to adverse condition of large cathode-to-anode area ratio.

The presence of pores in the galvanic metal coating can seriously reduce the design life of the component and may adversely affect surface wear properties. Causes of porosity in nickel or nickel-cobalt alloys deposits have been attributed to various factors including improper pretreatment, surface roughness, composition of plating path, design of the component and surface defects present on the substrate prior to coating. Efficient cleaning of steel surface is vitally important if no pores are to be formed during the deposition process. Rough surface tend to promote the development of pores.

Another factor which contributes to porosity is the hydrogen evolution during the electrodeposition process. Hydrogen is evolved concurrently with nickel deposition although it rate will depend upon bath variable such as pH and component species of plating bath. Surface defects that are already present in the substrate prior to coating can also lead to the production of pores via local disruption of metallic bonding with electrodeposited nickel.

Information on the amount of porosity and its distribution can assist in the prediction of corrosion performance. Corrosion testing is probably the most used method in industry for porosity assessment. Corrosion testing is either carried in the field or accelerated testing in the laboratory. Field testing gave the most reliable results but is too time consuming. Accelerated corrosion testing speeds up the corrosion process by adjusting laboratory parameters such as temperature, relative humidity and corrosive species. However, the interpretation and extrapolation of laboratory test results is more difficult. Examples of laboratory testing include salt spray, acid salt spray, sulphur dioxide. The major drawbacks to all these tests are restricted reproducibility and difficulties in quantitative interpretation of results.

Electrochemical test techniques have been introduced for the detection of porosity of coated metals. However, to date a few studies have reported on use of electrochemical test method for assessment of nickel or nickel-cobalt electrodeposits. For this reason, the present research work attempts to develop methods for this kind of assessment.

3.5.2 Coating thickness

As mentioned before that thickness of the coating plays an important role. The specification of the thickness can be assigned either as a local thickness or average thickness.

There are two methods for testing the thickness which are as follow:

A) Destructive Methods:

- Microscopic method for testing the thickness consists of sectioning the plated part, polishing and etching, mounting, applying the standard metallographic techniques and in the end the measurement of the thickness of the coating is done by the help of optical microscope.
- The coulometric method consists of equipment which separates a very small area. Than current is applied to anodically dissolve the coating and to measure the current and as well as measure the time before penetration is done to the substrate. For the indication of penetration changes in voltage are made.
- The use of scanning electron microscope can be done in order to measure the individual layers in the coatings which consists of multiple layers.

B) Non-destructive Methods:

These are also utilized when measuring the thickness of the coatings. These methods have an advantage which is being of getting the process done faster and it also is done without having to destroy any parts. These methods are:

- Magnetic attractive force
- Magnetic induction

- X-ray spectrometry
- Beta backscatter of particles

Today, a number of non-destructive methods which can be performed and can be applied for the measurement of thickness for nickel coatings. X-ray fluorescence (XRF), is one of the most valuable tool even though it is pretty costly (Nickel institute, 2014).

3.5.3 Microscopic examination

One of the most useful and important tool known as microscopic examination is used for studying and characterizing of materials. In this approach electron, optical and scanning probe microscopes are mostly used. By the help of these instruments the investigation of micro-structural features of all different types of materials can be done (Callister, 1940).

3.5.3.1 Optical microscopy

With the optical microscopy, microstructures are studied by using the light microscope; the basic elements of a microscope are the illumination and optical systems. The contrasts which are present in the image are result from various differences in the reflectivity of the different regions of the microstructure. The surface of the material should be grounded first, and made smooth through polishing. Then the microstructure of the material is revealed through a surface treatment called etching which can be done by using a chemical (Callister, 1940).

3.5.3.2 Electron microscopy

The upper limit to the magnification possible with an optical microscope is approximately 2000 times. Therefore, some structural elements are too fine or small to allow perception utilizing optical microscopy. Electron microscopes use electron beam instead of light, therefore much smaller wavelengths can be attained to see the nanometer size details of the microstructure (Callister, 1940).

3.5.3.3 Scanning electron microscopy

One of the most recent and very useful tool that has been in the market is known as the scanning electron microscope (SEM). The surface of the material being investigated via an electron beam, and the reflected beam is collected, and then it is displayed at the same rate on a cathode ray tube. The image which is displayed on the screen represents the features of the sample's surface structure and micro-details (Callister, 1940).

3.5.4 Adhesion

There is a strong bond between the substrate and the nickel electrodeposits unless the adhesion is poor between them, in this case these will always be a failure in the substrate or in the coating. Despite the importance of adhesion testing, there are no quantitative methods which are suitable for regular quality control purposes.

On the parts of the material where the mechanical tests cannot be applied, instead of the mechanical tests thermal shock testing can be done. Thermal shock test is performed by heating the played parts and then dipped in water, which causes an instant contraction of the metal, which causes the detaching of any poorly adhered coatings on the surface of the metal (Nickel Institute, 2014).

3.5.5 Microindentation hardness test

For measuring of small samples micro-hardness test is used, by having to forcing a pyramidal geometry of small diamond into the surface of the sample. The load which is applied in this method is much smaller than the one in Brinell and Rockwell methods. The range of the force loaded is from 1 g to 1000 g, the results are measured through the help of microscope, and in the end the measurements are converted in order to get the hardness value. It is also important to prepare the sample by grinding and polishing it (Callister, 1940).

3.5.6 Corrosion resistance

The corrosion resistance of coated components is strongly related to porosity in coating. Therefore, a galvanic corrosion cell can be formed in steel substrate coated by porous nickel deposit. This galvanic cell can promote steel substrate dissolution when immersed in acid media with simultaneous hydrogen growth or oxygen lessening on nickel coating. Because nickel is splendid with respect to steel, the coating ought to be pore-free to keep away from a lofty cathode-to-anode region ratio which may guide to extreme localized corrosion of iron substrate. It is not the case for galvanized steel because zinc metal is active to steel and the presence of pores in zinc coating leads to a high anode-to-cathode area ratio. Thus, galvanic corrosion current density is weak and no steel corrosion is expected. Instead, bare steel parts will be sacrificially protected by cathodic currents flowing between anode and cathode.

Test methods for assessment of porosity of metallic coatings on steel substrate can be classified into chemical and electrochemical tests; the chemical test include:

- Salt spray
- SO_2 exposure
- Use of ferroxyle indicator
- Corrodkote corrosion tests

The electrochemical test methods are rapid and more reliable. They include:

- Electrographic test
- Tafel extrapolation
- returning voltametry
- Linear division resistance
- Corrosion probable screening.

3.5.7 Electrochemical tests

Of course an electric current is accompanied with corrosion process (electrochemical reaction). For this reason it is possible to find corrosion rate if this current (current density) has been known. Current density can be defined the current per area of exposed surface of metal corroded (designated i). Unit of corrosion rate r is mol/m^2-s and can be determined by this expression

$$r = \frac{i}{nf} \qquad (3.4)$$

n is equal the number of electrons that accompanied the ionization of atoms and f is Faraday's constant = 96500 c/mol (Callister, 1940).

3.5.8 Linear polarization resistance

Linear polarization resistance (LPR) is a quick, nondestructive testing technique commonly used in material corrosion studies to gain corrosion rate data. For this method the material is polarized, typically on the order of ±10mV, relative to its Open Circuit (OC) potential—the potential measured when no [net] current is flowing. As the potential of the material (working electrode) is changed, a current will be induced to flow between the working and counter electrodes, and the material's resistance to polarization can be found by taking the slope of the potential versus current curve. This resistance can then be used to find the corrosion rate of the material using the Stern-Geary equation.

It is the laboratory nondestructive quick test which is usually used to investigate the corrosion rate, the way to conduct this test is polarizing the material 10 mV plus and mines to its open circuit potential (OCP). The OCP can be measured by potentiostat when there is no net current flow (Kharmachi, 2015).

CHAPTER 4
METHODOLOGY

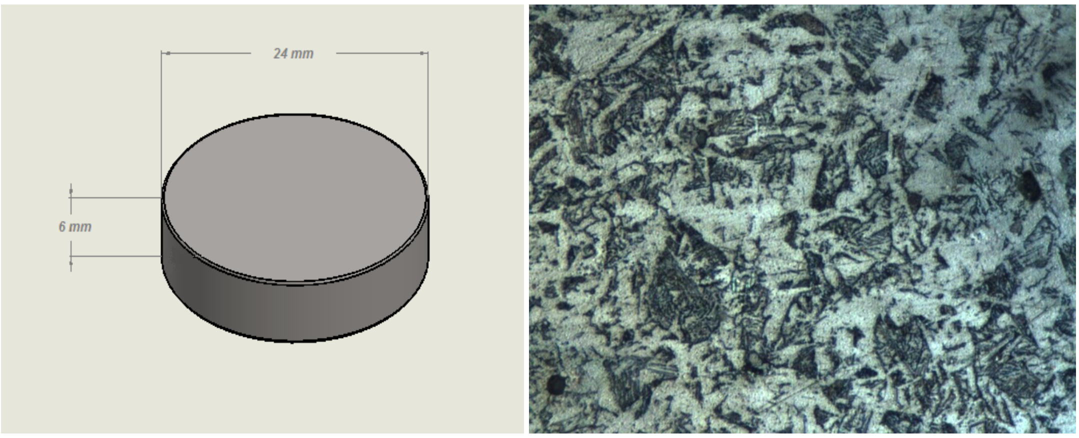
This chapter describes the materials and methods used in this research work. It includes the details of the design and construction of electroplating cell used for the purpose of this investigation. Since the aim of this work was to deposit and study deposited nickel and nickel-cobalt films, latter part of this chapter deals with various electrochemical and analytical methods for characterization electrodeposited layers.

4.1 Materials

Test material used in this investigation is a commercial quality AISI 1021 carbon steel rod. The chemical composition and dimension and microstructure of the steel are given in Table 4.1 and Figure 4.1 respectively. It's worth mentionable that the chemical composition of steel sample that given in table 4.1 was obtained by using ARL 3460 OES metals analyzer device. Test conducted in LISC, in Misruta, Libya.

Table 4.1: The chemical composition of the carbon steel tested

Element	Fe	C	Mn	Si	P	S	Ni	Cu	Cr
Wt%	98.86	0.21	0.87	0.15	0.03	0.05	0.11	0.45	0.10



(a) Sample dimensions (b) Optical micrograph of steel substrate (x1000)

Figure 4.1: Test sample

4.2 Sample Preparation

The received test sample were in the form of rods 40-50 cm long. These rods were cut using the cut-off wheel in the Department of Material Science and Engineering at the University of Tripoli into disc-shaped samples 24 mm in diameter and 6 mm thick as shown in Figure 4.1. The cutting operation was done under running water to avoid over-heating which may bring about changes in properties of the steel sample. Test samples were marked from SS1 to SS72 for conventional electrodeposition, then test samples were carried for surface preparation on emery paper and were successfully ground on emery paper size 120 down to 1000 grit. Following this, test samples were cleaned under running water, washed with distilled water. Following the mechanical surface preparation, the surfaces of test samples were ultrasonically cleaned in 5 wt% NaOH solution. The final cleaning step was done in 10% HCl solution, then washed with acetone and dried just before immersion in plating cell.

4.3 Cell Construction

The electro-deposition cell used for this work consisted of a half-liter beaker, a nickel or a platinum anode, and the steel disc sample (cathode). The cell and its contents were thermo-stated in WNB 22, 60529-IP 20, Memmert, Germany thermal bath with controllable temperature to within ∓0.1°C as shown in Figure 4.2. Test leads or electrical connections were connected to a 248615116 Electro-Automatic Laboratory Power Supply, China made.

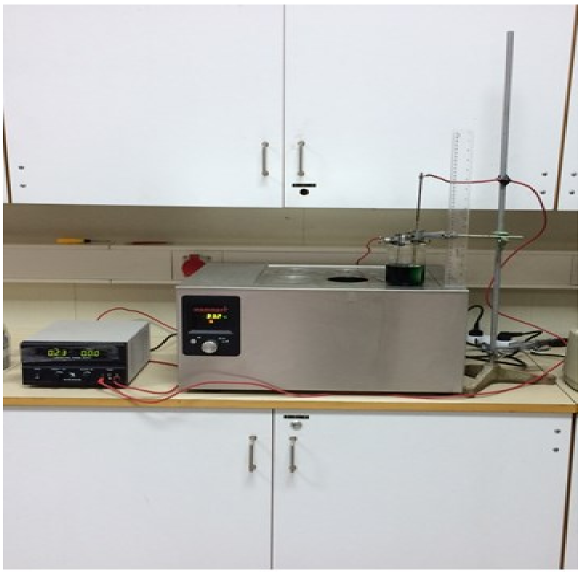
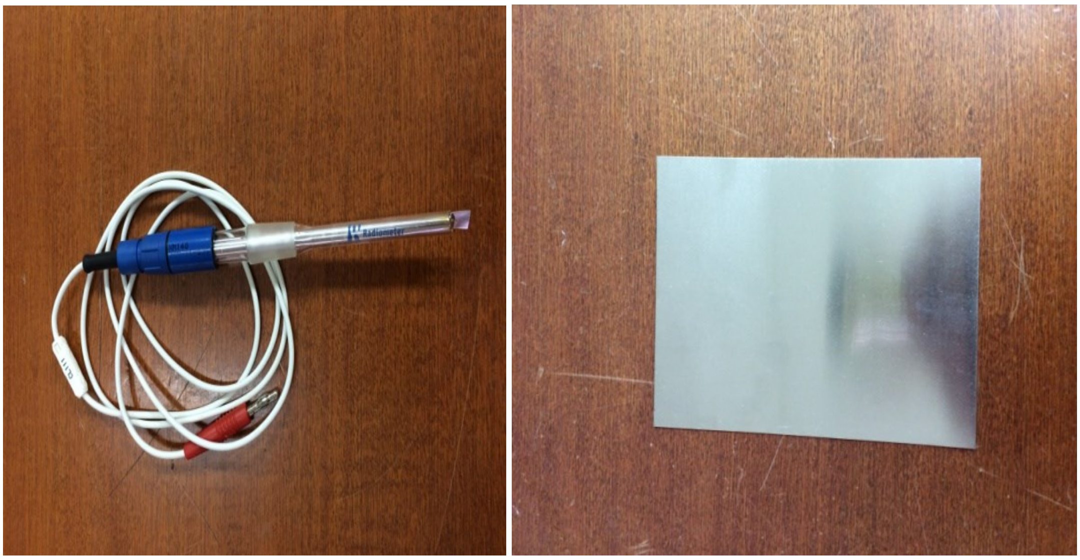


Figure 4.2: Experimental set-up prepared for the electrodeposition process

In the preliminary experiments, the anode was of platinum type electrode due to lack of Ni-anode. Later, a platinum anode was available that was manufactured by Radiometer Analytical Company, France. Eventually, a high purity 99.96% Nickel anode size 150 * 100* 0.6 mm was received, brand Tifoo that was manufactured in Germany and was procured from UK as shown in Figure 4.3.



(a) Insoluble Pt anode (b) Soluble Ni anode

Figure 4.3: Types of anode materials used

Test samples were fixed in a sample holder as shown in Figure 4.4 in next page. The sample holder was constructed from polypropylene plastic material fitted with an O-ring to isolate all sample surfaces except the exposed area to be coated. The holder was fitted with steel rod for electrical connection to ensure the minimum resistance bath for electrical connection. The holder was also inert to the chemical bath used for electrodeposition.

4.4 Bath Composition

Solutions used for electrodeposition of Nickel or Nickel-Cobalt coating were prepared from analytical grade reagents and distilled water. The composition of the first bath utilized is given in Table 4.2, the amount of chemicals of Watt's bath converted to molarities in order to conduct the experimental in half liter beaker and saving the used chemicals.

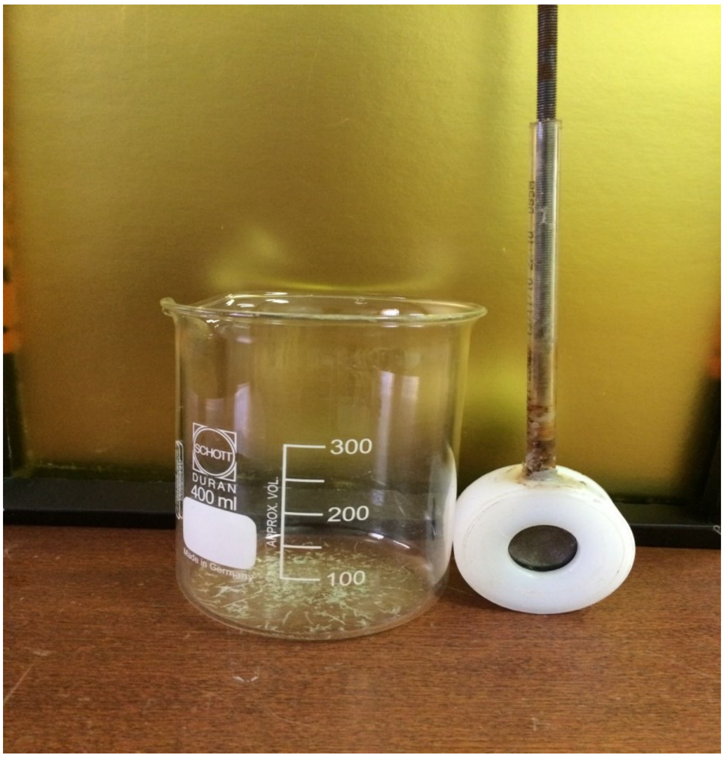


Figure 4.4: The holder made for samples

Table 4.2: The composition of the first bath for Ni-deposition

Bath composition	Molarity (M)
Nickel sulfate	1.3
Nickel chloride	0.3
Boric acid	0.48

The composition of the second bath is seen in Table 4.3.

Table 4-3: The composition of second bath (Ni-Co Binary Coating)

Bath composition	Molarity (M)
Nickel sulfate	1.3
Nickel chloride	0.3
Boric acid	0.48
Cobalt sulfate	0.071

The weight of chemicals needed for the preparation of baths were determined using an electrical balance which has the smallest division of 0.0001g.

4.5 Experimental Procedure

Right after completion of mechanical surface preparation and chemical cleaning, the test samples were washed with distilled water and immediately placed in the plating bath. The cathode (substrate) and anode were fixed in the bath at a distance of approximately 25 mm from each other. The initial weight of test samples was taken to the nearest 0.0001g. Then, test samples were fixed in place in the sample holder, immersed in the electrodeposition bath. The correct level of current density was adjusted on the power supply unit to allow changing the value of this parameter from 10 mA/cm^2 to 60 mA/cm^2 and temperature was set between 40-60^{o}C.

Bath temperature was adjusted by a temperature controller to the nearest 0.1°C. The pH of the bath was measured by HI98103 Hanna portable pH meter. The electrodeposition time was followed by a stop watch and was varied between 15 to 45 minutes without agitation. After electrodeposition, test samples were washed under running water, dried under a stream of hot air and weighed using an electrical balance.

4.6 Test Parameters

The electrodeposition process is highly influenced by the test parameters. Therefore, the test parameters below were followed closely for the control and assessment of the Nickel and Nickel-Cobalt electrodeposition processes.

- Current density
- Temperature of the bath
- Time of deposition
- Bath composition

4.7 Characterization of Deposition Layers

The sample preparation for microstructure examination, micro-hardness measurement and SEM examination was carried out as following:

Samples have to be made from cross section for study the deposition layer of coated samples. The non coated (as received) and coated samples were cut by using the cut-off wheel with the same procedure mentioned in Section 4.2. Afterwards, these samples were sent to Abosaliem Advanced Center for Technology in order to fabricate a convenient mount for grinding and polishing of the sample surfaces. In sequences steps, each metallographic sample (as received designated AR, nickel coated designated Ni C and nickel-cobalt coated designated Ni-CC) were ground, polished, etched, and finally examined in the optical microscope.

With running water, wet grinding operation was carried out on the SiC emery papers from coarse to fine grids, i.e. 120, 220, 320, 500, 1000 and 1200 mesh numbers. After grinding operations, the samples were polished using 1 μm particle size diamond paste, then, coarse and fine grades of aluminum oxide Al_2O_3 were applied for further polishing. The final polishing finish was performed on the polishing cloth using an alumina solution (0.25 μm), followed by cleaning the steel sample surface with water then alcohol, finally dried in the air drier.

The polished sample surfaces were etched in a 2% Nital solution, i.e. 2% nitric acid in methanol, the sample surfaces were again cleaned using water then acetone. After these surface preparation stages, the samples were ready to undergo optical microscope examination, micro-hardness measurements and scanning electron microscopy (SEM) observations.

4.7.1 Optical microscopy examination

The prepared metallographic samples were examined in a metallurgical light microscope. The micrographs of the electrodeposited layers and as received samples were taken by a camera fitted within the metallurgical light microscope.

4.7.2 Scanning electron microscopy (SEM)

As received and nickel-cobalt coated samples were sent to Libyan Petroleum Institute in Tripoli for examination in the scanning electron microscope. The morphologies of the coated samples were studied using a JEOL scanning electron microscope. Images were taken under 10KV electron beam energy.

4.7.3 X-Ray diffraction examination

Coated carbon steel samples were also taken to the XRD unit available at the Libyan Petroleum Institute for identification of deposited phase using the X-ray diffraction analysis. Test samples were scanned between (10 to 100°) 2θ degree diffraction angle.

4.7.4 Micro-hardness measurements

As received and nickel-cobalt electrodeposition coated samples were also sent to Abosaliem Advanced Center for micro-hardness measurements. The micro-harness of samples were measured by micro-hardness tester, Vicker micro-hardness technique by applying 300gf was performed. The final value quoted for micro-hardness were an average of twelve measurements performed on a different locations in the sample surface. Standard sample which is non coated(as received carbon steel) was tested to compare the improvement of hardness due to electrodeposition process.

4.8 Electrochemical Characterization

4.8.1 Setup and calibration the system

Potentiostat was connected to a dummy cell as shown in the Figure 4.5, the GAMRY software codes were entered to the computer used in this set up. All charts were identical with those counterparts in the potentiostat catalog which meant that our system did operate perfectly.

Figure 4.5: Calibration of the system with the dummy cell

4.8.2 Cell preparation and constructions

Electrochemical measurements were done in a stagnant 3% NaCl solution. The solution was prepared from analytical grade reagents and distilled water. A three electrode cell was constructed to conduct the electrochemical measurements. Platinum type counter electrode (CE) was used with an area of 1 cm2 where as saturated calomel electrode (SCE) was employed as a reference electrode (RE). Carbon steel (of commercial quality) in the shape of a disc sample of 24 mm diameter and 6 mm thick was used as the working electrode. Electrochemical test sample was located in the same flat sample holder that was used in the electrodeposition experiments seen in Figure 4.4 to form the working electrode. The reference electrode was prepared by adding crystals from KCl salt and shake it until these crystals did not dissolve anymore and become saturated, the reference electrode is shown in Figure 4.6. It had to be located as close as possible to the exposed area of the test sample as shown in Figure 4.7. The electrochemical cell connected to the S.N 06048, potentiostat/Galvanostat/ZRA Reference 600 Potentiostat produced by GAMRY Instruments is shown in Figure 4.8.

Figure 4.6: Reference electrode, i.e. Saturated Calomel Electrode (SCE)

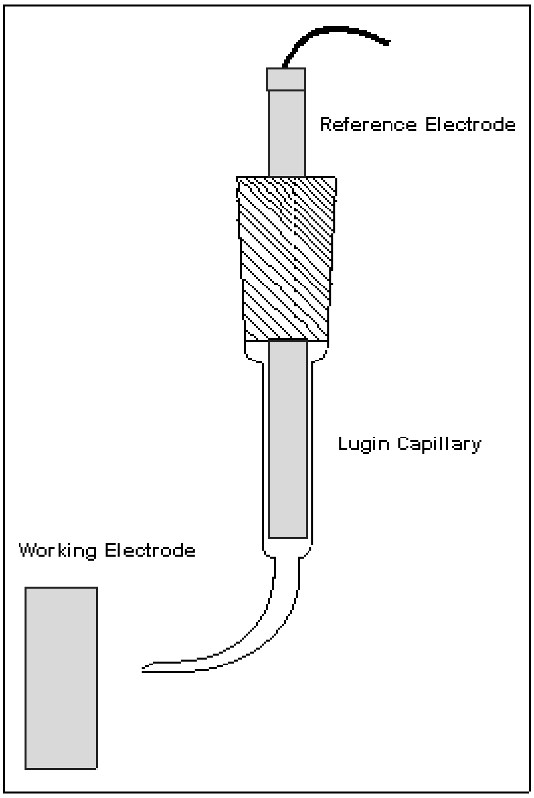


Figure 4.7: The position of the reference electrode relative to the working electrode (sample)

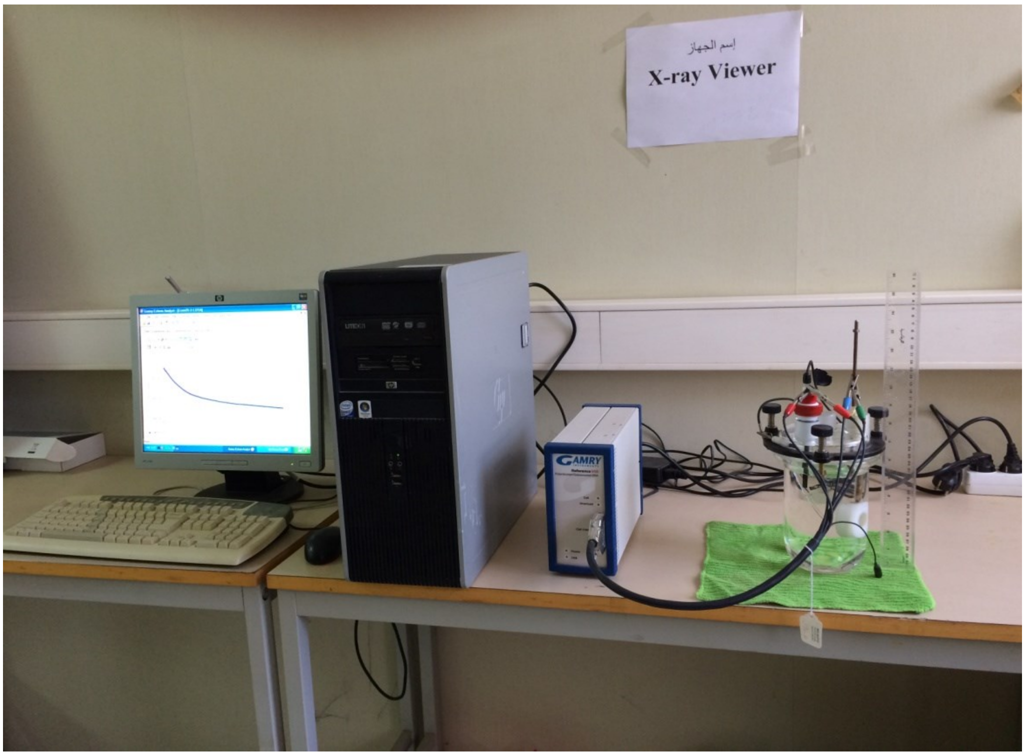


Figure 4.8: The parts of the electrochemical system

4.8.3 Electrochemical measurements

Using a three-electrode cell, two types of polarization measurements were carried out on the coated and bare steel surfaces. These measurements were performed using the Gamry Reference 600 Potentiostat/Galvanostat. The measurements were performed at room temperature (20ºC) in an open system (open to air). Prior to the electrochemical measurements all test sample were immersed in the test solution for the same period of time (pre-conditioning) to reach a stabilized corrosion potential value before start of polarization.

After stabilization of the open circuit potential cyclic and potentiodynamic scans were carried out at a scan rate 1 mV/s.

CHAPTER 5
RESULTS AND DISSCUSION

In this chapter, the results for two types of electrodeposition baths that were tried are presented. The first type of bath was for nickel coating deposition, whereas second was designed to deposit Ni-Co via electrodeposition.

5.1 Deposition Result for Ni-Bath

The data presented in Table 5.1 is for the electrodeposition of nickel on carbon steel substrate using platinum anode at a temperature of 40°C. The current density range for this set of deposition experiments was from 30 to 180 mA/cm^2. The time of deposition was fixed at 30 minutes according to the data given in Table 5.1, the deposition rate was increased from 1.5 mg/min at a current density of 30 mA/cm^2 to 10.2 mg/min at the maximum current density of 180 mA/cm^2.

When platinum was used as the anode material in the electrodeposition cell, a gradual decrease in the pH value was noted from 3.5 at the beginning of the experiments to pH= 1.1 in the last run. The change of the pH of plating solution to a very acidic value can be explained by the oxidation of water molecules at the anode surface according to the electrochemical reaction mentioned in equation 5.1.

Table 5.1: Ni-deposition on carbon steel substrate using Pt-anode at 40°C

Sample Number	Current Density(mA/cm^2)	pH	Temperature (°C)	Anode	Deposition Time(min)	Deposition Rate(mg/min)
1	30	3.5	40	Pt	30	1.50
2	60	2.3	40	Pt	30	4.25
3	90	1.8	40	Pt	30	5.72
4	120	1.6	40	Pt	30	7.11
5	150	1.2	40	Pt	30	8.43
6	180	1.1	40	Pt	30	10.20

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad (5.1)$$

A second set of runs for the electrodeposition of nickel on carbon steel substrate was carried out at 60ºC. The data for this set of runs is presented in Table 5.2. According to data given in Table 5.2 no appreciable changes in rate of deposition were recorded although the temperature was raised from 40 to 60ºC. This was probably due to the effect of the bath pH values changes because again under these experimental condition a gradual decrease in pH was recorded.

Table 5.2: Ni-deposition on carbon steel using Pt-Anode at 60ºC

Sample Number	**Current Density(mA/cm^2)**	**pH**	**Temperature (ºC)**	**Anode**	**Deposition Time(min)**	**Deposition Rate(mg/min)**
7	30	3.5	60	Pt	30	1.52
8	60	3.3	60	Pt	30	3.38
9	90	2	60	Pt	30	5.04
10	120	1.6	60	Pt	30	7.03
11	150	1.4	60	Pt	30	8.66
12	180	1	60	Pt	30	10.88

The variation of the coating thickness with the imposed current density is shown in Figure 5.1. The calculated nickel coating thickness increased steadily as the current density in both cases at 40 and 60ºC bath temperature, the quoted thickness values were given in microns.

The examination coating thickness of about 100 microns was recorded at the maximum current density of 180 mA/cm^2. As can be seen in Figure 5.1 no appreciable changes in the rate of deposition and consequently in coating thick can be observed as the bath temperature changed from 40 to 60ºC.

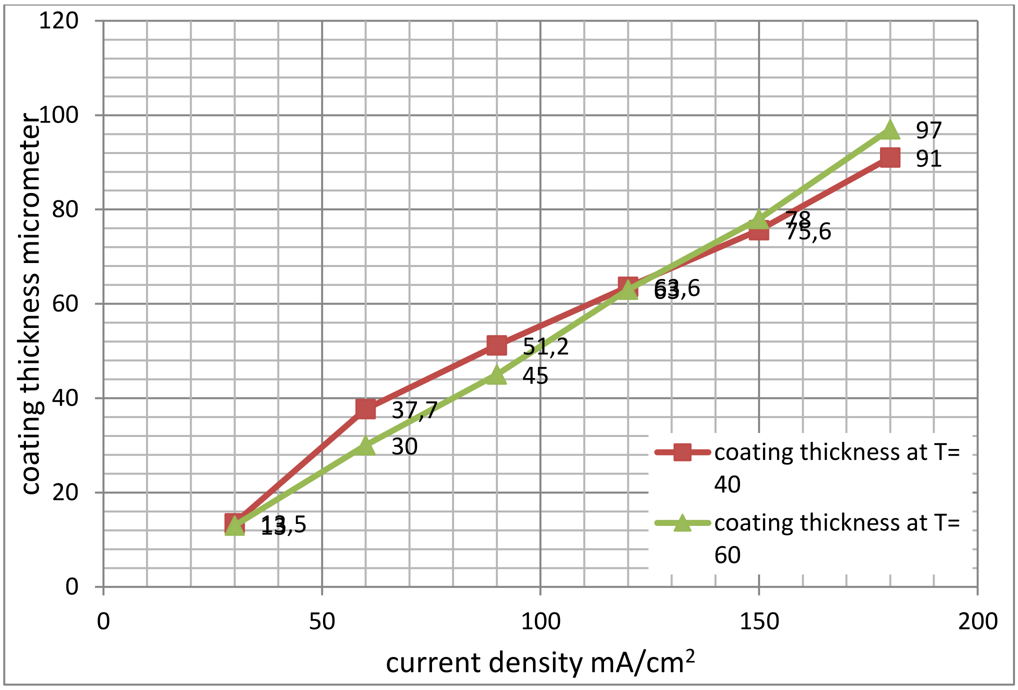


Figure 5.1: Current density vs the thickness Ni coating

5.2 Ni-Co Deposition

After the initial successful runs of electrodeposition from Ni-plating bath and after procurement of nickel anode which was imported from UK and produced by Tifoo Germany company, the testing program was directed towards the electrodeposition of Ni-Co deposition on carbon steel substrate. The first set of runs was carried out at 40ºC for 30 minutes as the time of deposition, as given in Table 5.3. The current density range was chosen between 10 and 50 mA/cm^2. Under this testing regime the pH of the electroplating bath was controlled to within 0.1 variation as can be read in column (3). The rate of deposition was varied between 0.5 to 2 mg/min.

Table 5.3: Electrodeposition of Ni-Co coatings using Ni-anode at 40ºC

Sample Number	Current Density(mA/cm^2)	pH	Temperature (ºC)	Anode	Deposition Time(min)	Deposition Rate(mg/min)
13	10	3.7	40	Ni	30	0.46
14	20	3.7	40	Ni	30	0.73
15	30	3.8	40	Ni	30	1.71
16	40	3.8	40	Ni	30	1.86
17	50	3.7	40	Ni	30	2.10

Using nickel as anode in the electroplating cell, a second set of electrodeposition runs was carried out at 50ºC at a fixed deposition time of 30 minutes. A similar observation was made on the effect of temperature on deposition rate as in the case of nickel electrodeposition as given in Table 4.4.

Table 5.4: Electrodeposition of Ni-Co coatings using Ni-Anode at 50ºC

Sample Number	Current density(mA/cm^2)	pH	Temperature (ºC)	Anode	Deposition Time(min)	Deposition Rate(mg/min)
18	10	3.6	50	Ni	30	0.61
19	20	3.7	50	Ni	30	0.82
20	30	3.6	50	Ni	30	1.76
21	40	3.7	50	Ni	30	2.10
22	50	3.6	50	Ni	30	2.26

Figure 5.2 shows the result on the effect of current density on coating thickness at 40ºC and 50ºC. It was interesting to note that under bath test parameters a sharp increase in coating thickness was recorded above the current density 20 mA/cm^2. It appears to be convenient to choose 30 mA/cm^2 as the optimum current density for electrodeposition of Ni-Co layers on carbon steel substrate for getting electrodeposition of about 15 microns thickness.

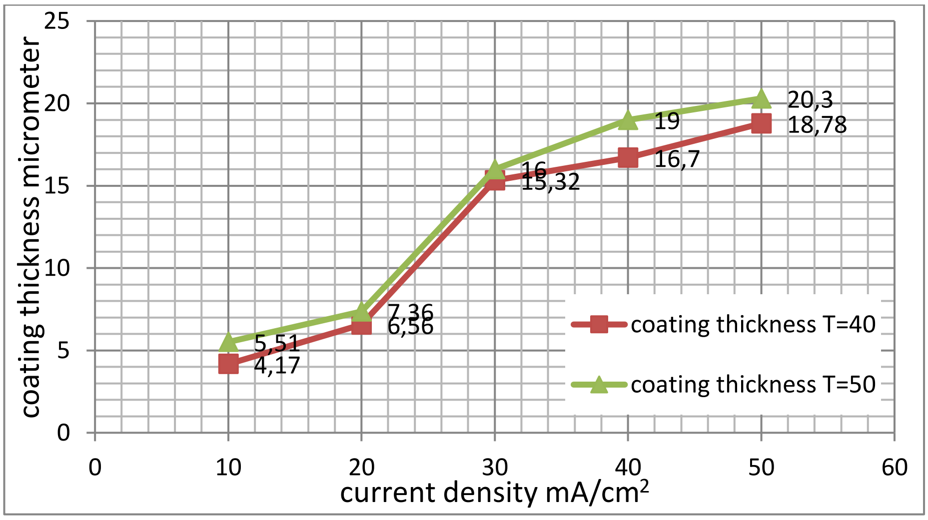


Figure 5.2: Current density vs the thickness of Ni-Co coating

The effect of time deposition on the thickness of deposited layer is given in Table 5.5 for three time periods. Figure 5.3 shows that as the time of deposition exceeded 30 minutes excessive thick layers can be deposited. For example, at 30 min the thickness of deposited Ni-Co layer was about 20 microns. As the time of deposition was increased to 45 minutes the thickness of deposited layer was more than 3 times the thickness obtained for 30 minutes. This means thicker deposited coating could be obtained at longer deposition time. The obtained result is matched well to Koay Mei Hyiea result in his research work.

Table 5.5: Optimum operating conditions with various deposition times

Sample Number	Current Density(mA/cm^2)	pH	Temperature (ºC)	Anode	Deposition Time(min)	Deposition Rate(mg/min)
23	30	2.8	40	Ni	15	1.34
24	30	2.8	40	Ni	30	1.71
25	30	2.8	40	Ni	45	6.53

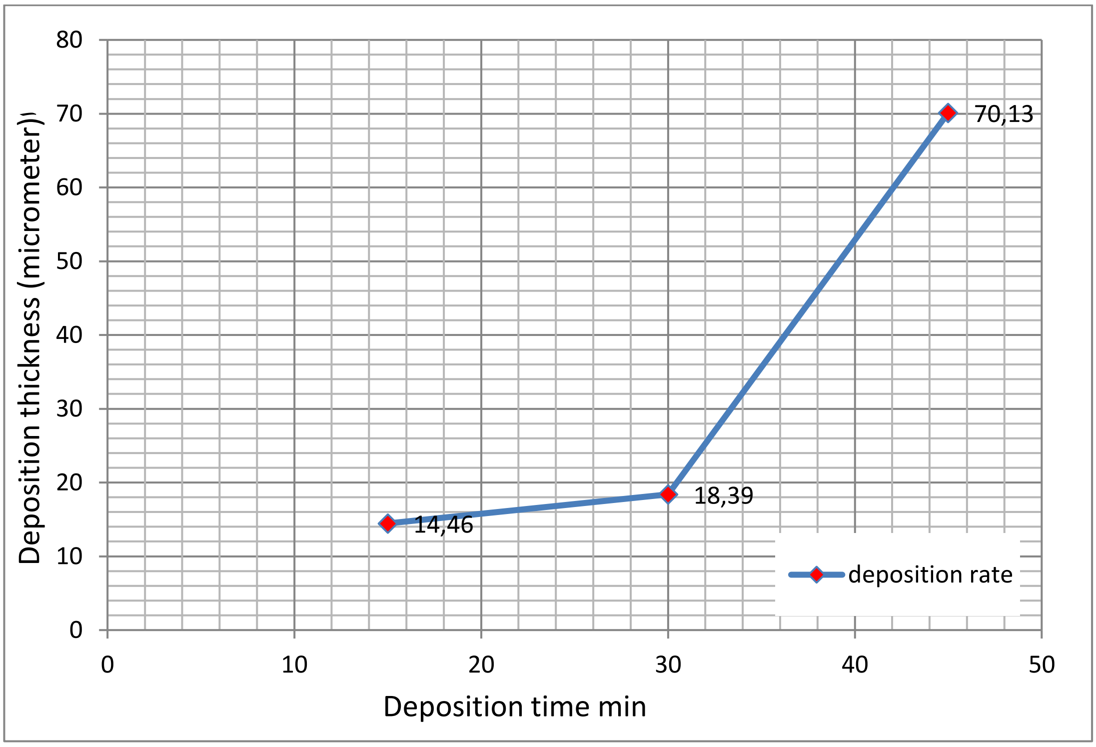


Figure 5.3: Deposition time vs deposition thickness

5.3 Effect of Current Density on Efficiency

The current efficiency was based on the following calculation:

$$\text{Current efficiency} = 100 \text{ x } (W_{\text{actual}}/W_{\text{theoretical}}) \quad (5.2)$$

$$\text{Actual weight} = (\text{Final weight - Initial weight}) \quad (5.3)$$

Theoretical weight =

(Current in Amp x time in sec x atomic weight of nickel)/(96500 x valency) (5.4)

Example; sample number 1:

$$(\text{actual weight}) \quad 17.2194 - 17.1742 = 0.0452 \text{ g}$$

$$(\text{Theoretical weight}) \quad (0.11*1800*58.59)/(96500*2) = 0.0602 \text{ g}$$

$$\text{Current efficiency} = 100*(0.0452/0.0602) = 75\%$$

Also

$$\text{Thickness} = (\text{Wactual x } 10{,}000)/ (\text{area x density of nickel})$$

$$(0.0452*10000)/(3.14*8.90) = 16\mu\text{m}$$

Figures 5.4 and 5.5 show the dependence of current efficiency on applied current density for Ni- coatings and Ni-Co coatings, respectively. A comparison of data provided in these two figures revealed that a higher deposition efficiency was achieved for Ni-coating on carbon steel when a maximum efficiency of 95% was recorded. On the other side, for the Ni-Co electrodeposition the maximum efficiency percentage was found as 84%.

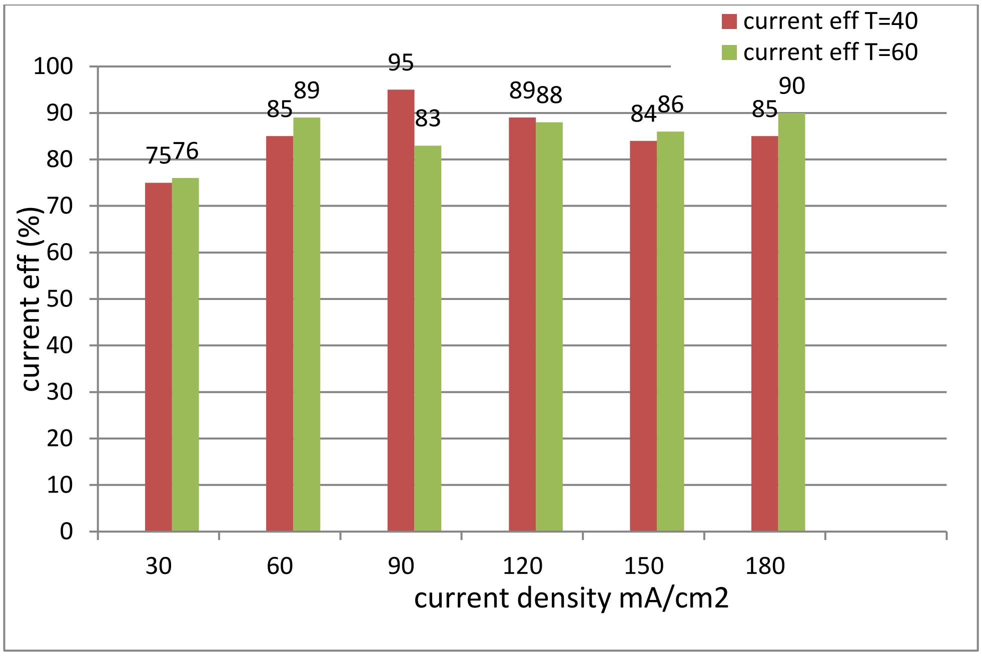


Figure 5.4: Current density vs current efficiency during Ni coating

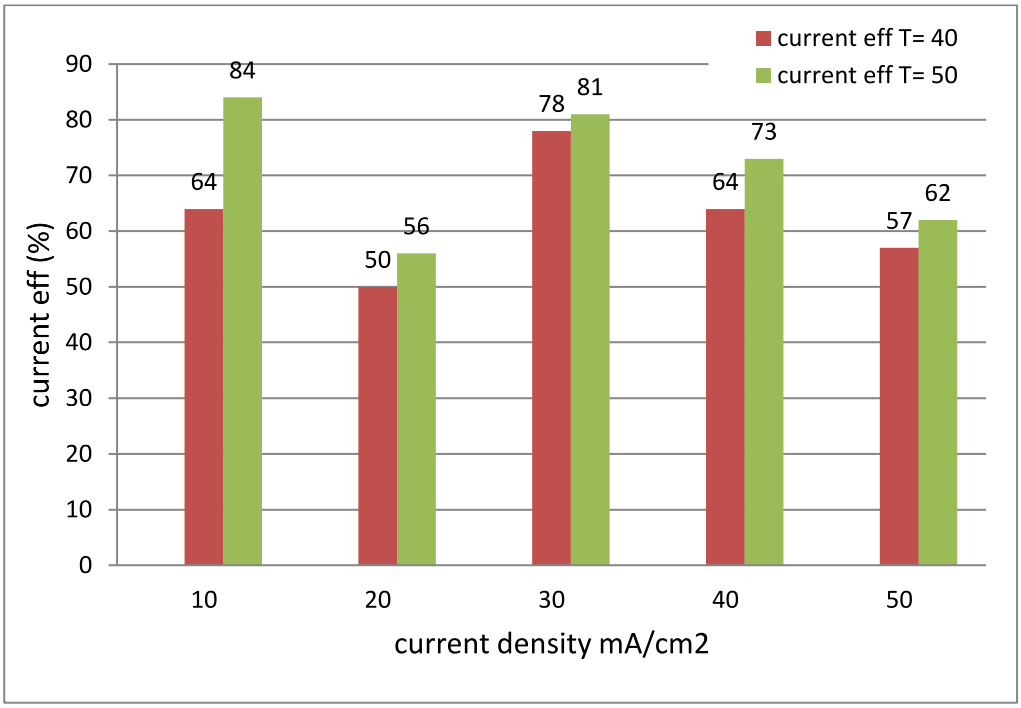


Figure 5.5: Current density vs current efficiency during Ni-Co coating

5.4 Effect of Anode Type

At the beginning of test program, an inert type of anode was used. However, such uses imposed a negative effect on the bath chemistry in terms of changes in pH values as explained previously in section 3.3.7. For running electrodeposition of nickel on carbon steel substrate covering a current density range from 30 to 180 mA/cm^2, a total of 150 minutes were needed. The pH changes in this time interval using platinum anode as shown in Figure 5.6. A sharp decrease in the pH values were noted in the first hour. Following this, the pH continued to fall down to about pH = 1 by the end of deposition experiments. This behavior was similar at both testing temperatures, namely 40 and 60ºC.

After the procurement of a new type of anode material these undesirable effects on the bath chemistry were avoided. The Ni-anode in the form of the plate was obtained and installed in the electrodeposition cell. Monitoring of the pH during the electrodeposition runs of Ni-Co alloye showed a more or less stable values of pH of the electrodeposition bath as shown in Figure 5.7 where an average value of pH = 3.7 can be seen. However, some researchers such as O. Sadiku-Agboola, E.R. Sadiku, and others suggest a pH of 4 to 5 for good results. The following equations can describe most reactions happened in electroplating cell (Popov, 2002).

Nickel plating cell with Pt insoluble anode follows the reactions below at the anode:

$$2SO_4^{2-} \rightarrow S_2\,O_8^{2-} + 2e^- \qquad (5.5)$$

$$2H_2O \leftrightarrow O_2 + 4H^+ + 4e^- \qquad (5.6)$$

On the cathode the following reactions are expected :

$$O_2 + 4H^+ + 4e^- \rightarrow 2H_2O \qquad (5.7)$$

$$Ni^{2+} + 2e^- \rightarrow Ni \qquad (5.8)$$

$$2H^+ + 2e^- \rightarrow H_2 \qquad (5.9)$$

$$SO_4^{2-} + 2H^+ + 2e^- \rightarrow SO_3^{2-} + H_2O \qquad (5.10)$$

In nickel-cobalt plating cell using with soluble anode Ni, the following reactions are possible at the anode:

$$2SO_4^{2-} \rightarrow S_2O_8^{2-} + 2e^- \qquad (5.11)$$

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^- \qquad (5.12)$$

$$Ni \rightarrow Ni^{2+} + 2e^- \qquad (5.13)$$

The possible reactions on cathode would be:

$$O_2 + 4H^+ + 4e^- \rightarrow\ 2H_2O \tag{5.14}$$

$$Ni^{2+} + 2e^- \rightarrow Ni \tag{5.15}$$

$$Co^{2+} + 2e^- \rightarrow Co \tag{5.16}$$

$$2H^+ + 2e^- \rightarrow H_2 \tag{5.17}$$

$$SO_4^{2-} +\ 2H^+ +\ \ 2e^-\ \ \rightarrow\ SO_3^{2-} +\ H_2O \tag{5.18}$$

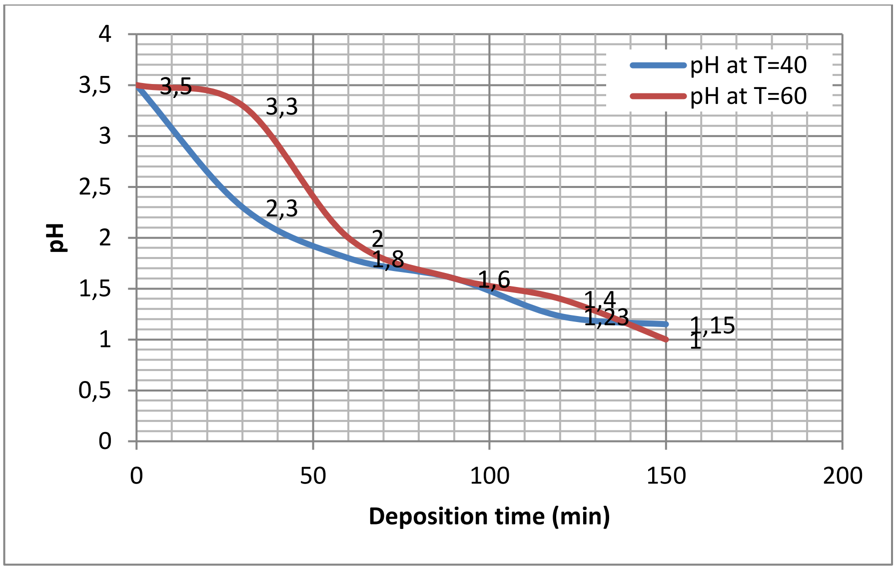


Figure 5.6: Deposition time vs pH during Ni coating

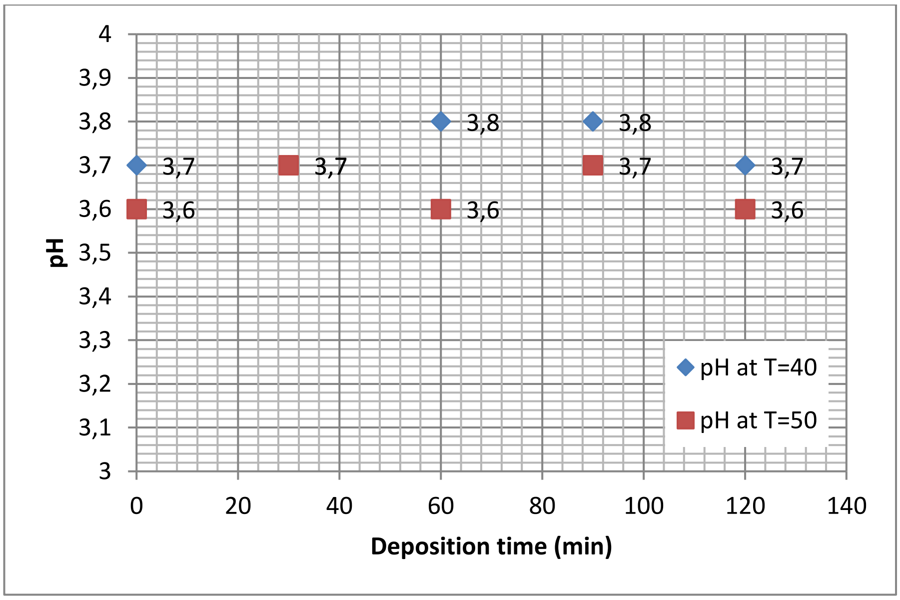


Figure 5.7: Deposition time vs pH during Ni-Co coating

5.5 Properties of Functional Ni-Co Coating

5.5.1 Result of hardness test

The results of hardness test of Ni-Co electrodeposites are shown in Figure 5.8.

Improvement in hardness values from 217 HV for non-coated steel to 250 HV for nickel-cobalt coated steel can be seen in these data. However, not much increase in hardness can be seen because, the electrodeposited layers were not subjected to heat treatment. These results are similar to Koay Mei Hyiea result.

In usual practice, electrodeposited layers are followed by a heat treatment for the purpose of improving hardness. By conducting a heat treatment the micro hardness can be improved to 450 HV.

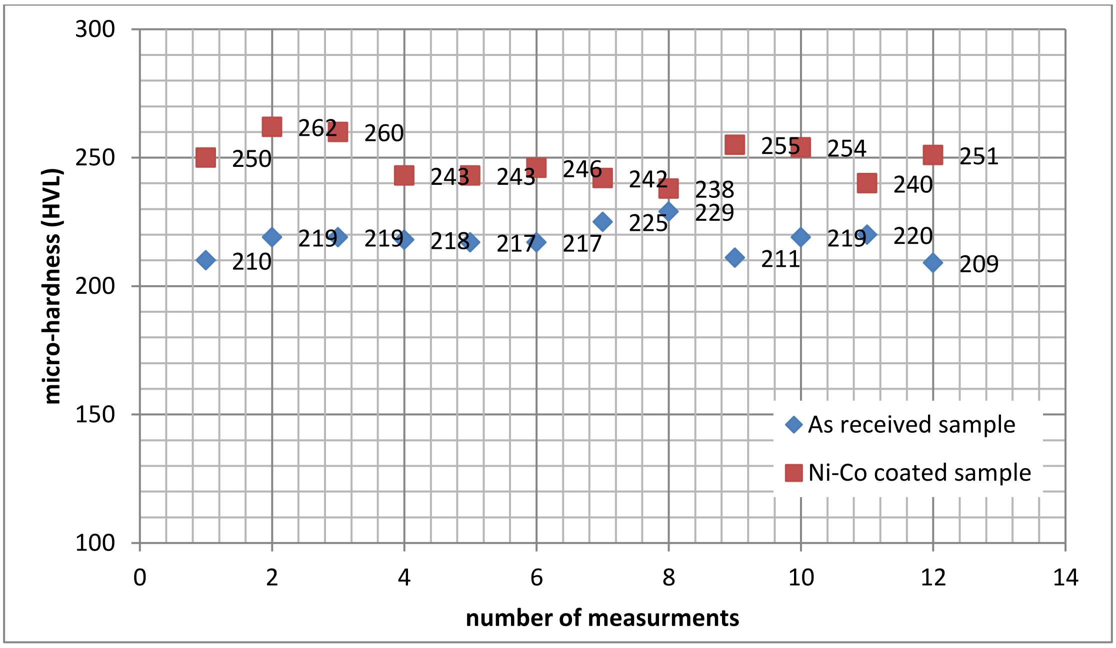


Figure 5.8: Micro-hardness improvement in the Ni-Co coated sample

5.5.2 XRD data

Figure 5.9 shows the surface X-ray diffraction pattern of Ni-Co composite coating deposited on carbon steel substrate from Watt bath electrolytes.

Four peaks with orientation (111), (200), (220) and (311) have been recorded on Ni-Co composite coating diffraction pattern. These were recorded at 2θ values of 45, 52, 77 and 93° corresponding to different crystal facets with the predominance of 200 planes which showed the highest peak intensity, this result has matched well with the standard Ni-Co structure in our data base.

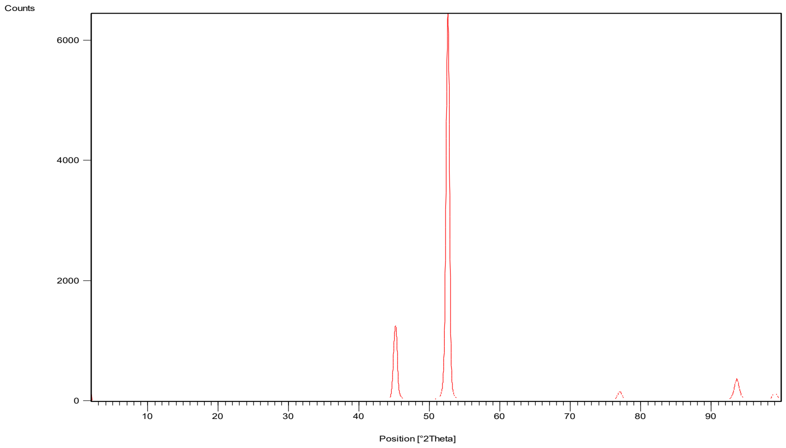


Figure 5.9: XRD patterns of Ni-Co coating at deposition condition current density = 50 mA/cm^2, deposition temperature 50°C and pH value = 3.6

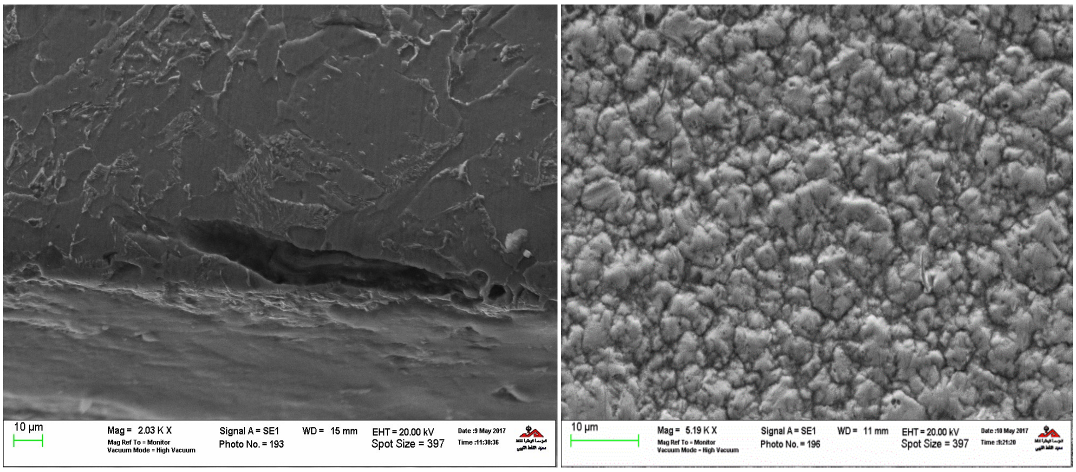
5.3.3 Surface morphology of electrodeposited coating

Figure 5.10 shows the surface morphology of Ni-Co films deposited on carbon steel at 50°C deposition temperature, pH of bath = 3.6, current density = 50 mA/cm^2 and using the nickel anode. As can be seen in the SEM image, a compact, porosity free layer was obtained. The coating was free of cracks and exhibited a good adhesion to the steel substrate. Also, The micrographs of nickel and nickel-cobalt electrodeposited layers were taken by a camera fitted within metallurgical light microscope.

5.3.4 Open circuit potential measurements

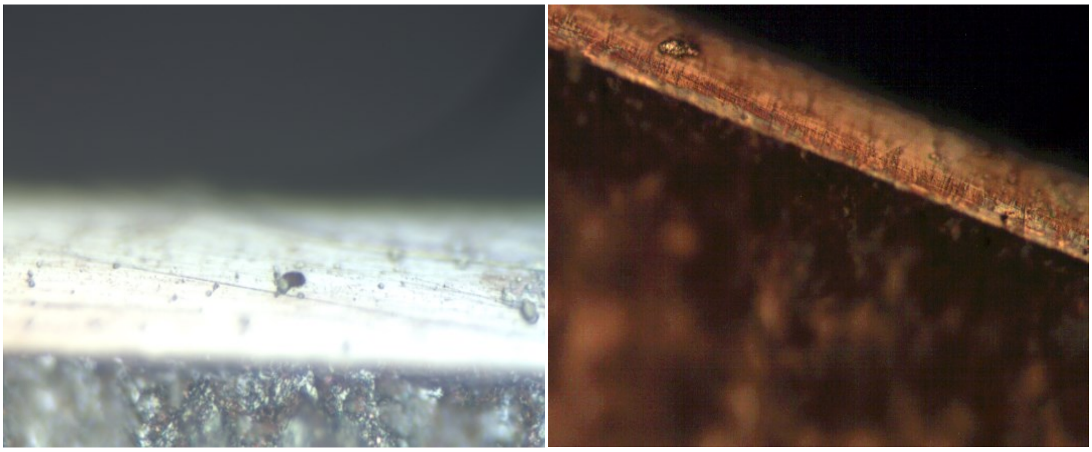
Figure 5.11 shows the corrosion behaviors of coated and bare carbon steel in the 3% NaCl, in terms of open circuit potential values. The noble behavior of the coated steel is evident. It can be seen that a potential difference of about 300 mV can seen which is a substantial improvement in the corrosion behavior in such environments. These results were recorded for a comparison of bare steel with the Ni-Co coated steel. A similar comparison given in Figure 5.12 for measurements with the Ni-coated steel substrate showed a lower resistance to the same test environment (3%

NaCl solution) as compared to Ni-Co coated samples since the difference in the open circuit potential values was only about 200 mV.



(a) SEM micrographs of the interface between Ni-Co deposited layer and carbon steel substrate

(b) SEM micrograph showing nickel-cobalt deposits obtained from second plating bath



(c) Grand and polished cross section of nickel coated sample under optical microscopy with magnification (x1000)

(d) Grand and polished cross section of nickel-cobalt coated sample under optical microscopy magnification (x1000)

Figure 5.10: Optical examination of deposited layer

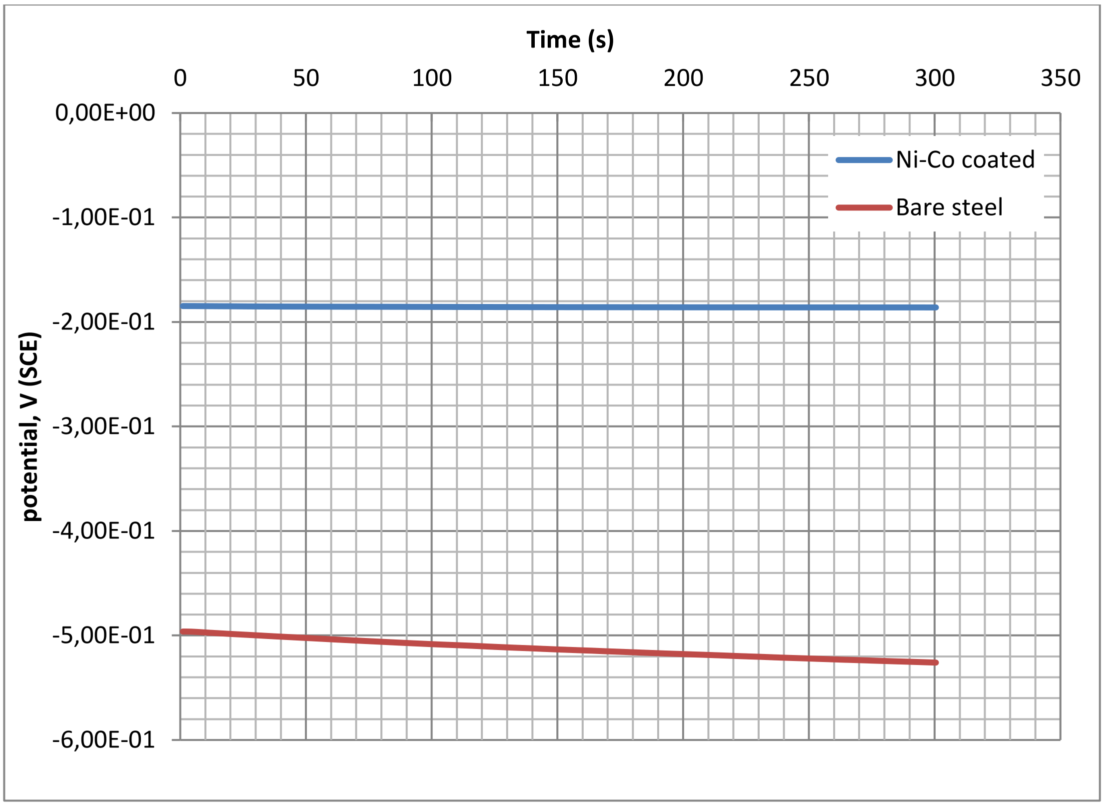


Figure 5.11: Variation of OCP with time for Ni-Co coated and bare steel in (3% NaCl)

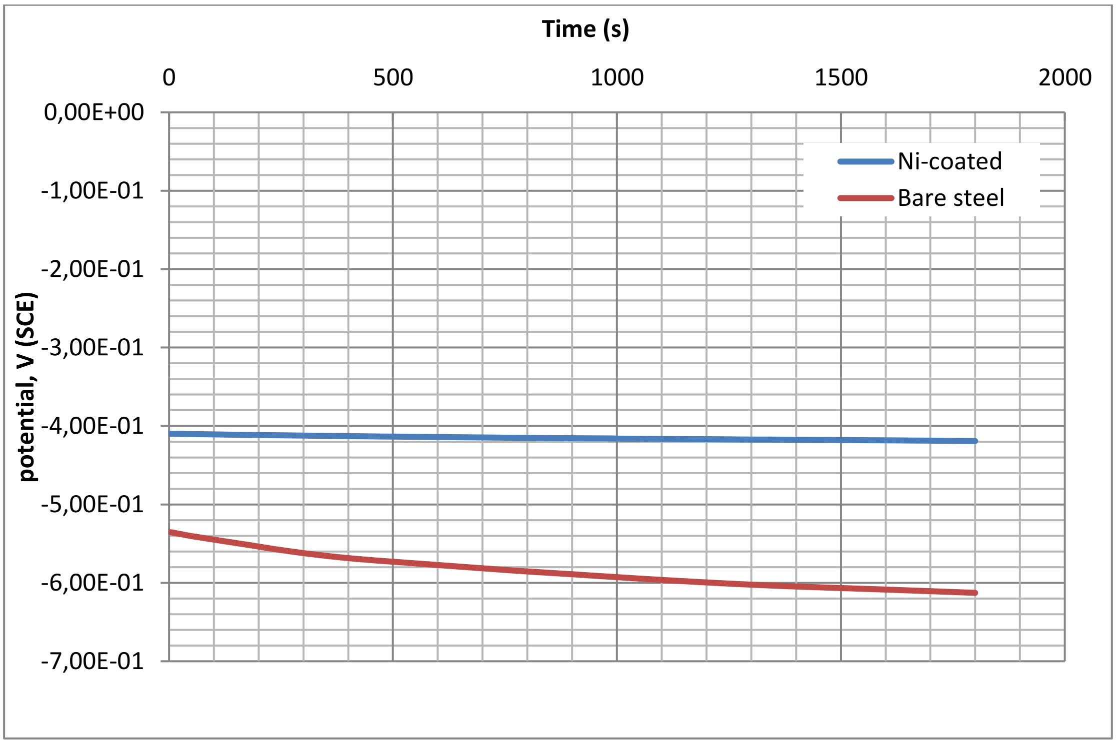


Figure 5.12: Variation of OCP with time for Ni-coated and bare steel in (3% NaCl)

CHAPTER 6
CONCLUSIONS AND FUTURE WORK

6.1 Conclusions

Nickel and nickel-cobalt functional coatings were prepared by conventional electrodeposition methods using inert and nickel anodes on carbon steel substrates. It was found that the current density had a major effect on the rate of deposition, an optimum value of 30 mA/cm^2 was recorded in the present work. Furthermore, insoluble anodes like platinum has a negative effect on pH stability and it could be used only for specific purposes for instance when nickel anodes are not practical such as internal plating or when the space between cathode and anode is limited. On the other hand, nickel anode provide more stability in pH value during Ni-Co electroplating process. The coating was crack-free and exhibited an excellent adhesion to the steel substrate.

One of the most interesting observation was the major effect of deposition time on coating thickness, as the time of deposition increased from 30 to 45 minutes the thickness of deposited film increased 3 times more before 30 minutes. However, temperature did not show appreciable effect on coating thickness during Ni coating because of ph fluctuate and slightly effect during Ni-Co coating. Improvement in micro hardness was not as expected because it was not followed by a heat treatment process.

A close examination corrosion behavior diagram (open circuit potential measurements) have indicated that the coatings can obviously improve the corrosion resistance of the carbon steel substrate in the marine environment. A comparison between two types of coating was conducted and it showed that Ni-Co coating has better corrosion resistivity than Ni coating, it was found that the Ni-Co corrosion potential E_{corr} difference is 300 mV compared to non coated steel and noble behavior is evident. However, Ni coated showed lower corrosion resistivity than Ni-Co coated and it recorded 200 mV deference in corrosion potential E_{corr}.

6.2 Future Work

The assessment of coating continuity of nickel and nickel-cobalt deposits is important because nickel is cathodic to carbon steel substrate. Therefore, additional experimental work may be needed on the characterization of coating porosity. Since electrochemical corrosion testing of deposited layer is a quick test method as shown in this survey, further tests by other gravimetric and physical methods are needed to support the data collected on coating performance in the test environment chosen. It's obvious there is a limitation in this work, for this reason a future work is needed. For instance, there was a sharp increase in deposition thickness between 20 and 30 mA/cm^2 of current density. Therefore, more details study can be conducted in this region to find the optimum value of current density. Also, a specific study may be recommended for an optimum deposition time between 30 and 45 minutes.

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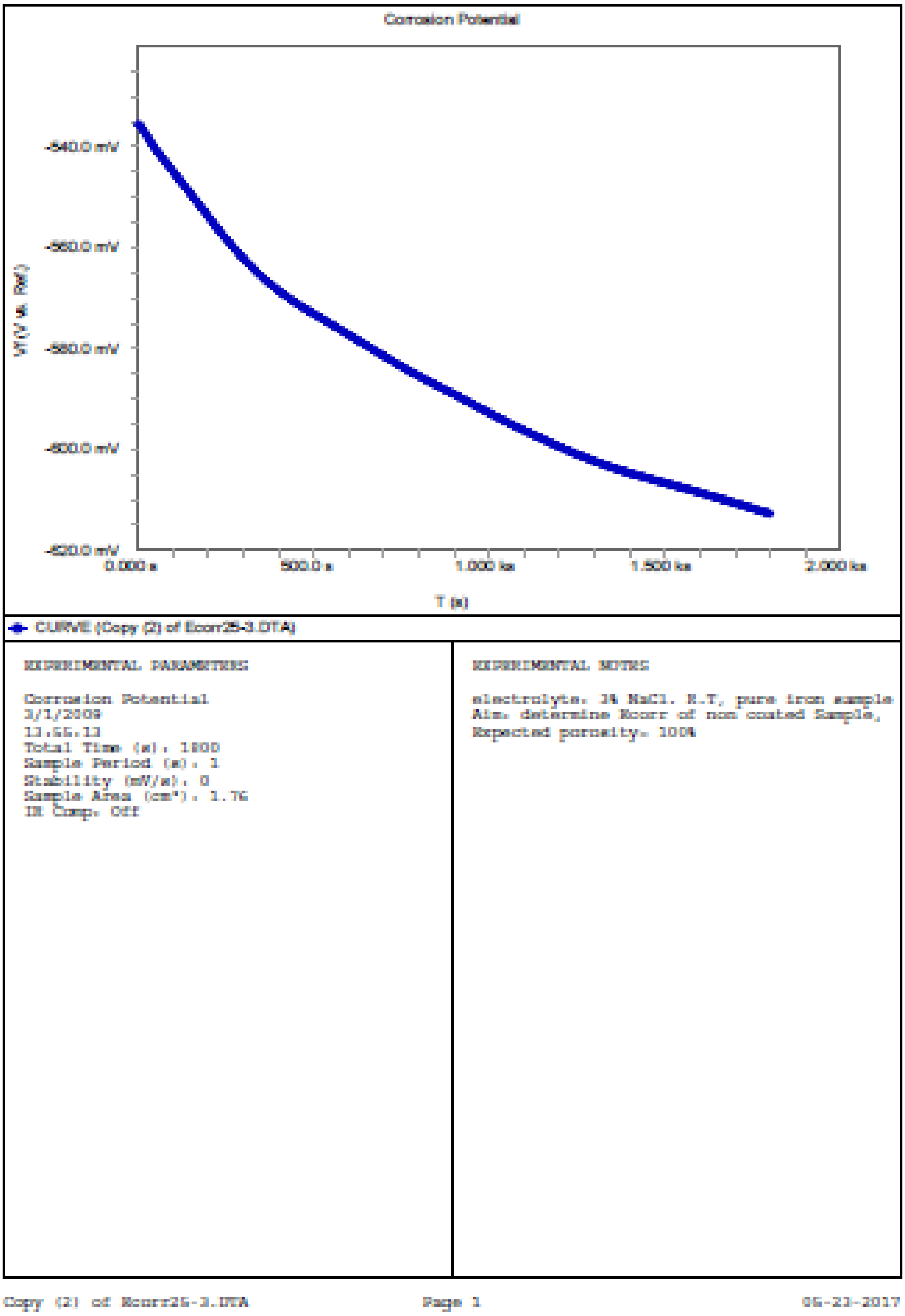
APPENDICES

APPENDIX 1

CORROSION POTENTIAL MEASUREMENTS IN 3% NaCl

GAMRY potentiostat charts used in this present study to determine E_{corr} by conducting the OCP experiment.



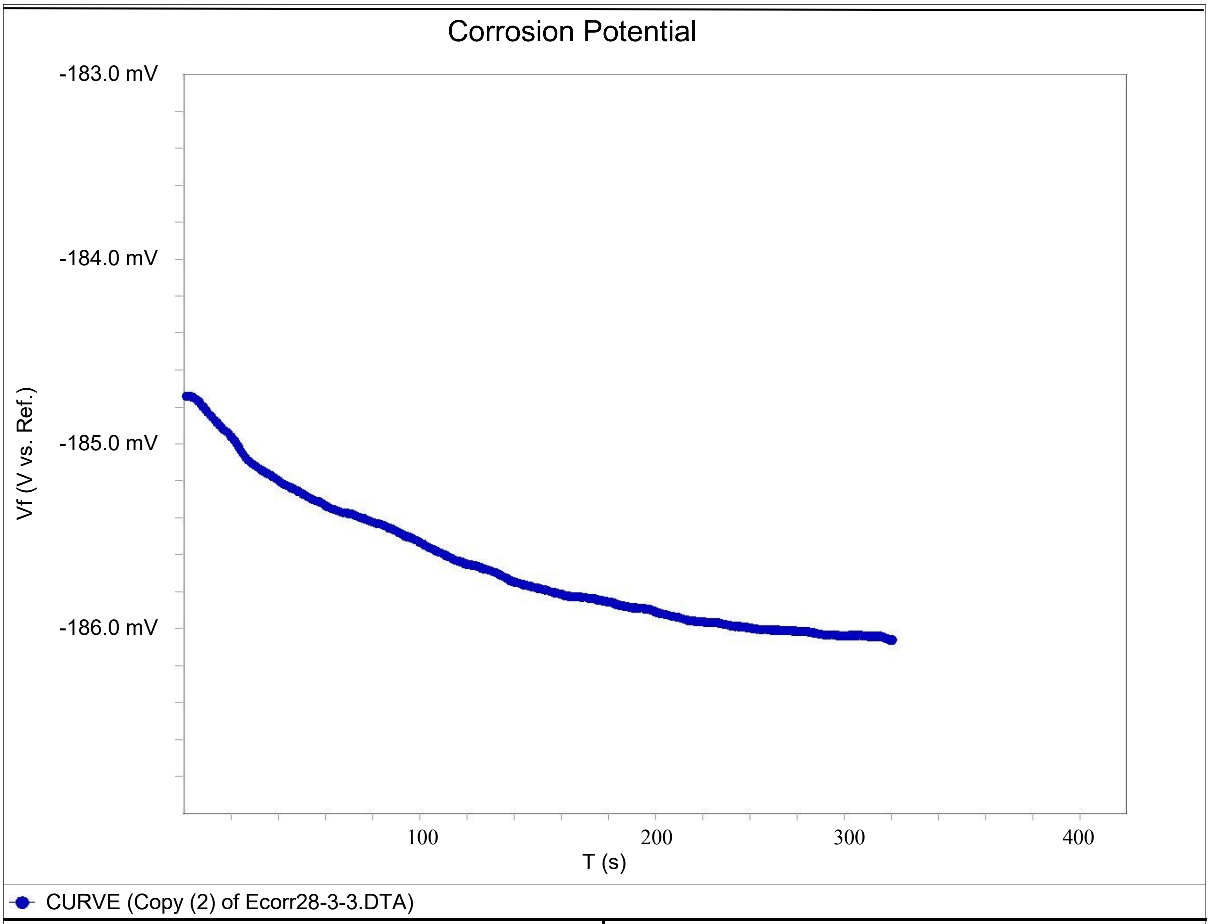
EXPERIMENTAL PARAMETERS

Corrosion Potential
3/1/2009
13:55:13
Total Time (s): 1800
Sample Period (s): 1
Stability (mV/s): 0
Sample Area (cm²): 1.76
IR Comp: Off

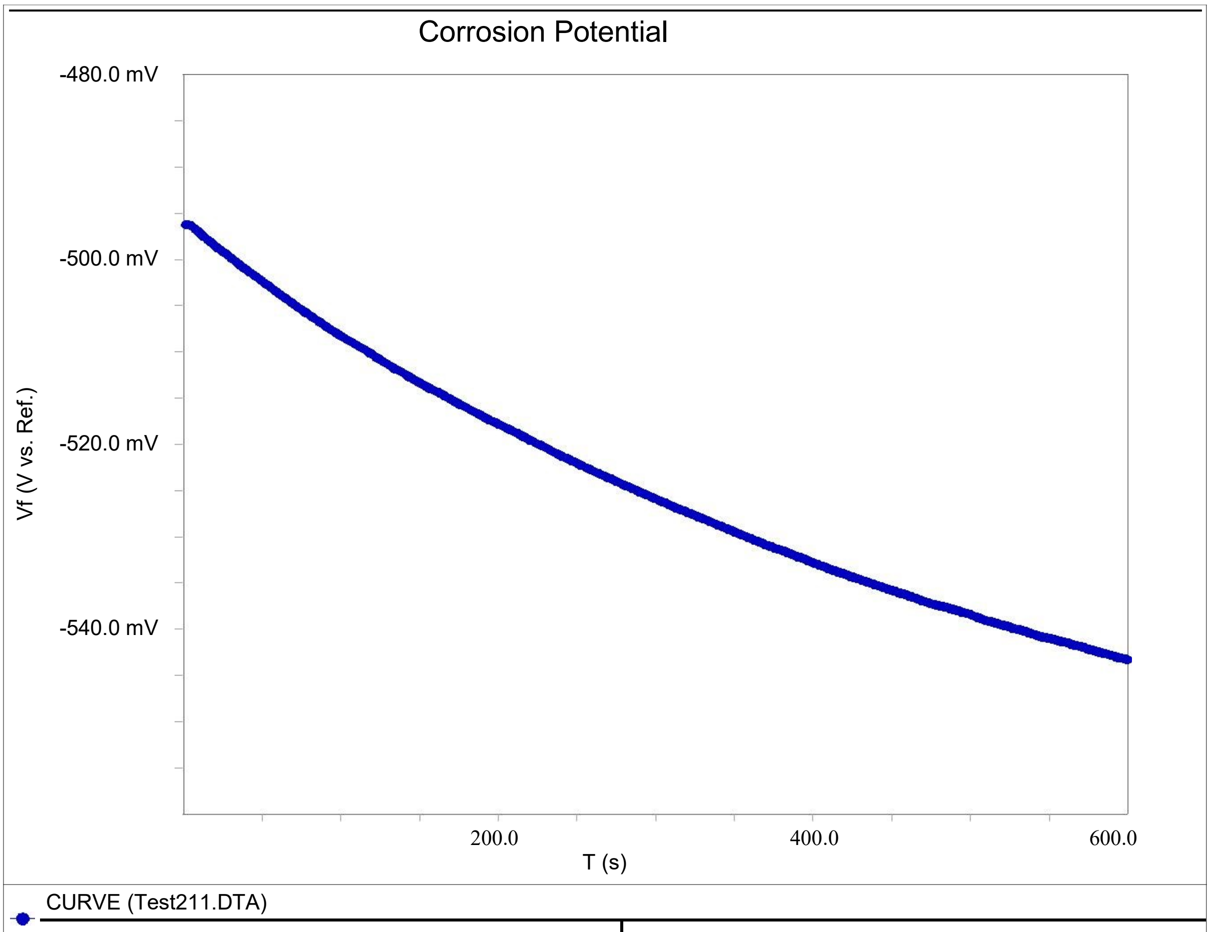
EXPERIMENTAL NOTES

electrolyte: 3% NaCl, R.T, pure iron sample
Aim: determine Ecorr of non coated Sample,
Expected porosity: 100%

Copy (2) of Ecorr25-3.DTA Page 1 05-23-2017



EXPERIMENTAL NOTES	EXPERIMENTAL PARAMETERS
electrolyte: 3% NaCl. R.T, Ni-Co coated sample Aim: determine Ecorr of coated Sample, Expected porosity= 0% for one hour	Corrosion Potential 3/28/2017 12:12:29 Total Time (s): 300 Sample Period (s): 1 Stability (mV/s): 0 Sample Area (cm²): 1.76 IR Comp: Off



EXPERIMENTAL NOTES

checking corr pot, 2/11/2016 morning
low carbon steel

EXPERIMENTAL PARAMETERS

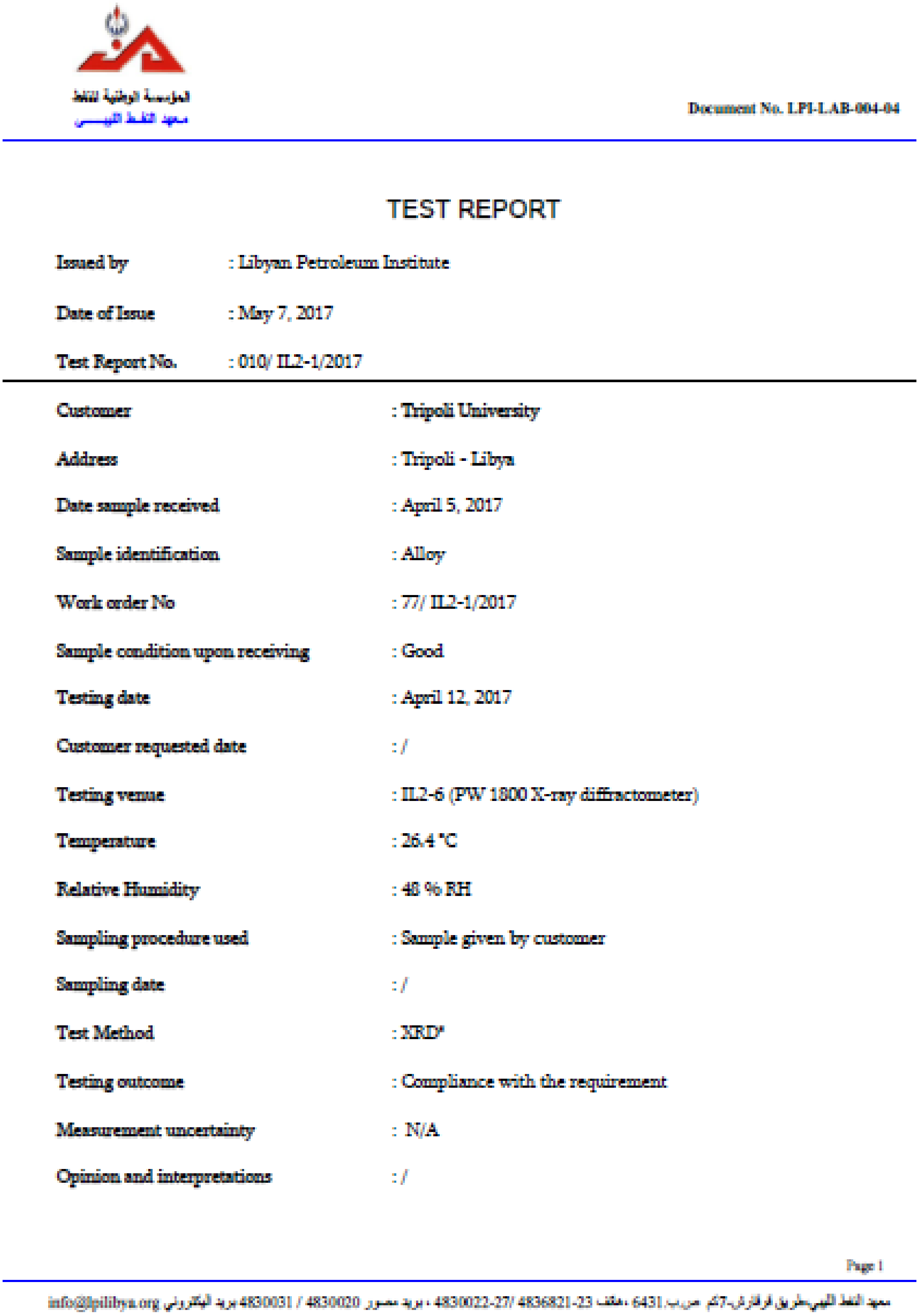
bare steel
11/2/2016
1:28:07
Total Time (s): 600
Sample Period (s): 1
Stability (mV/s): 0
Sample Area (cm²): 11.37
IR Comp: Off

Test211.DTA Page 1 05-23-2017

APPENDIX 2

XRD-CHART PERFORMED IN LPI

The XRD test that was performed in Libyan Petroleum Institute to evaluate the Ni-Co coating.



المؤسسة الوطنية للنفط
معهد النفط الليبي

Document No. LPI-LAB-004-04

TEST REPORT

Issued by : Libyan Petroleum Institute

Date of Issue : May 7, 2017

Test Report No. : 010/ IL2-1/2017

Customer : Tripoli University

Address : Tripoli - Libya

Date sample received : April 5, 2017

Sample identification : Alloy

Work order No : 77/ IL2-1/2017

Sample condition upon receiving : Good

Testing date : April 12, 2017

Customer requested date : /

Testing venue : IL2-6 (PW 1800 X-ray diffractometer)

Temperature : 26.4 °C

Relative Humidity : 48 % RH

Sampling procedure used : Sample given by customer

Sampling date : /

Test Method : XRD*

Testing outcome : Compliance with the requirement

Measurement uncertainty : N/A

Opinion and interpretations : /

Page 1

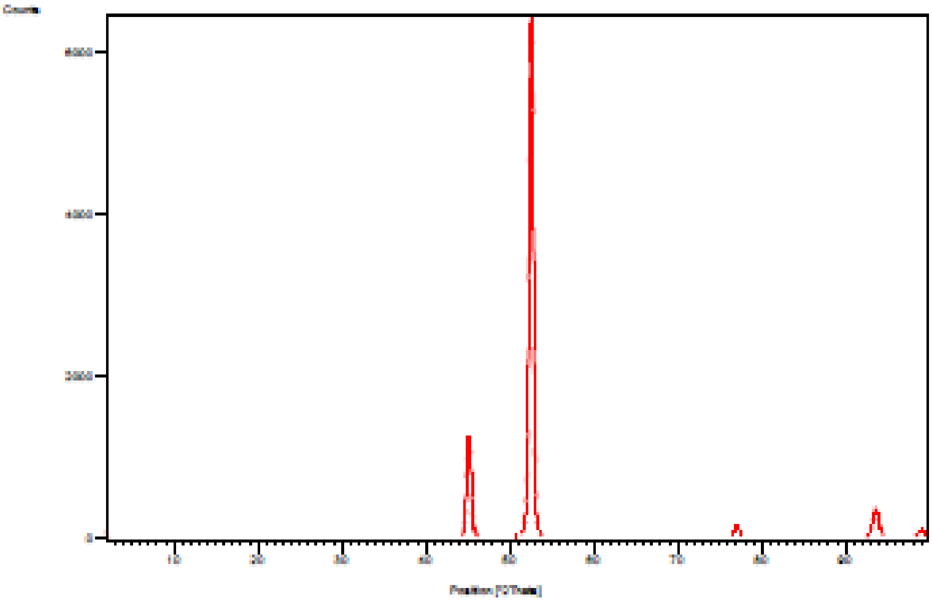
معهد النفط الليبي-طريق قرقارش-7كم. ص.ب 6431، هاتف 23-4836821 /4830022-27، بريد مصور 4830020 / 4830031 بريد الكتروني info@lpilibya.org

Issued by : Libyan Petroleum Institute

Date of Issue : May 7, 2017

Test Report No : 0010/ IL2-1/2017

Graphic & Phase identification of The Sample



Peak List

.1

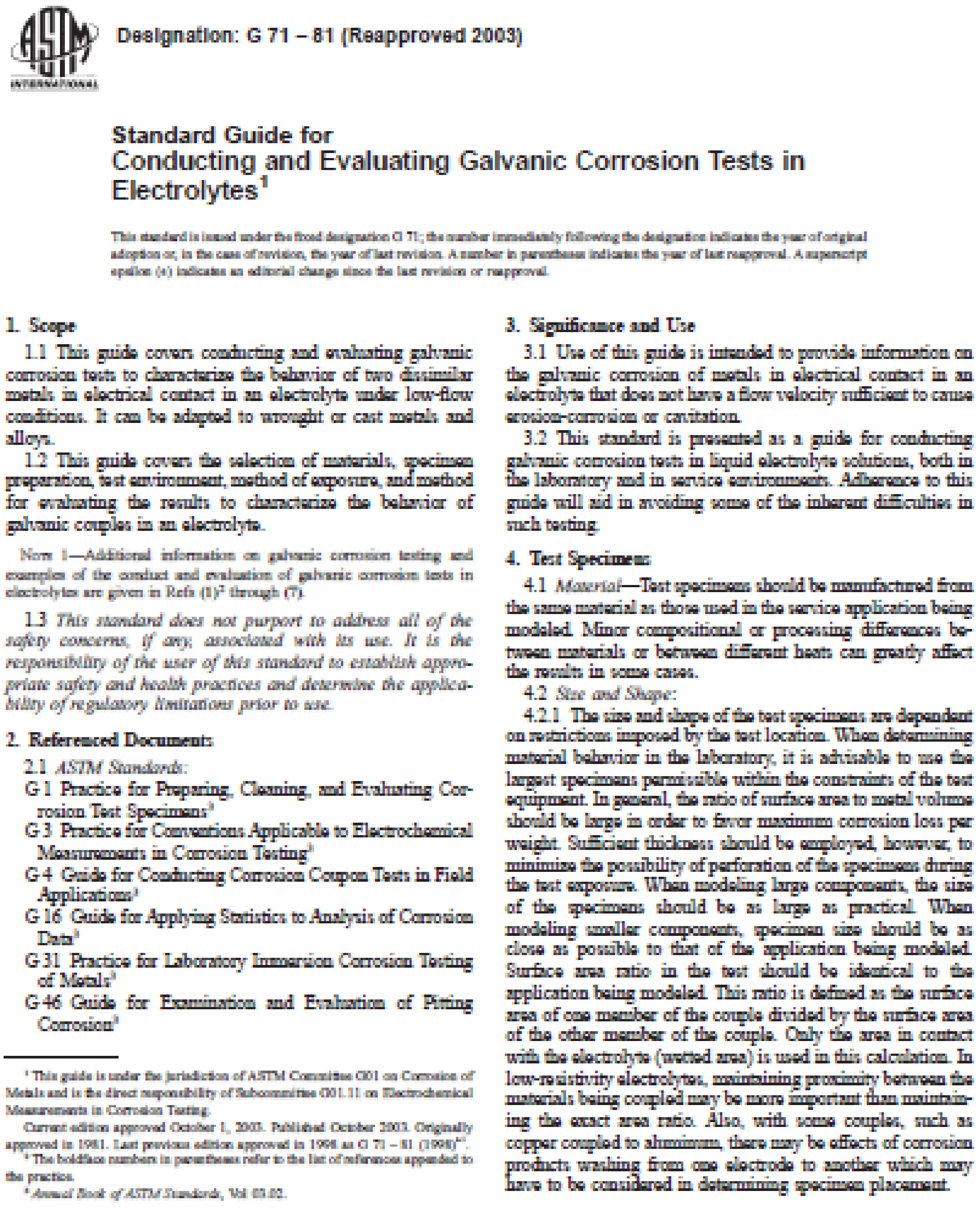
Pos. [°2Th.]	Height [cts]	FWHM [°2Th.]	d-spacing [Å]	Rel. Int. [%]
2.0343	93.77	0.0590	43.42802	2.00
45.0242	1096.78	0.2755	2.01353	23.36
45.3081	1057.37	0.2558	2.00157	22.52
52.7822	4694.38	0.5707	1.73441	100.00
65.3572	6.06	0.6298	1.42786	0.13
76.9870	139.75	0.5510	1.23860	2.98
82.6839	13.08	0.5510	1.16711	0.28
93.6682	313.33	0.7872	1.05698	6.67
98.9796	108.04	0.8640	1.01316	2.30

APPENDIX 3

ASTM G 71 – 81 (REAPPROVED 2003)

Standard Guide for Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes.

This guide covers the selection of materials, specimen preparation, test environment, method of exposure, and method for evaluating the results to characterize the behavior of galvanic couples in an electrolyte.



Designation: G 71 – 81 (Reapproved 2003)

Standard Guide for
Conducting and Evaluating Galvanic Corrosion Tests in Electrolytes[1]

This standard is issued under the fixed designation G 71; the number immediately following the designation indicates the year of original adoption or, in the case of revision, the year of last revision. A number in parentheses indicates the year of last reapproval. A superscript epsilon (ε) indicates an editorial change since the last revision or reapproval.

1. Scope

1.1 This guide covers conducting and evaluating galvanic corrosion tests to characterize the behavior of two dissimilar metals in electrical contact in an electrolyte under low-flow conditions. It can be adapted to wrought or cast metals and alloys.

1.2 This guide covers the selection of materials, specimen preparation, test environment, method of exposure, and method for evaluating the results to characterize the behavior of galvanic couples in an electrolyte.

NOTE 1—Additional information on galvanic corrosion testing and examples of the conduct and evaluation of galvanic corrosion tests in electrolytes are given in Refs (1)[2] through (7).

1.3 *This standard does not purport to address all of the safety concerns, if any, associated with its use. It is the responsibility of the user of this standard to establish appropriate safety and health practices and determine the applicability of regulatory limitations prior to use.*

2. Referenced Documents

2.1 *ASTM Standards:*

G 1 Practice for Preparing, Cleaning, and Evaluating Corrosion Test Specimens[3]

G 3 Practice for Conventions Applicable to Electrochemical Measurements in Corrosion Testing[3]

G 4 Guide for Conducting Corrosion Coupon Tests in Field Applications[3]

G 16 Guide for Applying Statistics to Analysis of Corrosion Data[3]

G 31 Practice for Laboratory Immersion Corrosion Testing of Metals[3]

G 46 Guide for Examination and Evaluation of Pitting Corrosion[3]

3. Significance and Use

3.1 Use of this guide is intended to provide information on the galvanic corrosion of metals in electrical contact in an electrolyte that does not have a flow velocity sufficient to cause erosion-corrosion or cavitation.

3.2 This standard is presented as a guide for conducting galvanic corrosion tests in liquid electrolyte solutions, both in the laboratory and in service environments. Adherence to this guide will aid in avoiding some of the inherent difficulties in such testing.

4. Test Specimens

4.1 *Material*—Test specimens should be manufactured from the same material as those used in the service application being modeled. Minor compositional or processing differences between materials or between different heats can greatly affect the results in some cases.

4.2 *Size and Shape:*

4.2.1 The size and shape of the test specimens are dependent on restrictions imposed by the test location. When determining material behavior in the laboratory, it is advisable to use the largest specimens permissible within the constraints of the test equipment. In general, the ratio of surface area to metal volume should be large in order to favor maximum corrosion loss per weight. Sufficient thickness should be employed, however, to minimize the possibility of perforation of the specimens during the test exposure. When modeling large components, the size of the specimens should be as large as practical. When modeling smaller components, specimen size should be as close as possible to that of the application being modeled. Surface area ratio in the test should be identical to the application being modeled. This ratio is defined as the surface area of one member of the couple divided by the surface area of the other member of the couple. Only the area in contact with the electrolyte (wetted area) is used in this calculation. In low-resistivity electrolytes, maintaining proximity between the materials being coupled may be more important than maintaining the exact area ratio. Also, with some couples, such as copper coupled to aluminum, there may be effects of corrosion products washing from one electrode to another which may have to be considered in determining specimen placement.

---

[1] This guide is under the jurisdiction of ASTM Committee G01 on Corrosion of Metals and is the direct responsibility of Subcommittee G01.11 on Electrochemical Measurements in Corrosion Testing.

Current edition approved October 1, 2003. Published October 2003. Originally approved in 1981. Last previous edition approved in 1998 as G 71 – 81 (1998)$^{\varepsilon 1}$.

[2] The boldface numbers in parentheses refer to the list of references appended to the practice.

[3] *Annual Book of ASTM Standards*, Vol 03.02.

APPENDIX 4

BS EN ISO 1456:2009 STANDARD PRACTICE FOR METAL COATINGS

This guide for conducting metallic coatings like nickel, nickel plus chromium, copper plus nickel, and of copper plus nickel plus chromium.

This International Standard specifies requirements for functional nickel, nickel plus chromium, copper plus nickel and copper plus nickel plus chromium coatings that are applied to iron, steel, zinc alloys, copper and copper alloys, and to aluminium and aluminum alloys, to provide an attractive appearance and enhanced corrosion resistance. Coating designations are specified that differ in thickness and type, and guidance is given on selecting the coating designation appropriate for the service conditions to which the coated product will be exposed.

BRITISH STANDARD

BS EN ISO 1456:2009

Metallic and other inorganic coatings — Electrodeposited coatings of nickel, nickel plus chromium, copper plus nickel and of copper plus nickel plus chromium (ISO 1456:2009)

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APPENDIX 5

USER MANUAL

This manual covers the installation, safety and use of Gamry Instrument Reference 600+ Potentiostate/Galvanostat/ZRA.

GAMRY
INSTRUMENTS
Reference 600+™
Potentiostat/Galvanostat/ZRA
Operator's Manual

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Revision 6.02
December 1, 2015
988-00006