ELECTRODEPOSITION OF NICKEL/COPPER MULTI-NANOLAYER BY DUAL BATH TECHNIQUE AT AMBIENT TEMPERATURE

SHARIFAH SAKINAH BINTI ABDULLAH

A thesis submitted in partial

fulfillment of the requirement for the award of the degree of
Master of Science

Faculty of Science, Technology and Human Development

Universiti Tun Hussein Onn Malaysia

APRIL 2017

ELECTRODEPOSITION OF NICKEL/COPPER MULTI-NANOLAYER BY DUAL BATH TECHNIQUE AT AMBIENT TEMPERATURE

SHARIFAH SAKINAH BINTI ABDULLAH

UNIVERSITI TUN HUSSEIN ONN MALAYSIA

ACKNOWLEDGEMENT

The success of any project relies heavily on the encouragement and guidelines of many others. I would like to take this opportunity to express my gratitude to all those people who made this thesis possible and gave me such an enjoyable experience.

First and foremost, I would like to express my highest appreciation and gratitude to my supervisor Dr. Suzi Salwah Binti Jikan for her patience, advice, encouragement, continuous guidance and supervision during this tough period to complete the project. There are no such words in the dictionary that can express my deepest appreciation. You are always the best. Secondly, I would like to thank my co-supervisor, Dr. Nur Azam Bin Badarulzaman, who gave me the golden kindness, advice, helps and support during this research. You are always the best.

In addition, warmest thanks to the metallurgy lab technician, En Abu Bakar Bin Ahmad for providing me a good research environment and facilities to complete this project. Also, thanks to the technician from material lab, Tuan Haji Tarmizi Bin Haji Nasir and En Khairul Anuar Bin Ismail for guiding me in carrying out the Scanning Electron Microscopy (SEM) and X-Ray Diffraction (XRD) analyses. Lots of thanks to all postgraduate students, especially Siti Rodiah, Ainor Hayat, Abdullah and Siti Salwa for their supports and kindness.

Last but not least, an honorable mention goes to my dad, Abdullah Bin Hassan for his understanding and support. Thank you so much to my mom, Samiah Bin Buniran for her love and trust. Not forgotten to my husband, En Arif Zakwan Bin Ashari for his moral support and the wise advice throughout this project. I would also like to express my gratitude for the assistance from Research Acculturation Grant Scheme (Vot RO18, Malaysia Ministry of Education) for funding this research. Without the help from those that I mentioned above, I would face many difficulties while doing this project. I hope, all the knowledge and experiences gained during this project may help me in the future time.

TABLE OF CONTENTS

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS AND ABBREVIATIONS

A	-	ampere
AC	-	alternating current
ASTM	-	American Society for Testing and Materials
Cu	-	copper
DC	-	direct current
EDS	-	Energy Dispersive Spectrometer
FSTPi	-	Fakulti Sains, Teknologi dan Pembangunan Insan
FIB-FESEM	-	Focus Ion Beam-Field Emission Scanning Electron Microscope
H_2	-	hydrogen
H_2O	-	water
H_3BO_3	-	boric Acid
HV	-	vickers hardness
L	-	length
Ni	-	nickel
$NiSO_4.6H_2O$	-	nickel sulfate hexahydrate
$NiCl_2.6H_2O$	-	nickel chloride hexahydrate
O_2	-	oxygen
SEM	-	Scanning Electron Microscopy
XRD	-	X-Ray Diffraction
%	-	percentage
a	-	area
d	-	density
˚C	-	degree celsius
g/l	-	gram/liter
kg	-	kilogram

nm	-	nanometer
mN	-	milinewton
mm	-	millimeter
μm	-	micrometer
t	-	time
h	-	height
I	-	current of electrodeposition
Z	-	electrochemical equivalent

LIST OF APPENDICES

ABSTRACT

The electrodeposition of Nickel/Copper (Ni/Cu) multi-nanolayer coating has been carried out on Cu substrate by using dual bath technique. The electrodeposition process was carried out at electrolyte temperatures of 25 °C, 40 °C, and 60 °C. The Watts electrolyte and Cu (II) sulphate solutions have been chosen for this experimental work because it produced a good surface coating. This work aims to produce different sublayer thicknesses (20 nm, 40 nm, 60 nm, 80 nm and 100 nm) with thickness ratio of 1:1. The work also involved a study on the effect of different sublayer thickness, the effect of multiple nanolayers with different compositions of layer thickness (Ni:Cu = 2:1, 1:1 and 1:2) and the effects of different electrolyte temperatures. The production Ni/Cu multi-nanolayer samples was conducted by using current densities of Ni and Cu at 0.0527 A·cm^{-2} and 0.0505 A·cm^{-2} respectively. The (FESEM) image of Ni/Cu multi-nanolayer coating showed that the sublayer thickness of 20 nm exhibited the smallest compact cluster of cauliflower-like appearance. The Focus ion beam FESEM images it was proven that all respective samples (20 nm, 40 nm, 60 nm, 80, and 100 nm) were truly exist and the multi-nanolayer structures are formed alternately of Ni and Cu layer. The uniformity of coating composition was studied using coating composition while phase deposition presence was evidence by using X-ray Diffraction (XRD) respectively. The double-like peaks of XRD data indicate the pattern of alternate multilayer which confirmed the existence of distinctive Cu and Ni layers with each of them having their own lattice parameter. The vickers hardness result showed that the sublayer thickness of 20 nm has highest hardness value of 504.32 Hv. The composition of the layer with the ratio of 2:1 for Ni/Cu coating was found to contribute the highest hardness value which is 507.54 Hv presenting an increase of 89 %. In addition, the microhardness of Ni/Cu multi-nanolayer reached its maximum hardness value 504.34 Hv at electrolyte temperature of 25 °C. The trends of the hardness values are in line with the corrosion resistance study on the coated samples. The corrosion

properties of corrosion current density and the corrosion potential for 20 nm showed a shift towards the more positive regions. So, the sublayer thickness of 20 nm had excellent effect on the corrosion resistance. Ni/Cu multi-nanolayer system with the ratio of 1:2 presented the highest corrosion resistance among other multi-nanolayer system. The best corrosion resistance was attributed to coating samples prepared at electrolyte temperature of 25 ℃, based on the results obtained from morphological analyses, hardness and corrosion. In conclusion, this study has evidenced that Ni/Cu multi-nanolayer successfully enhanced the physical and chemical properties of the coating. Ni/Cu multi-nanolayer.

ABSTRAK

Elektrosaduran Nikel/Kuprum (Ni/Cu) berbilang-lapisan nano telah dilakukan terhadap substrat Cu melalui teknik dua rendaman. Proses elektrosaduran dilakukan pada suhu-suhu elektrolit 25 °C, 40 °C, dan 60 °C. Elektrolit Watts dan larutan Cu (II) sulfat dipilih untuk ujikaji ini kerana ia mampu untuk menghasilkan permukaan salutan yang baik. Kajian bermatlamat untuk penghasilan sublapisan berketebalan 20 nm, 40 nm, 80 nm dan 100 nm, dengan nisbah ketebalan 1:1. Kajian juga melibatkan kesan kepelbagaian ketebalan sublapisan, kesan nano lapisan dengan komposisi ketebalan lapisan berbeza (Ni:Cu = 2:1, 1:1 and 1:2) dan kesan kepelbagaian suhu elektrolit juga dikaji. Kajian dilakukan pada sampel Ni/Cu berbilang-lapisan nano dengan menggunakan ketumpatan-ketumpatan arus Ni dan Cu iaitu 0.0527 A·cm^{-2} dan 0.0505 A·cm^{-2}, masing -masing. Imej daripada Mikroskop Imbasan Elektron Pancaran Medan (FESEM) memaparkan morfologi permukaan salutan Ni/Cu berbilang-lapisan nano serta menunjukkan sublapisan berketebalan 20 nm dengan kelompok terpadat berpenampilan 'kubis bunga'. Alur ion terfokus FESEM yang digunakan untuk kajian keratan rentas pelbagai ketebalan sublapisan salutan Ni/Cu menunjukkan kesemua sampel (20 nm, 40 nm, 60 nm, 80 nm, dan 100 nm) mempunyai struktur berbilang-lapisan nano dengan lapisan-lapisan Ni dan Cu yang berselang-seli. Keseragaman komposisi salutan dikaji menggunakan Spektrometer Serakan Tenaga (EDS) manakala kehadiran fasa terdeposit dikaji menggunakan Pembelauan Sinar-X (XRD). Puncak-puncak kembaran dalam XRD menunjukkan corak selangan berbilang-lapisan yang mengesahkan kewujudan lapisan-lapisan tersendiri Cu dan Ni dengan parameter kekisi masing-masing. Hasil ujian kekerasan Vickers menunjukkan sublapisan berketebalan 20 nm memiliki kekerasan tertinggi bernilai 504.34 Hv. Komposisi salutan Ni/Cu bernisbah 2:1 pula menunjukkan kekerasan tertinggi bernilai 507.54 Hv, iaitu 89 %. Mikro kekerasan Ni/Cu berbilang-lapisan pula mencapai nilai maksimum iaitu 504.34 Hv pada suhu elektrolit 25 °C. Pola nilai-nilai kekerasan adalah seiring dengan hasil kajian rintangan kakisan ke atas sampel-sampel salutan. Ciri-ciri kakisan iaitu ketumpatan arus kakisan dan keupayaan kakisan bagi 20 nm menunjukan perubahan kekawasan

yang lebih positif. Maka,sublapisan berketebalan 20 nm memberikan rintangan kakisan yang terbaik. Sementara itu, sistem Ni/Cu berbilang-lapisan nano bernisbah 1:2 menunjukkan rintangan kakisan tertinggi berbanding sistem-sistem berbilang-lapisan nano yang lain. Rintangan kakisan tertinggi didapati menerusi sampel-sampel salutan yang terhasil pada suhu elektrolit 25 °C berdasarkan keputusan yang diperoleh dari analisis morfologi, ujian kekerasan dan kakisan. Kesimpulannya, kajian ini telah berjaya membuktikan Ni/Cu berbilang-lapisan nano mampu meningkatkan sifat-sifat fizikal dan kimia salutan.

CHAPTER 1

INTRODUCTION

1.1   Research Background

Nickel (Ni) is one of the metal that has been recognized as an important raw material in many industries. The major countries that have reserved Ni ores are Canada, South Africa and Finland. Most of Ni consumption in the world is for producing stainless steel. Besides that, Ni metal exhibits unique properties such as fine hardness, strength, and also good resistance to corrosion (Loweinheim, 1978). Electrodeposited elemental Ni has been the material of choice to demonstrate a variety of microdevice prototypes, including micro-gears, and microcantilevers. Whereas, Copper (Cu) is produced worldwide, mostly in United States, Chile, Canada and Zaire. Cu is easily precipitated with metals that are higher in the electromotive force (EMF) series, because it has higher electropositive. It is known as native element. Cu is used in various technology applications for example, as the undercoat for plated player and as the conductor in print circuit boards. This fact shows that Cu coating is a relatively inexpensive metal material and can be deposited on top of various substrates (Gamburg & Zangari, 2011). Ni and Cu are important materials to many industries. The annual demand is bigger compared to those of many other metals. Thus, the study of Ni/Cu multi-nanolayer should be done in order to increase awareness of Ni and Cu potentials in electroplating industries.

The electroplating is also often called as electrodeposition. It is widely used for the production of a metal coating to a metallic or other conducting surfaces by an electrochemical process. This is one of the most promising techniques in producing nanostructured multilayer coating material. This technique has demonstrated to be very convenient because of its relatively low production cost and high production

rate, compared to that of vacuum evaporation, cold rolling, single roll rapid quenching and sputtering (Halim *et al.*, 2012 and Ghosh *et al.*, 2006). This technique has successfully proven by previous researchers in producing nanometallic films in various thicknesses ranging from hundreds of nanometers to tens of micrometers. Electrodeposition is versatile technique and well suited in the production of micro and nano technology. Electrodeposition has a lot of advantages such as low production cost and requires low temperature of an electrolyte (below 80 °C). In addition, through electrodeposition, the resulting multilayer is able to prevent interdiffusion and expected to have clear-cut interfaces than those prepared via dry process. So, it is capable to produce thin films in a large area and in an extremely short period of time. Moreover, this method is competent to fabricate quality structures of multilayers that give promise to the flexibility and capability of being used for parts of any size and geometry (Abdel-Karem *et al.*, 2011 and Alper, 2004). On top of that, the process can be performed at room temperature using different kinds of substrates and less hazardous electrolyte.

The structure of multilayer coating in nanometer range has shown promising alteration in its mechanical and chemical properties than samples coated with multilayer coating in micrometer range (Pellicer *et al.,* 2011). Multilayer in nanometer range has interesting mechanical properties which involve high hardness or flow stress when the bilayer thickness is decreased to nanoscale (Kaneko *et al.,* 2005). Moreover, these layered structures can exhibit and enhance properties such as mechanical strength, microhardness, giant magnetoresistance and corrosion resistance (Fei & Wilcox, 2006). It involves particularly multilayer with sublayer thickness that is confined to nanometer scale (Barshilia & Rajam, 2002). Barshillia & Rajam (2002) reported that, it was easy to form coherent multilayer of Ni/Cu because both of Cu and Ni have similar face centered cubic structures and lattices. However, this multilayer tended to form a solid solution over the entire composition range. The successful research work done by Barshillia & Rajam (2002) in producing compositions in which each layer consists of Ni/Cu proved that electrodeposition could be an efficient alternative method for producing multilayer products. Therefore, the studies on Ni/Cu electrodeposition has increased since Ni/Cu multilayer or alloy offers excellent corrosion resistance, good mechanical, electrical and catalytic properties compared to single deposit of either Ni or Cu (Ghosh *et al.,* 2006).

The production of multilayer structure can be conducted by single bath technique and dual bath technique. However, the dual bath technique has attracted many researchers in producing various multilayers, such as Zn/Co (Kirilova *et al.,* 1998), and Ni/Cu (Haseeb *et al.,* 1994 and Shu *et al.,* 2012). According to the position in the electrochemical series, Cu can easily be electroplated in aqueous solution, however there will be problems regarding on how to prevent the formation of deposits with Ni. Thus, it is impossible to deposit a Cu layer on Ni layer. Nonetheless, by using the dual bath technique, the electrolyte solutions do not have to be compatible, because the multilayers are obtained by repeatedly transferring the substrate from one electrolyte to another different electrolyte. There are lots of advantages of dual bath technique. It is a simple method that does not have limitations and it has a wide applicability for the production of multilayer coatings. It also offers a wider choice in the selection of multilayer components and it allows the deposition to take place on unalloyed materials due to the electrochemical limitations of these unalloyed materials (Haseeb *et al.,* 1994).

Therefore, this research work has chosen the dual bath technique to produce multilayer coating structures in nanometer range (20 nm, 40 nm, 60 nm, 80 nm, and 100 nm). This current research focuses on the element of Cu and Ni in order to form products for nanosystem applications. For this technique, the Ni/Cu multi-nanolayer can be produced by the sequential electrodeposition, where the steps start by electrodepositing the Cu substrate with the first layer in Ni electrolyte, followed by transferring into Cu electrolyte to form second layer. The layers were formed alternately. Ni/Cu multi-nanolayer is an interesting technological system because it is electrochemically easy to grow in a well-controlled environment. The coherency to form alternate layer of Ni/Cu attributed to the fact that Cu and Ni possess the same face centered cubic (F.C.C) structures (Barshilia & Rajam, 2002), identical atomic rays, electronegativity and similar electron valences. Moreover, the isomorphic mechanism of Ni/Cu multilayer is also able to complete the solubility of the two components in liquid and solid states (Melo *et al.,* 2011).

This production of multilayer coatings in nanoscale can be done at ambient temperature by controlling the deposition time in order to obtain the desired thickness. Hence, Faraday's Law was used in calculation of time for the production of the nanolayer thicknesses. So far, there is no research has been reported on the

production of multi-nanolayer coating at ambient temperature especially in the study on the effect of different sublayer thicknesses, the effect of different ratios of the sublayer thickness and the effect of the electrolyte temperatures on the properties of this multi-nanolayer coating.

1.2   Problem Statement

The development and characterization of nanostructure materials have been subjected as intensive researches in scientific and industrial communities (Rashidi & Amadeh, 2010). Nanostructured materials with sizes of less than 100 nm are important for various industrial applications. It is expected that these nanostructured materials can enhance the physical and chemical properties of the end products (Miyake *et al.,* 2001). Among various manufacturing methods, the electroplating has received considerable attention as this method is more practical and economical. The studies on Ni/Cu electrodeposition had been performed by other workers and they had reported the mechanism and characteristics of Ni/Cu electrodeposition (Tokarz *et al.,* 2007; Kim *et al.,* 2005; Kaneko *et al*., 2005; Ren *et al.,* 2004; Barshilia & Rajam, 2002; Lassri *et al.,* 2001; and Zhang *et al.,* 2009).

Ambient temperature has attracted interest to this research work as the electrolyte temperature for the electrodeposition because it portrays several satisfying properties such as no hydrogen evolution, high conductivity, non flammability and chemical stability over a wide temperature range (Koura *et al.,* 2003). Eventhough Beverskog & Puigdomenech, (1997) had stated that the possibilities of Ni deposited at below 30 °C, most of the research works were maintaining the usual temperature range of Watts electrolyte that is around 30 °C to 80 °C. In addition, other researchers and chemical producer companies practice the specified temperature range which is around 55 °C to 65 °C. Lower deposition temperature below the range of 55 °C to 65 °C has to be avoided as it will not produce a bright Ni or Cu layers by normal plating time.

Nonetheless, most research works focusing on the usual temperature range which is above ambient temperature due to increasing of deposition temperature will increase the deposition rate. In other view of works, besides the electrolyte temperature enhanced the production rate, it can also affect the quality of the coating.

The high temperature of electrolyte produces weak coating properties. It is due to the hydrogen evolution. The increase of the deposition temperature will increase the hydrogen evolution and may lead to an increase in the porosity and crack in the coatings. Zentner *et al.* (1953) mentioned that according to their research findings, it could be possible to successfully deposit metals at lower temperature than the usual deposition temperature. Their findings on depositing metals at lower temperature range suggested that the deposition process at lower temperature has the potential in obtaining harder Ni coating. Nevertheless, Badarulzaman *et al.* had successfully formed the coating at a lower temperature which is at ambient temperature. However, their work is not on multi-nanolayer coatings. Due to that reason, this research work has selected the ambient temperature in performing the research work in producing thin layer as thin as nanolayer.

The microstructure and surface texture can be tailored by controlling growth parameters such as deposition or electrolyte temperature in order to obtain the good desired coating properties. The electrolyte temperature is one of the important factors to produce the coating with desired properties. However, there are insufficient electrodeposition studies that were done at ambient temperature, thus deposition temperature at ambient temperature need to be investigated. Moreover, the results of the electroplating experiments obtained from previous researchers were difficult to optimize due to inconsistent or different data. Rashidi & Amadeh (2010) found that the grain size of the deposits increases by increasing the bath temperature. The results for plating temperature only for above 55 °C is consistent with other findings. Nonetheless, for plating temperature at lower than 55 °C, it displayed unexpected behavior which is an increase in the electrolyte temperature leading to grain refining of the Ni deposits. Moreover, there is less information discussing on the effects of electrolyte temperature to the deposits. Whereas, in some studies, they are more focusing on the deviation of more than 5 °C of plating temperature from the optimum temperature (Rashidi & Amadeh, 2010).

Therefore, thorough studies in this field can be useful in manufacturing components and devices coated with Ni and Cu. In this research work, detail studies have been performed in order to study the multi-nanolayers that were deposited using Watts electrolyte and Cu (II) sulfate solutions under different electrochemical conditions with the goal of controlling the sublayer thickness. Cu substrate was used in this research as cathode. The increase in the surface area can increase the rate of

plating process, and most Cu salts dissociate completely in water. Furthermore, the deposition current densities of Cu and Ni are some of the vital parameters in electrodeposition process. The deposition current densities obtained from the early stage of the research work will be implemented in all electrodeposition activities in this work. Thus, the obtained values of these deposition current densities lead to easier usage of different electrolytes. The experimental results are also expected to give valuable informations on the influences of electrolyte temperature, sublayer thickness and sublayer ratio. The enhancement in corrosion resistance and microhardness of Ni/Cu multi-nanolayer deposited on Cu substrate has been expected as the outcome of these research works.

1.3   Research Objectives

This research was carried out to achieve the following objectives:

1. To synthesise multi-nanolayer of Ni/Cu coated on the Cu substrate using dual bath technique (DBT). The multi-nanolayer of Ni/Cu coating produced forming different sublayer thickness with alternate layer of five different nanometer scale (20 nm, 40 nm, 60 nm, 80 nm, and 100 nm).

2. To study the effects of different sublayer thicknesses, different sublayer ratios of thickness and different electrolyte temperatures on the properties of multi-nanolayer of Ni/Cu coating.

3. To analyse the morphology, element, phase, hardness and corrosion properties of multi-nanolayer of Ni/Cu coating produced at different electrolyte temperatures with different sublayer thicknesses and different sublayer thickness ratios.

1.4   Research Scopes

This research works emphasize on the deposition and characterisation of different Ni/Cu multi-nanolayer structures. A multi-nanolayer structure consists of alternating Ni/Cu multilayer in nanosize scale. These Ni/Cu multi-nanolayer structures were deposited using dual bath technique. The effect of different sublayer thicknesses of

20 nm, 40 nm, 60 nm, 80 nm and 100 nm will be studied. The effect of different sublayer ratios of Cu and Ni with the ratios of 1:1, 1:2 and 2:1 will be investigated and finally, the effect of various electrolyte temperatures (25 °C, 40 °C and 60 °C) will be explored.

Part I- Preliminary experiment

(a) The decomposition potential test for Ni and Cu has been carried out in order to identify the most efficient current density during the electrodeposition process.

(b) The data was derived from the graph of current (ampere, A) against potential (volt, V).

Part II- Electrodeposition process to produce Ni/Cu multi-nanolayer coatings at various conditions:

(a) The Watts and Cu (II) sulfate solutions were used as the electrolytes.

(b) The different sublayer thicknesses (20 nm, 40 nm, 60 nm, 80 nm and 100 nm) were prepared.

(c) The different sublayer ratios of (Ni:Cu = 2:1, 1:1 and 1:2) were produced.

(d) The Ni/Cu multi-nanolayers of 20 nm were prepared in order to study the effects of electrolyte temperatures (25 °C, 40 °C and 60 °C).

(e) The individual layer thickness was controlled by adjusting their deposition time.

Part III-Characterisation

(a) Scanning Electron Microscope (SEM) was used to view the surface and the cross-sectional morphologies of the Ni/Cu multilayer coating.

(b) Focus Ion Beam Field Emission Scanning Electron Microscope (FIB-FESEM) to study the Ni/Cu multi-nanolayer by to distinguish the sublayer thicknesses of alternate nanolayers of Ni/Cu on a Cu substrate.

(c) Energy Dispersive Spectrometer (EDS) for elemental study

(d) X-ray Diffraction (XRD) for phase analysis.

(e) Vickers hardness for determined the hardness and strength studies

(f) Corrosion test to evaluate the corrosion properties and the corrosion behaviour of Ni/Cu multi-nanolayer in NaCl environment.

1.5   Application of Multilayer Coatings

Metallic multilayer coating has shown significant uses in various applications such as automotive, magnetic recording, media, X-ray mirrors, diffusion barrier coatings and wear resistant coatings due to its superior physical properties (magnetic, optical and mechanical) (Ren *et al.,* 2004). Multilayer coating with sublayer thickness in nanometer range has got tremendous attractions from scientific and engineering communities because of its improved mechanical properties such as strength, hardness, wear resistance and corrosion resistance (Ghosh *et al.,* 2007, Fei & Wilcox, 2006 and Zhang *et al.,* 1998).

It also involves the applications of multilayered construction of magnetic heads, disks in magnetic rigid disk drives, various components in micro electromechanical systems (MEMS) devices and head tape devices. Moreover, the tribological properties of these layered structures are important in these applications because the ratio of the layers to the substrate depend largely on the layer properties such as the layer thickness, surface roughness and elastic modulus. Due to these reasons, most of the researches conducted were to synthesis the layers for the applications of these devices are as thin as 1 nm (Ghosh *et al.,* 2007). In addition, the multilayered structures are also used in variety of applications such as X-ray mirrors and diffusion barrier coating due to its superior physical properties (Ren *et al.,* 2004). The multilayer's films are usually fabricated by dry processes such as sputtering, vacuum evaporation and molecular beam epitaxy (MBE) which are proven to be the most suitable techniques in order to produce high quality structures with atomic scale. However, the electrochemical deposition exhibits more interesting technique since the electrodeposition process can be altered to reduce the production time. Thus, this activity applies an economically technique (Miyake *et al.,* 2001).

The electrodeposition of Ni/Cu has a broad use in various seawater applications such as valves, condensers and heat exchanger tubes. It is highly corrosion resistant in seawater, acidic or alkaline media and in many oxidizing or reducing gas environments (Kaneko *et al.*, 2005). Nowadays, the study on Ni/Cu electrodeposition is important especially in the preparation of nanostructured materials as they are used in industrial and electronic applications such as notebooks and mobile phones (Melo *et al.*, 2011). Industries using nano technology claimed that Ni and Cu are promising high performance material, intelligent system, longer life,

safer and less raw material needed. Due to that reason, this study focuses on the nanolayer of Ni/Cu as a hope that the findings would be useful for nanotechnology applications.

In conclusions, it is well known that this process is low in cost, able to increase durability, produce high deposition rate and improve the appearance of plated piece. Therefore, industries are expected to gain many benefits such as reducing cost of production and improving the productivity (Ren *et al.,* 2004). This research focuses on the production of sublayer thickness in nanometer scale which is highly projected to enhance the physical and chemical properties of the product. This research will develop a more efficient electrodeposition process and good finishing product that can be applied in industries related to electroplating.

CHAPTER 2

LITERATURE REVIEW

2.1 Nickel (Ni)

Nickel (Ni) is the twenty-fourth most abundant element in the lithosphere (Lowenheim, 1978). It offers unique properties such as fine hardness, strength, and good ductility, and toughness, lustrous and good conducting electricity. Due to its unique properties, up to 70 % of Ni is widely used in the stainless steel production. In the earth crust, Ni exists about 0.01 % mainly as sulphide, oxide and silicate mineral. In natural geological activities, Ni is produced by weathering and volcanoes which lead to major Ni distribution in the natural environment (Schaumloffel, 2012). Ni has an atomic number of 28.

The retrospective on Ni started with Ni electrodeposition using ammonium sulfate solution that was developed by Dr. Isaac Adams, who was one of the first to commercialise Ni plating in the United States in 1869. In 1916, Professor Oliver Watts at the University of Wisconsin formulated Watts solution. Watts electrolytes are the combinations of nickel sulfate, nickel chloride and boric acid (Schlesinger & Paunovic, 2000).

Ni coatings are commonly used due to their high corrosion resistance and attractive visual appearance. The electrodeposition process of Ni is similar to other electrodeposition processes which involves soluble metal anode. It also requires conductive aqueous solution of Ni salts to channel the direct current between two electrodes. There are few types of solutions that are used for Ni electroplating;

- Watts Ni plating solution
- Ni sulfamate solution
- All-Chloride solution

- Sulfate-Chloride solution
- All-Sulfate solution
- Hard Ni solutions

Ni sulfate is a type of electrolyte that produces lots of Ni. It is a non volatile and the cheapest among the Ni salts. While, Ni chloride is a source of chloride ions that is required to prevent the passivity of the anode and to increase the conductivity of the electrolyte. The presence of chloride ion is due to addition of Ni chloride to the electrolyte. However, there are also other chemicals such as boric acid is being added in Watts solution to serve as a weak buffer and control the pH of the cathode. It is relatively very pure, inexpensive, stable and nonvolatile (Loweinheim, 1978 and Torabinejad *et al.,* 2017).

The electrodeposition of Ni has been carried out using sulfate solutions which contain some chloride and boric acids. Sulfate and chloride solutions are the best of choices for the electrodeposition process due to the economic aspects. Based on previous researchers, the electrodeposition of Ni has general advantages and disadvantages that are summarised in Table 2.1.

Table 2.1: List of advantages and disadvantages of Ni electrodeposition
(Loweinheim, 1978)

Advantages	Disadvantages
Relatively good wear resistance	The mechanical properties of the substrate can get worse if Ni was deposited on steel because of hydrogenation.
Relatively high hardness	Ni coating is not tolerant to mechanical work, such as elongation, bending or riveting
Good ductility, especially when deposited from sulfamate solutions	Ni becomes not stable in sulfur-containing media, in ammonia, in a humid chlorine atmosphere.
Ni has good anti-diffusion barrier and widely used as the barrier layer to prevent the diffusion of the substrate material to the deposit	Ni does not act as sacrificial corrosion protection of steel

The properties of Ni that are able to enhance surface conductance make it a relatively good electrical conductor	Ni is a magnetic metal; therefore it cannot be used when non-magnetic materials are necessary.
High corrosion resistance in conventional media, in high humidity environments or in alkali solutions or organic acids	Ni deposits may often peel away from the basis metal. Moreover, the adhesion of a subsequent deposit on top of a Ni surface is also problematic
Ni are easily deposited/soldered by using conventional method	Ni deposition is highly sensitive to impurities in the electrolyte.

Nickel and its alloys have received considerable attention among the industrialists and academicians as the most commonly used materials for anti-corrosion coatings (Qibo & Yinxin, 2013 and Jinlong *et al.,* 2016). The study on Ni electroplating was also done for the solar applications (Nandy *et al.,* 2016). Electrodeposition of Ni is one of the most commercial techniques that have been recognized previously as surface modification and surface finishing process. Owing to these potentials, Ni is the appropriate choice of element to be used in electrolysis reaction due to its chemical stability. The electroplating process is an effective method for obtaining Ni thin films having micro or nanostructures with good film quality and aspect ratio (Hili *et al.,* 2015). Ni electrodeposition falls into three functional categories which are: decorative, functional and electroforming (DiBari, 2010 and Ebrahimi, 2001). Therefore, the electroplating method is mostly preferred if compared to other Ni deposition techniques.

2.2   Copper (Cu)

Copper (Cu) has an atomic number of 29 and it is one of the elements in the periodic table. Cu exists in the earth's crust about 0.001 to 0.01 ppm mainly as sulphide, oxide and carbonates ore. The loss of *d* electron from multiple valences formed coloured ions, spontaneous complex formation and typical characteristics (Lowenheim, 1978).

There are three types of solutions that are commonly used in Cu deposition: acidic (sulfate), alkaline (cyanide and non-cyanide) and pyrophosphate (mildly alkaline) (Gamburg & Zangari, 2011). As expected, from the position in the

electrochemical series, Cu can easily be electroplated in aqueous solution but there will be a problem regarding on how to prevent the formation of deposits with less noble metal. The immersion deposits are usually non adherent and powdery. Most of researchers proposed the use of complexing agent to reduce the activity of Cu ions. Table 2.2 presents the list of advantages and disadvantages of Cu electrodeposition.

Table 2.2: List of advantages and disadvantages of Cu electrodeposition (Loweinheim, 1978)

Advantages	Disadvantages
Highest electrical and thermal conductivity	Under atmospheric condition, Cu deposit has a very low chemical resistance. The deposit cannot provide electrochemical protection to the substrate
Environmentally non hazardous	At higher temperature Cu coatings must have barrier layer to prevent diffusion into other metal
Cu metal indispensable component of multilayer deposits	The deposits form alloy with solders resulting in formation of intermetallic compounds
Cu deposits usually have low internal stresses; very thick layers of coating that easily produced	Cu is unstable when in contact with many organic substances.
It is suitable for various mechanical working processes. Cu is ductile and can be easily polished	Cu is not suitable for hermetic connections, for example welded joints.

Wendrock *et al.* (2000) has done a study on the electroplating of Cu layer at room temperature. The room temperature electroplating activity produced grain growth in thin electroplated Cu layers. This grain growth is believed to be driven by a very high defect density coupled with high grain boundary mobility. During the movement of a grain boundary in the materials, defects are healed. Thus, the total free energy is lowered than before.

2.3   Compositionally Modulated Multilayer (CMM)

Multilayer thin film coating has received attention among researchers over the few decades for its excellent mechanical properties. Multilayer coating consists of repeating different bilayer materials of different thickness. In electrodeposition of multilayer, accurate control of microstructure on the nanometric scale makes it possible to control not only its magnetic properties but also its mechanical properties (Chui & Chen, 2008 and Vella *et al.*, 2004). The properties of multilayer structures produced by the electrodeposition process are significantly affected by parameters such as the electrolyte concentration, the electrolyte pH, the deposition potentials, additives, substrates and the control methods (galvanostatic and potentiostatic) (Singh *et al.*, 2009).

In nanostructural materials, the microstructural length or grain size is about 100 nm (Tjong & Chen, 2004). They are divided into three main types which are one-dimensional structures (more commonly known as multilayers) which are made of alternate thin layers of different composition, two-dimensional structures (wire-type elements suspended within a three-dimensional matrix), and three-dimensional constructs, which may be made of a distribution of fine particles suspended within a matrix as described in Figure 2.1 (Schlesinger & Paunovic, 2000).
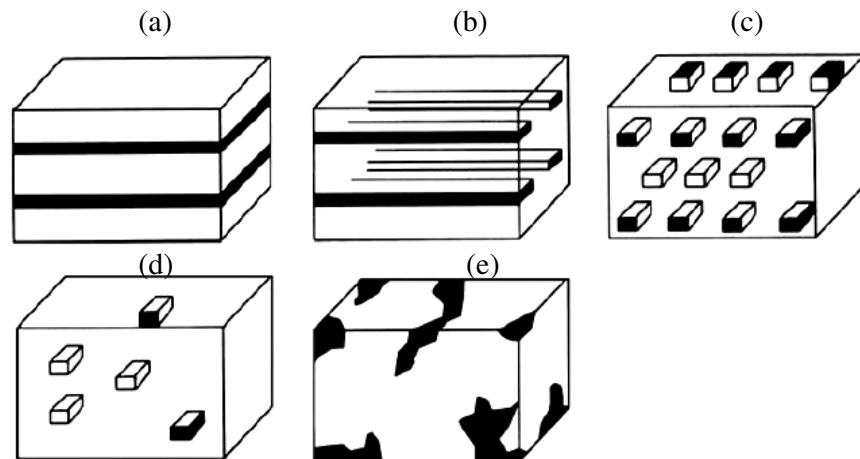
Figure 2.1: Several types of dimensional structures of nanostructured materials
(a) Quantum wells (b) quantum wires (c) ordered arrays of quantum boxes
(d) Random quantum dots and (e) an aggregate of nanometer-size grains
(Schlesinger & Paunovic, 2000).

Alternate layer of two different materials with different laminate thickness in the range of nanometer can be fabricated by electrochemical deposition. The electrodeposition is an inexpensive process for the production of advanced material. The multilayer can be produced in either dry or wet process. The dry process involves vacuum deposition such as evaporation, molecular beam epitaxy and sputtering. The wet process, especially electrodeposition of multilayer can be divided into two categories which are single bath technique and dual bath technique (Esmaili *et al.,* 2011).

The multilayer involves combination of several metal of interest to form alternate layers. Go'mez *et al,* (2002) investigated on the electrodeposition of Co/Cu multilayer from a single electrolyte containing the Co (II) and Cu (II) ions. Wen *et al.* (2002) also investigated the microstructure and mechanical properties of the multilayer structure of Ni/Ru which found that the multilayer formed coherent epitaxial on each other. The considerable interests in the production of nano-dimensional multilayer structured films show large potentials applications in various technologies based on different unique properties. Therefore, in this research dual bath technique has been selected in order to produce the multi-nanolayer structure of Cu and Ni.

2.4   Electrodeposition

Electrodeposition (also termed as 'electroplating' or 'electrochemical deposition') process is a study in the fields of electrochemistry, electrochemical engineering, solid state physics, metallurgy, material and electrical (Paunovic & Schlesinger, 2006 and Loweinheim, 1978). Electrodeposition refers to the formation of metallic coating on a base material occurring through the electrochemical reduction of metal ions from an electrolyte. Electrodeposition is simple and not expensive (Singh *et al.,* 2009). This process involves an electrolyte as ionic conductors to produce chemical species of metal of interest (Gamburg & Zangari, 2011). This electrochemical deposition technique is able to produce adhesive and compact coatings of metal, alloys and composites (Safiee *et al.,* 2016). Metal electrodeposition is one of the most interesting electrochemical processes owing to their widespread uses such as avoiding corrosion, improving the external appearance of diverse materials, in

metallic structures and engineering. Moreover, it is also used in jewelry, decoration, galvanization and cast replicates for electroerosion, plastic metallization and electronic industries. Recently, this electrodeposition has been found to be the most important method especially in producing coating for environmentally energy harvesting such as solar cells and thermo electric generators (Matsuoka *et al.,* 2015).

In general, electrodeposition process consists of dissolution of metal from an electrode (anode), into a solution containing ions of the same metal (cathode) which is in contact with the solution. The potential is applied between electrodes. Oxidation-reduction processes are produced at the electrodes. The oxidation occurs at the anode while the reduction takes place at the cathode. These reactions lead to a change in the metal oxidation state (Postigo, 2010).The electrodeposition comprises several important components which are anode, cathode, power supply and electrolyte as displayed in Figure 2.2.
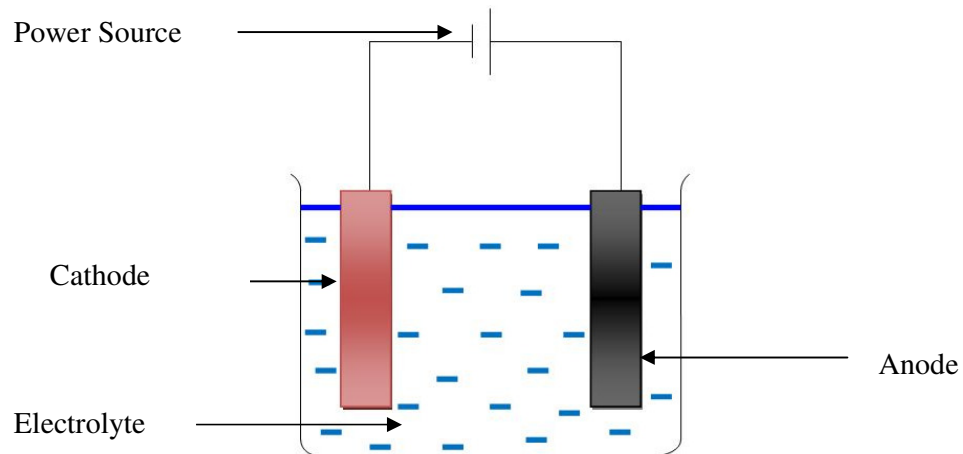
Figure 2.2: An electrolytic cell

The electrodeposition involves the process of metal deposit on a particular substrate when a current is passed through an electrolytic bath (Beltowska-Lehman *et al.,* 2015). Figure 2.2 is the electrolytic cell that composed of several parts. Generally, the anode is the metal that is placed at the positive terminal electrode where oxidations occur. The cathode workplace/ substrate is placed at the negative terminal of the AC or DC power supply. A voltage applied across the two electrodes will result in a potential difference. Then, the cations in the electrolyte move to the

cathode due to the electric field and causing the dissociated metal ions to gain electrons. At this stage, they oxidize on the surface of the cathode and form a deposited layer on the cathode metallic coating (Paunovic & Schlesinger, 2006 and Loweinhem, 1978). The movement of the cations and the electrons forms an electric current. This chemical deposition is a repeating process where the electrons flow out from the anode into the electrolyte back to the anode with the aid of the external circuit. Finally, they flow back to the cathode (Ping *et al.,* 2011).

The Faraday's Law is shown in equation (2.1) which relates the amount of electrical charges passed through the circuit during electrodeposition. It is used to calculate the duration of electrolysis in order to achieve a predetermined thickness.

$$m = \frac{QA}{nF} \tag{2.1}$$

Where,

m is the deposited metal mass (grams)

Q is the net charge passed through the circuit (coulombs)

A is the atomic weight of the metal

n is the number of electrons per molecule of the species being reacted

F is the value gained by multiplying the electronic charge by the Avogadro number means that 1 F equals to 96,485 C/ (mol of electrons)

At constant current

$$Q = It \tag{2.2}$$

The charge Q can be defined in terms of electric current as in Eq. (2.3).

$$Q = \int dIt \tag{2.3}$$

Where,

I is the total current in amperes (A)

t is the duration of the electrochemical process in seconds (s)

Other researchers are assuming 100 % efficiencies of current densities in electrodeposition process (Alper *et al.,* 2004 and Tsuru *et al.,* 2002). In this study,

the electrodeposition term is defined as a process in which the deposit of a thin layer (of metal) is formed 'electrolytically' on a metal substrate (Sahoo, 2008). Electrodeposition has a lot of advantages such as low production cost and requires low temperature of an electrolyte. The structures and compositions of the deposits are affected by electrolyte composition, agitation of the solution, current and potential during the process.

2.5   Electrodeposition of Ni/Cu Multilayer Systems

The increasing attention in order to enhance the performance of devices and coatings has prompted research into strategies that can be implemented to decrease the dimensions of thin films and coatings without compromising their mechanical performance. Electrodeposition is one of the best methods to prepare alternate layer of element in the range of hundreds of nanometers to tens of micrometers. For an example, a successful work has resulted in enhancing performances of the samples, such as improving corrosion resistance, tribological performance, thermal stability and having high strength and giant magneto resistance (Kurmanaeva *et al.,* 2016). This current research focuses on the elements such as Cu and Ni in order to form products for nanosystem applications.

The development of Ni/Cu multi-nanolayer has interest most researchers because this technological system can be electrochemically easy to grow in a well-controlled environment. The coherency to form alternate layer of Ni/Cu attributed to the fact that Cu and Ni possess the same F.C.C structures (Barshilia & Rajam, 2002), identical atomic rays, electronegativity and similar electron valences. Moreover, the isomorphic mechanism of Ni/Cu multilayer is also able to complete the solubility of the two components in liquid and solid states (Melo *et al.,* 2011). Nickel is an excellent choice as the first layer of the coating, for several commercial and industrial reasons (Bouyelfane & Zerga, 2014). Researches on the alternate layer of Cu and Ni have attracted attentions since few years ago. The Ni/Cu metal coating has been regarded as the next generation of the metallization process that can improve the efficiency with a low specific contact resistance. This coating is formed using low-cost electrodeposition.

According to Tench & White (1984) on the investigation of composite structures "periods" down to 100 °A, the presence of harder Ni layer in a softer Cu matrix for compositionally modulated multilayer exhibited the enhancement of their tensile strength. Yahalom & Zadok (1987) also developed a method to produce composition modulated alloys by electrodeposition of Cu and Ni which had unique properties similar to those produced via vapour deposition.

Tóth-Kádár *et al.* (2000) on his recent work also studied the characteristics of eletrodeposited Ni/Cu alloys and Ni-Cu/Cu multilayers. The findings proposed the growth of the multilayers via two pulse plating technique in the formation of chemically intermixed interface. They established the current density of the deposition from the measurement of the direct current. Moreover, the properties of the multilayer structure are critically dependent on the growth conditions of the Ni/Cu systems. The very perfect thin Ni–Cu/Cu multilayers can be prepared with coherent interfaces. Nonetheless, if the layer modulation wavelength is in the 10 nm range and at modulation thicknesses above 60 nm, the interfaces lose their nearly perfect coherency (Czira´ki *et al.,* 1998).

In this present work, the research focuses on the production of alternate layer of Cu and Ni layer at ambient temperature (room temperature). The ambient temperature has been selected for the electrodeposition temperature in this work with the resistance changes of up to 55 % and the sensitivies of up to 0.07 % as successful work of using this temperature in producing Co–Cu/Cu and Co–Ni/Cu multilayer has been reported by Czira´ki *et al.* (1998). Alternating layers of metal and electrodepositing the layers at various temperatures are the parameters that need to be taken into consideration in order to get a better quality deposit. In electrodeposition, there are two major techniques for the preparation of multilayer structures by using either single-bath technique or dual bath technique.

2.6   Dual Bath Technique (DBT)

There are two major techniques in preparing multilayer films by electrodeposition. The first one is the single-bath technique. In this technique, the deposition is carried out by alternately changing the cathodic current/potential in a single electrolyte containing ions of different constituents of the multilayer. The second technique is

the dual-bath technique, which is conceptually simple and it involves the deposition of the constituents by alternate immersion (Matsuoka *et al.*, 2015). Dual Bath Technique (DBT) has attracted many researchers to deposit various multilayers, such as Zn/Co (Kirilova *et al.,* 1998), Ni/Cu (Haseeb *et al.,* 1994 and Shu *et al.,* 2012) and Cu/Ni (Ren *et al.,* 2011). Historically, in 1921, Blum was the first person who employed the Dual Bath Technique (DBT) for the deposition of Ni/Cu multilayer structure. Blum's deposit was a minimum of 5 µm sublayer thickness (Haseeb *et al.,* 1994).

Although the single bath technique has attracted most researchers, the obvious disadvantage of the single bath technique is that more noble metal (nonmagnetic) is co-deposited during the deposition of the less noble metal component (magnetic). Thus, it is impossible to deposit a Cu layer in a Ni layer. Nonetheless, by using the dual bath technique, the more and less noble metal in the electrolyte solutions do not have to be compatible, because the multilayers are obtained by repeatedly transferring the substrate from one electrolyte to another different electrolyte. Therefore, most recent works have chosen the dual bath technique to produce multilayer structures. For this technique, each layer is deposited alternately on a particular substrate.

The condition of deposition such as current density, potential, or both parameters must be different enough to allow separate electrodeposition of each layer (Haseeb *et al.,* 1994). Table 2.3 summarizes the findings and studies of multilayer structures via dual bath technique.

Table 2.3: Summary of multilayer structures via dual bath technique

Multilayer Structures	Repeat Length	Deposition method	Solutions
NiFe/Cu	20 nm	Pulsed Galvanostic	Copper Sulphate
(Esmaili *et al.,* 2011)			Nickel Sulphate
			Iron Sulphate
Ni/Cu	18 nm	Pulsed	Nickel Sulphate
(Ghosh *et al.,* 2007)			Copper Sulphate
Ni-Cu Alloys and Ni-Cu/Cu Multilayers		Direct Current (DC) plating	Nickel Sulphate

		Two-pulse plating	Copper Sulphate
(Tóth-Kádár *et al.,* 2000)		Galvanostatic	
Cu/Ni	5-100 nm	Potentiostat	Copper Sulphate
(Haseeb *et al.,* 1994)		Galvanostatic	Nickel Sulphate
Zn/Co	0.3 and 3.0 µm	Galvanostatic	Zinc
(Kirilova *et al.,* 1998)			Cobalt

2.7   Direct Current (DC)Electrodeposition

The properties of the electrodeposited films are significantly affected by the deposition potential or current density, type of electrolyte and electrolyte temperature (Sarac & Baykul, 2013). In the conventional DC electrodeposition process, the electrical current is continuously exerted to the system in uninterruptible manner. The duty cycle is the ratio of current on time to the total time which is 100 %. Therefore the average current equals to the peak current density. This method is anold method and conventional that is used for the electrodeposition of metal and alloys. The advantage of direct current electroplating is that DC unit is cheaper than pulse generator. Moreover, this technique applies simple, economically affordable process and easy procedures in order to attain better results (Torabinejad *et al.,* 2017).

2.8   Current Density

Current density is one of the most important variable since it influences the deposition rate, microstructure, chemical composition, and cost as well as strongly affecting the properties of the coating. The current density is usually assumed to be uniformed across the surface of the coating (Paunovic & Schlesinger, 2006).

Current density governs the rate of the deposition process that is usually measured in mol/cm^2.s or in microns per hour which is usually expressed in amperes

per square meter A·m⁻². Thus, the current density is the most suitable measure for the rate of any electrochemical process. The equation 2.4 as follow:

Current Density, (CD)

$$i = \frac{I}{A}$$

(2.4)

Where,

        I is the current (A)

        A is the area (m²)

2.9   Decomposition Potential

The decomposition potential was discovered by Maxx Le Blanc (1865-1943). He discovered more about the phenomenon of polarization and the formation of gas films on the electrodes. Not only that, the applied EMF caused dissolution from one electrode and deposition of metal on the other. When H_2SO_4 solution was electrolysed by platinum electrodes, applying an external potential of 1.00 V, the current flowed but suddenly stopped due to the polarization. The H_2 and O_2 formed a layer at the surface of the electrodes. During the applied potential of the current, the current suddenly increased which is caused by the evolution of H_2 and O_2 at the electrodes (H_2 at cathode and O_2 at anode).

      Moreover, the term decomposition potential can be defined as the maximum potential that must be applied between two electrodes of an electrolytic cell to ensure the continuous electrolysis process. It is also known as deposition or discharge potential of the sums of potential of each electrode during the electrolysis that must be greater than the reversible electrode potential. The value of decomposition potential can be determined from a plot of current versus voltage as shown in Figure 2.3 (a). As the applied voltage increased, the flow of the current and the potential difference across the electrodes were measured. The experimental setup is shown in Figure 2.3 (b). The graph explains that the initial current flow is small until it reaches the decomposition voltage. The voltage region shows the almost complete

polarization for one or both electrodes. Beyond D the current increased rapidly (sudden jump) with further increase in applied e.m.f.
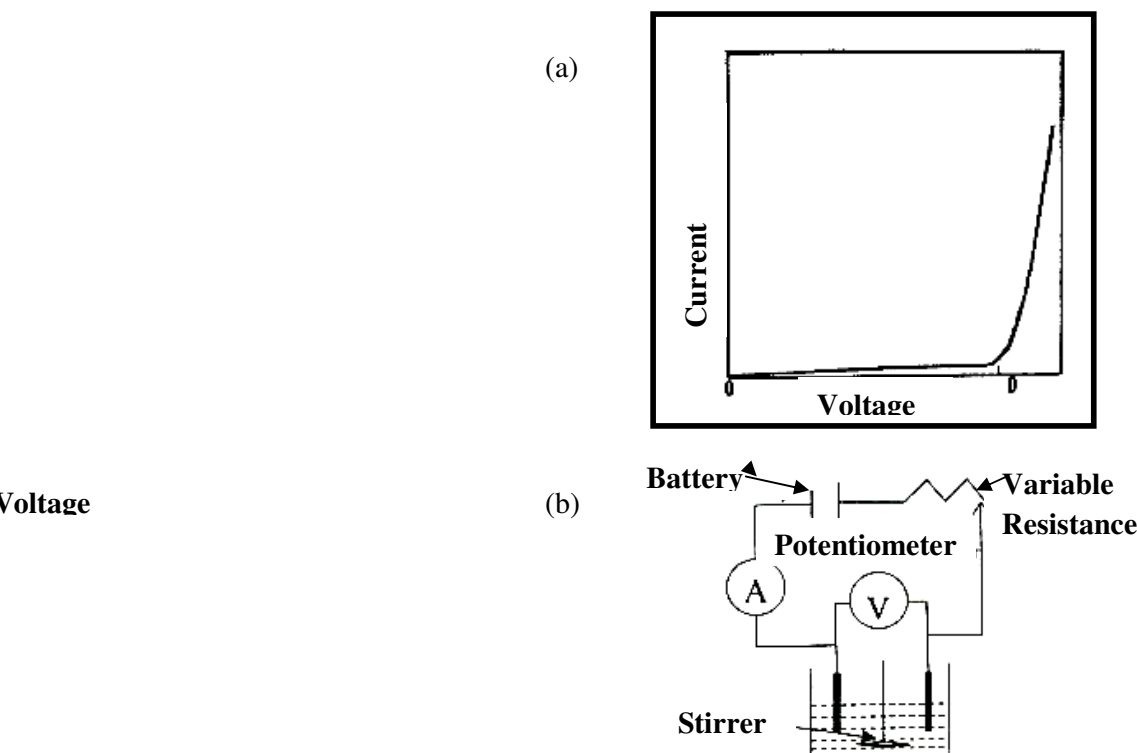
Figure 2.3: Measurement of decomposition potential (a) current –voltage diagram (b) Experimental set-up (Sivasankar, 2008)

Decomposition potential was involved in the preliminary work in order to obtain the best current density for the experimental works. Qian *et al.* (2011) determined the form of deposition rate for both electrolytes. The voltage values were connected with the critical deposition overpotential of each metallic ion. It was a concept where Ni was not deposited when the applied voltage was lower than 2.00 V whereas Cu was not deposited from the electrolyte until the voltage was higher than 1.00 V. The high concentration of metallic ion in the electrolyte contributed by the ion supplied to the cathode.

Badarulzaman *et al.* (2010) also discovered the decomposition potential of Ni. Based on the observation, it revealed that the decomposition potential was 2.00 V with 0.12 A. Moreover, Bonhote and Landolt, (1997) revealed that Cu reduction occurred in the plateau between -0.20 V and -0.70 V of the limiting current. The sudden increase in the current at the end of the plateau was due to the Ni deposition

that started at -0.70 V. Modulating current density between high values corresponded to the simultaneous deposition of Ni and Cu.

However, Lazzari and Pace, (1975) investigated the electrochemical properties of diethyl-triethylenediamine cuprous bromide (dtdBr$_2$-CuBr). The decomposition potential of the electrolyte appeared to be 0.70 V at 25 °C. Abrantes *et al.* (1986) also studied the variation of decomposition potential that involved in different electrolyte temperatures. This research revealed that below 65 ℃ the decomposition potential involved was influenced by the voltage stability window. Meanwhile, at a high temperature, the reduction process was caused by a change of anodic limit.

The decomposition potential or decomposition voltage is important as the predetermining step in this work. The increase of the voltage above the decomposition voltage will increase the rate of the reaction. It was also as an approximate characteristic of the industrial electrode during the electrodeposition process.

2.10   Hydrogen Evolution

During electrodeposition process, hydrogen is the second element that is electrochemically produced at the cathode. Hydrogen evolution affects the physical properties such as embrittlement (Gabe, 1997)**.** The mechanism of hydrogen evolution:

In acid solution

$$H^+ + e^- + M \rightarrow M - H + H_2O \tag{2.5}$$

In alkali solution

$$H_2O + e^- \rightarrow H_{ads} + OH^- \tag{2.6}$$

In the deposition of certain metals, hydride formations are formed by adsorbing hydrogen (H$_{ads}$). Increasing the solution temperature and current density will also increase the hydrogen adsorption. Excessive gas evolution can induce hydrogen embrittlement. Thus, low deposition rates can occur. Hydrogen bubbles may cause porosity, interface defect or voids in the coating due to the surface tension (Gabe, 1997).

REFERENCES

Abdel-Karim, R., Reda, Y., Muhammed, M., El-Raghy, S., Shoeib, M & Ahmed, H. (2011). Electrodeposition and Characterization of Nanocrystalline Ni-Fe Alloys. *Journal of Nanomaterials*, pp.1 - 8. doi:10.1155/2011/519274

Abrantes, M. A., Alcacer, L. J & Sequeira, C. A. C. (1986). Thin Film Solid State Polymer Electrolytes Containing Silver, Copper and Zinc Ions as Charge Carriers. *Solid State Ionics, 18(19)*, pp. 315 - 320.

Allahyarzadeh, M. H ., Aliofkhazraei, M., Sabour, R., Rouhaghdam, R & Torabinejad, V. (2016). Gradient electrodeposition of Ni-Cu-W (alumina) nanocomposite coating. *Materials and Design*, 107, pp. 74–81.

Alper, M., Baykul, M. C., Pe´Ter, L & Bakony, I. (2004). Preparation and Characterisation of Electrodeposited Ni–Cu/Cu Multilayers. *Journal of Applied Electrochemistry*, *34*, pp. 841 – 848.

Badarulzaman, B. A., Mohamad, A. A., Puwadaria, S., & Ahmad, Z. A. (2010). The Evaluation of Nickel Deposit Obtained via Watts Electrolyte at Ambient Temperature. *Journal of Coating Technology, 7 (6),* pp. 815 – 820.

Badea, G. E., Caraban, A., Sebesan, M., Dzitac, S., Cret, P., & Setel, A. (2010). Polarisation Measurements Used for Corrosion Rates Determination. *Journal of Sustainable Energy*, *1(1),* pp.1 - 4.

Barshilia, H. C & Rajam, K. S. (2002). Characterization of Cu/Ni Multilayer Coatings by Nanoindentation and Atomic Force Microscopy. *Surface and Coatings Technology, 155*, pp. 195 – 202.

Baskaran, I., Narayanan, T. S., & Stephen, A. (2006). Pulsed Electrodeposition of Nanocrystalline Cu–Ni Alloy Films and Evaluation of Their Characteristic Properties. *Materials Letters, 60*, pp. 1990 - 1995.

Beltowska-Lehman, E., Indyka, P., Bigos, A., Szczerba, M. J., & Kot, M. (2015). Ni–W/ZrO$_2$ Nanocomposites Obtained by Ultrasonic DC Electrodeposition. *Materials and Design, 80*, pp. 1 - 11.

Beverskog, B & Puigdomenech, I. (1997). Revised Pourbaix Diagrams for Nickel at 25 ℃ - 300 ℃. *Corrosion Science, 39 (5),* pp. 969 – 980.

Bicelli, L. P., Bozzini, B., Mele, C., & D'Urzo, L. (2008). A Review of Nanostructured Aspects of Metal Electrodeposition. *International Journal of Electrochemical Science*, *3*, pp. 356 - 408.

Bonhote, Ch. & Landolt, D. (1997). Microstructure of Ni/Cu Multilayers Electrodeposited from a Citrate Electrolyte. *Electrochimica Acta, 42(15),* pp. 2407 - 2417.

Bouyelfane, A & Zerga. (2014). A Ni/Cu Electroplating, a Worthwhile Alternative to use Instead of Ag Screen-Printed Front Side Metallization of Conventional Solar   Cells. *Materials Science in Semiconductor Process*sing. 26, pp. 312–319.

Boyapati, V. A. P & Kanukula. C. K. (2013). Corrosion Inhibition of Cu-Ni (90/10) Alloy in Seawater and Sulphide-Polluted Seawater Environments by 1, 2, 3-Benzotriazole. *ISRN Corrosion,* pp.1 - 22.

Bragg, W. L. (1913). The Diffraction of Short Electromagnetic Waves by a Crystal. *Proceedings of the Cambridge Philosophical Society, 17 (43).*

Chung, C., Chang, C. W. T & Hung , S. T. (2010). Electroplating of Nickel Films at Ultra Low Electrolytic Temperature. *Microsystem Technology*, 16, pp. 1353 – 1359.

Chui, X & Chen, W. (2008). Saccharin Effects on Direct-Current Electroplating Nanocystalline Ni-Cu Alloys. *Journal of The Electrochemical Society,* 155,pp133-139.

Czira´ki.A, Pierron-Bohnes, V, Ulhaq-Bouillet, C, To´th-K´ad´ar, E & Bakonyi, I. (1998). A Cross-Sectional High-Resolution Transmission Electron Microscopy Study of Electrodeposited Ni–Cu/Cu Multilayers. *Thin Solid Films* pp. 239–242.

DiBari, G. A. (2010). Electrodeposition of Nickel. In: M. Schlesinger and M, Paunovic. Modern Electroplating, 5th.ed. New York: John Wiley and Sons Inc.

Donald, L. S. (1995). Electroplating Nickel/Chromium for Automotive Industry. *Metal Finishing*, *93*, pp. 205 – 212.

Ebrahimi, F, & Liscano, A. J. (2001). Microstructure Mechanical Properties Relationship in Electrodeposited Ni/Cu Nanolaminates. *Materials Science and Engineering, 301*, pp. 23 – 34.

Ebrahimi, F., Bourne, G. R., Kelly, M. S., Matthews, T. E. (1999). Mechanical Properties of Nanocrystalline Nickel Produced by Electrodeposition. *Nanostructured Materials, 11(3),* pp. 343 - 350.

Esmaili, S., Bahrololooma, B. E & Kavanag, K. B. (2011). Electrodeposition, Characterization and Morphological Investigations of Nife/Cu Multilayers Prepared By Pulsed Galvanostatic Dual Bath Technique. *Material Characterization*, pp. 204 - 210.

Evans, G. P, Schecka, C, Schada, B, Zangaric, G. (2003). Electrodeposition of epitaxial nickel films. *Journal of Magnetism and Magnetic Materials, 260*, pp. 467 – 472.

Fei, J, & Wilcox, G. D. (2006). Electrodeposition of Zinc–Nickel Compositionally Modulated Multilayer Coatings and Their Corrosion Behaviours. *Surface & Coatings Technology, 200,* pp. 3533 – 3539.

Fullerton, E. E., Schuller, I. K., Vanderstraeten, H., & Bruynseraede, Y. (1992). Structural Refinement of Superlattices from X -Ray Diffraction, *Physical Review, 45 (16),* pp. 9292 - 9310.

Frankel, G. (2010). Coatings for Corrosion Protection. *The Electrochemical Society*, *25(29),* pp. 105-111.

Gabe, D. R. (1997). Role of Hydrogen in Metal Electrodeposition Processes. *Journal of Applied Electrochemistry*, *27*, pp. 908 - 915.

Gamburg, Y. D & Zangari, G. (2011). *Theory and Practice of Metal Electrodeposition.* ed. New York: Springer Science. Springer.

Ghosh, S. K. Limaye, P. K., Swain, B. P., Soni, N. L., Agrawal, R. G., Dusane, R. O & Grover, A. K. (2007). Tribological Behaviour and Residual Stress of Electrodeposited Ni/Cu Multilayer Films on Stainless Steel Substrate. *Surface and Coatings Technology*, *201*, pp. 4609 – 4618.

Ghosh, S. K ,Grover, A. K. Dey, A. K., Kulkarni, U. D, Dusane, R. O, Suri, A. K & Banerjee, S. (2006). Structural Characterization of Electrodeposited Nanophase Ni–Cu Alloys. *Journal of Material Research*, *21(1)*, pp. 45 - 61.

Go´mez, E., Labarta, A., Llorente, A & Valle´s, E. (2002). Characterisation of Cobalt Copper Multilayers Obtained by Electrodeposition. *Surface and Coatings Technology, 153*, pp. 261 – 266.

Goranova, D., Avdeev, G & Rashkov, R. (2014). Electrodeposition and characterization of Ni–Cu alloys. *Surface & Coatings Technology*. 240, pp. 204–210.

Guan, M. (2005). Electrodeposition of AuCo Alloys and Multilayers. University of Petroleum (East China). Master Thesis.

Halim, R. Karim, A. Raghy, S. Nabil, M & Waheed, A. (2012). Electrodeposition and Characterization of Nanocrystalline Ni-Mo Catalysts for Hydrogen Production. *Journal of Nanomaterials,* pp. 1 - 9.

Haseeb, A. S. M. A., Celis, J. P & Roos, J. R. (1994). Dual-Bath Electrodeposition of Cu/Ni Compositionally Modulated Multilayers. *Journal of the Electrochemical Society, 141*, pp. 230 - 237.

Hili, K, Fan, D, Guzenko, V. and Ekinci, V. (2015). Nickel electroplating for high-resolution nanostructures. *Microelectronic Engineering*. 141, pp.122–128.

Ibanez, A. & Fatas, E. (2005). Mechanical and Structural Properties of Electrodeposited Copper and Their Relation with the Electrodeposited Parameter. *Surface and Coating Technology, 191*, pp.7 - 16.

Iyer, D. S. (2001). *Electrodeposited Nanoscale Multilayers of Invar with Copper*. Bangalore University: Master Thesis.

Jayakrishnan, S., Krisna, N., Sujatha, K.P., Sriveeraraghavan, S., Krishnan, R.M. & Natarajan, S. R. May-Jun. (1996). Electroplating of Nickel-Copper Alloys. *Bulletin of Electrochemistry*, pp. 259-265.

Jinlong, L .,Tongxiang, L & Chen, W. (2016).Effect of Electrodeposition Temperature on Grain Orientation and Corrosion Resistance of Nanocrystalline Pure Nickel. Journal of Solid State Chemistry, *240,* pp. 109-114.

Kaura, N., Suzuki, Y., Idemoto, Y., Kato, T., and Matsumoto, F. (2003). Electrodeposition of Zn–Ni alloy from $ZnCl_2$–$NiCl_2$–EMIC and $ZnCl_2$–$NiCl_2$–EMIC–EtOH ambient-temperature molten salts. *Surface and Coatings Technology, 169 –170*, pp. 120–123.

Kaneko, Y & Mizuta. Y. (2005). Vickers Hardness and Deformation of Ni/Cu Multilayer Electrodeposited on Copper. *Material Science Journal*, *40(12),* pp. 3231 - 3236.

Kaneko, Y., Mizuta, Y., Nishijima, Y & Hashimoto, S. (2005). Vickers Hardness and Deformation of Ni/Cu Nano-Multilayers. Electrodeposited on Copper *Journal of Materials Science, 40,* pp. 3231 – 3236.

Kang, J. X., Zhao, W. Z, & Zhang G. F. (2009). Influence of Electrodeposition Parameters on the Deposition Rate and Microhardness of Nanocrystalline Ni Coatings. *Surface Coating Technology*, *203*, pp. 1815 – 1818.

Kim, M., Kim, J., Kim, C. K., & Kim, N. (2005). Study on the Effect of Temperature and Pressure on Nickel-Electroplating Characteristics in Supercritical CO_2 *Chemosphere*, pp. 459 – 465.

Kim, J., Yim, T & Lee, J. (2013). Effects of Bath and Operating Conditions on the Composition of Ni-Fe Alloy Electroplating for Solar Cell Substrate. *Current Applied Physics, 13*, pp. 5108-5110.

Kirilova, I., Ivanov, I., & Rashkov, S. T. (1998). Anodic Behaviour of Composition Modulated Zn/Co Multilayers Electrodeposited from Single and Dual Baths, *Journal of Applied Electrochemistry, 28,* pp.1359 - 1363.

Kurcharska, B., Kulej, E., & Gwozdzike, K. (2012). Evaluation of the Temperature Stability of a Cu/Ni Multilayer, *Journal of Metallurgy and Materials, 57.*

Kurmanaeva, L., McCrea, J, Jian, J .,Fiebig, J, Wang, H, Mukherjee, A. K. & Lavernia, E, J .(2016). Influence of Layer Thickness on Mechanical Properties of Multilayered NiFe Samples Processed by Electrodeposition. *Materials and Design* 90, pp. 389–395.

Lamovec, J., Jovic, J., Vorkapic, M., Popovic, B., Radojevic, V., & Aleksic, J. (2011). Microhardness Analysis of Thin Metallic Multilayer Composite Films on Copper Substrates. *Journal of Mining Metallurgy, 47 (1)*, pp. 53 – 61.

Lassri, H., Ouahmane, H., Fanity, E., Bouanani, M., Cherkaoui, F & Berrada, A. (2001). Ferromagnetic Resonance Studies of Electrodeposited Ni-Cu Multilayers. *Thin Solid Films*, *389*, pp. 245 - 249.

Lazzari, M & Pace, R. C. (1975). Electrochemical Properties of the n-n'-dimethyltriethylene- dibromide-cuprous bromide Solid Electrolyte. *Electrochimica Acta*, *20*, pp. 331 - 334.

Lins, V., Cecconello, E. S., & Matencio, T. J. (2008). Effect of Current Density on Morphology, Porosity, and Tribological Properties of Electrodeposited Nickel on Copper. *Journal of Material Engineering and Performance*, *17(5),* pp. 741 - 745.

Liu, Z., Zheng, M., Hilty, R. D., & West, A. C. (2010). Effect of Morphology and Hydrogen Evolution on Porosity of Electroplated Cobalt Hard Gold. *Journal of the Electrochemical Society, 157 (7)*, pp. 411 - 416.

Liu, Z., Zheng, M., Hilty, R. D., & Westa, A. C. (2010). Effect of Morphology and Hydrogen Evolution on Porosity of Electroplated Cobalt Hard Gold. *Journal of the Electrochemical Society*, *57*, pp. 11 - 16.

Low, C. T. J, Wills, R. J. A., & Walsh, F. C. (2006). Electrodeposition of Composite Coatings Containing Nanoparticles in a Metal Deposit. *Surface and Coatings Technology, 201*, pp. 371 - 383.

Lowenheim, F. (1978). *Electroplating Fundamental of Surface Finishing*. New York: McGrow –Hill Book Company.

Mansfeld, F. (2006). Classic Paper in Corrosion Science and Engineering with a Perspective by F. Mansfeld. *Corrosion, 62(10),* pp. 843.

Matsuoka, K, Okuhata, M & Takashiri, M. (2015). Dual-bath electrodeposition of n-type BieTe/BieSe multilayer thin Films. *Journal of Alloys and Compounds 649*, pp. 721-725.

Melo, L. C., De Lima-Neto, P., & Correia, A. N. (2011). The Influence of Citrate and Tartrate on the Electrodeposition and Surface Morphology of Cu–Ni layers. *Journal of Applied Electrochemistry, 41*, pp. 415 – 422.

Miyake, T., Kume, M., Yamaguchi, K., Amalnerkar, D. P., & Minour, H. (2001). Electrodeposition of CuNi–P multilayers by a Single Bath Technique. *Thin Solid Films*, *397*, pp. 83 –89.

Nageswar, S. (1975). Crystal Growth at the Cathode. *The Electrodeposition and Surface Treatment, 3*, pp. 417 – 433.

Nady, J. E, Kashyout, A., Ebrahim, Sh. & Soliman, M. (2016). Nanoparticles Ni Electroplating and Black Paint for Solar Collector Applications. *Alexandria Engineering Journal*, 55, pp. 723–729.

Nguyen, V.C., Lee, C. Y., Chen, C. S & Chang, L. (2013). An Electroplating Technique Using The Post Supercritical Carbon Dioxide. *Surface and Coating Technology, 232,* pp.234-239.

Nikolic, N. D., Popov, K. I., Pavlovic, L. J., & Pavlovic, M. G. (2006). The Effect of Hydrogen Codeposition on the Morphology of Copper Electrodeposits: The Concept of Effective Overpotential. *Journal of Electroanalytical Chemistry, 588,* pp. 88 – 98.

Nimmo, B & Hinds, G. (2003). Beginners Guide to Corrosion. NPL, pp. 1-10.

Nirvana, A., Al-ameer, A., & Uthman, A. (2011). The Influence of Various Parameters on Crevice Corrosion of Two Different Type Geometry of 304l Stainless Steel. *The Iraqi Journal for Mechanical and Material Engineering, 11(4),* pp. 720 - 729.

Oliver, W. C & Pharr, G. M. (2004). Measurement of Hardness and Elastic Modulus by Instrumented Indentation: Advances in Understanding and Refinement to Methodology. *Journal of Material Research, 19 (1).*

Panda, S. & Pattanayak, S. (2012). *Electrodeposition of Copper Thin Films Charge Transfer vs Mass Transfer Mechanism: a Structural Exploration.* National Institute of Technology Rourkela: Degree Thesis.

Paunovic, M. & Schlesinger, M. (2006). *Fundamentals of Electrochemical Deposition.* 2nd . ed. United States of America: Wiley Interscience. John Wiley & Son.

Pellicer, E., Varea, A., Pané, S., Sivaraman, K. M., Nelson, B. J., Suriñach, S., Baró, J., & Sort, J. (2011). A Comparison Between Fine-Grained and Nanocrystalline Electrodeposited Cu–Ni Films. Insights on Mechanical and Corrosion Performance. *Surface & Coatings Technology, 205*, pp. 5285–5293.

Pierce, P. E., Kovac, Z & Hingginbotham, C. (1978). The Kinetics and Mechanism of Film Growth During the Electrodeposition Process. *American Chemical Society, 17(4),* pp. 317 - 322.

P´eter, L, Pa´da´r, J, To´th-Ka´da´r, E., Czira´ki, A , S´oki, P., Pog´any, P., & Bakonyi, E. (2007). Electrodeposition of Co–Ni–Cu/Cu Multilayers. Composition, Structure and Magnetotransport Properties. *Electrochimica Acta. 52 ,*pp, 3813–3821.

Ping, N. L., Dan, Y. D., Feng, L., & MingZhe, Z. (2011). Electrodeposition of Ni Micro/Nano-Structures. *Inorganic Chemistry, 56(32),* pp.3246 - 3430.

Postigo, M. V. (2010). *New Methods for the Analytical Control of a Nickel Electroplating Bath. Application of Chemometric Techniques*. University Del Pais Vasco: PHD Thesis.

Qian, Y., Tan, J., Liu, Q., Yu, H., Xing, R., & Yang, R. (2011). Preparation, Microstructure and Sliding-Wear Characteristics of Brush Plated Copper–Nickel Multilayer. *Surface and Coatings Technology, 205*, pp. 3909 – 3915.

Qiao, X., Li,H., ZhaO, W., & Li, D. (2013). Effects of Deposition Temperature on Electrodeposition of Zinc–Nickel Alloy Coatings. *Electrochimica Acta, 89*, pp. 771 – 777.

Qibo, Z & Yixin, H. (2013). Electrodeposition Behavior of Nickel from a Low Temperature Urea-molten Salt. Materials and Product Engineering *Chinese Journal of Chemical Engineering*, 21(12), pp.1397-1403.

Rajasekaran, N & Mohan, E. S. (2009). Structure, Microstructure and Corrosion Properties of Brush-Plated Cu–Ni Alloy. *Journal of Applied Electrochemistry , 39*, pp.1911 – 1916.

Rao, I & Hazzledine, P. M. (2000). Atomistic Simulations of Dislocation -Interface Interactions in the Cu-Ni Multilayer System. *Philosophical Magazine*, *80(9),* pp. 2011 - 2040.

Rashidi, A. M & Amadeh, A. (2010). Effect of Electroplating Parameters on Microstructure of Nanocrystalline Nickel Coatings. *Journal Material Science Technology. 26(1),* pp. 82 - 86.

Rashidi, A. M & Amadeh, A. (2009). The Effect of Saccharin Addition and Bath Temperature on the Grain Size of Nanocrystalline Nickel Coatings. *Surface and Coatings Technology, 204*, pp.353 – 358.

Ren, F. Z., Liu, P., Zheng, M., Dong, Q. M., Zhou, G. S., & Yuan, Q. (2004). Electron Theory Based Explanation and Experimental Study on Deformation Behavior of Cu/Ni Multilayers. *Metals and Materials International, 10*, pp. 337 - 341.

Sahoo, R. K. (2008). *Sonoelectrochemical Synthesis of Metallic Multilayer Nanocomposite and Their Characterization*. National Institute of Technology Rourkela: Thesis Master.

Sarac, U & Baykul, M. C. (2013). Morphological and Microstructural Properties of Two-Phase Ni–Cu Films Electrodeposited at Different Electrolyte Temperatures. *Journal of Alloys and Compounds*, *552*, pp. 195 – 201.

Sarac, U, Oksuzoglu, R. M., & Baykul, M. C. (2012). Deposition Potential Dependence of Composition, Microstructure and Surface Morphology of Electrodeposited Ni–Cu Alloy Films. *Journal of Material Science Material Electron*, 23, pp. 2110 – 2116.

Sato, N. (2012*). Basics of Corrosion Chemistry*. 1st. ed. Green Corrosion Chemistry and Engineering: Opportunities and Challenges: Wiley-VCH Verlag GmbH & Co. KGaA.

Schaumlöffel, D. (2012). Nickel species: Analysis and toxic effects. *Journal of Trace Elements in Medicine and Biology*, 26, pp.1 – 6.

Schlesinger, M. & Paunovic, M. (2000). Modern Electroplating, 4th ed., New York John Wiley and Sons, pp. 139 - 193.

Schuller, I. K. (1980). New Class of Layered Materials. *Physical Review Letters, 44 (24),* 1597 - 1600.

Sen, R., Das, S., & Das, K. (2011). The Effect of Bath Temperature on the Crystallite Size and Microstructure of Ni–CeO$_2$ Nanocomposite Coating. *Material Characterisation, 62*, pp. 257 - 262.

Shafiee, Z , Bahrololoom, M. E & Hashem, B. (2016). Electrodeposition of Nanocrystalline Ni/Ni–Al$_2$O$_3$ Nanocomposite Modulated Multilayer Coatings. Materials and Design 108, pp.19–26

Shaw, B. A & Kelly, R. G. (2006). What is Corrosion? *The Electrochemical Society Interface*, pp. 24 – 26.

Shu, B. P., Liu, L., Deng, Y. D., Zhong, C., Wu, Y. T., Shen, B., & Hu, W. B. (2012). An Investigation of Grain Boundary Diffusion and Segregation of Ni in Cu in an Electrodeposited Cu/Ni Micro-Multilayer System. *Material Letters, (89),* pp. 223 - 225.

Singh, S., Basu, S & Ghosh, S. K. (2009). Structure and morphology of Cu/Ni film grown by electrodeposition method: A study of neutron reflectivity and AFM. *Applied Surface Science* 255, pp. 5910–5916.

Sivasankar, B. (2008). *Engineering Chemistry*. New Delhi: Tata Mc Graw-Hill Education.

Srinivas, P., Hamman, S., Matthias, W., Kieschnick, M., Ludwig, A., & Dey, S. (2013). Development of Ni/Cu Materials Library by Using Combinatorial Pulsed Electrodeposition. *Transactions of the Indian Institute of Metals , 66(4),* pp.429 - 432.

Tench, D. M. & White, J. T. (1984). Considerations in Electrodeposition of Compositionally Modulated Alloys. *Journal of Electrochemical society*, *12,* pp. 2039.

Tjong, S. C. & Chen, H. (2004). Nanocrystalline Materials and Coatings. *Materials Science and Engineering*, *45*, pp. 1–88.

Tokarz, A., Fraczek, T., Balaga, Z & Nitkiewicz, Z. (2007). Structure, Hardness, and Thermal Stability of Electrodeposited Cu/Ni Nanostructured Multilayers. *Material. Science Journal, 15*, pp. 247 – 252.

Torabinejad, Aliofkhazraei, V. M,, Assareh, S, Allahyarzadeh, M. & Rouhaghdam, H, A, S. (2017). Electrodeposition of Ni-Fe Alloys, Composites and Nano Coatings. *Journal of Alloys and Compounds* 691, pp.841-859.

Tóth-Kádár, E., Peter, L., Becsei, T., Toth, J., Pogany, L., Tornoczi, T., Kamasa, P., Bakonyi, I., Lang, G., Cziraki, A., & Schwarzacherd, W. (2000). Preparation and Magnetoresistance Characteristics of Electrodeposited Ni-Cu Alloys and Ni-Cu/Cu Multilayers. *Journal of the Electrochemical Society, 147(9),* pp. 3311 – 3318.

Tsuru, Y. Nomura, M & Foulkes, F. R. (2002). Effects of Boric Acid on Hydrogen Evolution and Internal Stress in Films Deposited from a Nickel Sulfamate Bath. *Journal of Applied Electrochemistry*, *32*, pp. 629 – 634.

Tsyntsaru, N., Belevskt, S., Cesiullic, H., Dikursarb., A., & Celisa, J. P. (2012). Cu/Co–W Nanolayers Electrodeposited from Single Bath and Investigations of Their Nanohardness. *Surface Engineering and Applied Electrochemistry, 48(5),* pp. 418 – 425.

Vany´sek, P. (2000). Electrochemical series. CRC PRESS LLC.

Vella, J. B., Mann, A. B., Kung, H., & Chien, C. L. (2004). Mechanical Properties of Nanostructured Amorphous Metal Multilayer Thin Films. *Journal of Material Resident. 19(6)*, pp.1840 - 1848.

Wang, L., Zhang, Y., Metro, A., Bonhommec, P., & Troyon, M. (1996). TEM study of Electrodeposited Ni/Cu Multilayers in the Form of Nanowires. *Thin Solid Films, 288*, pp. 306 – 314.

Wang, W & Singh, R. N. (1999). Influence of the Microstructure on the Mechanical Properties of Ni/Sn Multilayered Composites. *Materials Science and Engineering, 271(1),* pp. 306 - 314.

Wen, S. P., Zong, R. L., Zeng, F., Gu, Y. L., Gao, Y., & Pan F. (2002). Thermal Stability of Microstructure and Mechanical Properties of Ni/Ru Multilayers. *Surface and Coatings Technology*, *202*, pp. 2040 – 2046.

Wendrock, H,. Brtickner, W., Hecker, M., Koetter, T,G., Schloerb, H. (2000). Room Temperature Grain Growth in Electroplated Copper Thin Films. Microelectronics Reliability 40, pp. 1301-1304.

Wilcox, G. D. (2004). Surface Modification with Compositionally Modulated Multilayer Coatings. *Journal of Corrosion Science and Engineering, 6(52)*,

Yadla, S. V., Srideva, V., Lakshamni, M. V. V. C & Kumari, S. P. K. (2012). A Review on Corrosion of Metals and Protection. *International Journal of Engineering Science and Advanced Technology, 2(3)*, pp 637 – 644.

Yahalom, J. & Zadok, O. (1987). Formation of Composition-Modulated Alloys by Electrodeposition. *Journal of Materials Science*, *22*, pp. 499 - 503.

Zhang, W. & Xue, Q. (1997) .Tribological Properties of Nickel-Copper Multilayer Film on Beryllium Bronze Substrate. *Thin Solid Films*, *305*, pp. 292 - 296

Zhang, W., Xue, Q., & Zhang, X. (1998). The Influence of Brighteners on the Friction and Wear of Electrodeposited Multilayer Films. *Wear*, *214*, pp. 74 - 78.

Zhang, X. L., Jiang, Zh. H., Yao, Zh. P., Song, Y., & Wub, Zh. D. (2009). Effects of Scan Rate on the Potentiodynamic Polarization Curve Obtained to Determine the Tafel Slopes and Corrosion Current Density. *Corrosion Science, 51, pp.* 581 – 587.

Zhu, X. Y., Liu, X. J., Zonga, R.L., Zenga, F., & Pan, F. (2010). Microstructure and Mechanical Properties of Nanoscale Cu/Ni Multilayers. *Materials Science and Engineering, 527*, pp.1243 - 1248.

Zentner, V., Brenner, A., & Jennings, C. W. (1953). Physical Properties of Electrodeposited Metals. *Plating, 39,* pp. 865–894.