REVIEW ARTICLE

MECHANISM OF ELECTRODEPOSITION OF NICKEL IN AQUEOUS SOLUTION

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ARTICLE INFO	ABSTRACT
	Nickel deposition has been widely studied and much work has been devoted to the mechanism of the deposition process.In the present paper, we review studies of the electrode position of nickel and nickel based alloys in aqueous solution over the last two decades, which have built on the extensive pioneering work of DiBari, Evans, Bockris, Matulis, Heusler, Weil, and Ives and many others. The aim is to highlight new, and interesting, developments in nickel electrode position.

INTRODUCTION

Preface

Nickel is a silvery white and malleable metal. It has a high mechanical strength, is fairly hard paramagnetic at ordinary temperature. It oxidizes with difficulty when heated in air. Polished surfaces will however gradually corrode upon atmosphere exposure. Nickel is slowly soluble in hydrochloric and in dilute sulphuric acids. Dilute nitric Acid rapidly attacks nickel but immersion in concentrated sulphuric acid renderstheSurface of nickel passive which is not readily attacked.Nickel alloys were known and treasured by man for thousands of years before nickelwas identified as a metallic element.The first commercial application of Ni was in the making of copper-nickel-zinc alloy, known as German Silver or nickel silver, that began in the early nineteenth century.Nickel electroplating had come into commercial practice in the 1840's and by 1870 Become one of the principle end uses of nickel.(Nriago *et al*., 1980)

Uses of Ni

Ni is found in many objects in our daily life. It is used in electroplating and in certain Alloys as it renders strength and resistance to corrosion, the most common being the Stainless steel. Nickel is found in diverse commodities such as automobiles, batteries, Coins, costume, jewelry, inks and varnishes, dyes, surgical implants, sinks and Utensils.The major uses of refined nickel in industry include electroplating, alloyproductionand fabrication, the manufacture of Ni-cadmium batteries and electroniccomponents, and the preparation of catalysts for hydrogenation of fats andmethanation. The wastes generated from these industries contain Ni in various concentrations. In Absence of proper treatment and disposal methods, nickel contamination in soil or water would occur and cause toxic exposure to living organisms.(Griswell *et al*., 1980)

Background of the research

Wurtz discovered the deposition of power form metallic nickel from an aqueoussolution of its salts reduction of sodium hypophosphite at 1844. In 1946, Brenner andRiddel started to develop a practical system led to application of the electrolessnickeltechnology. The General American Transportation Corp first produced thecommercially available electroless nickel solution under the trade name "Kanigen" in1955. In the mid end of 1970's, the "Durnicoat" process using sodium hypophosphitereduction and the "Nibodur" process using sodium borohydridereduction were developed. The deposition coating on both metal and non-metal was investigated in 1957-1958. Interest in electroless nickel plating has continuedunabatedly since itsinvention by Brenner and Riddel. (Riedel *et al*., 1991) The properties of coatings depend largely on the composition of the bath usedand the deposition

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conditions (Chen *et al*., 2002, Lo *et al*., 1994, Zeller *et al*., 1994, Zeller *et al*., 1991). The small amounts of additives are usually used. Toprovide improved deposition rate, throwing power and brightness, finer grain structureand better corrosion resistance. Since electroless nickel plating process is chemicalreduction of nickel ions to the nickel results from the presence ofreducingagent in thesolution, it always concerns with hydrogen evolution during the plating process andformation of porous surface. It greatly reduces the corrosion resistance of the coating.To remove these hydrogen from the surface of substrate and to produce pit free Nickel deposits, surfactants were used as wetting agent into the plating bath (Riedel *et al*., 1991; Chen *et al*., 2002; Karppusamy *et al*., 1991; Hagiwara *et al*., 1997). Theeffect of cationic and anionic surfactants on plating have been known for Severalyears and investigated by several researchers. (Gutzeit *et al*., 1960; Tsuomi *et al*., 1992) Pitfree Nickeldeposits had been achieved by the addition of 150 ppm sodium dodecyl sulphate in the plating bath. The effects of additives in the electroless nickel deposition process have been studied by electrochemical analysis. It has been investigated that the additives influence significantly the anodic oxidation of the reducer, which is the main controlling step ofthe plating process. The higher the anodic oxidation current would be higher the oxidation speed, and hence the higher the deposition rate (Yu *et al*., 2002). In thedeposition process, increased in deposition rate by about factor of 25% wasfound bythe addition of Tween 20 at 5ppm level and smoother morphology were achieved byusing of surfactant in the acidic hypophosphite bath (Chen *et al*., 2002). Zeller andSavati found a very low corrosion rate, less than 2 µm/yr, for EN coatingin the 50% NaOH environment (Zeller *et al*., 1994). Lo and coworkers have examined roleof phosphorous in the electro chemical behavior of electrolessNi-P alloys in 3.5%NaCl solutions. It was found that chargetransfer resistance Rctand film resistance Rfvalues increased with increasing phosphorous content of coating (Lo *et al*., 1994).

Electroplating

Electroplating method is widely used to coat a metal, with a thin layer of another metal. The formation of metallic films and coatings is an important technology and has been applied in many industries. Several methods such as the vapor deposition and plasma spray have been developed, among which the electro-deposition of metals has several distinct advantages such as rapid deposition rates, cost effectiveness, andsimplicity of high level control over the thickness of the film (Li *et al*., 2006, Simka *et al*., 2009). Nickel is one of the most often employed to increase the corrosion resistance or electrical conductivity of the underlying substrate (Sadiku *et al*., 2004). It is also known that in acidic solutions Ni is capable of passivizing to a considerable extent.Another factor is the fact that in the electrochemical series Nickel is only moderately negative with respect to H^+/H_2 equilibrium.This means that in practice, the rate of dissolution of Nickel in acidic solutions is slow in the absence of oxidants more powerful than H+ or of a substance capable of making the reaction kinetically easy. (Abd el Haleem *et al*., 2004) The anodic behavior and the mechanism of passivation of Nickel and the properties of passive nickel have been studied a lot. Despite this, there is by no means agreement either on the mechanism of passivation of Nickel or on the composition and thickness of the passive layer. That is why we tried in this

work to make a survey of thereactions mechanism as well as the kinetics of Nickel electro-deposition from different baths.

Mechanism of Ni electrodeposition in aqueous solution and passivation behavior of Ni

Electrodeposited Charge because the electro-deposition process involves the transfer of electrons to an electrode, by measuring the current in the electrochemical cell, it is in principle possible to calculate the amount of material deposited. If no other reaction occurs in parallel, then we can assume that the reaction at the working electrode in aqueous electrolyte is just the simple reduction of a metal (M)

$$`` M^{n+} + ne^- \xrightarrow{} M^0$$
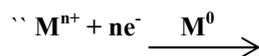
Where a metal ion M^{n+} is reduced to a metal atom M^0 after gaining n electrons. By assuming that all the metal ions reduced at the surface of the working electrode stick to this surface, the total amount of electrodeposited material can easily be calculated from the charge Q (in coulombs), which represents the product of the total amount of electrodeposited atoms N times the charge of n electrons, as given by the expression

$$Q = Nne$$

Electrodeposition of nickel has been investigated intensively for decades because of its particular mechanical properties in numerous applications in industry. Many experimental works were published (Scheck *et al*., 2003, Mohanty *et al*., 2002, Saitou *et al*., 1999, Orinakova *et al*., 2003, Galova *et al*., 2001) and many mathematical models of Ni electrodeposition process were suggested (Lux *et al*., 1998, Lemaire *et al*., 1997, Mokute *et al*., 2002). Although extensively used in practice, the nature and mechanism of the rather complicated process was not solved so far. The reaction pathway of Bockris *et al*. (Bockis *et al*., 1961) is assumed to be most relevant for nickel deposition. This mechanism incorporates the nickel monohydroxidecation, NiOH+, as an important species in the charge transfer.This monohydroxide is formed in the solution as a product of the first reaction step (1). In next reaction steps this species is adsorbedat the electrode (2) and discharged (3). The deposition of nickel at the electrode is the last reaction step (4).

$$Ni^{2+} + H_2O \leftrightarrow NiOH^+_{(aq)} + H^+ \tag{1}$$

$$NiOH^+_{(aq)} \leftrightarrow NiOH^+_{(ads)} \tag{2}$$

$$NiOH^+_{(ads)} + e^- \rightarrow NiOH \tag{3}$$

$$NiOH + H^+ + e^- \rightarrow Ni + H_2O \tag{4}$$
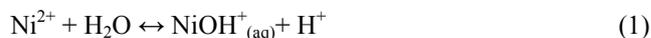
Discharge of hydrogen takes place also in several steps (Shreir *et al*., 1977). Two alternativesmechanisms are possible. Hydronium cations (H_3O^+) aredesolvated and partially discharged at the electrode surface (5a). Also their reaction with fresh nickel layer as catalyst is possible (5b). Next the hydrogen atoms combine in the adsorbed state to form adsorbed molecules (6a, 6b). The desorption of adsorbed hydrogen molecules as bubbles is the last step in hydrogen discharge mechanism (7).
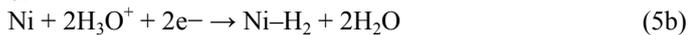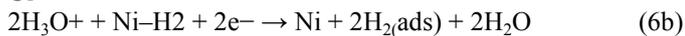
$$H_3O^+ + e^- \rightarrow H(ads) + H_2O \tag{5a}$$

or

$$Ni + 2H_3O^+ + 2e- \rightarrow Ni–H_2 + 2H_2O \qquad (5b)$$
$$2H(ads) \rightarrow H_2(ads) \qquad (6a)$$

Or

$$2H_3O+ + Ni–H2 + 2e- \rightarrow Ni + 2H_{2(ads)} + 2H_2O \qquad (6b)$$
$$nH_2 \rightarrow (H_2)n \qquad (7)$$

Before, during and after each reaction in both mechanisms, the transport of ions (Ni^{2+}, H_3O^+, $NiOH^+$, SO_4^{2-}, OH^-) from the bulk of solution to the diffusion layeror in opposite direction can take place. In both processes, the nickel deposition and the hydrogen evolution occur simultaneously, and individual reaction steps can intersect.So generally we can say that the main accepted molecular scale model for Ni electro-deposition is a multistep reaction:Before, during and after each reaction in both mechanisms, the transport of ions (Ni^{2+}, H_3O^+, $NiOH^+$, SO_4^{2-}, OH^-) from the bulk of solution to the diffusion layer or in opposite direction can take place. In both processes, the nickel deposition and the hydrogen evolution occur simultaneously, and individual reaction steps can intersect. So generally we can say that the main accepted molecular scale model for Ni electro-deposition is a multistep reaction:

$$Ni^{2+} + X^- \longrightarrow NiX^+ (a)$$

$$NiX^+ + e- \longrightarrow NiX_{ads} (b)$$

$$NiX_{ads} + e- \longrightarrow Ni + X^- (c)$$
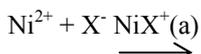
In which X denotes a ligand, probably an anion (SO_4^{2-}, Cl^-, OH^-) and NiX_{ads} an adsorbed Ni species (Bursteinl *et al.*, 2011; Allongue *et al.*, 2004). By comparing the experimentally determined kinetic parameters with those calculated for the various rate determining steps and ranges of coverage, they deduced that if a reaction mechanism of the general type (a)-(c) applied in watts bath (consisting of $NiSO_4+NaCl+H_3BO_3$).

i. The anion X- must be the chloride ion and
ii. The rate determining step was reaction (b), i.e the first electron transfer step.

Nickel is a very active metal, it is known to have strong corrosion resistance to aggressiveenvironments due to its easy passivation behavior. The anodic behavior and the mechanism of passivation of nickel and the properties of passive nickel have been studied extensively; perhaps more widely than any other element, except, possibly, iron. Despite this, there is by no means agreement either on the mechanism of passivation of nickel or on the composition and thickness of the passive layer (Gabe *et al.*, 1997). It is known that in acidic solutions; nickel is capable of passivating to a considerable extent. This is a feature not predicted by the potential-pH equilibrium diagram and is one reason why in practice the corrosion resistance of nickel in acid solutions is better than that predicted from considerations of thermodynamic equilibria.Another factor, is the fact that in the electrochemical series nickel is only moderthe state of passivity has intrigued corrosion scientists and technologists for a long time. Base metals, thermodynamically unstable with respect to their environment, are stabilised by formation of a solid-state surface film, itself formed by the corrosion interaction. Prediction of the formation of an oxide film is easy from a thermodynamic standpoint, where it can be shown via the conventional Pourbaix diagram that the oxide is the most thermodynamically favorable state if the conditions of

environment composition, temperature and electrode potential are appropriate. In dealing with such thermodynamics, it is nevertheless important to emphasize that passivity is in fact less easy to predict than that. Many metals are capable of passivation in solutions in which the solid oxide is thermodynamically completely unstable with respect to the dissolved metal ions: under these circumstances, passivity is not at all predictable from thermodynamic considerations alone. This has been long realized, but frequently ignored.Passivity and passivation are frequently investigated electrochemically by potential sweep methods, and a great body of published literature exists on the subject for very many metals and alloys. The technique requires careful consideration of the information sought in order to use the conventional polarization curve correctly. In particular, the potential sweep rate is critical. Aspects of passivity can in fact be completely overlooked by potentiostatic sweep methods. (Epelboin *et al.*, 1979)Sato and Okamotosuggest that the overall dissolution reaction to Ni $^{2+}$ proceeds in three steps involving the species ($NiOH_{(ads)}$ and $NiOH^+$).

Previous work showed that the potential decay curve for passive nickel electrodes consisted of three potential arrests, corresponding to the equilibrium potentials for NiO/Ni, Ni_3O_4/NiO and Ni_2O_3/Ni_3O_4. Bockris *et al* favour a dissolution-precipitation mechanism for the formation of $Ni(OH)_2$ from $NiOH^+$. They suggest that the cause of passivity is neither a monolayer nor a multilayer of oxide but is the conversion of the multilayer from an ionic to an electronic conductor at the passivation potential. The work of Ebersach *et al.* with a rotating nickel electrode suggests that passive films are formed by a solid state mechanism rather than by a dissolution-precipitation mechanism. Okamoto *et al.* suggested that passive nickel is covered by a compact pseudomorphic film. They showed that increasing the electrolyte temperature above 60°C resulted in crystallization of the film and the formation of "active patches" upon which the dissolution is concentrated. Metallographic studies by Myers *et al* (Myers *et al.*, 1981) supported the belief that "active patches" are generated in the transpassive dissolution region.

The table below is a review of numerous theoretical and practical studies of the electrodeposition of nickel over the last 10–15 years.

Electro-deposition of Ni based alloys

Nickel alloys with other metals and materials have made a significant contribution to our present day society and promise to continue to provide materials for an even more demanding future. Many works have been reported about optimal properties of nickel based alloy films.For example, structural and magnetic properties of nickel alloys ferrites synthesized by coprecipitation method were investigated by Shaikh. (Sheikh *et al.*, 2010) Campos reported an investigation of thin Ni and nickel alloys electrodeposited over flexible substrates. (Campos *et al.*, 2012) Sun fabricated a kind of nickel alloys permanent magnet arrays for sensors and actuators. (Sun *et al.*, 2012) Electrochemical deposition of CoNi as new materials for electrochemical sensing of glucose was studied by Vilana. (Vilana *et al.*, 2015) There are many methods that could be used to prepare nickel alloy films, such as plating, physical vapor deposition, molecular beam expitaxy and so on. Each approach contains its advantages and disadvantages.

Table 1. A review of numerous theoretical and practical studies of the electrodeposition of nickel over the last 10–15 years

Author	Work	Reference
Allongue *et al.*	Used in situ scanning tunneling microscopy (STM) and cyclic voltammetry (CV), investigated the growth mechanism of ultrathin layers of nickel and cobalt that were electrodeposited from dilute sulphate solutions onto gold.	(Allongue *et al.*, 2004)
Cui and Lee	Investigated nickel deposition from aqueous neutral chloride solutions in both the presence and the absence of oxygen. For voltammetric measurements, a rotating glassy carbon disc electrode or stainless steel electrode was used. Scanning electron microscopy (SEM) and stripping voltammetry were used for the analysis of the structure of the deposits and the determination of the current efficiency in deposition. In the presence of oxygen, the formation of a poorly steel electrode was used. Scanning electron microscopy (SEM) and stripping voltammetry were used for the analysis of the structure of the deposits and the determination of the current efficiency in deposition. In the presence of oxygen, the formation of a poorly conductive layer of Ni(OH)2 on the electrode surface was observed, prior to nickel deposition because of oxygen reduction. This Ni(OH)$_2$ layer inhibited the formation of a surface active nickel complex (formulated as Ni(OH)ads), and diminished both the nucleation and the growth of nickel. The effect was more pronounced in regions with little hydrogen evolution.	(Cui *et al.*, 1996)
Orinˇaˊkovaˊ et	Studied the electrolytic deposition of nickel from a Watts electrolyte solution onto a paraffin impregnated graphite electrode (PIGE) at pH 2, 3, and 4.	(Orinakova *et al.*, 2004)
Sˇupiçovaˊ *et al.*	Studied the electrolytic deposition ofNickelFrom the chloride electrolyte solution.	(Supicova *et al.*, 2006)
	assumed a reaction pathway assumed to be most relevant for nickel deposition	
	determined the nickel speciation in aqueous chloride solutions over a broad range of concentration and pH, and clarified the role of boric acid in nickel electrodeposition.	
Bockris *et al.*	They found that in concentrated NiCl$_2$ solution the predominant nickel species in the acidic region were Ni^{2+} and NiCl$^+$ and in a concentrated mixed sulphate-containing NiCl$_2$ solution, Ni^{2+}, NiCl$^+$ and NiSO4 were important.	(Bockris *et al.*, 1961)
Ji and Cooper	Studied the initial stages of the deposition of nickel onto vitreous carbon from an aqueous chloride solution. The morphology of the deposit was observed by scanning electron and optical microscopy.	(Ji *et al.*, 1996)
Goˊmez *et al*	Studied the mechanism of the Ni^{2+} reduction from acid sulphate, chloride and Watts electrolytes.	(Gomez *et al.*, 1992)
Epelboin and Wiart and coworkers	Studied the electrodeposition from a low concentration of nickel onto vitreous carbon at pH 3 and 5 and with different anions .	(Epelboin *et al.*, 1971,
Proud and Mü̈ller	Used EIS to characterize the deposition of nickel onto stainless steel cathodes from unbuffered acid sulphate electrolytes at pH from 2.0 to 3.5.	Epelboin *et al.*, 1979,
Holm and, O'Keefe	Studied Nickel nucleation onto glassy carbon substrates. Determined the concentration of nickel ad-atoms at the surface during the initial stages of nickel deposition onto glassycarbon substrates from the Watts electrolyte using both galvanostatic and potentiostatic pulse methods.	Epelboin *et al.*, 1983,
Bozhkov *et al*	Studied the initial stages of the electrocrystallization of nickel and cobalt onto a vitreous carbon substrate by simultaneous ellipsometric and amperometric measurements during potentiostatic deposition. Nickel electrodeposition was carried out from a mixed sulphate–chloride electrolyte, and cobalt electrodeposition was carried out from a sulphate electrolyte.	Froment *et al.*, 1963, Chassing *et al.*, 1983, Wiart *et al.*, 1990)
	Investigated the process of nickel electrochemical deposition from Watts-type electrolytes under the influence of high frequency ultrasound.	
Abyaneh and co-workers	An improvement in the distribution of the deposited Ni in millimeter-sized groove-features on the cathode surface was observed.	(Proud *et al.*, 1993)
Jensen *et al*	Focused their work on nickelelectrodeposition from an eutectic LiCl–KCl melt, which is the most frequently used molten salt in industrial processes.	
Lemaire *et al*	Described the growth of the nickel film prepared by electrodeposition.	(Holm *et al.*, 2000)
Saitou *et al*	Two kinds of growth rate were measured using columnar photoresists formed on indium–tin oxide glass plates.	(Bozhkov *et al* 1970)
Lantelme *et al*	analysed the potentiostatic current–time transient response on glassy carbon or titanium with respect to nucleation and radial growth and developed a potentiostatic model for the electrodeposition of nickel at a rotating electrode.	(Abyaneh *et al.*, 1983)
	It was shown that the nickel deposition from acidic solutions onto glassy carbon or titanium obeys nucleation and hemispherical growth principles.	(Jensen *et al.*, 2003)
Evans *et al*	Studied the structural and magnetic properties of Ni films grown by electrodeposition from sulphate solutions onto Ga As surfaces.	(Lemaire *et al.*, 1997)
Mockute and Bernotiene	Examined the interaction of additives with the cathode during nickelelectrodeposition in the Watts electrolyte.	(Saitou *et al.*, 1990)
Mockute and Bernotiene	Examined the reaction mechanism of some benzene sulphon amide and saccharin derivatives during nickel electrodeposition in the Watts electrolyte.	(Lantelme *et al.*, 1998)
Mohanty *et al*	Studied The effect of Cd^{2+} ions on the current efficiency, surface morphology and crystallographic orientation of the electrodeposited nickel from sulphate solutions.	(Evans *et al.*, 2003)
Froment and Wiart	Studied the effect of different organic inhibitors, especially2-butyne-1,4-diol on nickel deposits from a Watts electrolyte on the basis of differential interferometry.	(Mockute *et al.*, 2000)
Lin and co-workers	examined the influence of ammonium ions on the texture and structure of Ni deposits plated from a sulphamate bath onto a copper plate.	(Mockute *et al.*, 2002)
	Carried the electrodeposition of Al$_2$O$_3$ particle- Strengthened nickel films;using galvanostatic deposition in a stirred Watts bath, with pH values from 2.5 to 4.5. The nickel films deposited on copper substrates were analyzed by light and transmission electron microscopy and by energy dispersive X-ray (EDX) micro-analyses.	(Mohanty *et al.*, 2002) (Froment *et al.*, 1963)
Ferkel *et al*	Prepared composite Ni + Tiand Ni-P + Ti layers by simultaneous electrodeposition of nickel and titanium onto a steel substrate from a Watts bath under galvanostatic conditions.	(Lin *et al.*, 2001)
Serek and Budniok	Studied the influence of different metallic substrates on nickel electrodeposition from a chloride electrolyte. Cyclic voltammetry and potential step transient measurements were determined for platinum,nickel and iron electrodes.	(Ferkel *et al.*, 1997) (Serek *et al.*, 2002)
Goˊmez *et al*	Used chronoamperometry to study theELECTROCRYSTALLIZATION of both Ni and Co onto vitreous carbon and gold substrates from dilute chloridebaths. In addition, scanning electron microscopy and atomic force microscopy were used to visualise the morphology of the surface, in particular the overlap of growth centres.	(Gomez *et al.*, 1995) (Correia *et al.*, 2000)
	Measured the overpotential at nickel cathodes in aqueous solutions of HCl or NaOH.	(Bockris *et al.*, 1952)
Correia *et al*	Studied the mechanism of Ni^{2+} reduction from acid sulfate solution.	(Chassing *et al.*1981,
Bockris and Potter	Investigated the electro-deposition behavior of Ni on polycrystalline Cu and glassy carbon electrode in the air and water stable [EMIM][DCA] IL. SEM photos indicated that the morphology of nickel deposits depend on the deposition potential. XRD spectroscopy results showed that the nickel deposits had crystalline nature.	Chassing *et al.*, 1983, Wiart *et al.* 1990)
Wiart et a		(Saravanan *et al.*, 2012,
Deng *et al.*		Sravanan 2011)

However, considering about economy and convenience, plating technology is a kind of very effective and efficient ways to prepare alloy films which do not need too much equipment, but offer highly selective and conformal coatings.Some works have been reported so far about preparing nickel alloy films by electrodeposition methods.

For instance, J.Vazquez-Arenas investigated surface texture properties of CoNi alloys obtained by plating. (Yu*et al*., 2017) Ni-TiN thin films were electrodeposited by Fafeng Xia.(Xia *et al*., 2016) A kind of nanocomposite coatings based on NiW alloys were obtained by Wasekar (Wasekar *et al*., 2016) In addition, Zakeri prepared (Zn-Ni)/nano Al$_2$O$_3$ composite coatings by plating technology. (Ataie *et al*., 2016) Nickel based alloy films have been becoming the hot spot of functional films. Therefore, nickel based alloy films prepared by plating technology have been studied extensively. (Vilana *et al*., 2016, Sahin *et al*., 2015, Yu *et al*., 2013, Yu *et al*., 2014) However, it is found out that plating technology also possesses some disadvantages, such as particles aggregation, rough surface, concentration polarization, hydrogen evolution and so on. Along with the rapid development of electromagnetic technology, magnetic plating technology has gained much more focus which could ameliorate the problems during electrodeposition process. Magnetic field induced during electrodeposition process to prepare alloy thin films is called magnetic plating technology which could effectively improve deposition rate, refine coatings, and reduce concentration polarization and so on. Nickel and cobalt are typical elements with ferromagnetic properties. The effect of magnetic field on cobalt and nickel during plating process is conspicuous. Detail work about influences of magnetic fields on cobalt and cobalt alloys during plating process was investigated by our group. (Lu*et al*., 2015; Yu *et al*., 2016) According to our research, effects of magnetic fields on plating process with different electrochemistry and nucleation mechanism was totally different. Specific information about electrochemistry mechanism for cobalt electrodeposition process was reported in detail in some previous work. (Fanet *et al*., 1996) Currently more than 200 binary alloys are used in industry. The magnetic compounds are very interesting for various applications in computer technology and microelectronics, in the aircraft industry, and for coating plastics.The electrolytic deposition of these materials is a complex process and must be continuously controlled and regulated.

Electro-deposition of Ni-Co

Ni-Co alloys have been gaining popularity because they have been found to have a range of uses other than corrosion resistance for example they are used as electro catalysts as magnetic materials or have applications in hydrometallurgy. The development of the scientific and technological tendencies in the past few decades made claims on introducing more effective production processes or required the development of new types of materials. Experimental studies on the electrodeposition of Ni-Co alloy were carried out by a number of researchers (Bai *et al*., 2002; Jovic *et al*., 1997; Correia *et al*., 2000; Myung *et al*., 2001; Goldnisky *et al*., 2000; Correia *et al*., 2003; Zech *et al*., 1998) C. Fan and co-workers investigated the effect of trisodium citrate on the deposition of kineics of Ni(II), Co (II) and the Ni-Co alloy (Bai *et al*., 2002) A model for sulphate electrolytes by Zech *et al*. (Zech *et al*., 1998) showed that under kinetic deposition the higher co deposition rate suppressed by the deposition rate of the Ni.An

extensive voltammetry study by Bai *et al*. (Bai *et al*., 2002)was performed to examine the effect of temperature and potential range on the composition and the morphology of the alloys. The authors observed that if the applied potential range in the cyclic voltammetry experiments included the anodic oxidation region, anomalous deposition did not occur. Correia *et al.* (Correia *et al*., 2000) on the hand studied the effect of changing electrolyte formulation on deposit composition. They used different metal ion ratio of Ni(II) and Co(II), ranging from 1-5 and examined its effect on alloy composition and morphology. Myung *et al*. (Myung *et al*., 2001) investigated the relationship between the crystal structure phases and the corrosion resistance of the alloy. They found three different crystal structures, controlled by the Co content. Wang *et al*. (Wang *et al*., 2005) observed that the micro hardness of Ni-Co alloy represent a maximum at a Co content of 49 % in the alloy. Numerous works have examined the anodic-cathodic behavior of Co oxide/ hydroxide (Chang *et al*., 2006, Walson, 1994), Ni oxide / hydroxide (Vero and Kaldor, 1996; Cassela and Guascito, 1999) and Ni- Co oxide / hydroxide layers (Meier *et al*., 1982, Gorrigen *et al*., 1989, Chen *et al*., 1999, Hu *et al*., 2002, Castro *et al*., 2004, De Faria *et al*., 1998)

Serebrennikova *et al*. (Serebrennikova *et al*., 2000) doubted the Co inactivity during the electrochemical reaction using maximum film charge density measurement on Ni-Co oxide that was correlated with the complete Co and Ni content in films, they stated that Ni and Co oxidation/ reduction process occurred, which resulted in the precipitation of a mixture of Ni(OH)$_2$ and Co(OH)$_2$ on the surface.

The possible general oxidation process for Ni and Co is:

$$3H_2O + Me \xrightarrow{\quad\quad} Me(OH)_2 . H_2O + 2H^+ + 2e^-$$
and
$$Me(OH)_2 . H_2O + OH^- \xrightarrow{\quad\quad} MeOOH . (H_2O)_{1+X} + e^- + (1-X) H_2O$$
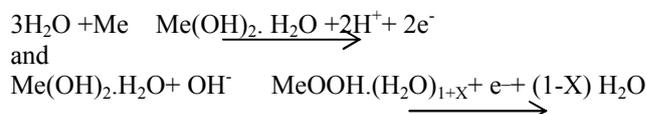
Electro-deposition of Ni-Cu alloys

In the past nickel–copper alloys were studied mainly for decorative purposes, but recently they have become of interest due to their mechanical, corrosion, electrical, and catalytic properties. Nickel–copper alloys are extensively used in industrial applications, such as ships, power stations, heat exchangers, and generally in saltwaterareas. With a relatively high Ni content, the alloy is frequently used with polluted water and in pipelines or marine applications. Further applications are the use ofNi–Cu condenser tubes for saline environments as well as being employed as hydrogenation and dehydrogenation catalysts (Kim *et al*., 1994). The widespread use of these alloysdepends on a combination of good corrosion resistance and excellent workability as well as high thermal and electrical conductivity (Brenner *et al*., 1963) The electrochemical preparation of these alloys has been widely studied. Citrate and pyrophosphate baths have been used most frequently and particular attentionhas been paid to the deposition of Ni–Cu coatings onto compact electrodes or substrates. Early work was reviewed by Roos (Ross *et al*., 1991) and Brenner (Brenner *et al*., 1963).

The standard reduction potentials for copper and nickel are far apart but to obtain good alloys the potentials need to be similar. This is usually achieved formixtures by shifting the deposition potential of the nobler component to a more negative value, either by changing the activity of the

discharging ions, by addinga suitable complex-forming substance, or by inhibiting the rate of reduction of the more noble metal. The influence of additives and changes on the electrolysisparameters are also important to produce homogeneous deposits without dendritic formations. Changing the current density of the process has been shown to be another route to make the deposition potentials more similar (Milosev *et al*., 1999). An increase in current density caused the cathode potential to become more negative and this condition should increase the proportion of less noble metal in the deposit. At a low current density, the coating was copper-coloured and was bright, uniform, smooth, and metallic. At a higher current density it was greyish with a black powdery nature. The effect of stirring the bath has also been studied. An increase in mass transfer during stirring increased the copper content of the deposit. The coating quality also changed from a non-metallic, black powdery in the unstirred condition to a metallic, reddishbrown coating under the stirred conditions.

Baths used in electro-deposition process of Ni coating and additives

The nickel electro-deposition process may be conducted using a few different types of aqueous baths (Badawy *et al*., 2005; Ross *et al*., 1991; Gosh *et al*., 2000). In addition, others aqueous solutions, deep eutectic solvents or even molten salt are still under research (Gosh *et al*., 2000; Nickel institute 2014; Schlesinger *et al*., 2010). The cathode current efficiency of different nickel electroplating solutions is usually above 90%. The lower efficiency is observed for some bright nickel solutions which have been formulated to provide a high level of brilliance. Values over 95% are usually achieved on additive-free nickel solutions. The important problems of nickel electro-deposition include: adhesion or even peeling off, and pitting on layer (Badawy *et al*., 2005; Ismail *et al*., 2004; Khosand *et al*., 2014; Abbot *et al*., 2015; Li *et al*., 2015; Mohanty *et al*., 2001). The most popular baths, among industrial methods of electro-deposition of nickel are Watts-type solutions. This type of bath was invented about 100 years ago by O.P. Watts. Basic compounds in this type of bath are nickel sulphate, nickel chloride and boric acid. These baths may contain many types of organic additives (Badawy *et al*., 2005; Ismail *et al*., 2004; Gosh *et al*., 2000; Khosand *et al*., 2014; Mohanty *et al*., 2001; Oloruntoba *et al*., 2011; Rashidi *et al*., 2010; Sadiku *et al*., 2012; Mockute *et al*., 2000; Wehner *et al*., 2003) These compounds are usually divided into two groups/types.

Type I serves as a carrier and reducer of the stresses occurring in the coating crystalline layer in the nickel electroplating bath. Internal stress refers to forces created in the layer as a result of the electrocrystallization process on another material and sometimes as a result of co-deposition of heteroatoms. This type of additive has usually an aromatic structure with sulphur, for example: benzene sulphonic acid, 1,3,6-naphthalene sulphonic acid (sodium salt), ptoluenesulphonamide, saccharin and allylsulphonic acid. Carriers introduce sulphur into the deposit. Type II additives are commonly known as brighteners. Today a wide range of organic compounds are used. They include: formaldehyde chloral hydrate, o-sulphobenzaldehyde, allylsulphonic acid, 2- butyne-1, 4-diol, thiourea, coumarin and many others. Brighteners are generally present in very low concentrations and are consumed by electrolysis. This generates problems with suitable additives determination in bath (Oliveira *et al*., 2006). The majority of nickel plating solutions, particularly those used for decorative plating, are based on the 'Watts' formulation developed by Professor Oliver P. Watts in 1916. The Watts electrolyte combines nickel sulphate, nickel chloride and boric acid. While the proportions may vary according to the application, a typical formulation together with operating parameters is given in Table 2.

Table 2. Typical formula and operating conditions for Watts nickel electroplating solutions

Nickel Sulphate (NiSO$_4$.6 H$_2$O)	240 - 300 g L^{-1}
Nickel Chloride (NiCl$_2$.6 H$_2$O)	30 - 90 g L^{-1}
Boric Acid (H$_3$BO$_3$)	30 - 45 g L^{-1}
Temperature	40 - 60 °C
pH	3.5 - 4.5
Cathode Current Density	2 - 7 A dm^{-2}
Deposition Rate	25- 85 μm h^{-1}

a)The nickel sulphate

Is the primary source of nickel ions (Ni^{2+}) with nickel chloride a contributing source. Nickel chloride has two major functions – it appreciably increases solution conductivity thereby reducing voltage requirements and it is important in obtaining satisfactory dissolution of nickel anodes. Boric acid is a buffer and has the major function of controlling the pH of the solution. As discussed in the previous section, due to the cathode efficiency being less than 100% there is a tendency for the pH to increase as some hydrogen ions (H$^+$) are discharged to liberate hydrogen gas. Regular additions of sulphuric acid are therefore required to adjust the pH (Pavlatou *et al*., 2007).

b)Boric acid: Limits the effect on the pH resulting from the discharge of hydrogen ions, thereby, simplifying pH control. The mechanism by which boric acid operates is complex, but it is generally understood that it exists in solution as a mixture of borate ions and non-ionized boric acid. When hydrogen is discharged some boric acid will ionize to replace the hydrogen ions lost and so the pH change is limited. At the same time, borate ions form. When acid is added to adjust the pH, these borate ions combine with hydrogen ions to reform boric acid. Boric acid is therefore only lost through drag out or other solution losses. (Nakamura *et al*., 1994) Deposits from Watts solutions without additives are soft and ductile but dull in appearance. The appearance and properties can however be dramatically changed by the use of addition agents. The addition agents consist of organic and certain metallic compounds selected to brighten and level the deposits. As will be discussed further in the section on decorative plating, addition agents may be used to produce semi-bright, bright or satin nickel coatings. (Vidal *et al*., 2010) There is a wide variety in the formulation of the organic compounds or additives for nickel baths, which are the responsible of the final quality of the plating. Their use in aqueous electroplating solutions is extremely important due to the effect they have in the growth and structure of deposits.Among their benefits, brightening the deposit, reducing grain size, reducing the tendency to tree-like structures or dendrites, increasing the current density range, promoting leveling, changing mechanical and physical properties, reducing stress, which is the amount of reversible work per unit area needed to elastically stretch a preexisting surface, and reducing pitting can be cited Nickel plating hand book (2014). Preferences for additives would depend on the purpose the deposits will have. In fully bright nickel deposits, for example, sulphur-content additives are frequently added. They can be divided into Class I and Class II brighteners and are responsible for brightness and levelling. (Savitzky *et al*., 1964)

Class I brighteners have two functions: to provide bright plating and to allow the second class of brighteners to be present over a wide range of concentrations. They include aromatic sulfonates, sulfonamides, sulfoimides, etc. as well as aliphatic or aromaticaliphaticolefinically unsaturated sulfonates, sulfonamides, sulfonimides, etc. They can be used singly or in suitable combinations and specific examples of this type of additives are: (Lendel *et al.*, 1998)

1. disodium 1,5-naphthalene disulfonate
2. trisodium 1,3,6-naphthalene trisulfonate
3. sodium benzene monosulfonate
4. o-benzoyl sulfimide (saccharin)
5. dibenzenesulfonimide
6. sodium 3-chloro-2-butene-1-sulfonate
7. sodium ß-styrene sulfonate
8. sodiumallylsulfonate
9. monoallylsulfamide
10. diallylsulfamide
11. allylsulphonamide

The Class II brighteners are used to obtain mirror-like platings. Nevertheless, they can promote brightlessness and stress in the deposits in the absence of a first class brightener.(Pasamontes *et al.*, 2006) They include products of epoxides with alpha-hydroxyacetylenic alcohol such as diethoxylated 2-butyne-1,4-diol N-heterocyclics, dye-stuffs, acetylenic amines, etc. Similarly to Class I brighteners, Class II can be used alone or in combination as well. (Gubeli *et al.*, 1991) Specific examples of such plating additives are: (Martens *et al.*, 2001)

1. 1,4-di-(ß-hydroxyethoxy)-2-butyne
2. 1,4-di-(ß-hydroxy-γ-chloropropoxy)-2-butyne
3. 1,4-di-(ß-,γ-epoxypropoxy)-2-butyne
4. 1,3-di-(β-hydroxy-γ-butenoxy)-2-butyne
5. 1,4-di-(2'-hydroxy-4'-oxa-6'-heptenoxy)-2-butyne
6. N-(2,3-dichloro-2-propenyl)pyridinium chloride
7. 2,4,6-trimethyl N-propargylpyridinium bromide
8. N-allylquinaldinium bromide
9. 2-butyne-1,4-diol
10. propargyl alcohol
11. 2-methyl-3-butyn-2-ol
12. quinaldyl-N-propanesulfonic acid betaine
13. butynoxy ethane sulfonic acids
14. propynoxy ethane sulfonic acids
15. quinaldine dimethyl sulphate
16. N-allylpyridinium bromide
17. isoquinaldyn-N-propanesulfonic acid betaine
18. isoquinaldine dimethyl sulphate
19. N-allylisoquinaldine bromide
20. 1,4-di-(β-sulfoethoxy)-2-butyne
21. 3-(β-hydroxyethoxy)-propyne
22. 3-(β-hydroxypropoxy)-propyne
23. 3(-β-sulfoethoxy)-propyne
24. phenosafranin
25. fuchsin
26. propargyl amine
27. 1-diehtylamino-2-methyl-3-pentyn-2-ol
28. 1-dimethylamino-2-pentyne
29. 1-dimethylamino-2-butyne

Anti-pitting or wetting agents are also used in bright nickel baths so that gas pitting is prevented or minimized in the baths. Furthermore, they may function to make the baths more compatible with contaminants, such as oil, grease, etc. by their emulsifying, dispersing, solubilising, etc. action on such contaminants, and thereby they promote sounder deposits. They include sodium lauryl sulphate, sodium lauryl ethersulfate and sodium dialkylsulfosuccinates. (Martens *et al.*, 2001) In general, these organic additives should be added in small amounts and frequently to maintain nickel plating quality, but there is not an established method to accomplish it in practice. (Wold, 2007)

Factors effecting Ni electroplating

- pH
- Temperature
- Current density
- Time
- Metal Ions
- Concentration Bath
- Agitation

Effect of the pH

The value of pH is depending upon the composition of Bath. The pH value should be maintained for good result. The pH of the bath influences the hydrogen evolution voltage, the precipitation of basic inclusion, the decomposition of the complex or hydrate from which the metal is deposited, and the extent of adsorption of additives. In a complex bath, pH may influence equilibrium between various processes. When the anode is insoluble, oxygen evolution takes place at the anode

$$2H_2O \rightarrow O_2 + 4H+ + e$$

On the other hand, hydrogen evolution at the cathode is accompanied by the production of hydroxide ion:

$$2H_2O+ 2e- \rightarrow 2OH- + H_2$$
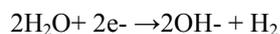
In a neutral bath, if the current efficiency is greater at the anode than at the cathode, the bath becomes more alkaline. If the electrode efficiencies are similar, the pH of the bath remains unchanged. Hence change in pH of a plating bath is a good indication of electrode efficiencies. In certain conditions precipitation of metal hydroxides may occur locally within the cathodic double layer, which get co-deposited with the plated metal and give defective deposit while increasing the pH due to hydrogen evolution. Thus buffers are necessary to minimize these pH changes. During Electro deposition of aqueous solution, hydrogen ions are discharged together with the ions of the metal being deposited. The hydrogen evolved not only has a detrimental influence on the plating rate and on the cathodic current efficiency, but it often also unfavorably affects the structure and properties of the metal being deposited by causing spongy or powdery deposits, pitting or other defects. In the Electro deposition, the metal of iron group or the-metal with 'low hydrogen overvoltage are very sensitive to the Concentration of hydrogen ions in the electrolyte, a change in the pH value considerably affects both the cathodic current efficiency and the structure of the electrodeposits. The pH value of the cathodic film is not always the same as that of the bulk of the electrolyte.The Hydrogen ions take part in the electricity transport and also affect the changes taking place in the electrode film. The pH value of the cathodic film will in principle be higher than the bulk of the Electrolyte, if the number of hydrogen ions transported by the current is smaller than the number of the hydrogen ions discharged in unit time

and vice versa. A change in the pH value of the cathodic film causes diffusion, which tends to equalize the activity of the hydrogen ionic discharged in the bulk of the solution and in the cathodic film. The difference between the PH values of the cathodic film and the bulk Solution, which tends to increase with the current density, either become stabilized or continues to increase, depending on the composition of the solution. (Lainer *et al*., 1970)

Effect of temperature

In general, an increase in bath temperature causes an increase in the crystal size. Increase in bath temperature increases solubility and thereby the transport number, which in turn leads to increased conductivity of the solution. It also decreases the viscosity of the solution, thereby replenishing the double layer relatively faster. High bath temperature usually decreases less adsorption of hydrogen on the deposits and thereby reduces stress and tendency toward cracking. By increasing the bath temperature from 45°C to 55°C, the grain size of deposit partial decreased, whereas further increase of bath temperature resulted in a contrary effect.

Effect of current density and distribution

In the electro deposition process the uniform coating of specimen is depend upon the current distribution parameter. In general, the metal ions are attached to the cathode at certain favored sites. This condition will possibly result to the presence of discontinuities in the form of pores, cracks or in other irregularities. Thus, In Electro deposition, current density and its distribution parameter play a centrally important role in determining the uniform coating of the final deposit. In the electro deposition process the current density over a cathode will vary from point to point. Current tends to concentrate at edges of the object. It tends to be low in recesses and cavities because current tends to flow more readily to points nearer to the opposite electrode than to more far points. In the Electro deposition process cathode current density must be held within the proper interval with respect to bath composition and temperature. Insufficient current for given specimen will result in poor coating, while the presence of excessive current does not necessarily result in increased plating rate and is liable to create other difficulties. Low current densities tend to result higher impurity presence in the deposits. The reason for this is that once over the limiting current density for good deposition, hydrogen ions discharge occurs, that in turn; increase the pH level at cathode andcausing metal hydroxide ions to be included in the deposit coating. To summarize, the optimum current density range for given plating bath is depending on composition of salt, operating conditions and the type of the plating sought. Anode current densities are also an important plating parameter and should be controlled properly. This can be done through the adjustment of the total anode area and the proportion of it made up of the metal being deposited.

Effect of Bath Concentration: Generally, in the Electro deposition process, bath concentration playing an important role to the plating performance. In normal plating condition, the increase of bath concentration will increase the Concentration of metal ions in solution. Therefore it will increase the deposition rate of the plating process.

Effect of Plating Time: In general, the plating thickness is increase directly proportionately to the plating time and current

According to the Faraday's Laws, quantity charge flow, Q in the solution is proportional to the current flow, l and also the Flow time, t as show in equation below:(Narendia *et al*., 1999)

$$Q = I \times T$$

Effect of Agitation

In General agitation provides sufficient mixing of metal salt so that the chemicals reagent becomes intimate and reacts with each other. In general, agitation of the plating solution replenishes metal salts or ions at the cathode and reduces the thickness of the diffusion layer. It reduces the gas bubbles, which may otherwise cause pits. Agitation helps increasing the operating current density and thereby permits a higher operating current density. These factors influences the structure of the deposit metal ion and also increase in the concentration of the metal, since it more rapidly compensates for the loss of the metal ions through discharge at the cathode. In the plating process, although agitation sometime cause the formation of coarse-grained deposits due to the mechanical inclusion of sludge and other impurities suspended in the electrode, it permits to use at high current densities plating process. The intensity of agitation should vary proportionately with the current densities with all other conditions remain unchanged. To reduce the defect of coarse-grained cause by impurities in the electrolyte, agitation is often accompanied by filtration electroplating; agitation promotes the deposition of the noble metal on the cathode Process. In brief, agitation system can greatly improve the plating performance since it provides sufficient mixing of the metal salt for the plating solution. However, this is true if the other parameters in the solution are controlled properly. (Paunovic *et al*., 1998)

Nature of the metal

Based on the magnitude of polarization, metals can be classified into three groups. Group I consists of metals like Ag, Pb, Cd, Sn etc., which are deposited at an overpotential of a few milli volts and rough deposits are obtained with grain size greater than 10-3 cm. Group III consists of metals like Ni, Co, Fe etc., which are associated with a large electrochemical polarization and are deposited as dense deposits with the grain size of around 10-5 cm. Cu, Bi, and Zn constituting the II group are intermediate metals with respect to the over potential value and grain size of the deposit. The interaction of the substrates with the deposited metal differs and this affect the kinetics of nucleation and hence the number of grains per unit area.By achieving the optimum condition for the plating solution, it can improve the plating quality and reduce the production cost. In general, high current density (below the limiting current density), high bath concentration, high bath temperature with the agitation is preferred to achieve the high cathode current efficiency. However, the detailed study must be carried out to get the optimum condition for these parameters. For the pH and plating time, there were no specify limitation but it is only depending on the type of solution used and regarded thickness in the process. However, the plating solution with alkaline base is most familiar since this type of solution has less effect caused by hydrogen evolution. several experiments were canied out by the researchers to study the effect of operating parameters in the electroplating process, such as Loshkarev, Gornostaleva and Kriukova have investigate the dependence of anodic and cathodic current efficiency on temperature, additives, current density and other

electrolysis parameters for nickel powder deposition. Kuznin and Motosova have studied the conditions of the deposition of alternate nickel and copper or zinc or iron layers.(Calusaru *et al*., 1979)It is found that Generally pH, Current density, Temperature are important factor of Electrode position process .The uniform coating of specimen is depend upon the current distribution parameter. The pH value should be maintained for good result. By increasing the bath temperature from 45°C to 55°C, the grain size of deposit partial decreased. Agitation helps increasing the operating current density and thereby permits a higher operating current density. Agitation is also important it reduces the gas bubbles, which may otherwise cause pits. Agitation helps increasing the operating current density and thereby permits a higher operating current density.

Future of bright nickel plating

The future of nickel plating will be influenced by changes in marketing conditions and technology. Technological developments that have been considered by researchers and electroplating/electroforming practitioners would foster the growth during the near future. These includes long term performances data on multi-layer nickel coatings, decorative plating of stainless steel, zinc/nickel alloy plating, new uses in battery, electronics, plated plastic and electroless nickel process improvements and the implementation of computer controlled manufacturing.The functional uses of nickel, whether as electroplated coatings or electroform artefacts are growing steadily, as the advantages of this metal in its naturally deposited form or as modified by various techniques become evident to design and production engineers (Dennis *et al*., 1993).

Conclusion

The paper summarized removal and recovery of nickel as based on recent literature. Nickel recovery from various types of aqueous solutions was described with emphasis on the hydrometallurgical approach.The high market price of nickel makes nickel recycling economically profitable. On the other hand, the environmental concerns and health risks related to nickel exposure impose the removal and recovery of nickel.

Acknowledgement

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