

Electro- and Electroless Plated Coatings for Corrosion Protection

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ELECTRODEPOSITION

Fundamentals of Electrodeposition

Electrodeposition can be defined as the deposition of an adherent metallic coating for the purpose of securing a surface with properties or dimensions different from those of the base material. Electrodeposits are applied to metal substrates for decoration, corrosion resistance, wear resistance, electrical properties, magnetic properties, solderability, etc. The ability of being decorative as well as protective to substrates distinguishes electrodeposited coatings from metallic coatings applied by hot dipping or spraying. The metallic luster, achieved by bright plating or by polishing after plating, lends a distinctive appearance not provided by other types of coatings. However, corrosion resistance is the primary reason for the use of electrodeposited coatings [1-5].

Metal deposition

In electrodeposition of metals, a direct current is made to flow between two electrodes immersed in a conductive aqueous solution containing the metal salts to be deposited. The flow of current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with the deposited metal. The metal to be deposited is present as positively charged ions. When the current flows, the positively charged ions react with the

electrons and are converted to metallic atoms at the cathode surface. The reverse occurs at the anode where the metal is dissolved to form positively charged metal ions which enter the solution. The schematic of an electrolytic cell employed for electrodeposition of metals is shown in Fig. 13.1.

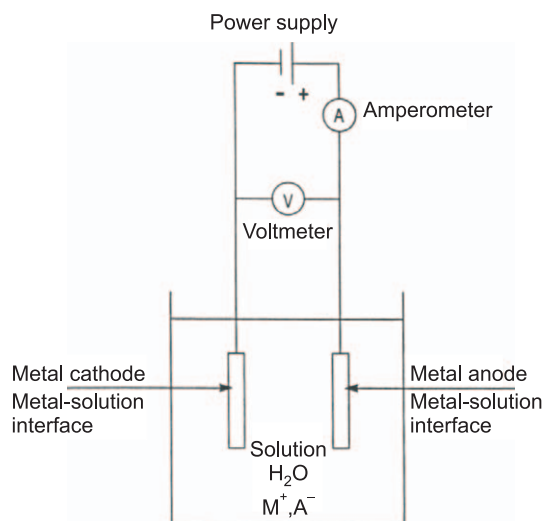


Figure 1 Schematics of an electrolytic cell for plating metal “M” from a solution of the metal salt “MA”
(Source: <http://electrochem.cwru.edu/ed/encycl> - Electrochemistry Encyclopedia)

The Faraday’s laws of electrolysis describe the basics of the electrodeposition of a metal as follows:

Faraday’s First Law: *The mass, m , of an element discharged at an electrode is directly proportional to the amount of electrical charge, Q , passed through the electrode.*

Faraday’s Second Law: *If the same amount of electrical charge, Q , is passed through several electrodes, the mass, m , of an element discharged at each will be directly proportional to both the atomic mass of the element and the number of moles of electrons, z , required to discharge one mole of the element from whatever material is being discharged at the electrode. Another way of stating this law is that the masses of the substances reacting at the electrodes are in direct ratio to their equivalent masses.*

By combining the principles of Faraday with an electrochemical reaction of known stoichiometry, the Faraday’s laws of electrolysis that relates the charge density (charge per unit area), q , to the mass loss (per unit area), “ m ” can be written as:

$$\Delta m = \frac{q(AM)}{nF}$$

The amount of metal deposited at the cathode and the amount of metal dissolved at the anode are directly proportional to the product of the current and time:

$$M = 1.095(a) (I) (t)$$

Where ‘ m ’ is the amount of metal deposited at the cathode (or dissolved at the anode) in grams, ‘ I ’ is the current that flows through the plating tank in amperes, ‘ t ’ is the time that the

current flows, in hours and 'a' is the current efficiency ratio. The proportionality constant (1.095) grams per ampere.hour equals M/nF where M is the atomic weight of the metal deposited, 'n' is the number of electrons involved in the electrochemical reaction and 'F' is the Faraday's constant (96500 coulombs).

Surface preparation for electrodeposition

Degreasing processes which remove the organic films, greases, etc. and pickling processes which remove dirt, oxide and corrosion products are the pretreatments employed before actual electroplating. Hydrocarbon or mineral oils are removed by solvents; vapour degreasing with chlorinated solvents or emulsification are common alternatives. Greases of animal or vegetable origin are removed by additions of hot aqueous solutions of alkalis. This is called as alkaline degreasing. Electrolytic alkaline degreasing is considerable faster than soak cleaning. Alkaline cleaning solutions are prepared from sodium hydroxide, trisodium phosphate, sodium silicate, sodium carbonate, soaps, detergents, etc. The higher the pH the more effective is the degreasing action, but with non-ferrous metals the greater is the danger of corrosion.

Oxide and corrosion-product films are removed by dissolution in aqueous solutions. Hydrochloric and sulphuric acid are the most common aqueous media used to remove oxides. Concentrations and temperatures are varied according to the substrate. Mixed acids containing wetting agents are supplied as proprietary mixtures. Electrolytic pickling is used for special purposes, but hydrochloric acid is unsuitable for this because of its volatility and evolution of chlorine gas. Cathodic pickling of steel in 10-20 wt.% sulphuric acid enables thick rust or scale to be removed without the loss of metal. Anodic pickling in 55 wt.% sulphuric acid is used to remove a thin surface layer from steel. A high current density is used. After 10-20 seconds, the metal becomes passive and dissolution ceases. Disordered and fragmented metal produced by abrasion or machining is removed to leave a surface which favours good adhesion of an electrodeposit. Oxide and corrosion products on copper alloys are removed in hydrochloric or sulphuric acids, less concentrated than used for steel.

Types of plating baths

Table 13.1 gives the various types of electrolyte solutions used for electrodeposition of metals. Among them, the simple acid solutions are less widely used. Although their polarization characteristics are low, they are less conducive to yield bright electrodeposits than those obtained from the complexant solutions. The complexant solutions offer increased metal solubility and give rise to higher limiting current densities.

The various constituents of the electrolyte solutions used for electrodeposition of metals are listed in Table 13.2. The metal salts are the source of metal ions. The complexant is vital to stabilize the metal ion in an appropriate form. The plating baths are usually designed to operate with excess of complexant to simplify bath control; depletion of complexant will give rise to greater amounts of uncomplexed metal ion in the solution and this may even arrest the process of electrodeposition. The complexant stabilizer may simply be excess complexant or a pH buffer. In plating baths containing cyanide, it is essential to maintain the $\text{pH} > 8$ with excess alkali to prevent the evolution of the detrimental HCN gas. In some cases a critical pH exists for optimum operation or optimum deposit properties. In Watts nickel plating where solutions have pH between 3.5 and 5, buffering with borate or boric acid is necessary. Depassivators like chloride and to a lesser extent tartarate or citrate are added to maintain smooth dissolution for soluble anodes. In the case of insoluble anodes, such depassivators must be eliminated. To

Table 1 Various types of electrolyte solutions used for electrodeposition of metals

Type	Metal that is getting plated	Electrolyte	Ions in the electrolyte
Simple acid	Cu	CuSO ₄	Cu ²⁺
	Sn	Sn(BF ₄) ₂	Sn ²⁺
	Ni	Ni(NH ₂ SO ₂ O) ₂	Ni ²⁺
Complexed acid	Cr	H ₂ CrO ₄	CrO ₄ ²⁻
	Cu	K ₆ Cu(P ₂ O ₇) ₂	Cu(P ₂ O ₇) ₂ ⁶⁻
	Ni	NiCl ₂	NiCl ₄ ²⁻
Alkaline hydroxide (amphoteric)	Sn	SnF ₄	SnF ₆ ²⁻
	Zn	Zn(OH) ₂	ZnO ₂ ²⁻
Complexed alkaline	Cu	CuCN	Cu(CN) ₂ ⁻

Table 2 Various constituents of the electrolyte solutions used for electrodeposition of metals

Constituent	Functions	Example
Metal salt	To supply metal ions	CuSO ₄ , NiCl ₂
Complexant	Stabilize metal in soluble form; affect mode of ion discharge	KCN, NaOH
Complexant stabilizer	Excess complexant, acid or alkaline reagent	KCN, NaOH
Buffer salt	Stabilize pH at optimum value	H ₃ BO ₃ , Na ₂ HPO ₃
Anode depassivator	Smooth anode dissolution and oxide film disruption	Chloride
Addition agents	Surfactant for hydrogen bubble dispersal, Brightener for bright deposits, Leveler for grain refinement Stress reliever	Detergent, Organic S and N containing compounds

control the properties of the deposit, the special addition agents are most important. Surfactants may be needed to minimize hydrogen absorption or pitting caused by bubbles. Organic additives bring about significant change in the mechanical properties.

The incorporation of byproducts from the additives has only a small effect on mechanical properties of the electrodeposits. However it severely alters the grain size and mode of growth of the electrodeposit resulting in a small-grained, smooth and bright surface. The mode of deposition is affected because the efficacy of an additive may often be indicated by its effect on the activation polarization of the cathode discharge reaction. A more highly polarized reaction (higher activation overpotential) for a given current will yield a brighter deposit. This general rule is valid for complexed-ion solutions also where polarization is high and deposits are brighter. By giving proper attention to such general principles, it is possible to virtually design an electrolyte for depositing any metal.

Throwing power

Metal distribution is influenced by cathodic polarization, the cathode efficiency-current density relationship and the electrical conductivity of the solution. The complex relationship

between these factors that influence current distribution and hence metal distribution is called as the throwing power. A plating solution with a high-throwing power is capable of depositing almost equal thickness on both recessed as well as in prominent areas.

Leveling and microthrowing power

The ability of an electroplating solution to fill in the defects and scratches present on the surface preferentially is called leveling. Organic additives present in the plating bath adsorb preferentially at micropeaks, the resulting increase in the local resistance to current flow increases the current density in microgrooves, thereby promoting leveling. Micro-throwing power refers to the ability of an electroplating solution to fill tiny crevices with deposits that follow the contour of a defect or scratch without any leveling action whatsoever.

Electrode reactions

In an ideal case, only metal ions will be discharged at the cathode and they will be completely reduced to atoms which become part of the growing electrode surface. However, many commercial processes are not ideal and many cathodic and anodic reactions do occur. The possible cathodic and anodic reactions that could occur during electroplating are given in Table 13.3.

Current efficiency

When two or more reactions occur simultaneously at an electrode, the number of coulombs of electricity passed corresponds to the sum of the number of equivalents of each reaction. The current efficiency for the deposition of a metal 'j' is defined as:

$$\text{Current efficiency (CE)} = \frac{W_j}{W_{\text{total}}}$$

Table 3 Electrode reactions that occur during electrodeposition

Type of reactions	Actual reaction	Remarks
Cathode reactions	$M^{n+} + ne^- \rightarrow M^0$	Main metal discharge and Deposition reaction
	$2H^+ + 2e^- \rightarrow H_2$	Main secondary reaction causing poor cathodic current density; may cause poor deposit properties
	$M^{n+} + e^- \rightarrow M^{(n-1)+}$	Partial ion reduction and source of inefficiency
Anode reactions	$M^0 \rightarrow M^{n+} + ne^-$	Metal dissolution at soluble anodes; maintains metal ion conc. in solution
	$2OH^- \rightarrow H_2O + \frac{1}{2} O_2 + e^-$	Oxygen evolution is the main reaction on insoluble anodes in basic medium
	$H_2O \rightarrow 2H^+ + \frac{1}{2} O_2 + 2e^-$	Oxygen evolution is the main reaction on insoluble anodes in neutral medium
	$M + H_2O \rightarrow MO + 2H^+ + 2e^-$	Passive oxide formation on anode; raises total cell resistance and inhibits anode dissolution
	$M + nOH^- \rightarrow MOH + ne^-$	Passive hydroxide film formation
	$M^{(n-1)+} \rightarrow M^{n+} + e^-$	Ion oxidation - removal of lower valency metal ions

where w_j is the weight of the metal 'j' actually deposited and w_{total} is that which would have been deposited if all the current had been used for depositing the metal 'j'. For example, during the electrodeposition of copper from a solution of cupric nitrate in dilute nitric acid, three cathodic reactions, namely, the deposition of copper, reduction of nitrate and reduction of hydrogen ions, occur. Hence, the current efficiency of the deposition process will be lesser than 100%, where the remainder of current is used for the side or competing reactions.

Growth mechanisms

The metal ion in plating solution is solvated. As the solvated metal ions approach towards the cathode, they lose some of their solvation sheath and get adsorbed on the cathode. The anion diffuses over the cathode surface until it reaches an atomic step. The anion loses more water of solvation and its freedom is reduced to diffusion along the step. Further desolvation and co-ordination follows when it reaches a kink in the step, at which stage it is immobilized. When other anions following this path eventually join and submerge the first, co-ordination with water in the electrolyte is exchanged fully for co-ordination with metal ions in the metallic lattice.

There are two basic mechanisms for the formation of a coherent electrodeposit [6]: layer growth and three-dimensional crystallites growth. In the layer growth mechanism, a crystal enlarges by spreading of discrete layers, one after another across the surface. In this case, a growth layer or step is the structural component of the coherent deposit. In 3D-crystallites growth mechanism, the structural components are 3D-crystallites built-up as a result of coalescence of these crystallites. The growth sequence of 3D-crystallites growth mechanism consists of four stages: (i) formation of isolated nuclei and their growth to 3D-crystallites; (ii) coalescence of 3D-crystallites; (iii) formation of linked network; and (iv) formation of a continuous deposit.

Role of additives

The use of additives in aqueous electroplating solutions is extremely important as they offer potential benefits which include brightening the deposit, reducing grain size, reducing the tendency to tree, increasing the current density range, promoting leveling, changing mechanical and physical properties, reducing stress and reducing pitting. The additives, when added in small concentrations make striking effects on electrocrystallization processes. Their adsorption on a high energy surface and deposition on growth sites produce a poisoning or inhibiting effect on the most active growth sites [7]. The additives can be organic or metallic, ionic or nonionic, and are adsorbed on the plated surface and often incorporated in the deposit.

Influence of additives on leveling and brightening

Normal electrodeposition accentuates roughness by putting more deposit on the peaks than in the valleys of a plated surface since the current density is highest at the peaks because the electric field strength is greatest in this region. In order to produce a smooth and shiny surface, more metal has to be deposited in the valleys than on the peaks, which is the opposite of the normal effect. The function of certain organic compounds is to produce this leveling in plating solutions. Leveling agents are adsorbed preferentially on the peaks of the substrate and inhibit deposition. An example is coumarin which is used in the deposition of nickel.

It adsorbs on depositing nickel by the formation of two carbon-nickel bonds and inhibits nickel deposition probably by a simple blocking action.

A bright deposit is one that has a high degree of specular reflection in the as-plated condition. Although brightening and leveling are closely related, many solutions capable of producing bright deposits have no leveling ability [1]. If the substrate is bright prior to plating, almost any deposit that is plated on it will be bright, as long as it is thin enough. However, a truly bright deposit will be bright over a matte substrate and it will remain bright even when it is thick enough to hide the substrate completely. Plating solutions without addition agents seldom or never produce bright deposits.

Classification and types of additives

Additives can be classified into four major categories: (i) grain refiners; (ii) dendrite and roughness inhibitors; (iii) leveling agents; and (iv) wetting agents or surfactants [6]. Typical example of grain refiners are cobalt or nickel codeposited in trace amounts in gold deposits. Dendrite and roughness inhibitors adsorb on the surface and cover it with a thin layer which serves to inhibit the growth of dendrite precursors. This category includes both organic and inorganic materials with the latter being more stable. Leveling agents, such as coumarin or butynediol in nickel solutions, improve the throwing power of the plating solution mostly by increasing the slope of the activation potential curve. The prevention of pits or pores in the deposit is the main purpose of wetting agents or surfactants [7].

Additives can act as grain refiners and levelers because of their effects on electrode kinetics and the structure of the electrical double layer at the plating surface [8]. Since additives are typically present in extremely small concentrations, their transport towards the electrode is nearly always under diffusion control and, therefore, quite sensitive to flow variations. The effects of additives are often manifested by changes in the polarization characteristics of the cathode. Many are thought to function by adsorption on the substrate or by forming complexes with the metal. This results in development of a cathodic overpotential which is maintained at a level which allows the production of smooth, non-dendritic plates having the desired grain structure [8].

Mechanisms of additives

Numerous mechanisms have been suggested to explain the behavior of additives: (i) blocking the surface; (ii) changes in Helmholtz potential; (iii) complex formation including induced adsorption and ion bridging; (iv) ion pairing; (v) changes in interfacial tension and filming of the electrode; (vi) hydrogen evolution effects; (vii) hydrogen absorption; (viii) anomalous codeposition; and (ix) the effect on intermediates. These are discussed in detail in a comprehensive review by Franklin [9]. An excellent coverage on the mechanism of levelling and brightening caused by the addition agents during plating is given by Oniciu and Muresan [10].

Properties of electrodeposited coatings

Structure of electrodeposited coatings

The properties of all materials are determined by their structure. Even minor structural differences often have profound effects on the properties of electrodeposited metals [11]. The four typical structures encountered with electrodeposited metals include; (i) columnar; (ii) fibrous; (iii) fine-grained; and (iv) banded [12].

Columnar structure

Columnar structures are characteristic of deposits obtained from simple ion acidic electrolyte solutions that do not contain any addition agents, e.g., copper, zinc, or tin from sulfate or fluoborate solutions, operated at elevated temperature or low current density. Deposits of this type usually exhibit lower strength and hardness than other structures but high ductility.

Fibrous structure

Fibrous (acicular) structures represent a refinement of columnar structure. This type of structure is obtained under conditions that favor the formation of new nuclei rather than growth of existing grains, such as the presence of addition agents, or use of low temperature and high current density. Properties of fibrous deposits are intermediate between columnar and fine-grained deposits.

Fine-grained structure

Fine-grained structures are usually obtained from complex ion solutions such as cyanide or with certain addition agents. These deposits are less pure, less dense and exhibit higher electrical resistivity due to the presence of codeposited foreign material. Deposits from simple ion acidic solutions, such as copper or nickel from sulfate solutions, develop this type of structure if the operating conditions are more extreme, such as, at very high current density or a higher pH [12]. The grain size of this type deposits is of the order of 10^{-5} to 10^{-6} cm. These deposits are usually relatively hard, strong and brittle.

Laminar structure

Laminar (or banded) structures are characteristic of bright deposits in presence of addition agents such as sulfur containing organic compounds in which the grains within the lamellae are extremely small. Gold-copper, cobalt-phosphorus, cobalt-tungsten, and nickel-phosphorus alloy deposits exhibit this type structure. These deposits usually have high strength and hardness but low ductility. Similar laminations can also be found in deposits obtained by pulse plating or periodic reverse current plating.

The crystal structure of electrodeposits strongly depends on the relative rates of formation of crystal nuclei and the growth of existing crystals [13]. Finer-grained deposits result under conditions that favor crystal nuclei formation while larger crystals are obtained under conditions that favor growth of the existing crystals. In general, factors which increase the cathode polarization enable a decrease in crystal size [13]. Fig. 13.2 shows a pictorial representation of the influence of plating variables on the grain size of electrodeposits [14].

Influence of the substrate

The structure of most electrodeposits is determined by epitaxial and pseudomorphic growth onto a substrate and by the conditions prevailing during deposition. Typically, a deposited metal will try to copy the structure of the substrate and this involves epitaxy, which occurs when definite crystal planes and directions are parallel in the deposit and substrate, respectively [2]. Epitaxy is the orderly relation between the atomic lattices of substrate and deposit at the interface, and is possible if the atomic arrangement in a certain crystal direction of the deposit matches that in the substrate. Another term, pseudomorphism, refers to the continuing of grain boundaries and microgeometrical features of the cathode substrate into the overlying deposit. A deposit stressed to fit on the substrate is said to be pseudomorphic [2]. Pseudomorphism persists longer than epitaxy.

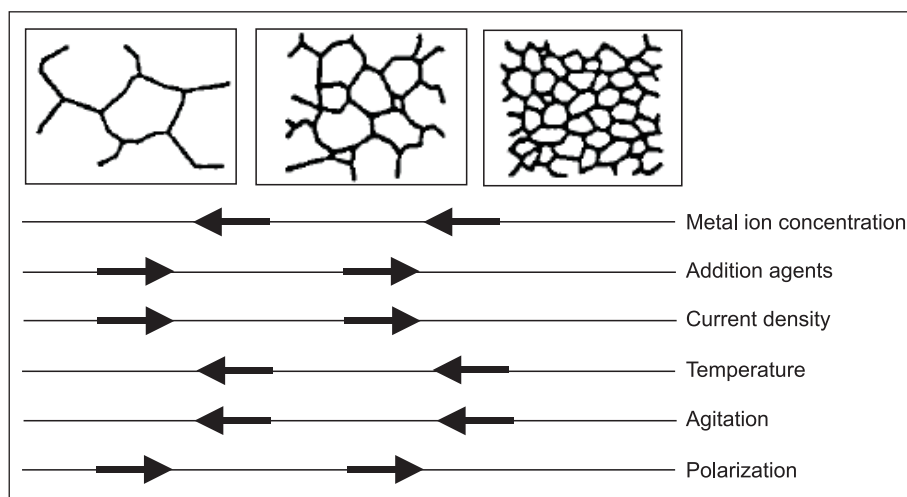


Figure 2 Pictorial representation of the influence of plating variables on the change in grain size of electrodeposits (adapted from Dini [14])

Texture of electrodeposited coatings

Texture, the preferred distribution of grains having a particular crystallographic orientation with respect to a fixed reference frame, is an important structural parameter for bulk materials and coatings [15, 16]. The texture of electroplated coatings can be markedly influenced by solution composition and operating conditions. Depending on pH and current density, five different textures can be obtained from a Watts nickel plating solution [17]. Texture is completely independent of the substrate orientation for thick deposits. Texture can influence a variety of functional properties of electrodeposits.

Mechanical properties

Moduli of elasticity

The moduli of elasticity of electrodeposits are generally smaller than those of the same metal formed in other ways. Irrespective of the method of formation, the moduli should be the same. The smaller moduli of elasticity of electrodeposits could possibly be due to the difficulty of obtaining accurate values and the possibility that the electrodeposits do not behave elastically.

Tensile strength

The tensile strength of electrodeposited metals depends on the operating conditions employed for electrodeposition of the individual metals. In many cases, the electrodeposit is two or three times as strong as the corresponding wrought metal. The primary reason for the higher strength of the electrodeposits when compared with their wrought counterparts is due to the fine grain size of the electrodeposits. The tensile strength of electrodeposited cobalt is more than four times the strength of annealed, wrought cobalt whereas some types of electrodeposited chromium are nearly seven times as strong as cast or sintered chromium.

The type of additives used in the plating bath and codeposition of impurities could significantly influence the tensile strength of electrodeposits. The tensile strength of

electrodeposited nickel coating varies from 39 to 250 MPa, depending up on the type additives used in the plating bath. In a copper pyrophosphate plating bath, addition of lower concentrations of dimercaptodiazole (DTMD) results in copper deposits with low tensile strength. However, when the concentration of DTMD is higher, the formation fine-grained copper deposits enables an increase in the tensile strength. Small amounts of co-deposited carbon in nickel and tin-lead electrodeposits influence the tensile strength. Increasing the carbon content of a sulfamate nickel electrodeposit from 28 to 68 ppm increased the tensile strength from 575 to 900 MPa. Similarly, increasing the carbon content of the tin-lead electrodeposit from 125 to 700 ppm increased the tensile strength from 29 to 41 MPa.

Ductility

Ductility is the amount of plastic deformation that can occur prior to fracture. Fine grained electrodeposits tend to be brittle because the plastic deformation which occurs primarily by dislocation motion is impeded by the grain boundaries. The ductility of electrodeposits, as evidenced by their percent elongation, is higher when they are attached to the substrate as they cannot exhibit highly localized plastic deformation prior to fracture. The lower ductility of electrodeposited free standing foils is probably caused by the more severe local plastic deformation, also called as necking, in the region where fracture occurs subsequently. The free standing foils of electrodeposited nickel and electroless copper have been found to exhibit severe necking. When the deposit adheres well to the substrate, necking is essentially prevented. The additives present in the plating bath have a significant influence of the ductility of the resultant deposits. In a copper pyrophosphate plating bath, addition of lower concentrations of dimercaptodiazole (DTMD) results in copper deposits with high ductility. However, when the concentration of DTMD is very high, the inclusion of excessive additive in the copper deposit causes the ductility to decrease.

Superplasticity

Superplasticity refers to large tensile elongations, typically 500%, that can be achieved in polycrystalline materials under certain conditions of strain rate and temperature. One of the main requirements for superplasticity is the presence of an ultrafine, equiaxed microstructure, typically 1 to 5 μm diameter that remains stable while being deformed at the superplastic temperature (usually around one-half the melting point). As many electrodeposited metals possess a smaller grain size, electrodeposition offers an exciting prospect for fabricating complex parts by combining a pre-forming by electrodeposition and final forming of the internal structure by superplastic deformation. The two electrodeposited alloys which meet these requirements and, therefore, exhibit superplastic behavior is Cd-Zn and Ni 40-60% Co. Although a number of alloys exhibit superplastic behavior, lead-tin, copper-nickel, and cadmium-tin are of particular interest since these alloy coatings can be deposited from aqueous solution. The growing field of electrodeposition of multilayer coatings by cyclic modulation of the cathodic current or potential during deposition also offers promise for the production of new superplastic alloys. Composition-modulated alloys (CMA) which have been produced by this process include Cu-Ni, Ag-Pd, Ni-Nip, Cu-Zn and Cu-Co.

Residual stress

Residual stress may be defined as a stress within a material which is not subjected to load or temperature gradients yet remains in internal equilibrium [5]. Residual stress in electrodeposits refers to forces created within the deposit as a result of the electrocrystallization

process and/or the codeposition of impurities such as hydrogen, sulphur and other elements. The residual stress is either tensile (contractile) or compressive (expansive) in nature. In tensively stressed deposits, the average distance between atoms in the lattice is greater than the equilibrium value, creating a force that tends to drive the atoms closer together. In compressively stressed deposits, the atoms are closer together and the force tends to drive them further apart. Dislocation theory provides a logical explanation of the origin of residual stress in electrodeposits [1].

Residual stresses in electrodeposited coatings can cause adverse effects on its properties. They may be responsible for peeling, tearing, and blistering of the deposits; they may result in warping or cracking of deposits; they may reduce adhesion, particularly when parts are formed after plating and may alter properties of plated sheet. Stressed deposits can be considerably more reactive than the same deposit in an unstressed state. Occasionally stress may serve a useful purpose. For example, in the production of magnetic films for use in high speed computers, stress in electrodeposited iron, nickel, and cobalt electrodeposits will bring about preferred directions of easy magnetization and other related effects [22].

There are a variety of steps that can be taken to minimize stress in deposits: (i) choice of substrate; (ii) choice of plating solution; (iii) use of additives; and (iv) use of higher plating temperatures. Typically, with most deposits, there is a high initial stress associated with lattice misfit and with grain size of the underlying substrate. This is followed by a drop to a steady state value as the deposit increases in thickness. With most deposits this steady state value occurs in the thickness regime of 12.5 to 25 μm . Atomic mismatch between the coating and substrate is a controlling factor with thin deposits. The type of anion in the plating solution can leave a marked influence on residual stress. For example, sulfamate ion provides nickel deposits with the lowest stress, followed by bromide [22]. There are numerous additives, particularly organic, which have a marked effect on the stress produced in deposits. Small quantities (0.01 to 0.1 g/l) of most sulfur bearing compounds rapidly reduce the stress in nickel deposits. When a sulfur compound reduces internal stress compressively, the resulting deposit is brighter. Increasing the plating solution temperature can also help to reduce the stress.

Adhesion

Adhesion of a coating or deposit is defined as the extent to which it sticks to the substrate. Adhesion can be regarded as a measure of the degree to which a bond has been developed from place to place at the coating-substrate interface. Good adhesion is often has no value unless the bond strength is satisfactory. If the electrodeposit separates from the substrate then the adhesion is poor and vice-versa. The adhesion of electrodeposits on metallic substrates is generally better whereas plating on plastics presents a serious adhesion problem. The main factors that are detrimental to adhesion are brittle layers, which can form by diffusion between the deposit and the substrate, especially if annealing is involved.

Porosity

Porosity is one of the main sources of discontinuities in electroplated coatings; the others are cracks arise due to high internal stress. In most cases porosity is considered undesirable as the pores can expose substrate underneath to corrosive agents, reduce mechanical properties and, deleteriously influence density, electrical properties and diffusion characteristics of the deposits. Kutzelnigg [18] suggests that pores may be broken down into two main categories,

transverse pores and masked or bridged pores. Transverse pores may be either of the channel type or hemispherical and extend through the coating from the basis metal to the surface of the deposit. They may be oriented perpendicular or oblique to the surface or may have a tortuous shape. Masked or bridged pores do not extend through the coating to reach the surface but either starts at the surface of the basis metal and become bridged or start within the coating and become bridged. Cracks may be regarded as pores much extended in a direction parallel to the surface, but they can also be divided into transverse cracks, enclosed cracks and surface cracks.

The porosity of electrodeposits depends on (i) the nature, composition and history of the substrate surface prior to plating; (ii) composition of the plating solution and its manner of use; and (iii) post plating treatments such as polishing (abrasive or electrochemical) and damage due to wear, deformation, heating and corrosion [19]. At low deposit thickness, porosity of electrodeposited films is largely controlled by the surface condition and characteristics of the underlying substrate. This condition persists up to a limiting thickness, after which the properties of the film itself, primarily crystallographic properties, determine the rate of pore closure [20]. The porosity of electrodeposits drops exponentially with increase in their thickness [21]. A convenient and often very effective way to modify the substrate and reduce porosity is to use an underplate.

Hardness

Hardness is one of the most important properties of electrodeposits, which is also indicative of the strength and ductility as well as the wear resistance of the deposits. The hardness value of electrodeposits is only of limited value unless it is experimentally related to the strength or the ductility of the specific material because for electrodeposits even the qualitative relationship that is commonly observed among hardness, tensile strength and ductility, do not always prevail. For example, it is usually expected that the hardness increases with the tensile strength and decreases with ductility. However, the reverse effect is also common in electrodeposits.

Hall-Petch equation relates the grain size, d , with the hardness, H , of the deposit as follows:

$$H = H_0 + K_H d^{-1/2}$$

where H_0 and K_H are the experimental constants and are different for each metal. The value of H_0 is characteristic of dislocation blocking and is related to the friction stress. K_H takes account of the penetrability of the boundaries to moving dislocations and is related to the number of available slip systems. The Hall-Petch equation has been found applicable for several polycrystalline materials and also for electrodeposited iron, nickel and chromium. Electrodeposited nickel exhibits Hall-Petch relation over a wide range of grain sizes from 12,500 nm down to 12 nm. A microhardness of approximately 700 kg/mm² was obtained with the smallest grain size.

Wear resistance

Wear, defined as the damage to the surface of a substrate due to the relative motion between that substrate and a contacting substrate or substances is a complex phenomenon and usually involves a progressive loss of material. The parameters that influence wear include: surface hardness and finish, microstructure and bulk properties, contact area and shape, type of motion, its velocity and duration, temperature, environment, type of lubrication and coefficient of friction. Electrodeposits offer some distinguishing features for wear resistant

applications. Chromium plating is more extensively used for wear resistance applications than any other electrodeposited coating. Typical uses include roll surfaces, shaft sleeves, pistons, internal combustion engine components, hydraulic cylinders, landing gear and machine tools. Although the thickness varies with the application, it is usually in the range of 20 to 500 μm . Chromium plating is very effective in reducing the wear of piston rings caused by scuffing and abrasion. The average life of a chromium-plated ring is approximately five times than that of the bare ring made of the same base metal. Hard chromium plating exhibits better resistance to low stress abrasion than hard anodized aluminum and heat treated electroless nickel. Electrodeposited chromium coatings also offer excellent scuffing resistance (evaluated by Falex test) compared to that of electro- and electroless deposited nickel. However, crack-free chromium coating exhibit high wear rate, which is related to its crystal structure. Crack-free chromium has a predominantly hexagonal close-packed crystal structure unlike conventional chromium which is body centered cubic. HCP metals tend to slip on only one family of slip planes, those parallel to the basal plane. This results in larger strains at a given stress level and less dislocation interactions. In addition, the strain-hardening rate is low, leading to rapid localization of deformation, early fracture and an increased wear rate.

Electrodeposited coatings are typically not effective for applications requiring wear resistance at temperatures above 500 to 600°C. Heat treatment of electrodeposited chromium coatings at 800°C for 1 hour drastically affects its hardness from 900 to 450 kg/mm^2 , which results in increasingly higher wear rate. However, electrodeposited composite coatings offers promise for higher temperature applications. Co-30Vol. % Cr_2C_3 composite coatings offer better wear resistance of aircraft engines at temperatures up to 800°C. The improved wear resistance is due to the formation of cobalt oxide glaze on the load bearing contact areas during interfacial motion. Electrodeposited composition modulated alloy coatings exhibit novel and interesting wear properties. The layer microstructure of these coatings provides internal barriers to wear damage and increases the wear resistance. Compositionally modulated Ni-Cu coating with alternate layers of nickel and copper having an equal layer spacing of either 10 or 100 nm on AISI type 52100 steel is found to be more wear resistant than either pure nickel or copper deposits.

Advantages and disadvantages of electrodeposition

Electrodeposition process is simple, versatile and cost-effective. It is a viable approach for preparing, coatings having a very high electrical conductivity that is commonly used in electronic circuitry, sacrificial anodic coatings that protect the base metal from corrosion, coatings with controllable thicknesses which are amenable to welding and soldering and, coatings with high hardness and wear resistance.

Some substrates like cast iron and some substrate conditions like porosity require special plating procedures. Large metal structures are beyond the capabilities of electrodeposition. The design and geometry of the parts might create problems to obtain uniform coating thickness.

ELECTRODEPOSITION OF ALLOYS

Alloy deposition is subjected to the same principles as single metal plating. The deposition potential of a given metal is determined by the standard electrode potential (E^0) and ionic activity. The ionic activity is proportional to the ionic concentration. The electrodeposition of

an alloy requires co-deposition of two or more metals. For achieving the deposition of an alloy, the metal ions must be present in the electrolyte solution that provides a cathode film where their individual deposition potential can be brought close to one another or become identical. If the deposition potential differs a lot then the only way to achieve deposition of the alloy is by controlling the activity of the ions by changing their concentration [23]. Alloy deposition often provides deposits with properties not normally obtained by employing electrodeposition of single metals.

The three main stages of alloy deposition are:

Ionic migration: The hydrated ions in the electrolyte migrate toward the cathode under the influence of the applied potential as well as through diffusion and/or convection.

Electron transfer: At the cathode surface are, the hydrated metal ions enter the diffusion double layer where the water molecules of the hydrated ion are aligned by the field present in this layer. Subsequently the metal ions enter the fixed double layer where because of the higher field present, the hydrated shell is lost. Then on the cathode surface, the individual ion may be neutralized and is adsorbed.

Incorporation: The adsorbed atom wanders to a growth point on the cathode and is incorporated in the growing lattice.

There are five types of alloy plating systems: (i) regular co-deposition; (ii) irregular co-deposition; (iii) equilibrium co-deposition; (iv) anomalous co-deposition; and (v) induced co-deposition.

Regular co-deposition

Regular co-deposition is characterized by deposition under diffusion control. The effects of plating variables on the composition of the deposits are determined by the changes in the concentrations of metal ions in the cathode diffusion layer and are predictable from simple diffusion theory. The percentage of the more noble metal in the deposit is increased by increasing the total metal content of the bath, decrease in current density, elevation of bath temperature and increased agitation of the bath. The effect of current density on the composition of alloys deposited from regular alloy plating systems consistently results in a decrease in the content of the more noble metal in the deposit. At low current density the deposit consists of the unalloyed noble metal; increase in the current density enables an increase in the content of the less noble metal.

Irregular co-deposition

Irregular co-deposition is mostly controlled by chaotic potentials of the metals rather than by the diffusion phenomenon. Irregular codeposition is most likely to occur with solutions of complex ions, particularly with systems in which the static potentials of the parent metals are markedly affected by the concentration of the complexing agents. The relation between current density and alloy composition in irregular co-deposition is complicated and usually unpredictable. The lack of a consistent trend in the content of the more noble metal in the deposit with current density stands in sharp contrast to the consistent behaviour of regular codeposition.

Equilibrium co-deposition

Equilibrium co-deposition is characterized by deposition from a solution which is in chemical equilibrium with both parent metals. The equilibrium plating system is unique in that the ratio

of the metals in the deposit (plated at low current density) is the same as their ratio in the bath. However, this equivalence exists only under static conditions (zero current density). Since electrodeposition is always accompanied by a departure of the electrode potential from the static potential, it cannot be expected that the two metals which were initially in static equilibrium in a solution will be in equilibrium with each other during codeposition. Therefore, it cannot be expected to obtain an alloy deposit having the same ratio as that of the bath, unless the deposition is carried out at such a low current density. At higher current densities, the composition of the deposit would be expected to depart to some extent from the equilibrium value.

Anomalous co-deposition

Anomalous co-deposition is characterized by the anomaly that the less noble metal deposits preferentially. With a given plating bath, anomalous codeposition occurs only under certain conditions of concentration and operating variables. Otherwise the codeposition falls under one of the other three types. The relation between alloy composition and current density is also unusual.

Induced co-deposition

Induced co-deposition is characterized by the deposition of alloys containing metals, such as molybdenum, tungsten or germanium which cannot be deposited alone. The relation between the composition of the deposit and the current density in induced codeposition is similar to that observed in irregular codeposition. The effect of current density is not large and there is no consistent trend of the content of the reluctant metal in the deposit with current density.

Some key issues in alloy deposition are as follows:

- (i) If an alloy plating bath, which is in continuous operation, is replenished with two metals in a constant ratio, the ratio of metals in the deposit will approach and ultimately take on that value.
- (ii) In alloy deposition, the ratio of the concentration of the more readily depositable metal to the other is smaller at the cathode-solution interface than in the bulk of the bath.
- (iii) An increase in the metal percentage of a parent metal in an alloy plating bath results in an increase in its percentage in the deposit.
- (iv) In the deposition of alloys from the normal alloy plating systems, the most fundamental mechanism is the tendency of the concentration of the metal ions at the cathode-solution interface to approach mutual equilibrium with respect to the two parent metals.
- (v) A variation in a plating condition that brings closer together the potentials for the deposition of the parent metals increases the percentage of the less noble metal in the electrodeposited alloy.

Influence of process variables on electrodeposition of alloys

Deposition potentials of metals usually become nobler with increase in temperature, because polarization is decreased. Whether the deposition of the nobler or less noble metal is favoured depends on which deposition undergoes the largest polarization. An increase in temperature increases the concentration of metal in the cathode diffusion layer, because the rates of diffusion and of convection increase with temperature. This is the most important way by

which temperature affects the composition of the electrodeposited alloys. Dense solution formed by the dissolution of the anode sinks to the bottom of the cell while the less dense solution from the cathode rises to the surface of the electrolytic cell. As the composition of the electrodeposited alloy is directly affected by the composition of the solution in contact, the dispelling of local variations in bath composition is more important in alloy plating than in deposition of single metal. Agitation of an alloy plating bath or rotation of the cathode can directly affect the composition of the alloy by reducing the thickness of the cathode diffusion layer. This is a purely mechanical action which does not change the electrochemical properties of the solution. Agitation has a more consistent influence on the composition of the deposit than either temperature or current density. Effect of pH on induced co-deposition is more complex than any other type of co-deposition of alloys. In induced co-deposition, the effect of pH exhibit a mixed trend of both an increase as well as a decrease in the alloy deposition.

Addition agents, used in low concentrations, do not affect the static potentials of the metal but usually increase the polarization associated with the deposition process. By using addition agents the dynamic potentials of more noble metals can be brought closer to the less noble metal, thereby making the co-deposition possible. Though the addition agents have some adverse effects like drastic reduction of the mechanical properties of the deposit, they play a very important role of bringing the deposition potentials of the constituent elements close and have a direct influence on the composition of the deposit. The concentration of the addition agent required to produce an appreciable effect is much smaller than that of a complexing agent. Addition agents are effective in baths containing metals as simple ions rather than as complexes.

PULSED CURRENT ELECTRODEPOSITION (PED)

Pulsed current electrodeposition (PED) is a method of depositing metal on a substrate using interrupted direct current [24-26]. The theory behind PED is very simple. The cathode film is kept as rich in metal ions as possible and as low in impurities as possible. During the period when the current is on, the metal ions next to the cathode are depleted and a layer rich in water molecules is left. During the portion of the cycle when the current is off, the metal ions from the bulk of the plating solution diffuse into the layer next to the cathode. Then the process is repeated. Also, during the time the current is off, gas bubbles and impurities that have adsorbed on the cathode have a chance to desorb [27, 28].

PED is accomplished with a series of current pulses of equal amplitude and duration in the same direction, separated by periods of zero current (Fig. 13.3). These pulses are often employed at a rate of 500 to 10,000 times per second. They favor the initiation of grain nuclei and greatly increase the number of grains per unit area. The intended result is a finer grained deposit with better characteristics and properties than conventionally plated coatings. The pulse rate (frequency) and 'ON' and 'OFF' times (duty cycle) are controllable to meet the needs of a given application. Typical on-time range from 0.1 to 9.9 ms, and typical off-times range from 1 to 99 ms. The physical and chemical properties of deposits can be controlled precisely through the careful selection of pulse-plating parameters.

In PED of metals the pulse on-time should be sufficiently short to stay well below the pulse limiting current density, but sufficiently long to fully charge the double layer. These two requirements determine the available parameter window. The upper limit depends heavily on the metal concentration in the electrolyte, while the lower limit is relatively independent of

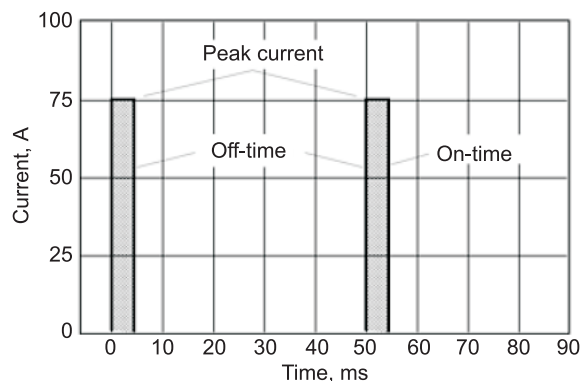


Figure 3 Constant-current pulse plating with an on-time of 5 ms, an off-time of 45 ms, and a peak current of 75 A (adapted from VanHorn [25])

concentration [29]. Electrolyte conductivity must be maintained at a high level to allow the peak pulse current to be completely effective. If the conductivity is not high enough, an excess voltage will be required to attain the desired peak current. Such peaks are power-inefficient and less effective. In periodic reverse plating, the polarity of a constant D.C. output is switched back and forth in a regular pattern. A comparison of the current patterns (ideal pattern) in conventional and periodic-reverse pulsed-current plating is given in Fig. 4. The duration of the current in each direction, called the forward and reverse envelopes, can be individually controlled from 0.1 milliseconds to 99.99 s. Within each envelope a square-wave pulse is generated. The frequency and the duration of the pulses are set independently for the forward and reverse envelopes (Fig. 13.5). Frequency range is from 10 to 9,999 Hz. Duty cycle settings in percentages determine 'ON' & 'OFF' for each pulse.

The average current density i_m in pulse and pulse reverse plating is given by the pulse current density i_p , the (anodic or cathodic) current that flows during the off-time i_{off} and the duty cycle (γ): $i_m = i_p \gamma + i_{off} (1 - \gamma)$. The pulse period is $t_{pp} = t_p + t_p'$ where $t_p = \gamma t_{pp}$ is the pulse on-time and t_p' is the pulse off-time. The pulse frequency n often used in the literature is simply the inverse of the pulse period, $n = 1/t_{pp}$.

PED offers increased nucleation rate, reduced diffusion layer thickness, higher diffusion limiting currents, decrease in grain size, reduced fluid dynamic effect on plating uniformity,

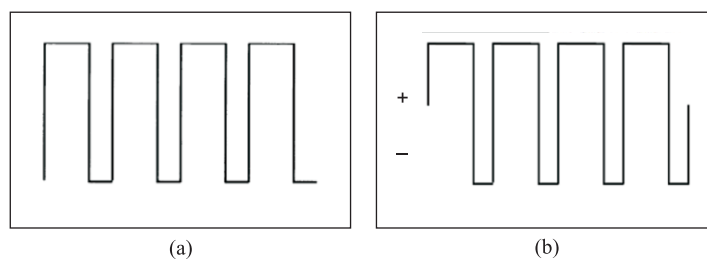


Figure 4 Current patterns in pulsed-current plating (Ideal pattern): (a) conventional plating; and (b) periodic-reverse pulsed-current plating (adapted from VanHorn [25])

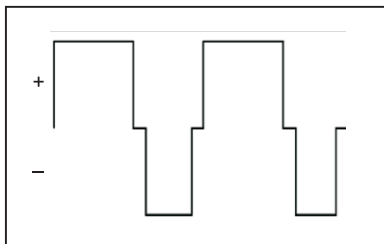


Figure 5 Square-wave current pattern of the forward and reverse envelopes in periodic-reverse pulse plating (adapted from VanHorn [25])

increased current yields, reduced hydrogen embrittlement and improved control in alloy plating. A well-known effect of pulse plating concerns the reduction of internal stresses resulting from codeposition of hydrogen. Using reverse pulses, one can selectively re-oxidize hydrogen dissolved in the deposit and thus reduce the tendency for cracking [30]. PED could dramatically influence the microstructure of the resultant deposits. Table 13.4 lists conditions that differ from d.c. plating (at same average current density) and how they could influence the physical phenomena that govern the development of the deposit microstructure. PED could also influence the composition of alloy deposits. The choice of applied pulse parameters greatly affects the composition of alloy deposits. To what extent the choice of pulse parameters influences the alloy composition depends on the kinetics of the partial reactions.

The advantages of PED compared to conventional electrodeposition are as follows:

- Deposits are smooth, dense, fine-grained, and almost completely free of pinholes.
- Variation in plate thickness from one part to the next is considerably reduced.

Table 4 Possible effects of pulse current electrodeposition on deposit structure (adapted from Landolt and Marlot [26])

Time interval	Conditions that differ from d.c. plating	Phenomena affected
On-time	Double layer charging Overvoltage Concentration profile near the electrode Adsorption (ions, additives, hydrogen)	Nucleation rate Growth mechanism (e.g., dendrites) Electrode reaction mechanism Codeposition rate (H, alloying elements), additive reactions
Off-time	Double layer discharge Potential relaxation Concentration profile relaxation Desorption (additives, ions, hydrogen)	Surface diffusion Surface recrystallization Corrosion, displacement reactions Passivation, Hydrogen diffusion
Pulse reverse-time	Anodic potential Sign change of double layer charge Concentration profile near electrode Desorption/adsorption (additives/ions)	Selective metal dissolution Hydrogen re-oxidation Additive oxidation Passivation

- Plating speeds can normally be increased.
- Current efficiency generally is improved.
- Use of organic additives, in most cases, can be reduced by 50 to 60%.
- Deposits are free from dendritic growth even if additives are not used.
- For some electrodeposits, such as gold, less metal is required in the plating solution to meet end-use specifications.

The main limitation of PED is that the cost of a pulsed-current rectifier is greater than that of a conventional dc unit.

PED can be used as a means of producing unique structures with improved properties, i.e., coatings with properties not obtainable by d.c. plating. PED can be used to improve the current distribution and to alter the prevailing mass transport conditions. It can also serve to control the microstructure and composition of electrodeposits, for example, nanocrystalline and multilayer deposits. PED permits control of the composition of electrodeposited alloys by varying the electrical parameters. PED has been reported to improve the deposition process and deposit properties such as porosity, ductility, hardness, and surface roughness. The benefits of PED are given in Table 13.5.

PED can be used to prepare multilayer alloy deposits from a single electrolyte containing a more noble metal in small concentration and a less noble metal in large concentration. The former deposits under mass transport control, the latter under activation control. Hence by periodically varying the potential (or the current) between the value where only the more noble

Table 5 Benefits of Pulsed current electrodeposition

Metallurgical	Denser deposit Finer grain deposit Lower porosity Higher tensile strength Higher elongation Reduced stress Reduce hydrogen embrittlement
Electrical	Higher conductivity Lower contact resistance Better bondability
Physical	Fills submicron trenches Improved adhesion of deposit Reduced stress on photo resists Increased throwing power Control of alloy composition Uniform thickness
General	Reduce additives Reduce plating time 10 - 20%

metal deposits and the value corresponding to deposition of both metals, it is possible to deposit multilayer deposits. In principle, parallel layers of alternating composition are obtained and their thickness, typically a few nanometers, depends on the charge passed during each pulse. At high pulse frequencies the amount of material deposited during one pulse is small, often less than one atomic layer, and alloy deposits of uniform composition are obtained. At low pulse frequencies, with pulse off-times of several seconds, the resulting alloy composition may vary periodically with pulse on-time and off-time leading to formation of multilayer deposits.

BRUSH PLATING

Brush plating, also called as selective plating, differs from conventional electroplating, in that the plating solution is brought to the job (cathode) and applied by a hand held anode instead of immersing both the cathode and anode in the plating bath. This method is usually adopted when the parts are too large to immerse in the plating bath or when a small area of a large part is to be plated or when touch up and repair of components is required. The anodes used in brush plating usually contains some absorbent materials so that the plating solution can be retained in them and can be applied over the cathode. The desired current for plating the metals can be supplied using a d.c. source. The plating solutions used for brush plating have a much higher concentration of metal usually as organometallic salts than do solutions used for tank plating. This permits the use of higher current density which results in faster deposition, better bond strength and less porosity than in tank plating. Continuous movement between the anode and cathode is a key element in obtaining high-quality brush plated deposits. A wide variety of metals and alloys such as, copper, nickel, cobalt, gold, platinum, palladium, silver, rhodium, cobalt-nickel, nickel-tungsten, etc. can be deposited by brush plating. Adhesion is good on most of the metals, except Ti, Ta and W, where only a limited adhesion could be achieved. The major advantage of brush plating is portability. Since this method offers precise thickness control, there is no need for subsequent machining. A comparison of the characteristics of conventional electroplating and brush plating is given in Table 13.6.

Table 6 Comparison of the characteristics of conventional electroplating and brush plating
(Source: Brush plating Course Manual, Liquid Development Co.)

Characteristic	Conventional electroplating	Brush plating
Precision buildup capacity	Fair to good	Excellent
Quality of bond	Good	Excellent
Speed of deposit	Slow	Fast
Density of deposits (porosity)	Moderately dense	Very dense
Portability	No	Yes
Requirement for post finishing	Usually required	Not required for thickness up to 0.01 inch on smooth surface
Hydrogen embrittlement	Yes	No

JET ELECTRODEPOSITION

Jet electrodeposition (JED) is a high-speed electroplating technique with special flow characteristics and in this respect it differs from conventional electrodeposition. Conventional electrodeposition is generally composed of three elemental steps: a transfer of metal hydration ions, a transfer of electrical charges and crystallization. The deposition rate is governed by the transfer of hydrated metal ions, which is the slowest of the three steps. The cathodic interface is characterized by a diffusion layer located between the cathode and bulk of the solution. The polarization curve, which exhibits the current-potential relationship, explains the phenomena occurring in the diffusion layer. It is necessary that electroplating is carried out at high current density to obtain a fast plating rate. However, if the current density exceeds the limiting current density, then it could lead to burnt deposits due to the depletion of cations at the cathode interface. At higher current densities diffusion is not fast enough to replenish the cations at the interface. Besides, hydrogen ions are also reduced to hydrogen gas. Replenishment of the interface by metal ions can be enhanced by reducing the thickness of the diffusion layer. In conventional electrodeposition, the diffusion layer thickness can be reduced by cathode movement or by adopting a rotating electrode or by ultrasonic agitation or by modifying the plating cell configuration. In jet electrodeposition, the electrolyte jet forcibly supplies a greater quantity of metal ions and makes the diffusion layer extremely thin. Consequently the limiting current density becomes very high. The increase in limiting current density can be up to several amperes per square centimeter. This enables an increase in the probability of nucleation, which results in the formation of fine grained deposits with increase in microhardness in accordance with the Hall-Petch relation. The grain-size refining effect of the jet electrodeposition is more efficient than conventional plating due to the much higher overpotential and current density.

Qiao et al. [31] have prepared nanocrystalline Ni-Co alloy deposits by JED with much higher current density. According to them, the limiting current density can be over 4.0 A/cm^2 and the highest deposition rate can be up to $47.3 \text{ }\mu\text{m/min}$, which is 90 times faster than that of conventional electrodeposition. The deposits are bright, show no burns, and have fine grain size. JED current density has little effect on the composition of the deposited alloy. Increase in current density from 2.39 to 4.77 A/cm^2 enables refinement of the grain size of the Co-Ni alloy deposits from 19 to 9 nm and an increase in the microhardness from Hv411 to Hv540. Only a few works regarding the use of JED for synthesis of nano-grained materials have been reported [32-36]. Takeuchi et al. [37] have studied the formation of compositionally graded Ni-P and Ni-P-SiC composite coatings by JED. Future development of this high-speed electrodeposition method requires better understanding of the effects of limiting current density and deposition rate on the composition, microstructure, and properties of the deposited alloys.

ELECTRODEPOSITION OF METALS USING IONIC LIQUIDS

The term "ionic liquids", formerly referred to room-temperature molten salts, is generally used for ionic melts with melting points below 100°C . Most of the liquids with which we are familiar (e.g., water, ethanol, acetone, benzene etc.) are molecular. Regardless of whether they are polar or nonpolar, they are basically constituted of molecules. However, the room-temperature ionic liquids are mainly constituted of ions. This gives them the potential to behave very differently from conventional molecular liquids, when they are used as solvents. In contrast to conventional molecular solvents, ionic liquids are usually nonvolatile, in most cases

nonflammable, less toxic, good solvents for both organic and inorganic materials, and can be used over a wide temperature range. Moreover, ionic liquids exhibit good electrical conductivity and have a wide electrochemical window whereas the electrochemical window of water is limited to only certain metals that can be deposited from aqueous media. Another advantage of ionic liquids is that problems associated with hydrogen ions in conventional protic solvents can be eliminated, because ionic liquids are normally aprotic. Therefore, ionic liquids have attracted considerable attention as solvents for a wide variety of applications including electrodeposition, batteries, catalysis, separations, and organic synthesis. Room temperature ionic liquids are the promising electrolytes for the ED of various metals because they have the merits of both organic electrolytes and high-temperature molten salts. They can be used in a wide temperature range, so temperature can be elevated to accelerate such phenomena as nucleation, surface diffusion and crystallization associated with the electrodeposition of metals. Since the ionic liquids are nonflammable and volatile, the process can be safely constructed.

A large number of studies on ED of metals from chloroaluminate ionic liquids have been reported whereas only a few studies have explored ED of metals from non-chloroaluminate ionic liquids such as tetrafluoroborate (BF_4^-), hexafluorophosphate (PF_6^-) and chlorozincate ionic liquids. Chloroaluminate ionic liquids are highly hygroscopic and upon hydrolysis produce toxic and corrosive hydrogen chloride. Hence they are not suited for practical use. In contrast to chloroaluminate, ionic tetrafluoroborate ionic liquids are more stable against moisture and are applicable for practical use. Moreover, codeposition of metals derived from the ionic liquids does not occur because the tetrafluoroborate anion is not reducible. However, tetrafluoroborate ionic liquids are limited only to a small number of metals for which the anhydrous tetrafluoroborate salts are available. Besides, it is difficult to adjust the Lewis acidity and basicity by the addition of BF_3 and this necessitates the addition of organic chlorides as a Lewis base to dissolve the metal chlorides, which act as Lewis acids to form their chlorocomplex anions. The hexafluorophosphate ionic liquids are similar to the tetrafluoroborate ionic liquids and they are more stable against moisture. However, they undergo hydrolysis when contacted with an acidic aqueous solution. They are not completely miscible with water and sometimes regarded as hydrophobic. Another type of ionic liquid used for electrodeposition of metals is a combination of various quaternary ammonium cations with bis(trifluoromethylsulfonyl)imide, $\text{N}(\text{CF}_3\text{SO}_2)_2^-$. These $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ionic liquids are not only stable against moisture but also immiscible with water. Therefore these $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ionic liquids are the promising candidates as supporting electrolytes for the practical electrodeposition processes.

A wide variety of metals such as Ti, Cr, Fe, Ni, Co, Cu, Zn, Pd, Ag, Cd, La, Pt, Au, Hg, alkaline and alkaline earth metals (Li, Na, K, Rb and Cs), Ga, In, Tl, Sn, Pb, Bi, Te are deposited using chloroaluminate ionic liquids [38, 39]. Electrodeposition of Cu, Fe, Co, Ag, Cd, Zn-Ni alloy, Te, Ge, Sb, In, In-Sb alloy, etc. has been explored using non-chloroaluminate ionic liquids. Electrodeposition of Ag, Cu, Co, Ni, Zn, Mg, Ga, Ga-As, In-Sb, Nb-Sn has been reported in $\text{N}(\text{CF}_3\text{SO}_2)_2^-$ ionic liquids. The possibility of electrodepositing metals using ionic liquids, which would otherwise be difficult to plate using aqueous electrolytes, opens up new avenues in surface modification to achieve desirable characteristics. One notable application is the electrodeposition of Ta on NiTi alloy. Ni-Ti alloys are widely used as orthodontic wires, self-expanding cardiovascular and urological stents, and bone fracture fixation plates and

nails. The biocompatibility of NiTi implants depends on their corrosion resistance. The major risk associated with Ni-Ti implants is the breakdown of the passive film, which occurs owing to the aggressiveness of the human body fluids, leading to release of Ni ions that may cause allergic, toxic and carcinogenic effects. Zein El Abedin et al. [40] have shown that ED of Ta using room temperature ionic liquid 1-butyl-1-methylpyrrolidinium bis(tri fluoromethylsulfonyl) imide ([BMP]Tf₂N) containing TaF₅ as a source of tantalum results in the formation of an adherent, dense and uniform layers of Ta of 500 nm thick, which offers better corrosion performance (higher open circuit potential, wider passive region and higher breakdown potential), than the uncoated alloy.

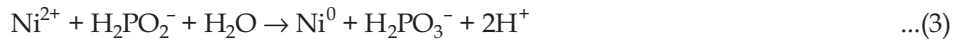
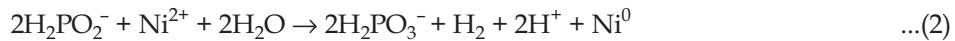
ELECTROLESS PLATING

Fundamentals of electroless plating

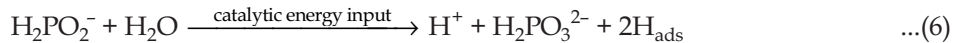
Electroless plating was an accidental discovery by Brenner and Riddell in the year 1946, when they tried to electroplate Ni-W alloy on the inner side of a steel tube using a citrate bath. As the Ni-W alloy deposit exhibits a high level of internal stress and cracking due to oxidation of the organic components in the bath, they attempted modification of the plating bath using several reducing agents including sodium hypophosphite. To their surprise, they found that the exterior surface of the steel tube was also coated and this had accounted for the increased current efficiency totaling up to 120% of the theoretical value. After careful analysis they concluded that the coating formed on the exterior of the steel tube might have formed by chemical reduction induced by hypophosphite, which happened to be a good reducing agent (the reduction potential of hypophosphite is 0.499 V vs. SHE at pH 4-6 and 1.57 at pH 7-10). In this process the chemical reducing agent provides electrons necessary to produce a metallic deposit rather than external electric current (as in electroplating). Hence the process was named as chemical nickel plating. Based on its analogy with electroplating process, William Blum coined the term as "Electroless Plating" for this process. Electroless plating process as we know today is an improved version of the process developed by Brenner and Riddell. Among the variety of metals that can be plated using this method, electroless nickel has proved its supremacy for producing coatings with excellent corrosion and wear resistance [41-43]. Compared to electrodeposition, coatings obtained using the electroless plating technique is uniform and they possess a very homogeneous distribution regardless of the substrate geometry [44]. Since no current flow is involved in the electroless deposition process, the rate of deposition on all areas should be equal as long as the solution conditions are maintained properly. This attribute of electroless plated coatings is beneficial when coating complex parts with critical dimensions, such as ball valves or threaded components.

Mechanism of electroless plating

Electroless plating is defined as the autocatalytic deposition (reduction) of metal ions in the presence of a reducing agent (hypophosphite, aminoborane or borohydride. Hypophosphite-reduced plating baths are the most commonly used for commercial electroless nickel plating. The mechanism of the electroless Ni-P deposition reactions taking place in the hypophosphite bath is not fully understood, but it has been postulated that it occurs in microcells of alternating anodic/cathodic polarity on the surface of the substrate. However, the occurrence of the following reactions is most definite as a result of the catalytic dehydrogenation of hypophosphite molecule adsorbed at the surface [43]:



Reaction (3), the simplified form of reactions (1) and (2), corresponds to nickel reduction while reaction (5) (a simplified form of reaction 4) corresponds to phosphorus reduction. The aforementioned reactions can be described as the following separate reactions [45]:



Reactions (6) to (8) are responsible for the formation of the Ni-P alloy coating. In reactions (7) and (8), the H_{ads} produced is consumed and Ni and P are deposited. Not all of the reactions occurring in the bath are favorable to EN deposition. Reactions (9) and (10) are deleterious to the deposition. In reaction (9), hypophosphite forms molecular hydrogen instead of atomic hydrogen, which diminishes the reducing power. As a result of reaction (10), nickel precipitates as nickel orthophosphite. This causes a reduction in the concentration of nickel ions in the bath. Also, the nickel orthophosphite precipitation occurring on the coating surface results in a defective and rough surface [45]. The unwanted occurrence of the reactions (9) and (10) causes a reduction in the efficiency of the electroless nickel coating deposition process.

Paunovic [46] was the first to identify electroless metal deposition in terms of mixed potential theory. He suggested that electroless metal deposition mechanisms could be predicted from the polarization curves of the partial anodic and cathodic processes. In simple terms, mixed potential theory leads to the assumption that electroless nickel plating can be considered as the superposition of anodic and cathodic reaction at the mixed (deposition) potential, E_m . Accordingly, the rates of the anodic reactions are independent of the cathodic reactions occurring simultaneously at the catalytic surface, and the rates of separate partial reactions depend only on the electrode potential, the mixed potential. The partial anodic and cathodic partial reactions are written as:

Anodic reaction



Cathodic reactions



The oxidation of hypophosphite (11) upon supply of sufficient energy (heat) provides the electrons necessary for reduction of nickel ions. Adsorbed nickel ions consume these electrons (12) and get deposited over the substrate surface with simultaneous hydrogen evolution (13). These electrons are also responsible for the deposition of phosphorus from hypophosphite (14).

Initiation of electroless nickel deposition occurs readily with metals such as iron, nickel, and cobalt. Once the initial nickel layer has deposited on the catalytic substrate, it acts as a catalyst for the process and the deposition continues unaided. This is referred to as autocatalysis of the deposition reaction. This unique property of EN plating makes it possible to coat internal surfaces of pipes, valves, nuts and bolts, and other complex geometries that are very difficult or impossible to be coated by conventional electroplating techniques.

Homma et al. [47] studied the reaction mechanism of electroless deposition using reductants like dimethylamineborane (DMAB), sodium hypophosphite etc., using a molecular orbital approach. It was indicated that the oxidation reaction for the reductants proceed via 5-coordinate intermediates and the calculated value of the heat of reaction could be used for quantitative evaluation of the reducibility of the reductants. Sodium borohydride and DMAB are the most widely used reducing agents for preparing electroless Ni-B coatings. Borohydride is a powerful reducing agent. The redox potential of BH_4^- is calculated to be $E^0 = -1.24$ V vs. SHE. In basic solutions, the decomposition of the BH_4^- unit yields 8 electrons for the reduction reaction.



However, it has been found experimentally that one mole of borohydride reduces approximately one mole of nickel. Based on this observation many mechanisms were proposed. The most widely accepted mechanism was proposed by Gorbunova et al. [48].



Equations (16) and (17) can be combined to give



Reduction of boron

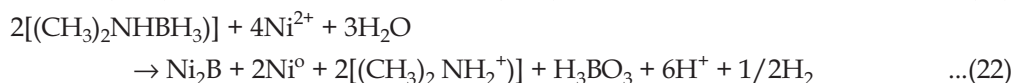


hydrolysis of borohydride

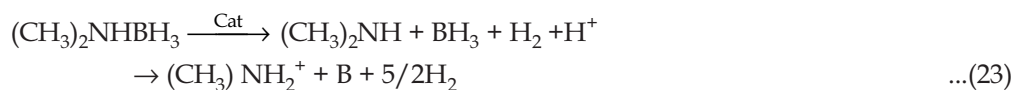


This mechanism indicates that the mole ratio of nickel reduced to borohydride consumed is 1:1, which was supported by experimental evidence [48].

DMAB has three active hydrogens bonded to the boron atom and, therefore, should theoretically reduce three nickel ions for each DMAB molecule consumed (each borohydride will theoretically reduce four nickel ions). The reduction of nickel ions with DMAB is described by the following equations:

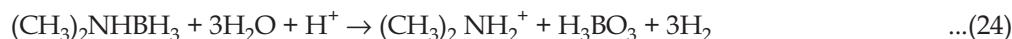


Boron reduction:

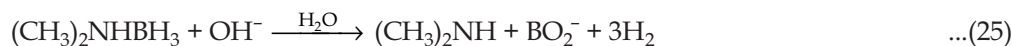


In addition to the above useful reactions, DMAB can be consumed by wasteful hydrolysis:

Acid:



Alkaline:



In acidic solutions, the first stage of the process is the dissociation of water ($\text{H}_2\text{O} \rightarrow \text{H}^+ + \text{OH}^-$) at the catalytic surface. The hydroxyl ions (OH^-) replace the hydrogen in the B-H bond of DMAB and as a result, an electron and a hydrogen atom are produced. The consumption of OH^- ions results in the accumulation of hydrogen ions (H^+) in the solution with a concurrent decrease in pH of the solution. In alkaline solutions, the sources of hydroxyl ions are the basic compounds (NaOH, NH_4OH , etc.) that are added to the plating solution to adjust the pH into the alkaline range of 7.0 to 14.0. As a result of the reaction of OH^- with the B-H bond, the pH also decreases in the alkaline solution. In this case, however, the pH decrease is due to the consumption of OH^- ions rather than the formation and accumulation of H^+ ions.

As can be deduced from reactions (3) to (5), (15) to (19) and (21) to (23), the electroless nickel coating is not pure nickel, unlike for electroplating, but a nickel-phosphorus or nickel-boron alloy coating. Electroless nickel processes are grouped as Ni-P, Ni-B and pure Ni, based, respectively, on the reducing agents used (i.e., hypophosphite, borohydride or dialkyl amino borane and hydrazine) in the plating bath. Hypophosphite reduced electroless nickel plating process has received commercial success because of its low cost, ease of control, and ability to offer good corrosion resistance [41-44]. Borohydride-reduced electroless nickel coatings also received considerable attention in recent years.

The essential components of the electroless plating bath (Table 13.7) are metal salt, reducing agent, complexing agent, accelerators, buffers, pH regulators, stabilizers and wetting agents. Most applications of the electroless coating are based on their wear and corrosion resistance. Table 13.8 enumerates the various applications of electroless nickel based coatings [49]. In as-deposited condition electroless nickel is a metastable, supersaturated metal-metalloid alloy. The properties of electroless nickel coatings are directly attributed to their microstructural characteristics. The phosphorus/boron content of electroless nickel coatings defines the physical, mechanical, and corrosion resistance properties of the coating [5].

Electroless Polyalloy Coatings

Development of electroless nickel polyalloy deposits is considered as the most effective method to alter the chemical and physical properties of binary Ni-P or Ni-B alloy deposits. There are many limitations to the production of ternary alloys. It is clear that the main metal (Nickel) must be capable of being catalytically deposited. The reduction of the second metal, which participates in the alloy, is determined by its electrochemical standard potential as well as its catalytic properties in relation to the reduction process. A few metals which do not

Table 7 The various components of electroless plating bath and their functions [43]

Component	Function
Nickel Ion	Source of Metal
Hypophosphite/Borohydride/DMAB	Reducing agent
Complexants	Stabilizes the solution
Accelerators	Activate reducing agent
Buffers	Controlling pH (longer term)
pH regulators	Regulates the pH of the solution
Stabilizer	Prevents solution breakdown
Wetting agents	Increases wettability of surfaces

Table 8 Application of electroless Ni-P coatings (adapted from Agarwala et al. [49])

Application avenue	Components	Coating thickness (μm)
Automotive	Heat sinks, carburettor components, fuel injection, ball studs, differential pinion ballx shafts, disk brake pistons and pad holders transmission thrust washers, synchromesh gears, knuckle pins, exhaust manifolds and pipes, mufflers, shock absorbers, lock components, hose couplings, gear and gear assemblies. Fuel pump motors, aluminum wheels, water pump components, steering column wheel components, air bag hardware, air conditioning compressor components, decorative plastics and slip yokes.	2-38
Air craft/ aerospace	Bearing journals, servo valves, compressor blades, hot zone hardware, pistons heads, engine main shafts and propellers, hydraulic actuator splines, seal snaps and spacers, landing gear components, turbine front bearing cases, engine mount insulator housing, flanges, sun gears, breech caps, shear bolts, engine oil feed tubes, flexible bearing supports, break attach bolts, antirotational plates, wing flap universal joints and titanium thruster tracks.	10-50
Chemical & petroleum	Pressure vessels, reactors, mixer shat, pumps and impellers, heat exchangers, filters and components, turbine blades and rotor assembles, compressor blades and impellers, spray nozzles, valves: ball, gate plug, check and butterfly, stainless steel valves, chokes and control valves, oil field tools, oil well packers and equipment, oil well turbine and pumps, drilling mud pumps, hydraulic systems actuators and blowout preventions.	25-125
Electrical	Motor shafts, rotor blades of stator rings	12-25
Electronics	Head sinks, computer drive mechanisms, chassis memory drums and discs, terminals of lead wires, connectors, diode and transistor cans, interlocks, junction fittings and PCB.	2-25
Food	Pneumatic canning machinery, baking pans, moulds, grills and freezers, mixing louts, bun warmers and feed screw and extruders.	12-25

Table 8 Contd.

Marine	Marine hardware pumps and equipment	25-50
Material handling	Hydraulic cylinders and shafts, extruders, link drive belts, gears and clutches and clutches	12-75
Medical & pharmaceutical	Disposable surgical instruments and equipment, sizing screens, pill sorters and feed screws and extruders.	12-75
Military	Fuse assemblies, tank tarred bearings, radar wave guides, mirrors, motors, detonators and firearms	8-75
Mining	Hydraulic system, jetting pump heads, mine engine components, piping connections, framing hardware.	3-060
Moulds & dies	Zinc dies, cast dies, glass moulds and plastic injection moulds of plastic extrusion dies.	15-50
Printing	Printing rolls and press beds.	~ 38
Rail road	Tank cars, diesel engine shafts and car hardware 20-90.	12-50
Textiles	Feeds and guides, fabric knives, spinnerets, loom ratchets and knitting needles.	~ 30
Wood & paper	Chain saw engine	~ 25
Miscellaneous	Drills and taps	~ 12
	Precision tools	~ 12
	Shower blades and heads	~ 8
	Pen tips	~ 5

possess the relevant catalytic properties in relation to the reduction process and are not catalytic poisons can also be codeposited with nickel. Ni-Re-P is an example of this type. When one of the metals is difficult to reduce, then its share in the alloy composition cannot be high. Ni-Cr-P is an example of this category. Electroless Ni-Cu-P, Ni-W-P, Ni-Mo-P, Ni-Zn-P, Ni-Sn-P, Ni-Re-P, Ni-Cr-P alloy coatings have been explored for a variety of applications. From corrosion protection point of view electroless Ni-Cu-P, Ni-W-P, Ni-Mo-P and Ni-Zn-P coatings assume significance [51-56]. Though alloying of Cu, W, Mo, etc. in the electroless Ni-P or Ni-B coatings enables an improvement in corrosion resistance, alloying of these elements results in a decrease in the P or B content of the coating.

ELECTROLESS COMPOSITE COATINGS

The idea of codepositing various second phase particles in electroless nickel deposit and thereby taking advantage of its inherent uniformity, corrosion resistance and hardenability has led to the development of electroless nickel composite coatings [41-44, 49, 57]. An essential advantage of preparing composite coatings by electroless codeposition compared to electrocodeposition is that the former allows accurate reproduction of the base geometry and eliminates the need for subsequent mechanical finishing. The electroless composite coating is formed by the impingement and settling of particles on the surface of the workpiece, and the subsequent envelopment of these particles by the matrix material as it is deposited. Several factors influence the incorporation of hard and soft particles in an electroless Ni-P matrix

including, particle size and shape, relative density of the particle, particle charge, inertness of the particle, the concentration of particles in the plating bath, the method and degree of agitation, the compatibility of the particle with the matrix, and the orientation of the part being plated [57].

ELECTROLESS DUPLEX, GRADED AND MULTILAYER COATINGS

Sankara Narayanan et al. [58] have explored the possibility of preparing electroless Ni-P/Ni-B duplex coatings using dual baths (acidic hypophosphite- and alkaline borohydride-reduced electroless nickel baths) with both Ni-P and Ni-B as inner layers and with varying single layer thickness. The duplex coatings are uniform and the compatibility between the layers is good. Sankara Narayanan et al. [59] have also explored the possibility of preparing electroless Ni-P graded coatings by sequential immersion in three different hypophosphite-reduced electroless plating baths. One important aspect of depositing electroless Ni-P graded coatings is the application of a nickel strike between each layer, so that the deposition proceeds without any hindrance when the substrate is sequentially immersed in electroless plating baths. The graded electroless Ni-P coatings are uniform and the compatibility between the three layers is good. Chen et al. [60] have studied the utility of multi-layered electroless Ni-P coatings to improve the corrosion resistance of powder-sintered Nd-Fe-B permanent magnet. Gu et al. [61, 62] have studied the role of multilayer coatings consisting of different layers of Ni-P and Ni obtained by electro- and electroless deposition processes to improve the corrosion resistance of steel as well as EL Ni-P coatings on AZ 91D Mg alloy.

CORROSION PROTECTION BY COATINGS

Corrosion is affected by a variety of factors including metallurgical, electrochemical, physical chemistry and thermodynamic. When selecting a coating it is important to know its position with respect to its substrate in the galvanic series for the intended application. Coatings are either anodic or cathodic to the substrate. Coatings that are anodic to a substrate in one environment may be cathodic to the same substrate in another environment. The environment itself may change from the surface of the coating to one that exists within any defects like pits, scratches and cracks. These defects are particularly important if the coating is cathodic to the substrate; in this case, if the substrate becomes exposed, rapid corrosion of the substrate may occur as it attempts to protect the coating. On the other hand, if the coating is anodic to the substrate, defects are less important, although they still must be considered.

If the substrate becomes exposed, it will be protected by the corrosion of the coating. Besides galvanic effects, the substrate and the interfacial zone between it and the coating can noticeably affect the growth and corrosion resistance of the subsequent coating since corrosion is affected by structure, grain size, porosity, metallic impurity content, interactions involving metallic underplates and cleanliness or freedom from processing contaminants. The nature of any corrosion products formed also must be taken into account. For example, in industrial environments, zinc is more protective of steel than cadmium is because the zinc sulphate corrosion product formed has a lower solubility than cadmium sulphate. Thus zinc sulphate provides a blocking action to reduce subsequent corrosion. This solution is reversed in marine environments, where the corrosion products are carbonates and chlorides. And, zinc provides more soluble corrosion products than cadmium does in this environment. The most desirable

situation is to have the coating anodic to the material beneath it and at the same time to have a very low corrosion rate.

CORROSION PROTECTION BY ELECTROPLATED COATINGS

Electroplated coatings offer corrosion protection of substrate metals in three possible ways: (i) cathodic protection; (ii) barrier action and (iii) environmental modification or control [62, 63]. Cathodic protection is provided by sacrificial corrosion of the coating, e.g., cadmium and zinc coatings on steel. Barrier action involves use of a more corrosion resistant deposit between the environment and the substrate to be protected such as zinc alloy plated automotive parts, copper-nickel-chromium and nickel-chromium coatings over steel. A typical example for environmental modification or control in combination with a non-impervious barrier layer is electrolytic tinplate used in food packaging [1]. The corrosion performance of electroplated coatings is influenced by a variety of factors, which include structure, crystallographic texture, grain size, porosity, impurities and triple junctions, interactions involving metallic underplates and cleanliness or freedom from processing contaminants [64].

Electrodeposits with a dense non-columnar structure offers better corrosion protection compared to deposits with a columnar structure in a water vapor corrosion test. The presence of large voids between the columns in deposits with a columnar structure offers only a minimum protection. Conditions that favor non-epitaxial growth could cause the formation of porosity and voids at the interface between the substrate and deposit. A prolonged acid dip treatment of copper causes pronounced etching and results in the development of the surface having large areas with (111) planes. Such substrates tend to promote non-epitaxial growth of subsequently deposited films with loose adhesion [65].

Texture can noticeably affect the corrosion resistance of electrodeposited coatings. It has been reported that the rate of anodic dissolution of electrodeposited nickel increases in the order (111) < (100) < (110) [66]. The ability of the zinc alloy coating to act either sacrificially or as a protective corrosion barrier is influenced by its texture. Zinc grains with a near (0001) orientation were found to have much lower corrosion currents in sodium hydroxide solutions, than those of other orientations [67]. The corrosion current density in 0.5 N NaOH decreased with increase in packing density of the zinc coating. Raeissi et al. [68] have studied the influence of texture on the corrosion resistance of zinc electrodeposits. Electrodeposition of zinc has resulted in a full epitaxial growth at 10 mA/cm², a completely non-epitaxial growth at 200 mA/cm² whereas both epitaxial and non-epitaxial components coexist at 100 mA/cm². The coatings electrodeposited at 10 and 200 mA/cm² have only one texture component and reveal higher corrosion resistance. High percentage of (00.2) basal planes parallel to the substrate provides higher corrosion resistance for the zinc coating obtained at 200 mA/cm². However, the full epitaxial growth with fewer grain boundaries offers a higher corrosion resistance for coatings obtained at 10 mA/cm². In contrast, the zinc coating formed at 100 mA/cm² allows easier hydrogen discharge and exhibit a relatively lower corrosion resistance compared to those obtained at 10 and 200 mA/cm².

The small grain size and high-volume fraction of grain boundaries could cause a significant influence on the corrosion behavior of electrodeposits as they would allow easier access of the corrosive species to the coating-substrate interface. Grain boundaries in an electrodeposit tend to corrode preferentially and if there is a range of grain sizes, the fine-

grained region tends to corrode faster [69]. The crevices in fine-grained deposits also corrode preferentially. This is due to the fact that the grains in the crevices are even smaller than in the rest of the deposit and they also have a different chemical composition following the incorporation of addition agents [70].

Recently, electrodeposited nanocrystalline (NC) coatings have been identified as promising candidate materials for a variety of applications. It will be of much interest to know how the small grain size and the high-volume fraction of grain boundaries of the nanocrystalline deposits is going to influence their corrosion behavior compared to their polycrystalline counterparts. Studies on the corrosion behaviour of nanocrystalline coatings are rather limited. Only a few studies have addressed the corrosion behavior of nanocrystalline materials [71-78]. Some studies have reported that electrodeposited nanocrystalline coatings offer a better corrosion resistance [72, 74, 75], while some other studies [71-73] report that they are inferior to the conventional polycrystalline coatings.

Rofagha et al. [72, 79] investigated the corrosion behavior of NC nickel (99.99%, 32 nm grain size) and coarse grained nickel (99.99%, 100 μm grain size) in sulphuric acid media. They found that the corrosion potential of NC nickel was shifted about 200 mV positive than that of polycrystalline nickel. Nanocrystalline nickel of grain size 32 nm displayed typical active-passive polarization behavior like pure coarse-grained (100 μm) polycrystalline nickel, but nanocrystalline Ni exhibited higher passive current density [72, 79]. Wang et al. [80] have reported that the corrosion resistance gradually increased with the reduction of grain size from 3 μm to 16 nm. The corrosion resistance of NC Ni is believed to be improved by the rapid formation of continuous Ni hydroxide passive films at surface crystalline defects and the relatively higher integrity of passive films as a result of the smooth and protective nature of the passive films formed on NC Ni coatings. Mishra and Balasubramanian [81] have reported that the passive current densities for nanocrystalline nickel were higher than that for bulk nickel and this has been related to the defective nature of passive film on nanocrystalline nickel. The breakdown potential for fine grain sized nanocrystalline nickel was higher than coarse-grained polycrystalline nickel. The corrosion rate of freshly exposed nanocrystalline Ni was lower compared to bulk Ni, indicating a higher hindrance to anodic dissolution from the nanocrystalline Ni surfaces.

Youssef [78] has reported that NC Zn coatings exhibited improved corrosion resistance compared to electrogalvanized steel in deaerated 0.5 N NaOH solution. The estimated corrosion rate of NC zinc was found to be about 60% lower than that of EG steel, 90 and 229 $\mu\text{A}/\text{cm}^2$, respectively. The passive film formed on the NC zinc surface seems to be a dominating factor for the observed corrosion behavior. The corroded surface of NC zinc exhibits discrete etch pit morphology, while a uniform corrosion was observed on the EG steel surface.

Vinogradov et al. [82] have shown that the corrosion behavior of NC Cu does not change significantly in comparison with coarse-grained polycrystalline Cu and highly localized corrosion is observed in ordinary polycrystalline Cu with relatively large grains. Yu et al. [83] have reported that the surface of NC copper is more active during initial immersion that leads to the formation of a passive film quickly. The uniform passive film then protects the NC copper from further serious corrosion. Stable passivation does not occur on the surface of conventional polycrystalline copper. Therefore, corrosion pits, formed on grain boundaries, impurities, triple junctions and surface defects are more severe on a polycrystalline surface.

A recent study has shown that the superior corrosion resistance of NC Ti in HCl and H₂SO₄ can be attributed to the rapid passivation of NC Ti and the impurity segregation to grain boundaries in polycrystalline Ti [84]. Aledresse and Alfantazi [85] showed that both NC Co (67 nm grain size) and NC Co-P (50 nm grain size, no bulk P concentration given) did not passivate and the corrosion current densities for NC Co and Co-P alloys markedly increased by a factor of about 2 and 20 times, respectively, when compared to that of polycrystalline Co in 0.25M Na₂SO₄ solution (pH 10.5). NC Co and Co-P specimens show more cathodic potential than conventional polycrystalline Co. Scanning electron micrographs of the NC and polycrystalline Co showed excessive uniform corrosion in nanocrystalline specimen, while less of the same type of corrosion was observed for the polycrystalline Co.

Porosity is one of the main sources of discontinuities in electrodeposits and is an important factor that can influence the corrosion behaviour. The factors that influence porosity in electrodeposits include the substrate, the plating solution and its operating characteristics, and post plating treatments. For sacrificial coatings such as zinc or cadmium on steel, porosity is not usually a problem since these coatings cathodically protect the substrate at the bottom of an adjacent pore. However, with noble coatings such as those used in electronic applications, substrates are subject to corrosion at pore sites. Porosity also permits the formation of tarnish films and corrosion products on surfaces, even at room temperature. Pore corrosion in thin gold plated electrical contacts is a well know example. An effective way to minimize porosity is to use an underplate. Another possibility is to deposit coatings with specific crystallographic orientations which can strongly influence covering power and rate of pore closure. Porosity is related to the thickness of electrodeposits. Generally, thicker coatings are less porous and offer better corrosion protection for the substrate. However, thickness alone is not sufficient enough to offer a better corrosion resistance. For example, the corrosion resistance of a chromium deposit depends not so much on its thickness but on its physical state. If the chromium is crack-free or non-porous, then its corrosion resistance is excellent. However, chromium deposits typically do not remain crack-free in service. A small number of cracks are detrimental; however, the presence of many fine microcracks may be beneficial. This is due to the fact that microcracked chromium deposits cause the galvanic corrosion action to be spread over a very wide area. Therefore, localized corrosion is avoided.

Co-deposited metallic impurities can noticeably influence the corrosion performance. For example, small amounts of sulfur in bright nickel deposits noticeably change the corrosion potential. Bright nickel with 0.04-0.15% sulfur displays a more active dissolution potential than semi-bright nickel containing about 0.005% sulfur [86]. If the two deposits are electrically connected, the rate of corrosion of the bright, nickel is increased, whereas the rate of corrosion of the semibright nickel is decreased [87]. Small amounts of copper in bright nickel plating solutions cause significant reductions in salt spray resistance, e.g., 10 ppm of copper results in a 20% reduction whereas 25 ppm of copper enables a 50% reduction.

Underplates are used for a variety of purposes such as improving adhesion of the plated system, as diffusion barriers, or for improving mechanical properties. They are also important in improving corrosion resistance. One example is the use of a nickel layer between a copper substrate and a final gold deposit to prevent diffusion of the copper to the surface where it would subsequently tarnish [64].

Internal stresses can also be harmful. Bright electrodeposits often possess high tensile internal stress and this leads to stress relaxation by way of cracking, which lowers the protective ability of the deposit. When the combined tensile stresses exceed the tensile strength of the plating, cracks can develop and these expose the base metal to corrosive attack. This is particularly serious in the case of chromium electrodeposits where internal stresses often exceed the yield stress, resulting in cracked deposits. The corrosion of gold plated spectacle frames is yet another example for the effect of stress on the deposit. One source of corrosive attack on spectacle frames is the formation of cracks which exposes the substrate to corrosive attack through perspiration. Substrates with locked-in stresses reduce the corrosion resistance of electroplated coatings relative to the same coating on an annealed substrate. Stressed metal is anodic to annealed or lesser stressed metals and is therefore more prone to corrosion in unfavourable service conditions.

The surface of a substrate must be free from soil and oxides before being plated. Besides assuring good adhesion this also prevents contaminants from being trapped at the interface and subsequently causing corrosion problems. Plating salts on the surface or in the pores of an electrodeposit also need to be adequately removed since they can increase the conductivity of adsorbed water and increase the probability of electrolytic or galvanic corrosion [65].

Electrodeposited Coatings Commonly used for Corrosion Protection

Nickel is widely used as a corrosion-resistant coating and as an undercoat for subsequent coatings. It is not resistant in HNO_3 or in environments containing Cl^- ions. However, it corrodes slowly in environments that do not contain Cl^- ions. Nickel is widely used in automotive industry as an underlayer for microcracked chromium to protect steel. Nickel is usually plated as part of a multilayer coating system in which the electrode potential of each layer is different from those of other layers. The outer layer is more anodic than the layer beneath it. Electrodeposited nickel-phosphorus coatings offer much better corrosion resistance than that of electrodeposited nickel in all environments. If the phosphorus content is above about 10%, the coating is amorphous and therefore lacks grain boundaries or other crystalline defects at which corrosion can be initiated.

Cadmium is generally preferred for the protection of steel in marine environments and aircraft components while zinc is preferred in industrial environments. Both Zinc and cadmium could offer sacrificial protection to the steel components under corroding conditions. Cadmium is much more toxic than zinc and tends to embrittle high-strength steel more than zinc does. It is better to avoid cadmium in applications in which its corrosion products may get into the environment. Generally corrosion performance of both zinc and cadmium is enhanced by chromate conversion treatments. Electrodeposited zinc has been widely used for protection of steel from corrosion. A drawback with zinc plating however, is the large amount of corrosion products formed and the very high dissolution rate of zinc when coupled with iron due to the large potentials difference between these two metals. Zn-Ni alloy coatings offer much better corrosion resistance compared to the conventional zinc. The presence of nickel also imparts a good barrier resistance to the coating. The concentration of the alloying metal (Ni) is critical in determining the corrosion resistance properties of the coatings. An enhancement in noble metal composition would lead to a shift in the open circuit potential towards the noble direction, which in turn will reduce the driving force for the galvanic corrosion. Also, the

barrier properties associated with such deposits will be superior compared to other coatings. Zn-Ni-X (X = Cd, Cu, P) ternary or quaternary alloy coatings would induce barrier properties to the sacrificial Zn-Ni alloy thereby extending the life of the coating.

Chromium is resistant to atmospheric corrosion, but is soluble in HCl or in alkaline (caustic) solutions. Its resistance to corrosion is because of the formation of an amorphous chromium oxide that acts as a passive film to protect the metal. Chromium is deliberately deposited for decorative and wear applications as a microcracked coating over nickel so that corrosion currents are uniformly distributed over a large area. Tin is widely used as a barrier and as an anodic coating for steel and copper. Since tin is readily solderable and its oxide is conducting, it finds application in electrical conductors and contacts. Its corrosion products are non-toxic. Therefore tinned containers are widely used in the food industry. Lead is stable in most atmospheres and in both chromic acid and sulphuric acid electrolytes. However, it is affected by chlorides. Lead electrodeposits form very inert passive films that tend to reduce the effects of galvanic corrosion.

Copper is not very good at resisting corrosion in the atmosphere and it tarnishes rapidly. When used alone, it should be protected by a suitable corrosion inhibitor. On the other hand, copper is often present in a coating system because, its small grain size reduces the porosity and thus improves the corrosion resistance of subsequent coatings. Gold is often used for decorative purposes and for electrical contact applications. Gold that is plated directly over copper will increase the corrosion rate of the copper through the unavoidable porosity of the gold deposit. Also, gold will diffuse rapidly into copper base metal. Therefore, electroplated nickel or cobalt coatings are normally plated beneath the gold coating.

COMPOSITIONALLY MODULATED MULTILAYER COATINGS

Compositionally modulated multilayers (CMM) are coatings that consist of a number of layers each composed of two sublayers of different metals or alloys. These coatings are produced using either a single bath or dual baths. In dual bath technique, the substrate is successively transferred between two separate plating baths and each layer is deposited alternatively to laminate the sublayer from the relevant bath. Dual bath technique has the disadvantage that it is susceptible to the formation of an oxide layer on the substrate during the transfer between the baths. Such an oxide layer can deteriorate the quality of the multilayers. In the single bath technique, an electrolyte containing two or more metals can be used. Deposition of multilayers from a single bath is normally carried out by periodically varying the current density owing to the difference in the reduction potential of the metal ions present in the electrolyte. Multilayer coatings have better corrosion resistance and physicomechanical properties than those observed in common alloys [88-90].

The use of CMM Zn-Ni alloy coatings for protection of steel substrate from corrosion has been extensively investigated. The cross-sectional morphology of Zn-Ni CMM coating with 12 individual layers is shown in Fig. 13.7. Kalantary et al. [91] obtained zinc-nickel CMM coatings with an overall thickness of 8 mm by electrodepositing alternate layers of zinc and nickel from zinc sulphate and nickel sulphate electrolytes. Due to the finer structure in each thin layer and the multiple layer effect, a significant improvement in the corrosion resistance is observed for Zn-Ni CMM coatings compared to pure Zn coatings. Chawa et al. [92] have also reported that the corrosion resistance of Zn-Ni CMM coatings obtained from zinc sulphate and nickel

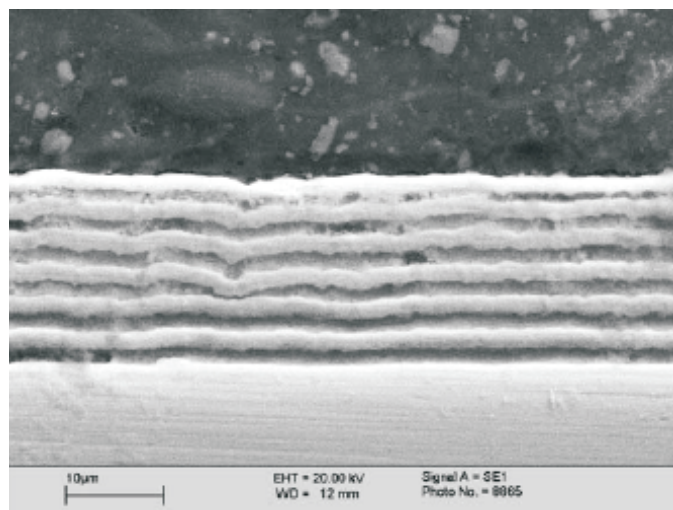


Figure 7 Cross-sectional morphology of Zn/Ni CMM coating with 12 individual layers (reprinted with permission of Elsevier Science, Inc., New York)

sulfamate baths was better than that of zinc or nickel monolithic coatings of a similar thickness. Zhong et al. [93], have studied the corrosion performance of Zn-Fe CMM coatings while Kirilova et al. [94] and Kirilova and Ivanov [95] have reported on the formation and corrosion behaviour of Zn-Co CMM coatings. Ivanov et al. [88, 89] have studied the corrosion performance of zinc-nickel CMM coatings obtained from a single and dual baths. According to them, CMM Zn-Ni coatings consisting of a large number of thin sublayers (11 or 12 of about 0.7 μm thick) are more corrosion resistant than the CMM Zn-Ni coatings consisting of a few thick sublayers (five or six of about 3 μm thick) with the same total thickness. CMM Zn-Ni coatings ending with a Ni oversublayer offer better corrosion resistance than CMM Zn-Ni coatings ending with Zn oversublayer.

Fie and Wilcox [90] have evaluated the corrosion performance of CMM Zn-Ni coatings using a salt spray test. According to them, the corrosion resistance of CMM Zn-Ni coatings was much better than that of a single-layer zinc or nickel deposit, and among the CMM Zn-Ni coating systems, coatings with a nickel sublayer adjacent to the steel substrate and zinc as the top layer (Ni/Zn CMM coating system) have the best protective performance than those with zinc sublayer adjacent to the steel and nickel as top layer (Zn/Ni CMM coating system). For either Zn/Ni or Ni/Zn CMM coating system, the zinc-nickel CMM coatings with the individual sublayer thickness of 2 μm have the longest time to red rust amongst the samples tested. Fie and Wilcox [90] have proposed a probable mechanism to account for the corrosion behaviour of zinc-nickel CMM coatings. Fig. 13.8 illustrates schematics of the probable corrosion mechanisms for zinc-nickel CMM coatings during corrosion process.

Diagrams A and B show the structures of two Ni/Zn CMM coatings with different individual layer thicknesses. Initially, zinc top layers corrode completely, then the zinc sublayers dissolve through the pores in the nickel sublayers. Diagrams C and D exhibit the structure of two Zn/Ni CMM coatings, with different individual layer thicknesses. The zinc

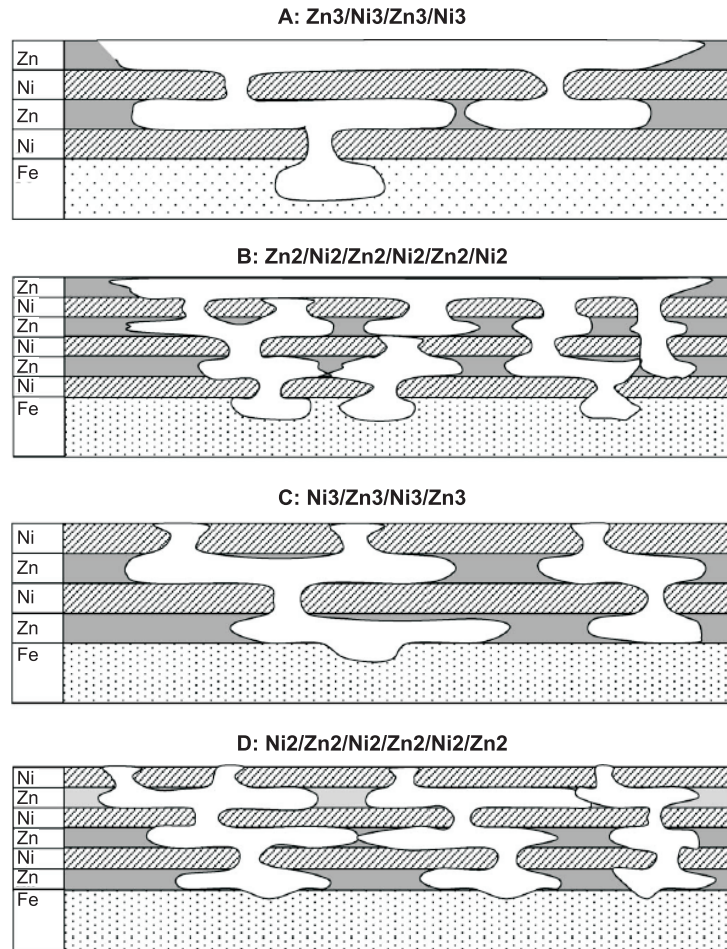


Figure 8 Probable corrosion mechanism diagram for Ni/Zn and Zn/Ni CMM coatings (reprinted with permission of Elsevier Science, Inc., New York)

sublayer beneath the nickel top layer dissolves through the pores existed in the nickel deposits during corrosion process. As a whole, the protection efficacy of zinc–nickel CMM coatings may be thought to depend on the barrier effect of the nickel sublayers and the sacrificial effect of zinc sublayers. Hence it appears that pores and microcracks of the nickel sublayer play an important role in deciding the corrosion resistance of Zn–Ni CMM coatings. Increase in thickness of the nickel sublayer could reduce the porosity but it may lead to the formation of microcracks following tensile stress. It is now observed that the electrodeposition of Zn–Ni CMM coatings with greater than twenty individual layers is quite possible. Attempts on electrodeposition of compositionally modulated alloy multilayer (CMAM) coatings by depositing alloy sublayers under different plating conditions from single bath has also been made.

CORROSION PROTECTION BY ELECTROLESS PLATED COATINGS

Electroless nickel coatings have excellent corrosion resistance in many industrial environments and is not susceptible to stress corrosion cracking. They are widely used either as protective or decorative coatings in many industries, such as petroleum, chemical, plastic, optics, printing, mining, aerospace, nuclear, automotive, electronics, computer, textile, paper, and food [96, 97]. Recently, the use of EL Ni coatings for corrosion protection of steel reinforcement bar has been suggested by Singh and Ghosh [98]. The corrosion protective ability of electroless Ni-P coatings to improve the life-time of components and assemblies used in a variety of industries is given in Table 13.9. Electroless nickel does not perform as a sacrificial coating in the same way that electrodeposited Zn or Cd performs on steel substrate to provide protection against corrosion. It behaves as a true barrier coating, protecting the substrate by sealing it off from the corrosive environments. Consequently, the thickness of the deposit and the absence of porosity are of great importance. The electroless nickel coating shows superior corrosion resistance compared to electroplated nickel coatings. The most important factors that determine the corrosion resistance are [42]:

- Substrate composition, structure and surface finish
- Pretreatment of the substrate to achieve a clean, uniform surface
- Adequate deposit thickness to meet the severity and time of exposure
- The properties of the deposit (composition, porosity, internal stress etc.) which depends on pH, formulation and prolonged use (turnover) of the plating solution
- Post plating treatments of the coating such as passivation and annealing
- The aggressiveness of the corrosive environment condition

The corrosion resistance of electroless Ni-P coatings varies with the phosphorus content of the coating: relatively high for a high phosphorus but low for a low-phosphorus electroless nickel coating. The better corrosion resistance of electroless Ni-high P coating is a result of its amorphous nature and passivity of the surface film formed on it. Amorphous alloys offer better resistance to corrosion attack than equivalent polycrystalline materials because of the freedom from grain or phase boundaries and because of the glassy film which form on and passivate their surfaces [99].

In general, high phosphorus (10-12 wt.% P) electroless Ni-P coatings are more resistant to acidic environments and products that hydrolyze readily to form acids. Low phosphorus (1-3 wt.% P) electroless nickel coatings are more resistant to strong alkaline environments than medium (6-8 wt.% P) and high phosphorus electroless nickel coatings [100-102]. It is important to recognize here that coating porosity is most significant in acidic environments when ferrous substrates are involved. In alkaline environments porosity is not normally a factor. The assumption that high phosphorus electroless nickel coatings always enhance corrosion resistance is misplaced as low phosphorus electroless nickel coatings are being successfully used in a variety of environments in the caustic soda production industry; corrosion performance of medium phosphorus and high phosphorus electroless nickel coatings in sodium hydroxide environments being relatively inferior.

The better corrosion resistance offered by electroless Ni-high P coatings can be explained as follows: Electroless Ni-P coatings undergo preferential dissolution of nickel even at open circuit potential, leading to the enrichment of phosphorus at the surface layer. The enriched

Table 9 The corrosion protective ability of electroless Ni-P coatings to improve the life-time of components and assemblies used in a variety of industries [97]

Type of industry or application	Component or assembly and its purpose	Type of environment or problem and its severity	Materials used and the normal service life	Recommendations for improvement in service life and the performance of electroless Ni coatings
Chlor-alkali industry	Steel compressors-diaphragm	Build-up of sodium sulphate and ferric chloride resulting in corrosion and erosion.	Steel - Needs repair in less than one year; total life time with repair is 8 years the	High P EL Ni deposits - double compressor life - 15 years - significant cost reduction and production savings
	Control valve used to concentrate NaOH	34% NaOH and 7% NaCl in water; 95°C; 380 L/min at a rate of 1.75 m/sec.	316 SS - 2 weeks N08020 alloy 20 - 3 months coating	A 50 micron low P EL Ni has significantly increased the life time
	Components or assemblies used in transporting brine	Saturated brine; pH :5.6; temperature: 70°C	316 SS - pitting corrosion N02200 - not suitable Rubber lining - 8 years	75 microns high P EL Ni. The life time is increased to 15 years.
	Cooling towers used to reduce the temp. of NaOH	Cooling tower water; 35°C; air, Na ₂ CO ₃ and NaCl; pH: 8.5; Flow rate:1.83 m/sec.	Steel pumps - within 2 years - corrosion erosion and cavitation	75 microns high P EL Ni - No corrosion or service problems even after 3 years
Transportation of chemicals by rail cars or tank cars	Nuts and bolts - loading valves on tank cars used for shipping	50% NaOH	641400 (ASTM 193-7) alloy steel - corroded within a short time; risk of failure in transit	25 microns Low P EL Ni - no failure after 3 years; after 5 years - 70% of the bolts are in satisfactory condition
	Safety vents; unloading connections/ barges; valve assemblies	50% NaOH or high purity NaOH	Poor corrosion resistance - discolouration due to iron contamination	50 micron low P EL Ni - Excellent corrosion resistance - prevented discolouration due to iron contamination
Chemical plants	Seawater cooling - Hot taps	Chloride ions - severe crevice corrosion - stagnant seawater	Steel	75 microns high P EL Ni - excellent corrosion resistance - no corrosion or leakage for over 3 years

Table 9 Contd.

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Distillation of organic compounds	Flow meters	Aqueous solutions containing 31% KOH plus 19% K ₂ CO ₃ ; 105°C	316 SS – stress corrosion cracking (SCC) failure	Low P EL Ni - much lower corrosion rate compared to 316SS; Combination of low P EL Ni-316SS -very successful
Food Processing industry	Distillation column	Monochlorotoluene; Severe plugging of the column due build-up of corrosion products	Mild steel – Frequent and plant shutdown	75 microns high P EL Ni – no plugging of corrosion products and no plant shutdown for over 4 years
Oil and gas industry - Surface and offshore operations	Packaging equipment – bearing, rollers, conveyer systems, hydraulics & gears	NaCl, nitrates, citric acid and acetic acid; humid atmosphere: up to 200°C	Stress corrosion cracking and fatigue failure of process equipment	High P EL Ni – Excellent corrosion resistance - replacement for Cr plating in bakery industry
	Ball valve	Crude oil production - associated gas contains 55% H ₂ S; 80°C; Pressure: 3000 psi	mild steel ball valves –3 months maximum - failure due to corrosion, surface cracking and erosion	75 microns of EL Ni extended the life of the assemblies enormously - No surface deterioration was after two years of continuous service.
	Ball valve used for seawater injection system	Pumping seawater under high pressure	Mild steel	A 75 micron EL Ni coating on the valves – No degradation for more than 4 years of operation.
	Valves, chokes	Khuff gas – 6 mole % CO ₂ and 0.1 mole % H ₂ S; Condensate – Hexane 28 L/Mm ³ & 7 L/Mm ³ water; Pressure: 5000 psi; 90°C; gas velocity: 6 m/sec.	Carbon steel – severe pitting corrosion and corrosion rate: 3-5 mm/year erosion;	25 micron EL Ni for chokes 75 micron valve – No corrosion for at least 6 years
	Tubular component	H ₂ S, CO ₂ , Cl ⁻ ; 260°C	Mild steel – corrosion and erosion; Stainless steel – pitting and galling	50-100 micron high P EL Ni – significantly improves the life-time
	Pumping systems – housing, impellers and discharge barrels	Mixture of clay and water – corrosive and abrasive – a combination of O ₂ and H ₂ S; high pressure	AISI 8630 steel – corrosion fatigue or stress corrosion in seal areas – after 3 months of operation	25-75 micron high P EL Ni – increase the service life of mud pumps for more than 18 months

Table 9 Contd.

Table 9 Contd.

Automotive industry	Pistons, carburetor parts, fuel injectors, engine bearings, gear assemblies	Corrosion of carburetor due to alcohol fuel; corrosion the products plug the narrow channels and orifices	Zinc diecast	5-9 micron high P EL Ni – improve performance of the carburetor
Aerospace industry	Compressor components	Corrosive atmosphere and erosive particles; 425°C; non-uniform thickness; Cd embrittlement	410 SS – Ni/Cd alloy coating by diffusion of Alumidecoating	High P EL Ni – excellent corrosion resistance
	high-pressure compressor stator assemblies	Refurbishing	410 SS	8-16 microns High P EL Ni (9-11%) compressively stressed deposit provides excellent gas flow path; greatly enhance the corrosion and erosion resistance for 5800 take-offs and landings
	High-pressure compressor spacer	Overhauling/repair	AMS 6304 alloy	High P EL Ni – uniform coverage and protection that was not possible with other coating systems
	Commercial and military aircraft engine	Compressor case components Corrosion and erosion at 425°C	Martensitic and ferritic iron base alloys and wrought alloy steel	8-25 microns high P EL Ni – improve the performance
	Landing gear of Boeing 727	Corrosion and erosion	High strength steel – ED Cd	8-16 micron high P EL Ni – improve the performance
	Support equipment – catapult covers and tracks used for launching of planes from aircraft carriers	Salt water/Steam at 230°C; force: 4.45 MN Wear and corrosion;	Galvanic corrosion between the track and covers Failure - Within 6-12 months	100 micron EL Ni 12 micron Cd and chromated – 14 to 18 years
Textile industry	Drop wires and needles	Weaving process – various chemicals applied to the fabric; corrosive	Steel – rusting could cause stain in the fabric	High P EL Ni

phosphorus surface reacts with water to form a layer of adsorbed hypophosphite anions (H_2PO_2^-). This layer in turn block the supply of water to the electrode surface, thereby preventing the hydration of nickel [103, 104], which is considered to be the first step to form either soluble Ni^{2+} species or a passive nickel film. Such a condition of phosphorus enrichment at the surface would enable hydrolysis of phosphorus and retard hydrolysis of nickel.

Electroless Ni-B coatings are considered to have lesser resistance to corrosion compared to electroless Ni-P coatings. The difference in corrosion resistance between electroless Ni-P and Ni-B coatings is due to the difference in their structure. Since the electroless Ni-B coating is not totally amorphous, the passivation films that form on its surface are not as glassy or protective as those that form on electroless high-phosphorous coatings [105, 106, 58]. The phase boundaries present in these deposits also produce passivation film discontinuities, which are preferred sites for corrosion attack to begin. Also, the inhomogeneous distribution of boron and thallium create areas of different corrosion potential on the surface, leading to the formation of minute active/passive corrosion cells and accelerated the corrosion attack.

Porosity is an important factor that influences the corrosion resistance of electroless nickel coatings [107]. In general, thicker coatings have fewer pores and hence provide a better corrosion resistance [41, 108, 109]. To achieve better corrosion resistance the minimum thickness recommendations are typically 40 μm in mild and moderate environments; but in severe corrosive environments a thickness of 75 μm is preferred. Besides porosity and coating thickness, the corrosion performance of electroless nickel coatings also depends on the surface finish. Generally, smoother substrate surface provide better quality deposits. Mechanical surface treatments and fabrication procedures, such as, grit blasting, casting, rolling, stamping, shearing, lapping, drawing, machining, etc., could create surface imperfections. These surface imperfections could lead to entrapment of solutions which could cause a premature failure. For a given roughness the corrosion potential was found to shift to nobler values and the corrosion current decreased considerably with the increase in thickness of electroless nickel coatings [108]. The tramp constituents co-deposited in electroless nickel matrix influence the corrosion resistance of the resultant coatings. Most of these tramp constituent originate from the stabilizers used in the plating bath. Non-metallic inclusions in the surface of the substrate material such as, carbides, sulphides etc., emanating from alloying elements or impurities can breed pores in the electroless coating, resulting in a decrease in corrosion resistance. Ageing of electroless nickel bath also has a pronounced and detrimental influence on the corrosion resistance of the resultant deposits [110].

For achieving better hardness and improved wear resistance, electroless nickel coatings are usually heat-treated around 400°C for 1 hour. During heat treatment the electroless nickel coatings undergo shrinkage in volume which may cause cracks through the coating, particularly when the microhardness exceeds 900 HV_{100} [96]. This impairs the corrosion resistance of such heat treated electroless Ni-P deposits [41-44]. Low temperature post-plating baking (preferably in vacuum) at temperatures around 200°C provides the optimum corrosion resistance to low and medium carbon steels. When corrosion resistance along with additional hardness is required, a heat treatment temperature of approximately 300°C is recommended to prevent micro-cracking and to limit porosity. At very high temperatures a tenacious oxide film will rapidly form on the coating surface. This film helps to seal the pores and create a passive surface so that electroless Ni-P coatings can withstand the corrosive attack. At temperatures above 650°C the Ni-Fe intermetallic formed at the interface is ductile and dense and reportedly

has very good corrosion resistance [102]. Proper and careful post plate treatments can appreciably enhance the corrosion resistance of electroless Ni-P coatings. A 15 minute immersion treatment in hot 1 wt.% CrO_3 solution after plating doubles the salt spray resistance of electroless Ni-P coatings on carbon steel.

Electroless Ni-P and Ni-B based ternary/quaternary alloy coatings, electroless composite coatings, duplex coatings, graded coatings and multilayer coatings are some of the promising developments in electroless plating processes for achieving improved corrosion resistance. The corrosion resistance of the electroless ternary alloy coatings is governed by the phosphorus/boron content as well as the alloying element. The most important factors that determine the corrosion resistance of electroless nickel coatings are also applicable for electroless ternary alloy coatings [111].

The corrosion resistance of as plated electroless Ni-Cu-P deposit is superior to electroless Ni-P deposit or 1Cr18Ni9Ti stainless steel in 50 wt.% NaOH [51]. Liu and Zhao [112] have reported that the anti-corrosion performance of Ni-Cu-P coatings with 17.2 wt.% Cu is superior to the Ni-P coatings and copper in 1 N HCl and 20% NaCl. They have also reported that alloying of Cu in Ni-P and Ni-P-PTFE composite coatings exhibit improved corrosion resistance in HCl and NaCl [113, 114].

Lee and Liang [52] have studied the corrosion resistance of electroless Ni-Mo-P alloy deposits and found that these deposits are more resistant to corrosion attack than are electroless Ni-P deposits. Lu and Zangari [53] have reported that addition of Mo to Ni-P alloys has little or no beneficial effect on corrosion properties.

Aoki and Takano [115] and Bangwei et al. [116] found out that codeposition of tungsten along with nickel and phosphorus in an electroless deposit, increases the protective effect of the film on steel and the extent of protection offered is a function of the tungsten content of the film. The protective effect of electroless Ni-W-P was also addressed by Mallory and Hajdu [42]. Accordingly, deposits containing about 20 wt.% tungsten were resistant to attack by concentrated HNO_3 and 7N HCl. An electroless nickel deposit containing 9.1 wt.% tungsten and 8.2 wt.% phosphorus was considerably more protective to steel than the electroless Ni-P deposit. Tungsten addition increases the corrosion resistance of electroless Ni-P and Ni-B coatings [117].

Tungsten and molybdenum addition are known to improve resistance to uniform, pitting as well as crevice corrosion of Ni in non-oxidizing acid solutions [56]. However, they offer only a limited improvement in corrosion resistance in oxidizing electrolytes. Heat treatment of EL Ni-W-P and Ni-Mo-P coatings also reduces their resistance to corrosion.

Electroless Ni-Zn-P deposit is recommended as a protective coating against corrosion for automobile components [54, 55]. This deposit can be used as a potential alternative for cadmium plating for uniformly coating complex shapes and threaded parts [42]. Veeraraghavan et al. [118] have suggested that EL Ni-Zn-P coatings with 16.2 wt.% Zn could be used as a sacrificial coating for the protection of steel. The high nickel content (74 wt.%) offers better corrosion resistance compared to conventional zinc based coatings.

There is a general belief that the corrosion resistance of electroless Ni-P composite coatings is lesser than that of electroless Ni-P coatings. The codeposited second phase particles present in the electroless nickel matrix are thought to reduce passivity and corrosion resistance. Hence

for applications requiring good corrosion resistance, a duplex coating, consisting of an initial electroless Ni-P coating followed by an electroless Ni-P composite coating, is recommended in place of electroless Ni-P composite coatings [119, 120]. However, the corrosion performance of electroless Ni-P composite coatings was found to be satisfactory by Hubbell [121], Hussain and Such [122] and Shoeib et al. [123]. Studies on the corrosion resistance of electroless Ni-P-Si₃N₄ composite coatings in 3.5% sodium chloride solution also revealed a marginal increase in corrosion resistance compared to plain electroless Ni-P deposit of similar thickness [124]. Evaluation of the corrosion resistance of electroless Ni-P-Si₃N₄, Ni-P-CeO₂ and Ni-P-TiO₂ composite coatings by electrochemical impedance spectroscopy suggest that these composite coatings provide better corrosion resistance than plain electroless Ni-P coatings [125].

Sankara Narayanan et al. [58] have studied the corrosion behaviour of electroless Ni-P/Ni-B duplex coatings in comparison with Ni-P and Ni-B coatings of similar thickness (Table 13.10). Amongst the two sets of duplex coatings, better corrosion resistance is offered by the duplex coating having Ni-P coating as the outer layer and its thickness is 10 μm or higher. The duplex coating having Ni-B as the outer layer also offers better corrosion resistance than EL Ni-B deposits. Though heat-treatment (400°C for 1 hour) tends to reduce the extent of corrosion resistance, the performance of duplex coatings is not drastically reduced. Hence, the electroless Ni-B/Ni-P duplex coating will be a useful replacement for Ni-B and Ni-P coating.

Table 10 Corrosion resistance of electroless Ni-P, Ni-B, Ni-P/Ni-B and Ni-B/Ni-P duplex coatings in as-plated and heat-treated conditions in 3.5% NaCl

System studied	Thickness (μm)	E _{corr} (mV vs.SCE)	i _{corr} (μA/cm ²)	R _{ct} (Ohms.cm ²)	C _{dl} (F) × 10 ⁻⁴
Ni-P as-plated	20	-354	3.62	7960	1.85
Ni-P heat-treated	20	-492	6.89	6498	2.36
Ni-B as-plated	20	-508	9.15	3844	3.53
Ni-B heat-treated	20	-519	14.60	1232	4.22
Ni-P/Ni-B as-plated	10 + 10	-386	3.86	7638	1.89
Ni-P/Ni-B heat-treated	10 + 10	-432	4.93	5339	2.44
Ni-B/Ni-P as-plated	10 + 10	-311	2.46	10130	1.61
Ni-B/Ni-P heat-treated	10 + 10	-356	3.24	7024	1.96

Table 11 Corrosion resistance of non-graded and graded electroless Ni-P coatings in 3.5% sodium chloride solution

System studied	E _{corr} (mV vs. SCE)	i _{corr} (μA/cm ²)	R _{ct} (KΩ.cm ²)	C _{dl} (μF)
EL Ni-Low P coating (L)	-536	4.22	6.90	289
EL Ni-Medium P coating (M)	-434	1.17	24.86	55.60
EL Ni-High P coating (H)	-411	0.60	37.45	49.10
EL Ni-P graded coating (LMH)*	-403	0.41	38.22	36.70
EL Ni-P graded coating (HML)*	-481	1.70	14.77	103

* LMH - Low-Medium-High P; HML - High-Medium-Low P.

Sankara Narayanan et al. [59] have studied the corrosion behaviour of EL Ni-P graded coatings in comparison with EL Ni-P coatings with different P contents (Table 13.11). The EL Ni-P graded coatings offer a better corrosion resistance compared to EL Ni-P non-graded coatings. Among the two types of EL Ni-P graded coatings, the coating system with EL Ni-high P coating as the outer layer offers better corrosion resistance than its counterpart. However, the corrosion resistance of EL Ni-P graded coating with EL Ni-low P as the outer layer is better than that of electroless Ni-low P coating, due to the barrier properties of the underlying Ni-medium P and Ni-high P layers. Based on their ability to offer corrosion resistance the coatings can be ranked in the following order:

EL graded Ni-P(LMH) > EL Ni-high P > EL Ni-medium P > EL graded Ni-P(HML) > EL Ni-low P

Heat-treatment of electroless Ni-P graded coatings is likely to modify the graded layers so that the gradation is lost. Hence the concept of graded electroless Ni-P coatings is valid only in as-plated condition. Besides, heat-treatment (400°C for 1 hour) drastically reduces the corrosion resistance of these coatings.

Chen et al. [60] have explored the possibility of using multi-layered electroless Ni-P coatings to improve the corrosion resistance of powder-sintered Nd-Fe-B permanent magnet. Since Nd-Fe-B reacts quickly with Cl⁻ and SO₄²⁻ ions in acidic solutions, the Nd-Fe-B magnet was first treated with an alkaline electroless nickel plating bath to deposit a low-P electroless nickel layer. Subsequently, a high-P electroless nickel layer was deposited using an acidic electroless nickel plating bath. Good adhesion of the coating is achieved by the intermediate low-P electroless Ni coating. The electroless Ni-P multilayer coating offers excellent corrosion resistance to Nd-Fe-B magnet. Though there is a loss in magnetic properties due to the multilayer coating, the remaining values are still very attractive for practical applications.

Gu et al. [61] have studied the role of multilayer coatings consisting of different layers of Ni-P and Ni obtained by electro- and electroless deposition processes to improve the corrosion resistance of steel. The difference in the corrosion potential among layers plays a very important role in protecting the steel substrate from rusting. The three-layer coating consists of electroless Ni-low P/electrodeposited Ni/electroless Ni-high P layers, from the surface to substrate, respectively, offers excellent corrosion resistance to the steel substrate. In the salt spray test, the time of the emergence of the first red rust spot for this multilayer coating is about 936 hours, which is 3.5 times of that of Ni-high P coating.

The mechanism of corrosion resistance of this multilayer coating can be explained as follows: when corrosion occurs on the upper electroless Ni-low P layer, some corroded pinholes would lead to localized galvanic corrosion and penetrates vertically from the upper surface layer. When these pinholes meet the electrodeposited Ni layer, the mode of corrosion changes from the original longitudinal corrosion to the extended transverse corrosion since the electrodeposited Ni layer would corrode easily due to its lowest corrosion potential (E_{corr}). This corrosion mode is described in step 1 of Fig. 13.9, which is similar to that observed in duplex nickel coatings consisting of semi-bright nickel and bright nickel layers [126]. The transverse corrosion of the electrodeposited Ni layer disperses greatly the corrosion current and provides a sacrificial protection for the upper electroless Ni-low P layer. As a result, the outer surface of coating maintains its original appearance. When the electroplated Ni layer was consumed out by corrosion in some local regions, the upper electroless Ni-low P layer starts to corrode and continues to protect the bottom layer from corroding (step 2 in Fig. 13.9). Thus, the upper and

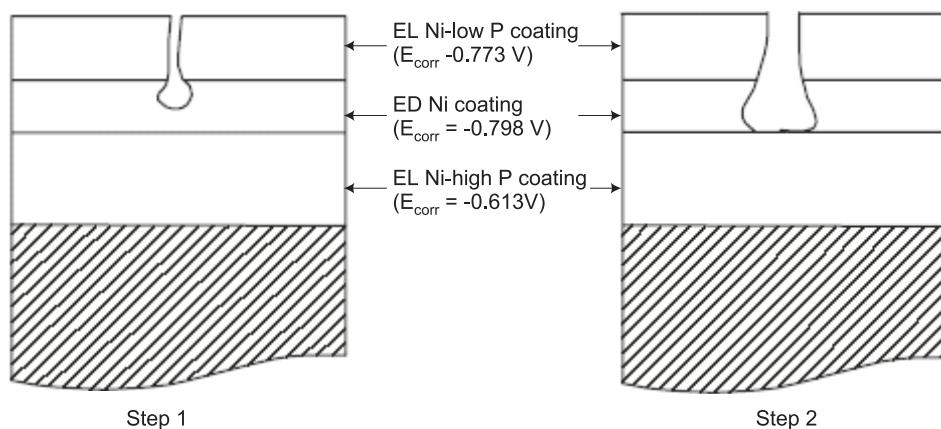


Figure 9 Schematic of the corrosion mechanism of EL Ni-low P/ED Ni/EL Ni-high P coating; Step 1: ED Ni-layer emerged through the pinhole corrosion and corrosion of ED Ni-layer occurs; Step 2: When corrosion reaches the third layer of EL Ni-high P layer, both upper EL Ni-low P and intermediate ED-Ni layers corrode alternately
Source: [61] (reprinted with permission of Elsevier Science, Inc., New York)

the middle layers corrode alternately in a low corrosion rate and delay the rusting of the steel substrate. Besides, the corrosion products formed during the corrosion process could also block some pinholes and delays the rusting of the steel substrate [127].

Gu et al. [62] have also reported the corrosion protective ability of a 45 μm thick multilayer coating on AZ91D Mg alloy prepared by electroless deposition process. The composition of this multilayer coating from substrate to surface was a protective layer of EL Ni-P deposit, a Ni-P layer with 9.2 wt.% P and another Ni-P layer with 5.4 wt.% P, respectively. Since the corrosion potential of the surface layer (EL Ni-5.4 wt.% P) was lower than that of the middle layer (EL Ni-9.2 wt.% P), when the pitting corrosion penetrates from the surface layer to the middle-layer, the surface layer would corrode preferentially. As a result, the pinning corrosion will not develop vertically to the coatings. This mechanism offers a better corrosion resistance for the AZ91D Mg alloy.

CONCLUDING REMARKS

This chapter presents an overview of the fundamental aspects of electro- and electroless deposition process, the mechanism of deposition, alloy deposition, etc. and the utility of these coatings for corrosion protection. Both electro- and electroless deposition techniques are simple, cost-effective and offer unique advantages for preparing deposits with desirable qualities. In electrodeposition, the plating rate, stability of the bath and the number of turnovers are very high but the resultant coatings lack uniformity on complex shapes and blind holes and they need a post-finishing treatment to achieve the desired performance.

In electroless deposition, the plating rate, bath stability and the number of turnovers are relatively less but the resultant coatings are more uniform and do not require post-finishing treatment. Electroplated coatings offer corrosion protection to the substrate metals in three possible ways: (i) cathodic protection; (ii) barrier action; and (iii) environmental modification

or control. The corrosion performance of electroplated coatings is influenced by a variety of factors, which include structure, crystallographic texture, grain size, porosity, impurities and triple junctions, interactions involving metallic underplates and cleanliness or freedom from processing contaminants. Electroless nickel does not perform as a sacrificial coating in the same way that electrodeposited Zn or Cd performs on steel substrate to provide protection against corrosion. It behaves as a true barrier coating, protecting the substrate by sealing it off from the corrosive environments. Consequently, the thickness of the deposit and the absence of porosity are of great importance. The electroless nickel coating shows superior corrosion resistance compared to electroplated nickel coatings. The most important factors that determine the corrosion resistance of electroless plated coatings are: substrate composition, structure and surface finish; pretreatment of the substrate to achieve a clean, uniform surface; adequate deposit thickness to meet the severity and time of exposure to the corrosive environment; the properties of the deposit (composition, porosity, internal stress etc.) which depends on pH, formulation and prolonged use (turnover) of the plating solution; post plating treatments of the coating such as passivation and annealing; and the aggressiveness of the corrosive environment condition. Electro- and electroless deposited ternary/quaternary alloy coatings, composite coatings, duplex coatings, graded coatings and multilayer coatings are some of the promising developments to achieve improved corrosion resistance.

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