Electroless alloy/composite coatings: A review

R C AGARWALA* and VIJAYA AGARWALA

Metallurgical and Materials Engineering Department, Indian Institute of
Technology, Roorkee 247 667, India
e-mail: ramesfmt@iitr.ernet.in

Abstract. Since the inception of electroless coating by Brenner & Riddell in 1946, it has been the subject of research interest and, in the past two decades, emphasis has shifted to the studies of its properties and applications. The co-deposition of particulate matter or substance within the growing film has led to a new generation of electroless composite coatings, many of which possess excellent wear and corrosion resistance. This valuable process can coat not only electrically conductive materials including graphite but also fabrics, insulators like plastics, rubber etc. The low coating rates with these can provide better reflectivity of plated surfaces and many more applications. Coatings can be tailored for desired properties by selecting the composition of the coating alloy/composite/metallic to suit specific requirements. The market for these coatings is expanding fast as the potential applications are on the rise. In the present article, an attempt has been made to review different electroless alloy/composite coatings with respect to bath types and their composition, properties and applications. Different characterisation studies have been conducted on various electroless nickel-based coatings with emphasis on wear and corrosion properties.

Keywords. Electroless nickel; electroless bath; composite coating.

1. Introduction

Electroless coatings can be divided into three main categories like (i) alloy coatings, (ii) composite coatings and (iii) metallic coatings. Electroless coating technology is credited mainly to Brenner & Riddell (1946). By the controlled chemical reduction reaction, the electroless coating chemistry has emerged as one of the leading growth areas in surface engineering, metal finishing etc. and is estimated to grow at a rate of beyond fifteen percent per annum, certainly no other chemistry is growing at this rate. Electroless coatings has unique physicochemical and mechanical properties for which they are being used increasingly. Some of the properties which render them usable are:

- Uniformity ($\pm 2 \cdot 5\ \mu$m)
- Excellent corrosion resistance
- Wear and abrasion resistance

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*For correspondence

- Solderability
- High hardness
- Amorphous, microcrystalline deposit
- Low coefficient of friction
- High reflectivity
- Resistivity
- Magnetic properties

Most applications of the electroless coating are based on their wear and corrosion resistance. However, the characteristic like luminescence has a great potential in defence and aerospace applications. Table 1 enumerates the various applications of electroless nickel based coatings (Agarwala *et al* 1999).

2. Alloy coatings

Apart from plating by reduction reaction, two other methods have also been reported. These include immersion plating on steel from solutions of nickel chloride and boric acid, and decomposition of nickel carbonyl vapour on steel substrate (Parker 1972; Gaurilow 1979). However, the latter is hazardous and former is poorly adherent and non-protective. The advantage of using the autocatalytic reduction reaction is in maintaining overall uniformity of coating in composition and thickness which is independent of the thickness variations of the substrate (Agarwala 1987). Several binary and ternary alloys have been deposited, these include the investigations of Ni–P (Brenner & Riddell 1946; Graham *et al* 1962, 1965; Henry 1984; Harris 1985; Bakonyi *et al* 1986; Agarwala 1987; Husheng *et al* 1991; Andre *et al* 1993; Paunovic *et al* 1995; Puchi *et al* 1997; Chitty *et al* 1997; Bozzini & Boniardi 1997; Bozzini *et al* 1999; Balaraju & Sheshadri 1999; Apachitei & Duszczyk 2000), Ni–B (Datta *et al* 1991; Srivastava *et al* 1992; Di Giampaolo *et al* 1997; Vasudevan *et al* 1998), Ni–Cu–P, Ni–Re–P (Gorbunova *et al* 1966), Ni–W–P (Pearlstein *et al* 1963; Li *et al* 1996), Co–P, Co–B (Brenner *et al* 1950), Fe–Mo–W–B (Wang *et al* 1997), Ni–Co–P (Kim *et al* 1995; Wang *et al* 1997), Fe–Sn–B, Fe–W–B, Fe–Mo–B (Wang *et al* 1997) and Ni–Sn–Cu–P (Bangwei *et al* 1999).

Different alloys are coated for desired physical and mechanical properties. Nickel turns out to be the single most widely coated element with phosphorous. Apart from nickel, many alloys contain at least one of the elements Co, Cu, Pd, Pt, Au or Ag.

2.1 *Bath composition and characteristics*

Mainly two types of baths have been used for depositing alloys. These include acidic and alkaline baths. Electroless alloy coatings are produced by the controlled chemical reduction of metallic ions onto a catalytic surface, the deposit/coating itself is catalytic to the reduction reaction and the reaction continues as long as the surface remains in contact with the bath solution or the solution gets depleted of solute metallic ions. The coating is uniform throughout the contours of the substrate because no electric current is used. Therefore, all parts of the surface area of substrate which are equally immersed in the bath have equal probability of getting ions deposited.

The bath (electrolytic) characteristics have been considered by taking nickel as an example. A source of nickel ions, usually nickel sulphate or nickel chloride is used other than this the electroless bath solution comprises of different chemicals each performing an important function (Agarwala 1987) as below.

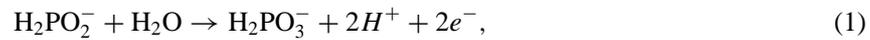**Table 1.** Application of electroless Ni–P coatings.

Application avenue	Components	Coating thickness (μm)
Automotive	Heat sinks, carburettor components, fuel injection, ball studs, differential pinion ball 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, aluminium 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, pilot tables, gyro parts, engine mounts, oil nozzle 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 shafts, 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 preventors	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
Marine	Marine hardware, pumps and equipment	25–50
Material handling	Hydraulic cylinders and shafts, extruders, link drive belts, gears and clutches	12–75
Medical & pharmaceutical	Disposable surgical instruments and equipment, sizering screens, pill sorters and feed screws and extruders	12–25
Military	Fuse assemblies, tank tarred bearings, radar wave guides, mirrors, motors, detonators and firearms	8–75
Mining	Hydraulic systems, jetting pump heads, mine engine components, piping connections, framing hardware	30–60
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	
Textiles	Feeds and guides, fabric knives, spinnerets, loom ratchets and knitting needles	12–50
Wood & paper	Knife holder corer plates, abrading plates and machine parts.	∼ 30
Miscellaneous	Chain saw engine	∼ 25
	Drills and taps	∼ 12
	Precision tools	∼ 12
	Shower blades and heads	∼ 8
	Pen tips	∼ 5

- A reducing agent to supply electrons for the reduction of nickel
- Energy (heat)
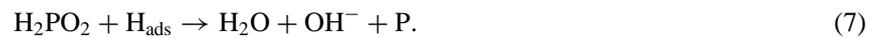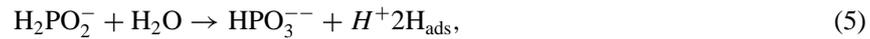- Complexing agents (chelates) to control the free nickel available to the reaction

2.1a *Reducing agents:* Several reducing agents have been used in electroless coating of alloys. Four types of reducing agent have been used for electroless nickel bath including sodium hypophosphite, amineboranes, sodium borohydride, and hydrazine.
Sodium hypophosphite baths – More than 70% electroless nickel is deposited from solutions reduced by sodium hypophosphite. The main advantage of these solutions over those reduced by borohydride or hydrazine includes lower costs, greater ease of process control etc. Several mechanisms have been proposed for the chemical reactions that occur in hypophosphite reduced electroless nickel plating solutions. Most widely accepted mechanisms are illustrated by the following equations (Gutzeit 1959, 1960).

 (i) Electrochemical mechanism, where catalytic oxidation of the hypophosphite yield electrons at the catalytic surface which in turn reduces nickel and hydrogen ions is illustrated below:

$$H_2PO_2^- + H_2O \rightarrow H_2PO_3^- + 2H^+ + 2e^-, \tag{1}$$

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

$$2H^+ + 2e^- \rightarrow H_2, \tag{3}$$

$$H_2PO_2^- + 2H^+ + e^- \rightarrow P + 2H2O. \tag{4}$$

(ii) Atomic hydrogen mechanism, where atomic hydrogen is released as the result of the catalytic dehydrogenation of hypophosphite molecule adsorbed at the surface is illustrated below.

$$H_2PO_2^- + H_2O \rightarrow HPO_3^{--} + H^+2H_{ads}, \tag{5}$$

$$2H_{ads} + Ni^{++} \rightarrow Ni + 2H^+, \tag{6}$$

$$H_2PO_2 + H_{ads} \rightarrow H_2O + OH^- + P. \tag{7}$$

The adsorbed active hydrogen, (6) then reduces nickel at the surface of the catalyst.

$$(H_2PO_2)^{2-} + H_2O \rightarrow H^+ + (HPO_3)^{2-} + H_2. \tag{8}$$
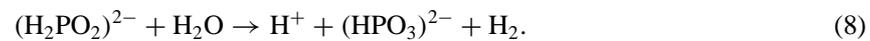
Simultaneously, some of the absorbed hydrogen reduces a small amount of the hypophosphite at the catalytic surface to water, hydroxyl ion and phosphorus, (7). Most of the hypophosphite present is catalytic, which is oxidized to orthophosphite and gaseous hydrogen, (8), causing low efficiency of electroless nickel solutions for alloy coating while the deposition of nickel and phosphorus continues. Usually, 5 kg of sodium hypophosphite is required to reduce 1 kg of nickel, for an average efficiency of 37% (Mallory 1974; Gaurilow 1979). The coefficient of utilization of hypophosphite vary a little with the nature of buffer additive; the highest degree of utilization of the hypophosphite was observed in the solution containing sodium acetate, the lowest is that with sodium citrate. The main characteristic of the process is the change in the composition of the solution. The concentration of nickel salt and hypophosphite is decreased and the concentration of acid is increased during the progress of deposition. This causes the lowering of deposition rate (Mallory 1974). Tables 2 and 3 record the different compositions

Table 2. Compositions of the acid nickel solutions (pH: 4–6, temperature: 90–92°C).

Components of the bath	Concentration g/l			
	I	II	II	IV
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30	30	30	-
Nickel sulphate, $NiSO_4 \cdot 7H_2O$	-	-	-	30
Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$	10	10	10	10
Sodium glycolate, $CH_2OHCOONa$	50	10	-	-
Sodium acetate $CH_3COONa \cdot 3H_2O$	-	-	-	10
Sodium citrate, $Na_3C_6H_5O_7 \cdot 5 1/2 H_2O$	-	-	10	-
General appearance of the coating	Semi-bright	Semi-bright	Semi-bright	Coarse uneven

of the bath used for nickel coating in acidic and alkaline baths (Brenner & Riddell 1947; Agarwala 1987).

Amineborane baths – Use of amineboranes in electroless Ni plating solutions have been limited to two compounds: N-dimethylamine borane (DMAB)–$(CH_3)_2NHBH_3$, and H-diethylamine borane (DEAB)–$(C_2H_5)_2NHBH_3$ (Gaurilow 1979; Mallory 1979; Stallman & Speakhardt 1981). DEAB is used primarily in European establishments, whereas DMAB is used generally in USA. DMAB is readily soluble in aqueous solutions while DEAB should be mixed with a short chain aliphatic alcohol such as ethanol, before mixing into plating bath. The amineboranes are effective reducing agents over a wide range of pH but due to evolution of hydrogen, there exists a lower limit of pH up to which the plating process can be carried out (Mallory 1979). Nickel, in the deposit increases as pH of the bath increases. Usually, the amineborane baths have been used in the pH range of 6 to 9. Operating temperatures for these baths range from 50–80°C, however, they can be used at temperature as low as 30°C. Accordingly, amineborane baths are very useful for plating non-catalytic surfaces such as plastics, nonmetals, which are their primary applications. The rate of depositions varies with pH and temperature, but is usually 7 to 12 μm/h.

Sodium borohydride baths – The borohydride ion is the most powerful reducing agent available for electroless nickel plating. Any water-soluble borohydride can be used; however, for optimum results sodium borohydride is preferred (Mallory 1974). In acid or neutral solutions, hydrolysis of borohydride ions is very rapid. In the presence of nickel ions nickel boride may form spontaneously. If the pH of the solutions is maintained between 12 and 14 the formation of nickel boride is suppressed and the reaction product is principally elemental nickel.

Table 3. Alkaline ammonical nickel solutions (pH: 8–9, temperature: 90°C).

Components of the bath	Concentration g/l		
	I	II	III
Nickel chloride, $NiCl_2 \cdot 6H_2O$	30	30	30
Sodium hypophosphite, $NaH_2PO_2 \cdot H_2O$	10	10	10
Ammonium chloride, NH_4Cl	50	100	--
Sodium citrate, $Na_3C_6H_5O_7 \cdot 5 1/2 H_2O$	100	--	100
Appearance of the coating	Medium dark	Bright	Bright

One mol. of sodium borohydride can reduce approximately one mol. of nickel, it can be deduced that the reduction of 1 kg of nickel requires 0·6 kg of sodium borohydride while 5 kg of hypophosphite is required. Deposits from borohydride reduced electroless nickel contain 3 to 8 wt% boron. To prevent precipitation of nickel hydroxide, complexing agents such as ethylenediamine, that are effective between 12 to 14 pH must be used. The presence of such complexing agents, however reduces the reaction rate thereby lowering the rate of deposition. At operating temperatures of 90°C the rate of deposition lies somewhere 25 to 30 μm/h.

During the course of reduction, the solution pH invariably decreases, requiring continuous additions of an alkali hydroxide. The highly alkaline nature of these baths poses difficulties for use with aluminium substrates.

Hydrazine baths – Hydrazine has also been used to produce electroless nickel deposits (Levy 1963; Dini & Coronado 1967). These baths operate in the temperature range of 90–95°C and pH range of 10–11. Their rate of deposition is approximately 12 μm/h. Because of the instability of hydrazine at high temperatures, these baths tend to be very unstable and difficult to control. The deposit contains high amounts of nickel but does not look metallic. The deposit is brittle and highly stressed for practical applications.

2.1b *Energy:*   Amount of energy or temperature of electroless nickel solutions is one of the important factors affecting the rate of deposition. The rate of deposition is low at temperatures below 65°C, and increases with the increase in temperature. This is true for almost all the systems. Generally the operating temperature is about 90°C, above which the bath tends to become unstable (Boudrand 1994).

2.1c *Complexing agents:*   One of the difficulties of reduction reactions or chemical plating is the maintenance of the bath composition. As the plating proceeds, continuous lowering of the rate of reduction of nickel occurs. The solutions cannot be replenished due to the formation of nickel phosphite. If nickel phosphite is precipitated in the bath, the surface quality of coating deteriorates resulting in rough and dark coatings. Moreover, the nickel concentration in the solution also decreases and the bath goes to the verge of total decomposition. Sodium citrate reduces the formation of nickel phosphite and reduces the rate of deposition (Gutziet & London 1954). The ability to form nickel complexes has been attributed to some of the proposed additives like salts of glycolic, succinic or malonic acids, however, these fail to stop the precipitation of nickel phosphite.

The best results are obtained when the sodium citrate concentration is about 30 g/l. It helps in checking the coating from becoming porous and dull. Because of the reduction in rate of deposition, accelerators like salts of carbonic acids, soluble fluorides and inhibitors like thiourea can also be added to avoid the total decomposition of the bath.

Bi, Pb, Cd and Te additions act as bath stabilisers (Lanzoni *et al* 1997). Bismuth and Te seem to be less effective than Pb and Cd in bath stabilization. These stabilizers are added in concentrations of only a few parts per million.

2.2 *Factors affecting the coating process*

Bath composition is the major parameter affecting the coating process; however, other factors like pH, temperature, bath loading factor, i.e., the surface area of the substrate also affect coating process in a major way.

Variation in nickel salt concentration has no noticeable influence on the rate of reduction of nickel but variation in hypophosphite concentration affects the process considerably. Although increase in hypophosphite concentrations improves the rate of reduction of nickel, extra

amounts of reducing agents should not be used as this may cause reduction to take place in the bulk of the solution. The appropriate amount of hypophosphite can be adjusted by observing the bath condition during the course of reaction. Weak hydrogen evolution is an indication of a low concentration of hypophosphite and a vigorous hydrogen evolution indicates excess hypophosphite.

Nickel deposits obtained from acid solutions have a very bright and smooth surface; coatings obtained from alkaline solution have a bright surface. As the alkalinity of the solutions increases, the nickel content of the deposit increases or the phosphorus content decreases. Phosphorus may be present as a phosphide or as solid solution. The concentration of nickel salts has slight influence on the rate of deposition. Large concentrations of nickel salts cause deterioration in the quality of the coatings with the formation of rough deposits. Sulphate and chloride baths are used for depositing amorphous alloys. The results by use of the sulphate baths are found to be systematic while with chloride baths, the results are arbitrary (Cziraki *et al* 1980). Deposits on aluminium substrates exhibit higher magnetization than on brass substrate.

Temperature has a considerable influence on the rate of process. The rate of the process increases with increase in temperature and attains a maximum at about 92°C. Beyond this temperature, it becomes difficult to maintain the pH of the solution and, therefore, the quality of the coating deteriorates. As the bath loading increases the rate of deposition increases. There is a critical bath loading factor above which the bath decomposes totally.

3. Electroless composite coating

The co-deposition of particulate matter with electroless nickel coatings dates back to the 1960's (Odekerken 1966). In his pursuit to improve corrosion resistance, of nickel chromium electrodeposits, he used an intermediate layer containing finely divided Al_2O_3 and PVC particles distributed within a metallic matrix. This intermediate layer was deposited using the electroless coating technique. Various systems have been used since for obtaining composite coatings, $Ni–P–Al_2O_3$ (Odekerken 1966; Apachitei *et al* 1998b), $Ni–P–SiC$ (Apachitei *et al* 1998b; Li 1997; Grosjean *et al* 1997), $Ni–P–B_4C$ (Ge *et al* 1998; Bozzini *et al* 1999), $Ni–P–B$ (Apachitei *et al* 1998b), $Ni–P–C$ (Cziraki *et al* 1980), $Ni–P–PTFE$ (Parker 1972; Narayana & Pandey 1997; Pena-Munoz *et al* 1998; Zhang *et al* 1998) and $Ni–P–MoS_2$ (Moonir-Vaghefi *et al* 1997). The most important ones include hard particle like: oxides, carbides, ceramics, insoluble powders, boron, diamonds, while recent ones are $Ni–P–Al_2O_3–ZrO_2$ (Sharma *et al* 2001a, b) and silver-graphite (Agarwala *et al* 1997) composite coatings. The soft particles contain powders of polyterafluoroethylene (PTFE), fluorinated carbon (CF_x) and fluoride salts.

Lately composite coatings of Ni–B with a few other elements have also been reported and are used as light emitting coatings. Successful co-deposition depends on various factors like catalytic or inert nature of particles and their size distribution, bath composition, and the compatibility between dispersoids and metal matrix.

It is possible to incorporate graphite in silver coatings by suspending graphite particles in the electroless plating bath. The plating bath contains silver cyanide, sodium cyanide, DMAB, sodium hydroxide and thiourea. The temperature used generally is around 70°C.

Electroless composite coating uses the conventional reduction reaction process with suspensions of particles. Generally, co-deposition of particle concentration in deposits of electroless coatings depends on various factors, like bath chemistry, particle characterization,

operating conditions etc. Each combination between a certain type of particles and the Ni–P matrix can lead to a new set of properties (Apachitei *et al* 1998b).

4. Electroless metallic coatings

Electroless copper coatings are being used before electroplating on plastics, ceramics polymers and other non-conducting materials (Henry 1984; Pedraza & Godbole 1990; Ramasubramaniam *et al* 1999). Electroless copper coating is also utilized for shielding electronic devices. The thickness of these coatings generally varies from $0 \cdot 12$ to $3 \cdot 0 \, \mu$m.

The plating bath contains a source of metallic ions, a reducing agent, complexing agent and a stabilizer. Copper sulphates, acetates, or nitrates are used as a source of copper ions. The reducing agent generally used is formaldehyde, but other reducing agents like DMAB, sodium hypophosphite etc. can also be used. Sodium hydroxide and potassium titrate are generally used complexing agents. Thiourea or vanadium oxide are used as bath stabilizers. The composite coating can be carried out with the bath at room temperature to a temperature as high as 70°C. The pH should be maintained at higher levels of about 12 to obtain bright coatings, however, the bath is more stable at a pH of about 9.

5. Structure of electroless coating

5.1 *As-coated electroless nickel coatings*

During the deposition of electroless nickel films, the growth of the film starts at isolated locations on the substrate. The whole substrate is then covered by lateral growth. The alloys containing lower phosphorus concentrations are characterized by the presence of crystalline and microcrystalline nickel, which indicates that the numbers of phosphorus atoms are not sufficient to distort the nickel lattice to an extent where amorphous nickel can be obtained. However, some very small pockets of amorphous nickel have been observed in coatings having $10 \cdot 8$ at. % P (Agarwala & Ray 1988; Hur *et al* 1990; Bozzini & Cavallotti 1997). As the phosphorus content increases to $23 \cdot 4$ at. % P, the amorphous nickel region goes on increasing due to increase in lattice distortion caused by phosphorus atoms situated in the interstitial position of nickel. In the as-deposited films a number of crystalline non-equilibrium phases like Ni, Ni_3P, Ni_5P_{12} etc. have been observed. The appearance of a number of phases may be due to the compositional inhomogeneities prevailing in the film in the as-deposited state. Otherwise, these precipitates would be observed while annealing electrodeposited (ED) Ni-films. But it may be noted that all the earlier workers have observed such transition phases like Ni_xP_y (Makhsoos *et al* 1978), Ni_5P_5 (Bakonyi *et al* 1986) even in ED films. The presence of inhomogeneities in electroless films may energetically as well as kinetically favour different local equilibria in different regions of the film leading to the formation of different phases depending on the actual composition. However, the precipitates other than Ni_3P are metastable transition phases because on continued heating for very long time, the precipitates disappear or transform to equilibrium Ni_3P. These observations are made by Kuo *et al* (1984, 1985) and Makhsoors *et al* (1978), for ED Ni–P films, which however do not show such a multiplicity of transition phases.

The width and the shift of the rings, obtained for different polycrystalline electroless Ni–P deposit with varying phosphorus contents, have been determined from the SAD patterns of TEM by the travelling microscope and are reported in table 4 along with the shift of these

Table 4. The variation of 2θ and θ shift for different phosphorus contents in the Ni–P deposit in TEM study.

Sample composition at % P	$\Delta 2\theta$	θ Shift	% Shift
14·3	0·07	0·07	14·92
15·3	0·09	0·08	17·63
17·8	0·12	0·07	15·59
19·8	0·16	0·07	15·13
22·4	0·21	0·11	22·01
23·4	0·22	0·10	21·91

rings as compared to pure nickel (Hur *et al* 1990; Agarwala & Ray 1992). From this table it can be shown that a linear relation of $\Delta 2\theta$ as a function of phosphorus content exists. X-ray analysis also shows a similar kind of intensity peak broadening behaviour with increase in phosphorus for electroless nickel deposits. The variation of height to breadth ratio, (H/B), of the broad X-ray diffraction peak near (111) reflections of crystalline nickel, in deposits with different phosphorus contents has been seen by Agarwala & Ray (1992). As the phosphorus content increases the Bragg's peak becomes more diffused and variations of H/B reduces systematically.

The structural condition of the deposit depends on composition and other factors like driving force for composition invariant crystallization, nucleation possibility and growth velocity. At low phosphorus contents, it is possible for nickel to crystallize in a composition invariant manner.

5.2 *Heat-treated electroless nickel coatings*

When electroless nickel films of different phosphorus contents are heat treated at various temperatures, the phases present in the as-deposited films undergo definite structural changes (Hur *et al* 1990).

The crystallization behaviour of electroless Ni–P film can be tentatively divided into two broad categories: (i) the alloys having microcrystalline nickel as a major constituent in the as-deposited state and (ii) alloys constituted mainly of an amorphous phase which do not have microcrystalline nickel as major constituent. The alloy containing 10·8 at. % P contains micro-crystalline nickel as a major constituent. When this alloy is annealed at lower temperature range of 200° to 300°C for 4 h, $Ni_{12}P_5$, microcrystalline nickel, and Ni_3P are seen as common phases at all temperatures. While after annealing at higher temperatures of 400 and 600°C, the commonly observed phases are crystalline nickel and Ni_3P. From this, the following can be inferred: Crystalline nickel and Ni_3P are the phases which are obtained after complete crystal-lization of the alloy (Kuo *et al* 1984, 1985; Bakonyi *et al* 1986). The only transition phase in this case is $Ni_{12}P_5$. It may, however, be noted that there has been no transition precipitates during annealing ED microcrystalline Ni–P films (Makhsoos *et al* 1978). The formation of the tran-sition phase $Ni_{12}P_5$ may be taken as the common characteristic transition precipitate formed while heating electroless microcrystalline nickel in the temperature range of 200° to 300°C.

Several transition phases are observed to form during heating of amorphous Ni–P films in as-deposited state, at low temperatures. In the case of the Ni 14·3 at. % P film, the transition precipitates from the amorphous phase are Ni_5P_4 and Ni_2P formed in the temperature range of 250° to 300°C. The presence of the transition $Ni_{12}P_5$ phase at lower temperature has been

attributed to the presence of microcrystalline nickel in the As-deposited Ni–P films. But in case of Ni–17·8 at. % P films, the transition precipitate Ni_5P_2 is formed during annealing in the temperature range of 200° to 300°C. Therefore, it appears that the precipitates formed from the amorphous phase depends on the overall composition of the film or more particularly, on the composition of the amorphous phase. It is further indicated that just by the presence of $Ni_{12}P_5$ alone during annealing of an alloy containing 19·8 at. % P at low temperatures of 200° to 300°C, it cannot be presumed that these precipitates have solely come from the annealing of minor amounts of microcrystalline phases but $Ni_{12}P_5$ partially could have been formed also from the amorphous phase at this composition of the film. Ni_7P_3 is observed in the alloy containing 22·4 at. % P during low temperature annealing but in the films containing 23·4 at. % P, only equilibrium precipitates of Ni_3P are seen even at lower temperature of 200° to 250°C annealing.

The results indicate that the formation of a particular transition phase from the amorphous phase will depend on the composition. All these transition phases start to disappear and the stable Ni_3P phase forms at about 250° to 300°C. The temperature at the start of this transformation decreases with increasing phosphorus content and for films containing 23·4 at. % P, this temperature is even below 200°C. At temperatures above 350°C, there exists only two stable phases that is crystalline nickel and Ni_3P for all the films investigated, irrespective of their composition.

From the above it is evident that an inhomogeneous electroless film on annealing leads to a number of transition phases which are not observed in ED films. But it is not clear, whether inhomogeneous films are inherent products of electroless technique or whether it is possible to produce a more homogeneous film with a strict control of the parameters. In that case, it is apparent that the simplicity of the technique will be lost.

Irrespective of phosphorus content of the deposit and the phases present in the as-deposited films, during the course of heat treatment all the phases undergo through an intermediate metastable phase before becoming Ni_3P. So at the end of the heat treatment i.e. when the equilibrium state has been attained, only two phases namely crystalline nickel and Ni_3P are observed (Hur *et al* 1990; Agarwala & Ray 1992). The same may be applicable for other alloy systems like Fe–Mo–W–B (Brenner *et al* 1950).

6. Properties of electroless coatings

Earlier research reported on electroless coatings are largely on the process and practically no attention has been paid to the mechanical properties. Even now considerable attention is being paid to the electroless process; however, some work has also been directed towards the studies on physicochemical and mechanical properties of electroless coatings. Studies have observed an increase in hardness of electroless nickel after heat treatment. Initially the data of the effect of time and temperature on hardness gives rise to the belief that the enhanced hardness is due to a process similar to precipitation hardening. Later it has been pointed out that certain electroless nickel coatings are amorphous to start with and for precipitation hardening a crystal lattice is required. Therefore, the structure and its correlation with mechanical properties after heat treatment should be depending on phosphorus content in order to study the mechanical properties of electroless coatings.

Electroless coatings have been largely characterised in the later half of the past decade. Various properties like wear resistance, reflectivity, luminescence etc. have been included in the subject of these studies. Table 5 reports the properties studied in this respect (Agarwala *et al* 1999; Feldstein 1999).

Table 5. Electroless nickel based coatings and their corresponding aspects considered for study.

Property								System					
	Ni–P	Ni–B	Ni–P–B	Ni–P–Al$_2$O$_3$	Ni–P–SiC	Ni–P–MoS$_2$	Ni–P–C	Fe–Ni–P	Ni–P–Si$_3$N$_4$	Ni–W–P	Ni–Sn–P	Ni–P–B –Others	Ni–PTFE
Structure (*)	•												
Structure (#)	•												
Microhardness	•	•			•		•				•		
Wearability	•	•	•	•	•		•		•	•	•		•
Coating rate	•	•			•	•	•						•
Morphology	•	•	•	•	•		•						•
Ductility	•	•		•	•								•
Corrosion resistance	•	•		•				•				•	
Magnetic property	•	•						•					
Porosity	•	•			•								
Adhesion	•	•			•								
Resistivity	•				•		•	•					
Scratch resistance	•				•								
Tensile strength	•												
Thermal stability	•												
Fatigue strength	•												
Solderability	•									•			
Machineability	•												
Wettability	•									•			
Flatness	•												
Luminescence	•											•	

• Indicates the particulars under study by different researchers; (*) indicates as-coated and (#) indicates heat-treated deposits.

Table 6. Properties of electroless nickel based coatings (source – home page: www.microplating.com).

Property	Coating System				
	Ni–3P	Ni–8P	Ni–11P	Ni–0·5B	Ni–5B–5Tl
Composition range:					3–5 %B,
balance nickel	3–4 %P	6–9 %P	11–12 %P	0·5–1·0 %B	3–5 %Tl
Structure*	m–c	m–c–a	A	c	m–c–a
Internal stress (MPa)	−10	+40	−20	+500	+110
Final melting point (°C)	1275	1000	880	1440	1170
Density (gm/cm^3)	8·6	8·1	7·8	8·6	8·25
Coefficient of thermal					
expansion (mm/m-°C)	12·4	13·0	12·0	ND	12·1
Electrical resistivity (mW-cm)	30	75	100	10	89
Thermal conductivity (W/cm-K)	0·6	0·05	0·08	ND	ND
Specific heat (J/kg-K)	1000	ND	460	ND	ND
Magnetic coercivity (A/m)	10000	110	0	ND	ND
Tensile strength (MPa)	300	900	800	ND	110
Ductility (%)	0·7	0·7	1·5	ND	0·2
Modulus of elasticity (GPa)	130	100–120	170	ND	120
Hardness as-deposited (HV$_{100}$)	700	600	530	580	700
Hardness heat-treated (HV$_{100}$)	960	1000	1050	500	1200

*a: amorphous; m–c: microcrystalline; m–c–a: mixed crystalline and amorphous; c: crystalline; ND: not determined.

Several mechanical properties of these deposits, along with a few other properties, are listed in table 6. Amongst them, hardness and fatigue properties have been studied extensively. There is a general agreement that for electroless nickel based coatings, heat-treated at 400°C for 1 to 4 h for any content of phosphorus, produces maximum obtainable hardness. This can be attributed to the formation of an equilibrium mixture of crystals consisting of solid solution of phosphorus in nickel (with low phosphorus content) or nickel and crystals of the intermetallics compound Ni$_3$P. But the same is not true for the substrate like aluminium. As commercially pure aluminium substrates undergo coarsening of grains due to annealing, this causes reduction in the hardness. The hardness of electroless nickel coatings are listed in table 7. The hardness of the high melting particles co-deposited remains the same, i.e., before and after heat treatment. Hence the hard particles incorporated into the Ni–P matrix increases the hardness of as-deposited and heat-treated layers of composite coatings (Apachitei *et al* 1998b).

6.1 *Wear and friction behaviour of electroless coatings*

Nickel–phosphorus (Ni–P) and Ni–P–X (X–hard particles) coatings produced by electroless technique tend to be extensively used as wear resistant materials. Several studies have been

Table 7. Hardness of electroless nickel coatings in as-coated and heat-treated conditions in response to phosphorus content.

Phosphorus content	Hardness HK$_{100}$ (as-coated)	Hardness HK$_{100}$(heat-treated)
2–3%P	700	1000
6–9%P	550	920
10–12%P	510	880

performed on Ni–P coatings (Brenner & Riddell 1946, 1947; Henry 1984; Apachitei *et al* 1998a). The electroless Ni–P based composite coatings possess better wear resistance than Ni–P alloy coatings (Balaraju & Sheshadri 1999). However, due to the complexity of the structure, wide variety of wear apparatus, loading conditions, environment during the wear tests, substrate and counter face material used, and consolidation of the vast knowledge on wear of electroless coatings is difficult. The wear behaviour of electroless composite coatings has yet to receive adequate attention from research community to fully exploit the potential it contains. In a few cases, tests have been developed to give measurements that can be directly related to in-service performance (Moonir-Vaghefi *et al* 1997; Balaraju & Sheshadri 1999).

It is experienced that, adhesion is the main cause of wear of electroless coatings against steel but no direct correlation between wear rate and hardness have been observed during the tests (Gawne & Ma 1987). It has been experimentally observed that regardless of phosphorus content, the composite coatings are more wear resistant, than base Ni–P alloy as a consequence of high hardness of the co-deposited particles. Suh (1973) explained the delamination theory of wear, accordingly to which, the dislocation density builds up at the sub-surface layer leading to formation of cracks and voids, and these cracks may link together resulting in their sheet-like wear particles. In a recently developed Ni–P–Al_2O_3–ZrO_2– Al_3Zr composite coating (Sharma *et al* 2001c, 2002), it is observed that the wear rates of aluminium and steel substrates are significantly higher than that of the corresponding electroless Ni–P–Al_2O_3–ZrO_2– Al_3Zr coated pin samples. These composite coatings exert better wear resistance while comparing with that of the electroless Ni–P coated pin samples.

Balaraju & Seshadri (1999) – had prepared electroless Ni–P coating by an acidic hypophosphite-based bath to produce 10–12% P in the electroless nickel coating. The wear resistance of the samples, in as-deposited and heat-treated (at 400°C for 1 h) conditions are assessed using a disc-on-disc method under unlubricated sliding conditions for 30 min. The counter disc, of diameter 35 mm, was made from heat-treated high-carbon, high-aluminium steel having 60 HRC hardness value. Different normal forces of 20, 40 and 60 N against the test disc specimen, which was rotated at 1000 rpm has been used. Substantially low specific wear rate of electroless Ni–P in heat-treated condition is observed when compared to that with as coated samples, which is considered to be due to very low mutual solubility of nickel phosphide and iron thus presenting a relatively incompatible surface. When heat-treated Ni–P coating (400°C) is run against carburised steel ring using 0·5 kg load, it shows the polished appearance of a worn surface and fine scratches are also observed on the block surface, but when the load exceeds 2·0 kg, moderate adhesive transfer occurs (Moonir-Vaghefi *et al* 1997). When the load is increased to about 8 kg, a high wear rate on heat-treated Ni–P coating occurs. Presence of shallow craters filled with wear debris are markedly noticed.

Electroless coated samples using an acid bath based on $NiCl_2$ (Staia *et al* 1997) are heat-treated at 260° and 400°C for 25 and 1 h respectively and subjected to wear studies. The modified ball cratering method, using a mixture of 10 ml ethylene glycol and 1 g of 3 μm diamond paste, is used to determine abrasive resistance of these coatings. A ball bearing is used as the tribological pair. The individual wear constants are determined by the use of recorded plots of the crater depth against sliding distance. In the same work by Staia *et al* (1997), comparisons of Rutherford and Hutchings results with the above results are reported which have been used for assessing the wear constant. The samples heat-treated at 400°C for 1 h are reported to be better, in terms of resistance to wear, without significant influence on coefficient of friction (Staia *et al* 1996).

The effect of temperature on wear of as-deposited electroless Ni–P coating under lubricated reciprocating sliding conditions are investigated using the ball-on-block test method by

Yugang & Tandon (1996). The studies reveal that the temperature increase from 25° to 100°C reduced the lubricated wear coatings, especially at higher loads. The wear mechanism also changes as temperature rises to 100°C. Higher sulphur and phosphorus contents on the wear track at high temperature reduces friction and wear of the electroless coating.

Bin-Sudin *et al* (1996) reported that the substrate roughness can be optimized to achieve the best electroless Ni–P interlayer, which is beneficial in isolating the substrate from wear surface effects and in permitting the use of rougher surface finish. They have carried out scratch adhesion and wet sand–rubber wheel abrasive tests.

Co-deposition of tungsten in electroless Ni–P matrix seems to reduce the phosphorus content in coating and such addition of tungsten affects the crystalline structure of low phosphorus Ni–P deposits (Jun, *et al* 1996). By Tabor abrasion test, it is confirmed that tungsten improves the wear resistance.

Bozzini *et al* (1999), investigated the tribological behaviour of electroless Ni–P composite coating by dry sliding tests with a slider-on-cylinder tribometer in laboratory air at room temperature against a PVD TiN coated HSS cylinder. Friction and wear data discussed on the basis of mechanical properties include microhardness, plasticity parameter and fracture toughness of coatings, which are derived by indentation measurements at low loads. Wear depth increases with increase in annealing time, for both pure matrix and B_4C-rich composite layer. The wear volume, Q, is correlated to mechanical properties using Archard-type equations as,

$$Q = k\,[W/HV],\qquad(9)$$

where, k is the wear coefficient, W is applied load and indentation hardness is referred as HV. Wear scar depth of Ni–P coatings is found to be one order of magnitude higher than those of corresponding composite coatings reinforced by B_4C particles. In both the cases the tendency for the wear scar depth to decrease with increase in heat treatment time is reported. SEM and OM observations show no evidence of delamination phenomena or any sign of detachment of the reinforcing particles along the wear scars produced in the testing conditions.

The morphology of wear scar suggest that the removal of material by plastic deformation is the main cause of wear in both Ni–P coatings and Ni–P–B_4C, hence it is reasonable to use an Archard-type wear equation to correlate the wear volume and the indentation hardness of the coating. During sliding, the hard particles can move into the matrix, behaving like cutting edges, thus enhancing the wear of the coating. The wear volume seems to increase linearly with increase in applied load. Only at the highest load (i.e. 25 N), a few isolated cracks are found to nucleate on the wear surfaces of the composite coatings.

Electroless Ni–P–SiC composite coatings containing 25–30 vol % SiC have been reported by Li (1997). According to them, Ni–P–SiC coatings possess greater hardness, higher porosity, as well as lower adhesion and corrosion resistance. Heat treatment at relatively higher temperature, i.e. 650°C for 1h, seems to improve adhesion and wearability of the composite coating. After heat treatment, presence of Ni_3Si compound is reported.

Reddy *et al* (1998), studied the specific wear rate of electroless Ni–P/diamond coating by disc-on-disc type wear tests with counter disc of high strength tool steel (hardness 800VHM). The wear tests are carried out at 250 rpm and 5 N load without lubrication. The wear rate is correlated with the coating composition, diamond particle size and annealing temperature. The above study reveals that Ni–P diamond electroless coating containing 9–10% P and 3–6 μm size diamond particles gives least wear rate in as-coated and annealed condition, i.e. after heat treating at 350°C for 2h followed by air cooling. The heat treatment gives rise to improved wear resistance when compared with corresponding as-coated conditions and is

due to complete crystallization of the coating. But less phosphorus ($\sim$ 6–7%) content in the coatings does not show the encouraging specific wear rate. In this study the heat treatment at 250° or 400°C for 2 h shows more specific wear rate.

Pena-Munoz *et al* (1998), reported the study of wear resistance properties of electroless Ni-PTFE coatings, while Zhang *et al* (1998) and Narayana & Pandey (1997), have reported the wear and friction properties of electroless Ni–P–PTFE coating. The hardness and wear resistance of these coatings in scuffing wear conditions with mildly abrasive conditions are simulated by Tabor wear test for low duration (20000 cycles) by Narayana & Pandey (1997). Addition of 18% PTFE and above found to be beneficial, where as 28% PTFE appeared to be more wear resistant. However, under abrasive wear conditions simulated by reciprocating, wear test, addition of both 18 and 28% PTFE reduces the wear resistance of electroless nickel. The reciprocating tests with loads 400, 700 and 1400 g, conducted in the presence of lubricant and water film reports that oil has beneficial effect with Ni–18% PTFE film where as water has a slightly detrimental effect. Further, the work also explains the effect of heat treatment, thickness and counterface/rubbing surface on wear resistance. Under abrasive wear conditions, heat treatment increases wear resistance of composite coatings, but under adhesive wear conditions, heat treatment has practically no effect. However in dry sliding wear, heat treatment of the coated samples increases coefficient of friction. About 10 *m thickness coatings shows optimum performance by a low and almost constant coefficient of friction. The work states that the wear rate increases on increasing the hardness of the opposite rubbing surface for Ni–PTFE coatings.

Moonir-Vaghefi *et al* (1997) explained the results of block-on-ring test to evaluate frictional and wear characteristics of electroless Ni–10wt.% P-MoS_2 composite coatings technique using 2 and 8 kg of loads. At higher loads, in case of Ni–10wt.%P coatings (under dry condition) the worn surface exhibited severe adhesive transfer of iron. Incorporation of MoS_2 particles into the Ni–P matrix improves the wear and friction properties of the coating. The heat treatment (400°C, 1 h) reduces the wear. The Ni–P–3% MoS_2 against itself has proved to have lower wear rate and coefficient of friction. The electroless Ni–P–MoS_2 heat-treated coatings also appears to behave in the same manner as the Ni–P coatings, excepting that, presence of MoS_2 reduces the friction and wear by minimizing the metal to metal contact due to wetting with dry lubricant on the contacting surface, however it does not show the improvement in wear characteristic at higher loads i.e. 8 kg. When heat-treated electroless Ni–P–3%MoS_2 coating run against itself, the wear rate and coefficient of friction are reported to be the lowest. It may be probably due to the presence of the MoS_2 film, which prevents spelling of the oxide layer on the carburised steel ring. The wear rate of annealed Ag-graphite coated specimens are about ten times lower than that of annealed silver coating (Agarwala *et al* 1997).

6.2 *Corrosion characteristics*

In order to achieve best corrosion protection with a thin coating, as electroless nickel, which has no complete tight cover of fluorocarbon coating, it is important that the substrate has a smooth, clean and pore-free surface. Non-metallic inclusions in the surface of the substrate material, carbides, sulphides etc. emanating from alloying elements or impurities, as well as a porous or rough surface can breed pores in the coating resulting in less corrosion protection. Corrosion rate of the coating is though in general very low in most environment as shown in table 8, the presence of oxygen and phosphorus atoms in respect of nickel atoms, invariably gives the corrosion product in the form of $Ni(OH)_2 + Ni_3(PO_4)_2$ at the outer layer and $NiO + Ni_3(PO_4)_2$ as the inner layer in electroless Ni–P coatings (Lanzoni *et al* 1997).

Table 8. Corrosion data of electroless nickel based plating (Source: web pages, www.nedox.com).

Corrosive liquid	Corrosion speed (μm/y)
Acetic acid	0·6
Acetone	0·06
Aluminium sulphate, 27%	5·0
Ammonium hydroxide, 25%	16·0
Ammonium nitrate, 20%	15·0
Brine, 3·5% CO_2 saturated	5·0
Brine, 3·5% H_2S saturated	0·0
Calcium chloride, 42%	0·02
Citric acid, saturated	7·0
Copper chloride, 5%	25·0
Ethylene glycol	0·6
Ferric chloride, 1%	200·0
Ferric acid, 88%	13·0
Hydrochloric acid, 5%	24·0
Lactic acid, 85%	1·0
Nitric acid, 1%	25·0
Oxalic acid, 10%	3·0
Phosphorus acid, 85%	3·0
Sudium carbonate, saturated	1·0
Sodium hydroxide, 45%	0·0
Sodium hydroxide, 50%	0·2
Sodium sulphate	0·8
Sulphuric acid, 65%	9·0
Water, distilled N_2-degassed	0·0
Water distilled	0·0
Sea water (3·6% salt)	0·0

Initially pore-free deposits with high internal tensile stresses offer less protection than the deposit having lower compressive internal stresses. The internal compressive stress is lower when phosphorus content in the deposit is higher, which has been revealed from the work of Parkar & Shah (1971). The resistance to chemical attack in various corrosive media is attributed to the inherent low porosity of these deposits as well as change in chemical properties of nickel due to presence of phosphorus.

Heinz & Heinrich (1990) reported that when phosphorus content is more than 10%, the corrosion resistance improves. Mallory (1974), observed that the corrosion characteristic of the deposit is more dependent on the complexing agent used in the plating bath than on deposit thickness. Ternary alloys like Ni–W–P, Ni–Cu–P and Ni–Sn–P seem to greatly enhance the protective value of electroless deposits on aluminium. The corrosion rate is observed to be lesser for electroless silver coated aluminium and aluminium alloys (Agarwala *et al* 1997).

The latest developments indicate that the electroless coatings can be used to coat intelligent materials used in defence industry. The composite coatings can provide an excellent layer of coating containing nickel and other components to be used for defence purposes. Since 1946 till today the electroless coating has been accepted as a standard process. The new century may find its role as intelligent coating on which the work is going on presently and as stated earlier the emphasis now is on applications of its valuable properties.

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