



Electroless Ni–P composite coatings

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Abstract

This review outlines the development of electroless Ni–P composite coatings. It highlights the method of formation, mechanism of particle incorporation, factors influencing particle incorporation, effect of particle incorporation on the structure, hardness, friction, wear and abrasion resistance, corrosion resistance, high temperature oxidation resistance of electroless Ni–P composite coatings as well as their applications. The improvement in surface properties offered by such composite coatings will have a significant impact on numerous industrial applications and in the future they will secure a more prominent place in the surface engineering of metals and alloys.

1. Introduction

Electroless plating is a chemical reduction process, which depends on the catalytic reduction of a metallic ion from an aqueous solution containing a reducing agent, and the subsequent deposition of the metal without the use of electrical energy. During the past five decades electroless plating has gained popularity due to its ability to produce coatings that possess excellent corrosion, wear and abrasion resistance. 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 [1, 2]. 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. Although electroless Ni–P deposits give satisfactory performance for several applications, enhancing their performance to suit different end uses warrants further development. This is achieved either by adding additional alloying element(s) or by incorporating hard/soft particles in the Ni–P matrix. A detailed account of electroless nickel composite coating was presented earlier by Feldstein [3]. This review outlines the development of electroless Ni–P composite coatings with the incorporation of various hard and soft particles in the Ni–P matrix to maximise the coating performance to meet the demanding needs of engineering applica-

tions. The method of formation, mechanism of particle incorporation, factors influencing particle incorporation, effect of particle incorporation on the coating structure, hardness, friction, wear and abrasion resistance, corrosion resistance, high temperature oxidation resistance and applications are discussed.

2. History of electroless Ni–P composite coating

The idea of codepositing various second phase particles in electroless nickel deposits and thereby taking advantage of their inherent uniformity, hardenability, wear resistance and corrosion resistance, has led to the development of electroless nickel composite coatings. Work dealing with the incorporation of second phase particles in the electroless nickel matrix began in the 1960s [4]. The initial attempts made to produce such deposits were not successful and often resulted in decomposition of the bath. This is not surprising as the methodology pursued for producing the composite coatings were similar to those prevailing in conventional electroplating. Dispersion of finely divided particles increases the surface area loading of the electroless plating bath by 800 times that normally acceptable for conventional electroless plating and this ultimately leads to homogeneous decomposition of the bath [5]. However, with the help of suitable stabilizers, electroless nickel composite coatings were prepared. An essential advantage of preparing composite coatings by electroless deposition compared to electrocodeposition is that the former allows accurate reproduction of the base

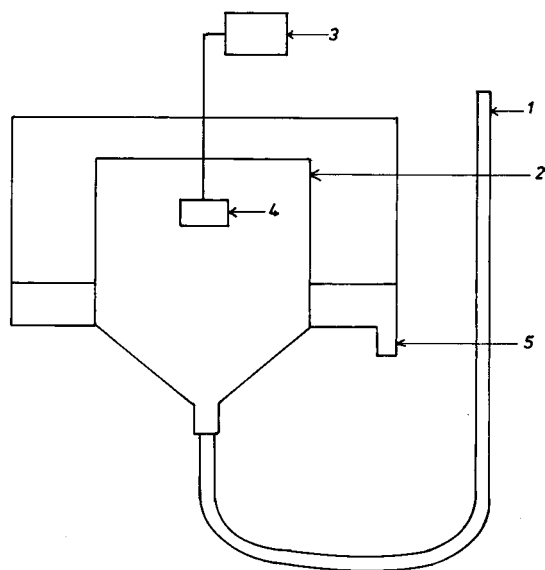


Fig. 1. Experimental set-up recommended for producing electroless composite coatings. (Adapted from Indira Rajagopal [5].) Key: (1) inlet for thermostated electroless composite bath, (2) overflow level, (3) Mechanical arrangement for the slow rotation of component, (4) component subjected to electroless composite coating, and (5) outlet for solution.

geometry and eliminates the need for subsequent mechanical finishing [1–3].

3. Preparation of electroless Ni–P composite coatings

An example of an experimental set-up used for producing electroless nickel composite coatings, similar to the one described by Metzger and Florian [4], is shown in Figure 1. Grosjean et al. [6, 7] used a similar cell assembly for incorporating silicon carbide particles in Ni–P matrix. This arrangement consists of a cylindrical vessel with a conical bottom and an outer jacket. The electrolyte with dispersed particles, at the appropriate temperature, is pumped through the bottom. The outer jacket collects the electrolyte that over flows. The substrate to be coated is suspended in the inner compartment. To keep the particles in suspension the electrolyte is agitated mildly. The conical shape at the bottom of the reaction vessel helps in collecting the dispersed particles, which settle due to gravity and redispense in the electrolyte with the aid of air agitation. Although vertical orientation of the substrate is sometimes adopted, it is generally advised that the substrate be rotated so as to ensure that the dispersed particles are incorporated uniformly.

4. Mechanism of particle incorporation

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. There

is no molecular bonding between particles and metal matrix [8, 9]. The mechanism of particle incorporation in electroless Ni–P matrix has received very little attention. Grosjean et al. [10] have studied the incorporation of SiC in an electroless Ni–P matrix using Guglielmi's mathematical model [11], which is proposed for composite coatings obtained via electrodeposition process. They suggest that the experimental results are in agreement with the mechanism proposed by Guglielmi [11].

5. Factors influencing particle incorporation

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 [12].

The size of the particles has a definite impact on their incorporation in the electroless Ni–P matrix [6, 13–15]. In general, it is recommended that particles must be large and heavy enough to settle in the solution yet not so large as to make the deposit rough or make it difficult for them to be held in suspension [13]. Also, the size of the particles should be selected with reference to the thickness of the electroless nickel deposit, as attempts made to incorporate 10 μm size particles in a 7 μm thick electroless nickel deposit resulted in unsatisfactory deposit and incorporation of 10 μm size particles even in a 25 μm thick deposit physically weakened the deposit [13]. It is suggested that particles in the size range of 2–7 μm might be suitable for codeposition in an electroless nickel matrix, with particles in the size range 4–7 μm being easiest to work with [13]. Grosjean et al. [6] have suggested that whatever the concentration of silicon carbide particles in the bath, the majority of the particles incorporated in the Ni–P matrix are in the range 0.3–1.8 μm diameter. Apachitei et al. [14] have found that, under similar operating conditions, smaller particles in a narrow size distribution yield maximum incorporation. Reddy et al. [16] recommended that for achieving a better integrity between the particles and the electroless Ni–P matrix, the size of the particles should be small so that they can be firmly held by the matrix.

Particle shape also plays a vital role in determining their incorporation level. It is generally believed that angular shaped particles will have a greater tendency to hold on to the surface upon impingement than round ones. Apachitei et al. [14, 15] have, however, shown that spherical shaped alumina particles resulted in better incorporation than irregular ones. The difference in particle shape also has a bearing on the type of finish of the deposit. Very smooth and very rough surfaces were obtained, respectively, from small rounded particles and large angular particles.

The other important factor that determines particle incorporation is the orientation of the work piece. Samples held vertically under uniform agitation, showed good incorporation. However, surfaces held horizontally and facing upwards were found to contain twice as many particles in comparison with those obtained using the vertical orientation [17]. Nevertheless, in such an orientation, very few particles were incorporated on the surface facing downwards. Hence it is recommended that the objects be rotated and/or tumbled in such a way that all parts of the surface are regularly presented upwards [18].

Agitation of the plating solution is also a key factor in determining particle incorporation. Various methods of agitation employed include circulation by pumping, purging of air, oxygen, nitrogen, ultrasonic agitation, and the plate-pumper technique. In practice, circulation by pumping or controlled air sparging is the best way to agitate the plating bath for obtaining maximum incorporation of particles in the Ni-P matrix. In general if the agitation is too slow (laminar flow), the particles in the bath may not disperse completely, except when their density is low. On the other hand, if the agitation is too high (turbulent), particles will not have sufficient time to get attached to the surface, and this results in poor particle incorporation. Figure 2 shows the level of incorporation obtained for silicon nitride, ceria and titania in a Ni-P matrix obtained at a fixed stirring speed (600 rpm) [19]. The lesser incorporation levels obtained for titania particles are due to the fact that these particles, being relatively smaller in size ($2.7 \mu\text{m}$) compared to silicon nitride ($7.0 \mu\text{m}$) and ceria ($7.9 \mu\text{m}$), are swept away from the electrode surface. This shows that the stirring speed should be optimized based on the size of the second phase particles to be incorporated. Kalantary et al. [20] have suggested that the laminar-

turbulent transition region is the most effective agitation condition for maximizing incorporation of particles in electroless composite plating. Xiang et al. [21] studied the effect of various modes of agitation on the level of incorporation of nano-sized diamond particles in the Ni-P matrix. Mechanical agitation resulted in lesser incorporation due to the directional flow in the bath. Although agitation by nitrogen avoids the directional flow, it does not help to decrease the extent of aggregation of nano-sized diamond particles in the bath. Injection agitation mode helps to shatter the aggregation of nano-sized diamond particles and results in higher levels of incorporation of particles in the electroless Ni-P matrix.

Concentration of the dispersed particles in the electroless nickel bath also plays a major role in influencing the incorporation level. Incorporation of Si_3N_4 , CeO_2 and TiO_2 particles in electroless Ni-P matrix (Figure 2) was found to increase with increase in their concentration in the bath up to 10 g l^{-1} , beyond which there seems to be saturation in spite of a continuous increase in their concentration up to 25 g l^{-1} . Several researchers [1, 19, 22–27] have also observed a similar trend of saturation in the incorporation level of various hard and soft particles. However, the critical concentration at which these particles exhibit saturation in incorporation is not very different. Hence, it is evident that the particle flux available for impingement at the electrode surface, as well as the time these particles are held on the surface, determines their level of incorporation rather than their type and nature. The observed increase in incorporation level up to a critical concentration can be ascribed to the increased flux of particles adjacent to the electrode surface. However, beyond this critical concentration, there is a possibility of grouping or agglomeration of these second phase particles due to the decrease in the mean distance between them resulting in settlement of the particles, causing either a saturation or slight decrease in the level of incorporation. Compared to electrodeposited nickel composite coatings, incorporation of particles for a given concentration is considerably higher for electroless Ni-P deposits. Moreover, it is observed that to obtain a particular level of incorporation, a greater amount of particles in the bath is required in the case of electrocodeposition than electroless codeposition [1, 5, 22–24].

Besides the above factors, some special additives, mostly surfactants, also play a major role in deciding the incorporation of second phase particles. These additives are especially important in the incorporation of soft particles like polytetra fluoroethylene (PTFE), graphite and molybdenum disulphide [25, 28–35]. Wu et al. [36] have used sodium dodecyl sulphate to increase the dispersion and wettability of the silicon carbide particles. Grosjean et al. [37] have shown that with the addition of 'Forafac-500', the incorporation of silicon carbide particles could be raised from 19 to 53 vol %. Ger et al. [34] have suggested that, though surfactant additives enable a higher level of incorporation of PTFE

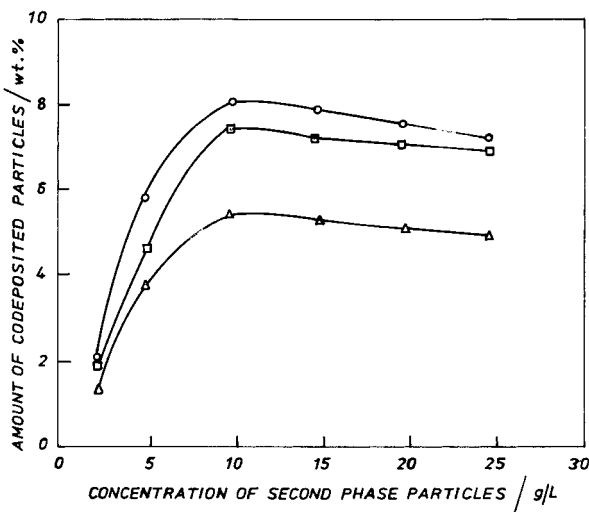


Fig. 2. Variation of the level of incorporation of Si_3N_4 , CeO_2 and TiO_2 particles in electroless Ni-P matrix as a function of their concentration in the plating bath, obtained at a fixed stirring speed (600 rpm). (Adapted from Balaraju [19].) Key: (○) Ni-P- Si_3N_4 ; (□) Ni-P- CeO_2 ; (△) Ni-P- TiO_2 .

particles, their concentration in the bath is critical. Beyond a certain concentration, the adsorption of surfactant additives on the substrate leads to increased surface coverage and acts as a barrier for the codeposition of PTFE particles in the Ni–P matrix. Hence, it is recommended that while modifying the electroless nickel plating bath using special additives, such as, surfactants, a better understanding of the adsorption of surfactants and the resultant surface coverage on the substrate is essential to achieve higher levels of incorporation.

It is clear from the above that several factors influence the incorporation of second phase particles in the electroless Ni–P matrix and under actual process conditions more than one factor plays a predominant role. A thorough knowledge of the influence of process parameters and conditions on electroless nickel deposits and the characteristic properties of the second phase particles used for incorporation are an essential prerequisite to achieve maximum incorporation.

The extent of particle incorporation in the Ni–P matrix determines its characteristics and a variety of methods have been used to determine the same. The amount of hard and soft particles incorporated in the electroless Ni–P matrix is determined by dissolving a known weight of the deposit in nitric acid and then filtering the particles through a weighed 0.1 μm membrane. From this, the percentage weight of particles incorporated in the deposit is estimated [19]. Dennis et al. [22] have used an electron microprobe analyser (EPMA) to determine the incorporation level of Cr_3C_2 in electroless Ni–P matrices. The proportion of the particles in the Ni–P matrix could also be quantitatively determined from the cross-section of the coating using image analysis. This method, developed by Bozzini [38], was also used by Pena Munoz et al. [39] and Grosjean et al. [6] to determine the extent of particle incorporation in the coating. The use of the plasma emitting spectrum analyser, which provides a direct analysis of the composite coating constituents, was adopted by Yu and Zhang [40]. The method of particle counting by observation of the coating surface morphology was adopted by Losiewicz et al. [41] in the case of TiO_2 and PTFE particles. Serhal et al. [42, 43] have used infrared reflection absorption spectroscopy to determine the PTFE content of electrodeposited Au–Co–PTFE coatings. These methods could be extended for determining the particle content of composite coatings prepared by electroless deposition.

6. Structure and properties of electroless Ni–P composite coatings

6.1. Structure

Hansen and Møller [44], Balaraju [19] and Balaraju and Seshadri [26] have studied the effect of incorporation of TiC , Si_3N_4 , CeO_2 and TiO_2 particles and suggest that incorporation of these particles does not alter the structure of the electroless Ni–P matrix. SAD patterns



Fig. 3. SAD pattern of as-plated electroless Ni–P– Si_3N_4 composite coating. (Adapted from Balaraju [19].)

obtained on the Ni–P matrix of the Ni–P– Si_3N_4 composite coating exhibit diffuse rings resembling that obtained for plain electroless Ni–P coatings (Figure 3). However, incorporation of B_4C particles is found to affect the orientation of nickel crystallites without influencing the crystallite dimensions; nickel tends to be less oriented in layers with B_4C particles [45]. Incorporation of SiC particles helps to increase nucleation centres, degree of crystallization, microstructural stability and prevents grain growth and aggregation of the matrix [36].

6.2. Hardness

The hardness of electroless Ni–P composite coatings increases with the incorporation of ceramic (hard) particles whereas with soft particles, the hardness tends to decrease [4, 8, 9, 13–15, 18, 19, 21, 22, 24–28, 32, 33, 36, 46–66]. The hardness of several electroless Ni–P composite coatings is presented in Table 1. The level of incorporation of particles, the phosphorus content of the matrix and heat-treatment determines the hardness of these coatings. For ceramic (hard) particles, like SiC , an increase in the level of incorporation increases the hardness of the coating [59], whereas for soft particles, like PTFE, the reverse is true [28]. The plot of level of incorporation of Si_3N_4 , CeO_2 and TiO_2 particles against increment in hardness (Figure 4(a–c)) further supports the fact that the increase in hardness is mainly a function of the level of incorporation rather than the hardness of the ceramic (hard) particles [19]. When ceramic (hard) particles are incorporated in the Ni–P matrix, an increase in hardness is noticed in all the deposits irrespective of their phosphorus content (2–13 wt % P) [55]. However, the influence of phosphorous can be seen on annealing these coatings arising from the formation of large amounts of hard Ni_3P phase when the phosphorus content of the coating is higher than 7 wt %.

Table 1. Hardness of electroless Ni-P composite coatings

Type of electroless Ni-P coating	Phosphorus content of the coating (wt %)	Particle content in the Ni-P matrix	Hardness (VHN ₁₀₀)		Reference
			As plated	Heat treated*	
Ni-P	8.00–9.10	–	410–600	979–1136	14, 15, 21, 22
Ni-P-nano diamond	7.60	0.52 wt %	470	939	21
Ni-P-nano diamond	6.27	2.21 wt %	755	966	21
Ni-P-SiC (irregular)	8.22	19.6 vol %	705 ± 42	1143 ± 20	14, 15
Ni-P-Al ₂ O ₃ (irregular)	8.22	9.7 vol %	643 ± 11	1139 ± 30	14, 15
Ni-P-Al ₂ O ₃ (spherical)	8.22	28.6 vol %	743 ± 15	1248 ± 68	14, 15
Ni-P-Al ₂ O ₃ (fibres)	8.22	10.7 vol %	640 ± 26	1147 ± 31	14, 15
Ni-P-Cr ₂ C ₃	7.20	27.0 vol %	645	1195 ^a	22
Ni-P-PTFE	9.5–10	25.0 vol %	275(b)	450 ^{b, c}	52
Ni-P-BN(h)	5.5	33.0 vol %	486(d)	753 ^d	62
Ni-P-Si ₃ N ₄	10.10	8.01 wt %	720	1171	19, 95
Ni-P-CeO ₂	10.18	7.44 wt %	676	1136	19
Ni-P-TiO ₂	10.40	5.42 wt %	642	1104	19
Ni-P-carbon nanotube	>7.00	12.0 vol %	520	1035	66

*Heat treated at 400 °C for 1 h unless otherwise indicated: (a) 500 °C/12 h; (b) load 50 g; (c) 350 °C/2 h; (d) knoop hardness.

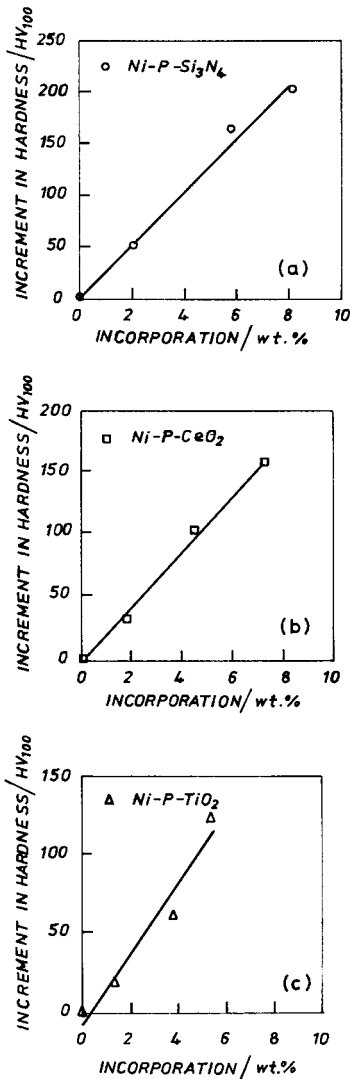


Fig. 4. Increment in hardness obtained as a function of level of incorporation of second phase particles in the electroless Ni-P matrix. (Adapted from Balaraju [19].) (a) Ni-P-Si₃N₄; (b) Ni-P-CeO₂, and (c) Ni-P-TiO₂.

The influence of heat treatment on the hardness of electroless Ni-P-SiC and Ni-P-PTFE coatings in comparison with electroless Ni-P coating is shown in Figure 5. The change in hardness with heat treatment temperature exhibits a similar trend for these coatings, which suggests that the hardening mechanism upon annealing is the same for both electroless Ni-P and Ni-P composite coatings. Increase in hardness up to 400 °C is due to precipitation hardening because of the formation of the intermetallic Ni₃P phase. The decrease in lattice defects and coarsening of the Ni₃P particles cause a reduction in hardness when these coatings were annealed beyond 400 °C.

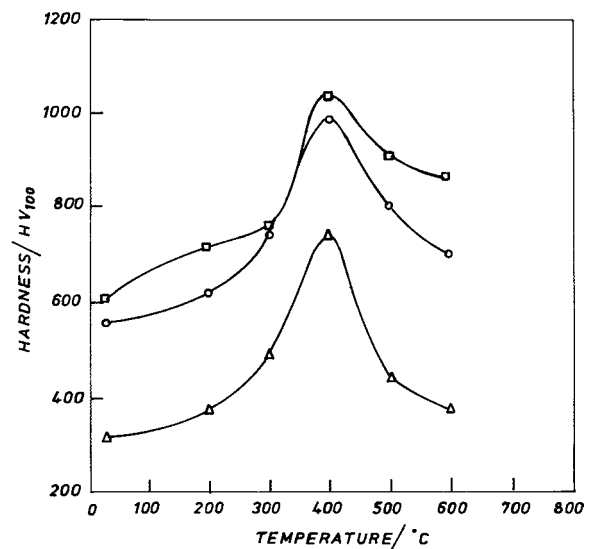


Fig. 5. Comparison of change in hardness with heat treatment temperature for electroless Ni-P, Ni-P-SiC and Ni-P-PTFE. (Data adapted from (a) Nishira and Takano [28] and (b) Li [58].) Key: (○) Ni-P; (□) Ni-P-SiC; (△) Ni-P-PTFE (a).

6.3. Young's modulus, plasticity and fracture toughness

Bozzini et al. [45, 67] evaluated the Young's modulus, plasticity and fracture toughness of electroless Ni–P–B₄C and Ni–P–diamond coatings and established their relationship with the tribological behaviour. The Young's modulus and fracture toughness of electroless Ni–P matrix increase with the incorporation of B₄C and diamond particles, both in the as-plated and heat-treated conditions and is found to be a function of particle content in the matrix [45, 67]. The plasticity of electroless Ni–P matrix is found to increase slightly with the incorporation of B₄C and diamond particles and the increase in plasticity is not measurably influenced by their volume fraction. In general, incorporated second phase particles tend to stiffen and harden the structure. The peculiar behaviour of increase in plasticity of these composite coatings is attributed to the partial removal of the plastic instabilities, which are typical for Ni–P coatings and strips [45, 67].

6.4. Surface finish

Incorporation of hard and soft particles in the electroless Ni–P matrix alters the surface finish both in terms of brightness and surface roughness (R_a) and in this respect, hard particles (SiC, Si₃N₄ etc.) increase the surface roughness whereas soft particles such as MoS₂, PTFE, etc. cause a reduction in surface roughness when compared to that of plain electroless Ni–P coating [19, 68, 69]. Surface roughness (R_a) is an important parameter as it determines the metal contact area between materials, which in turn increases the friction resistance, friction coefficient etc. [68]. The extent of change in roughness with the incorporation of hard and soft particles is dependent upon various parameters such as the type of particle, particle size, volume fraction of the particles and the thickness of the coating [69]. Xiang et al. [21] suggest that with the incorporation of nano-sized diamond particles (0.52–2.21 wt %) in the electroless Ni–P matrix the surface is changed from bright and smooth to foggy and rough with nodular protrusions covering the entire surface.

6.5. Friction, wear and abrasion resistance

Friction is the resistance to motion when bodies slide over one another [70–72]. Modification of the surface to impart dry lubrication is best achieved with the use of coatings. The natural lubricity of phosphorus enables electroless Ni–P coatings to exhibit a good lubrication property. However, under unlubricated conditions, prolonged testing results in galling or seizure failure of electroless Ni–P coatings [1, 2]. One of the options available to reduce such failures is the use of electroless Ni–P composite coatings.

Electroless Ni–P composite coatings containing ceramic (hard) particles such as SiC generally exhibit poor lubrication property when compared with electroless

Table 2. Friction coefficient for electroless Ni–P–PTFE composite coating measured by pin and ring machine (after [48, 49])

Coating on pin	Coating on ring	Coefficient of friction
Electroless Ni–P	Cr steel	0.6–0.7
Electroless Ni–P–PTFE	Cr steel	0.2–0.3
Electroless Ni–P–PTFE	Electroless Ni–P–PTFE	0.1–0.2
Electroless Ni–P–PTFE*	Cr steel	0.2–0.5
Electroless Ni–P–PTFE*	Electroless Ni–P–PTFE	0.1–0.7

* Heated at 400 °C for 4 h.

Ni–P coating, regardless of the extent of particle incorporation (7–20 vol %), due to their high surface roughness and high mechanical interlocking force [61, 68]. In contrast, electroless Ni–P matrix incorporated with soft particles like PTFE and graphite provide good lubrication when tested under unlubricated conditions due to their ability to prevent adhesion between the mating surfaces [25, 29, 40, 47, 48, 49, 52, 73–78]. Tulsi [48, 49, 73], Hadley and Harland [51] and Ebdon [74, 75] have suggested that the low coefficient of friction is due to the transfer of PTFE to the counterface material (Table 2). Nishira and Takano [28] suggest that these coatings have lower coefficient of friction compared to electroless Ni–P coatings, in both as-plated and heat-treated (400 °C, 1 h) conditions and the coefficient of friction is an inverse function of PTFE content. These coatings possess excellent lubrication properties in the temperature range from cryogenic to 290 °C. Izzard and Dennis [25] observed that electroless Ni–P–graphite (6 vol %) coatings fail to provide efficient lubrication when run against a steel counterface and the coefficient of friction is low when electroless Ni–P–graphite composite coating is run against itself. Hexagonal boron nitride, molybdenum disulphide, inorganic fullerene-WS₂ and carbon nanotubes are the other particles capable of providing a low coefficient of friction when incorporated in the electroless Ni–P matrix [35, 62, 64–66, 79].

Wear is defined as ‘damage to a solid surface, generally, involving the progressive loss of material, due to relative motion between that surface and a contacting substance or substances’ [80]. Adhesive and abrasive wear are the most frequently encountered wear mechanisms in electroless Ni–P coatings. Metzger and Florian [4], Brown [13], Parker [81] and Feldstein et al. [69] reviewed the wear resistance of electroless nickel composite coatings with various ceramic (hard) particles (Table 3). Gould [82] has reviewed the suitability of these coatings to combat adhesive and abrasive wear. The wear resistance of electroless Ni–P composite coatings is influenced by the type of ceramic (hard) particle incorporated in the deposit, its level of incorporation, its size and hardness, as well as hardness of the matrix [8, 9]. Straffelini et al. [83] suggest that wear of electroless Ni–P composite coatings occurs in two stages. During stage I, the deposits undergo a mild

Table 3. Abrasive wear of electroless Ni–P composite coatings (After Parker [81])

Type of coating	Taber wear index*	
	As plated	Heat Treated†
Ni–P	18	8
Ni–P–Cr ₃ C ₂	8	2
Ni–P–Al ₂ O ₃	10	5
Ni–P–TiC	3	5
Ni–P–SiC	3	2
Ni–P–B ₄ C	2	1
Ni–P–Diamond	2	2
Hard chromium	3	–
Aluminium hard coat	2	–

* Weight loss in mg/1000 cycles (average of 5000 cycles) with CS 10 wheels and a 1000 g load.

† Heated 10–16 h at 290 °C.

abrasive wear whereas during stage II the wear is severe and characterized by the brittle detachment of debris. Stage I represent the initial wear damage and reflect the surface durability.

Wear resistance of electroless Ni–P–SiC composite coatings has been studied by several authors [47, 55–58, 68, 84–88]. Increase in wear resistance with increase in SiC incorporation level is reported by Sale [84]. Wu et al. [68] suggest that the dispersion strengthening effect of SiC particles and the strengthening effect of the Ni–P alloy matrix enables such coatings to provide better wear resistance. Zonggang and Xinmin [55, 56, 88] argue that the Ni–P matrix should possess high phosphorus content (>7 wt %) in order to be capable of supporting the SiC particle to offer superior wear resistance, both in as plated and heat-treated conditions. The effect of heat treatment on the wear resistance of electroless Ni–P–SiC composite coatings reveals that wear resistance increases with increase in heat-treatment temperature up to 350 °C. Further increase in temperature (up to 600 °C) results in increase in the wear rate with further deterioration at higher temperatures (~800 °C). The possibility of reaction between nickel and SiC around 580 °C and a partial melting of Ni–P eutectic at 880 °C are responsible for the poor wear characteristics at high temperatures [47]. The formation of nickel silicide (Ni₃Si) is governed by the diffusion of nickel atoms into the SiC lattice and it occurs at the SiC/Ni–P matrix interface upon heat-treatment at 500 °C for 1 h. The Ni₃Si formation increases the adhesion between the reinforcement and the matrix and decreases the abrasive wear behaviour [85, 86]. Chen et al. [87] have identified the formation of γ -Ni₅Si₂ and β ₁-Ni₃Si phases on annealing above 450 °C. However, further annealing at 500 °C leads to the incorporation of phosphorous into the Ni₅Si₂ lattice and results in the formation of Ni₅(Si_{1-x}P_x)₂ solid solution.

The incorporation of Cr₃C₂ particles (27 vol %) in the Ni–P matrix is found to increase the wear resistance when evaluated by pin-on-disc and simulated hot forging tests [22]. Heat-treatment at 400 °C for 1 h

further enhances the wear resistance of these coatings. Leon et al. [52] suggest that even in as-plated condition, electroless Ni–P–hexagonal boron nitride composite coating is capable of providing higher wear resistance than plain electroless Ni–P coating heat-treated at 400 °C for 1 h. Wear decreased by nearly two orders of magnitude when the Ni–P matrix is incorporated with 33 vol % hexagonal boron nitride particles [62, 89]. Increase in wear temperature decreases the wear resistance. At high temperatures of the order of 400 °C, a mixed adhesive and fatigue wear mechanism, accompanied by a large plastic deformation of coatings and high coating transfer to the counterface material was observed [90]. This indicates that the tribological response of composite coatings at high temperatures is related to the mechanical properties of the Ni–P matrix, that is, to its behaviour to withstand the applied stresses as the temperature increases, irrespective of the nature and properties of the codeposited particles. Incorporation of inorganic fullerenes-WS₂ nanoparticles in the electroless Ni–P matrix increases the wear resistance under oil lubricated conditions and in this respect these coatings are better than Ni–P, Ni–P–2H–WS₂ and Ni–P graphite coatings. The improvement in wear resistance following the incorporation of inorganic fullerenes-WS₂ nanoparticles is due to its ability to serve as spacers between the asperities of two mating metal surfaces [79]. Carbon nanotubes, when incorporated in an electroless Ni–P matrix (12 vol %), increases the wear resistance both in as-plated and heat-treated conditions [64–66]. The wear resistance offered by these coatings is better than that of electroless Ni–P–SiC and Ni–P-graphite coatings.

Graham and Gibbs [91] investigated the difference in wear behaviour of electroless Ni–P composite coatings having natural and shock synthesized diamond particles by examining the yarnline wear groove with the help of SEM. Synthetic diamond particles appear to give a superior wear resistance. This has been ascribed to the much stronger bonding between the Ni–P matrix and the rough and irregularly shaped synthetic diamond particles. In contrast, natural diamond particles, which are relatively smooth, are incorporated only to a lesser extent and such coatings wear to a greater extent, under identical testing conditions. Reddy et al. [16] studied the wear resistance of electroless Ni–P composite coatings incorporated with diamond particles of different size ranges (3–40 μ m). Coatings incorporating finer diamond particles (3–6 μ m and 6–12 μ m) are more wear resistant compared to those with coarse diamond particles (20–40 μ m). This effect is largely a function of the degree of incorporation of diamond particles for a given coating thickness, which is higher for finer diamond particles. For achieving higher wear resistance, the integrity between particle and the electroless Ni–P matrix should be better, which is decided by the ratio of the coating thickness to the size of the particles.

Incorporation of ceramic (hard) particles might also have a deleterious effect. Hard particles, such as, tungsten carbide and diamond cause pronounced

abrasion of the counterface materials [81]. Similarly, higher levels of B₄C particles incorporated in the Ni–P matrix is reported to increase the wear rate, due to the protrusion of the B₄C particles, which increases the supporting points and causes increased wearability [59]. The results of the Falex test performed on electroless Ni–P and Ni–P–Si₃N₄ coatings suggest that these coatings are safer to use only under lubricated condition [19].

6.6. Corrosion resistance

In general, the corrosion resistance of electroless Ni–P composite coatings is believed to be less than that of electroless Ni–P alloy 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 [75, 92, 93]. However, the corrosion performance of electroless Ni–P composite coatings was found to be satisfactory by Hubbell [8, 9], Hussain and Such [18] and Shoeib et al. [94]. 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 (Table 4) [95]. 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 [96].

6.7. High temperature oxidation resistance

The oxidation behaviour of electroless Ni–P composite coatings has received considerably less attention. Frolova et al. [97] suggested that addition of B₂O₃ to a Ni–P glass mixture decreased the extent of oxidation. Similarly, it was found that incorporation of Si₃N₄ (8.01 wt %), CeO₂ (7.44 wt %) and TiO₂ (5.42 wt %) in an electroless Ni–P matrix increases the oxidation resistance and the extent of increase is a function of the amount of particles incorporated in the Ni–P matrix [19].

6.8. Magnetic behaviour

Bozzini et al. [98] suggest that electroless Ni–P–B₄C coating in the as-plated condition exhibit a strong dependence of magnetic susceptibility on the applied magnetic field due to its large structural inhomogeneity when compared to plain electroless Ni–P coating. However, after crystallization, plain electroless Ni–P coatings become homogeneous and attain ferromagnetic nature, whereas composite coatings preserve field dependence and exhibit typical super paramagnetic be-

Table 4. Corrosion resistance of electroless Ni–P composite coatings

Type of coating	Method of evaluation	Result	References
Electroless Ni–P–SiC	Neutral salt spray test; As per ASTM B-117	Same degree of protection offered by electroless Ni–P coating having similar thickness	8, 9
Electroless Ni–P–TiO ₂	CASS test for 16 h; As per ISO 3770: 1976	Same degree of protection offered by electroless Ni–P coatings having similar thickness	18
Electroless Ni–P–PVA	Immersion test in deionized water for 7 days	Corrosion rate is 0.0602 mg cm ⁻² per day	94
Electroless Ni–P–PAm	Immersion test in deionized water for 7 days	Corrosion rate is 0.0150 mg cm ⁻² per day	94
Electroless Ni–P–PAm	Immersion in artificial sea water (33.5 g l ⁻¹ NaCl) for 28 days; As per Egyptian standard ES 823: 1996	Enhanced corrosion protection property	94
Electroless Ni–P–Si ₃ N ₄	Potentiodynamic polarization study in 3.5% NaCl solution	Corrosion current density is 2.5 μA cm ⁻²	19, 95
Electroless Ni–P–CeO ₂	Potentiodynamic polarization study in 3.5% NaCl solution	Corrosion current density is 4.0 μA cm ⁻²	19
Electroless Ni–P–TiO ₂	Potentiodynamic polarization study in 3.5% NaCl solution	Corrosion current density is 6.0 μA cm ⁻²	18
Electroless Ni–P–Si ₃ N ₄	Electrochemical impedance study in 3.5% NaCl solution	R _{ct} is 90 535 Ω cm ² C _{dl} is 11 F cm ⁻²	19, 96
Electroless Ni–P–CeO ₂	Electrochemical impedance study in 3.5% NaCl solution	R _{ct} is 90 700 Ω cm ² C _{dl} is 11 F cm ⁻²	19, 96
Electroless Ni–P–TiO ₂	Electrochemical impedance study in 3.5% NaCl solution	R _{ct} is 58 991 Ω cm ² C _{dl} is 17 F cm ⁻²	19, 96

haviour. The observed difference in magnetic behaviour between these coatings is because the B₄C inclusions (25 vol %) in the coating act as centres for precipitation of nickel phase.

7. Applications of electroless Ni–P composite coatings

The applications can be broadly classified into three categories; these provide (a) wear resistance, (b) a surface with a desired friction coefficient, and (c) a hard surface for machining and finishing tools [4, 9, 48, 99, 100]. The life of moulds for plastics, rubber etc., which usually last for 10 000 mouldings, is increased by 15 times when they are coated with a 50 µm thick Ni–P–SiC coating [4]. Similarly, Ni–P–SiC coating prevents accelerated corrosion of abrasion moulds in the plastics industry and in this respect it is superior to chrome plating. The ability to coat even large parts enables electroless nickel composite coating to be given to automobile components like reinforced plastic front-end pieces [9]. Electroless Ni–P–SiC coating has been used to overcome problems due to pickup and galling, which arise during forming and drawing operations [9]. The same coating has been used in foundries for reducing wear and helping to release sand cores, without breakage, from core boxes [9].

Electroless Ni–P–PTFE coatings offer non-stick, nongalling, higher dry lubricity, low friction, good wear and corrosion resistant surfaces. Applications for which the electroless Ni–P–PTFE composite coatings have been used include moulds for rubber and plastic components, components for pumps and valves, butterfly valves for the oil and gas industry, fasteners, precision instrument parts, aluminium air cylinders, carburettors and choke shafts [48]. The coatings can be used under a wide range of temperatures from cryogenic to 290 °C. A Ni–P–PTFE composite coating applied to a butterfly valve prevents pick up and galling and decreases the leak rate and enables safe operation of the valve for cryogenic applications. Carburettor parts are being coated with Ni–P–PTFE for its nonstick, dry lubrication and low coefficient of friction properties, which minimizes build-up of gummy deposits on the choke shafts. Electroless Ni–P–PTFE coatings also find application in chains, lock parts, valves, pistons and piston rings, roller bearings, mining equipment parts and dies for striking coins. The internal surfaces of long aluminium cylinders were protected by a thin coating of electroless nickel composite against the wearing action of rubber pistons oscillating in the cylinder.

Ni–P–diamond composite coatings are applied to improve the wear resistance of reamers made of highly abrasive aluminium alloys, broaching tools for graphite, valves for viscous rubber masses, and thread guides for use in textile machines and friction texturizing discs [99]. Ni–P–diamond coatings enable slipless transmission of very high rotational speed, an essential requirement of yarn brakes, infinitely variable gears, and friction

clutches in the textile industry [99]. Use of electroless Ni–P–diamond composite plating is almost mandatory for making profiled diamond tools used for microfinishing screw threads, ball-guiding grooves and other profile sections where high accuracy is demanded and which is difficult to achieve by conventional electroplating [99].

8. Concluding remarks

The present review outlines the method of formation of electroless Ni–P composite coatings, the mechanism of particle incorporation, factors influencing it and their effect on coating characteristics. The property enhancement offered by these coatings has paved the way for their use in numerous industrial applications. Further developments in this field will secure a prominent place for these coatings in the surface engineering of metals and alloys.

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