Accepted for ***Surface and Coatings Technology January 23, 2019***

**Electrodeposition of Ni-P Alloy Coatings: A Review**

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**Abstract**

Ni-P coatings are extensively employed in engineering, owing to their mechanical and tribological properties which confer protection against corrosion and wear. Classically, such deposits can have a thickness of <500 m, although there is a trend to thinner coatings to achieve faster deposition and lower costs. Depending on their composition and structure, as-plated deposits demonstrate good mechanical, tribological and electrochemical features, catalytic activity but also beneficial magnetic characteristics. Following thermal treatment, the hardness of Ni-P metal deposits can approach or exceed that of hard Cr coatings. This paper provides a general survey of research on the electrodeposition of Ni-P binary alloy coatings. Proposed phosphorus incorporation mechanisms, Ni-P alloy microstructure before and after thermal treatment. Mechanical, tribological, corrosion, catalytic and magnetic properties are considered, as are the key process variables influencing the phosphorus content of deposits and the roles of the major electrolytic bath constituents. The merits of employing pulse plating and fabrication of newer (layered and functionally graded) structures are concisely explored. Interaction of four aspects (substrate state, electrolyte composition, process conditions and deposit properties is seen to be important during electrodeposition of Ni-P alloys; areas deserving further study are identified.

**Keywords:** coatings; electrochemical; electrolyte; engineering; mechanical properties; tribology.

**Highlights**

 The electrodeposition of Ni-P alloy coatings and their use are reviewed.

 Substrate, electrolyte, process conditions and deposit properties are important.

 Electrode reactions, bath composition and additives are considered.

 Developments include pulse plating, layered and multifunctional layers.

 Aspects deserving further R & D are identified.

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*(Approx. 21,000 words, 15 reactions/equations, 2 tables, 17 figures and 155 refs).*

**Nomenclature**

Symbol Meaning Units

*A* Projected electrode area cm2

*F* Faraday constant A s mol-1

*I* Total current A

*j* Overall current density A cm-2

*jH2*Partial current density for hydrogen evolution A cm-2

*jHPO3-*Partial current density for reduction of hypophosphite ion A cm-2

*M* Molar mass of material g mol-1

*n* Amount of material mol

*q* Electrical charge A s

*t* Time s

*T* Temperature oC

*x* Mean deposit thickness cm

*z* Electron stoichiometry Dimensionless

** Density of material g cm-3

** Cathode current efficiency for nickel deposition Dimensionless

**Abbreviations**

CVD Chemical vapour deposition

DC Direct current

DES Deep eutectic solvent ionic liquids

EP Electroplated

EPMA Electron probe microanalysis

fcc Face centred cubic

PC Pulsed current

PFOS Perfluorooctanesulfonic acid

PRC Periodic reverse current

PS Plasma sprayed

PVD Physical vapour deposition

XPS X-ray photoelectron spectroscopy

SEM Scanning electron microscopy

**1**. **Introduction**

In the modern world, billions of dollars per year are lost due to maintenance or premature failure of components due to corrosion, wear, fatigue and rupture. Surface degradation affects many industrial sectors and can account for up to 3-4% of the Gross Domestic Product in developed economies [[1](#page58), [2](#page58)]. The degradation of material surfaces can be lessened by strategic application of a coating that will mitigate the influence of the surrounding environment and working conditions, prolonging the service life and reliability of the equipment.

The wide variety of techniques for deposition of coatings include mechanical, physical, chemical and electrochemical processes [[3](#page58)]. Among them, direct electroplating offers many advantages [[4](#page58)–[6](#page58)]. Electrodeposition of the coating takes place at relatively low cost, usually in an aqueous solution, at atmospheric pressure and at modest temperatures (20-60 oC), which makes it suitable for industrial scale-up [[7](#page58)–[9](#page58)]. A particular advantage of electroplating is the possibility of customising appearance and properties of the coating by modifying the composition of the electroplating bath and/or the electroplating conditions to produce a wide range of metals, alloys, conductive polymers and composites. Deposition rates in the order of several tens of micrometres per hour can be routinely achieved [[10](#page58)].

In aerospace, automotive and general engineering sectors of industry, functional Cr coatings are widely employed due to their properties, such as hardness, corrosion-, wear- and heat resistance together with a low friction coefficient against steel [[7](#page58)].

The traditional commercial Cr electrodeposition process employs an aqueous bath containing Cr(VI) in acid solution. This hazardous solution, being carcinogenic, corrosive and strongly oxidising, imposes serious health, safety and environmental concerns [[11](#page58)]. As a consequence, the use of hexavalent chromium has been limited by the European Union Restriction of Hazardous Substances Directive [[12](#page58)] and by increasing international legislation. In addition, the typical wetting agent perfluorooctanesulfonic acid, PFOS employed in Cr electroplating to reduce acid mist generated during plating is being prohibited due to its chemical stability, which presents a problem for the environment [[7](#page58)]. Presently, much attention is focused on finding alternatives to Cr deposition, while maintaining the need to meet excellent functional properties of coatings.

It has been reported by many authors that certain binary, ternary or quaternary alloy coatings may present a suitable replacement for hard Cr and may possess an interesting combination of features that can culminate even in a possible improvement in terms of performance characteristics [[13](#page59)–[16](#page59)]. Extensive studies have shown that coatings based on Ni-P, with careful tailoring of composition and structure, can offer adaptive solutions to a wide range of environmental and working conditions [[17](#page59), [18](#page59)]. Compared to Cr coatings obtained from hexavalent Cr baths, effluents resulting from Ni electroplating involve simpler treatment, such as Clean Technologies (based on electrodialysis) [[19](#page59)]. Ni-P coatings exhibit many interesting features, depending on the electroplating conditions and the applied post-treatment. Deposits are often characterised by good mechanical properties, high wear- and corrosion resistance, electrocatalytic activity and favourable tribological features. With adequate attention to composition, structure and subsequent thermal treatment, the hardness of Ni-P electrodeposits can approach or surpass that of hard Cr coatings [[20](#page59)]. Ni-P alloy electrodeposits find applications as protective, functional and decorative coatings, primarily in automotive, aerospace and general engineering industries. Notably Ni-P deposits are used in the fabrication of decorative coatings for automotive industry, high precision components, diffusion barriers, catalytic coatings for hydrogen evolution in water electrolysis, thin film magnetic memory discs, microbatteries and sensors [[21](#page59)].

In order to enhance Ni-P deposit properties, it is essential to control the coating composition and microstructure. This can be achieved by controlling the electroplating bath composition and deposition conditions followed by applying appropriate post-treatment. Codeposition of nanometre, sub-micron or micron sized particles and fabrication of composite coatings are important trends. While classical industrial demands on hard, homogeneous, wear resistant coatings and corrosion protection are still valid, added capacities in terms of: chemical stability, biocompatibility, microstructured surfaces and functional (e.g., self-lubricating or magnetic) coatings are in high demand. This is where the production of composites but also compositionally modulated coatings, characterised by variable configuration across their thickness, can offer new possibilities and new combinations of properties that can be adapted to satisfy the increasing demands on multi-functional coatings.

**2. The benefits of electroplating and its prospects**

The beginnings of modern electroplating can be traced back to the start of the 18th century, when Brugnatelli performed the first documented electrodeposition of gold metal from a saturated gold solution [[22](#page59)]. In 1840, Henry and George Elkington were awarded the first patent for gold and silver deposition using potassium cyanide electrolytes. Electroplating quickly spread throughout the world and became a common process for depositing precious and non-precious metals, including copper, gold, nickel, brass, tin, and zinc. Adams’ patent for Ni ammonium sulfate electroplating bath (1869), Weston’s addition of boric acid to the Ni plating bath (1878) but also the studies on anode behaviour and chlorides introduction of chloride ions (1906) all paved the way establishing a sustainable Ni electroplating industry [[23](#page59)]. Introduction of the famous plating formulation for rapid nickel plating from an acid sulphate bath by the Watts in 1916 [[24](#page59)] provided the basis for research and production of most Ni coatings and remained a ’go-to’ composition owing to its stability and versatility. A wide range of coatings can be cathodically deposited from an undivided Watts nickel-based electroplating bath by appropriate control over operational conditions, including the temperature and current density, together with the type and degree of agitation [[25](#page59)]. In 1946, Brenner and Riddell discovered ‘autocatalytic’ or ‘electroless’ metal deposition by adding sodium hypophosphite as a reducing afent to a nickel bath [[26](#page60)]. Further studies by Brenner led to development of a Ni-P alloy electrodeposition process and first attempts at stating the alloy formation mechanism and deposit optimisation [[27](#page60), [28](#page60)]. After the pioneering work of Brenner, many authors continued the quest for elucidation of alloy codeposition paths and the influence of deposition conditions on microstructure and properties, owing to the alloy’s many benefits. This led to modern Ni-P deposits, recent advancements being considered in this review. Figure [1](#page72) provides a timeline for the evolution of Ni-P alloy electroplating, from the early beginnings of the metal electrodeposition towards modern Ni-P coatings.

Conventional electroplating possesses many advantages in terms of versatility, ease of use and cost effectiveness. The technique has many assets when compared to physical methods such as magnetron sputtering and chemical methods such as chemical vapour deposition. Physical vapour deposition is a high cost line-of-sight process with possibly poor throwing power, while in chemical vapour deposition high operating temperatures may cause substrate softening [[3](#page58), [29](#page60)]. Heat resistance of the substrate may very much limit the choice of the deposition technique, in particular for metals such as Al, Cu, Mg for which maximum deposition temperature is approx. 100 oC. Disadvantages of electroplating include problems with current efficiency below 100%, restricted throwing power, inadequate substrate adhesion and nonuniform coating thickness.

Dini [[30](#page60)] performed a comparison of coatings produced by various deposition techniques (PVD, CVD, PS and EP), considering a wide range of properties, including structure, porosity, density, stress, corrosion, adhesion, tribology, fatigue and thermal conductivity. His findings indicated that no coating technology provides superior results in terms of all considered parameters. Rather, the choice of coating technique must be made by taking into consideration a number of factors, such as substrate compatibility, adhesion, porosity, possibility of repair or re-coating, inter-diffusion, effect of thermal cycling, resistance to wear and corrosion, whilst simultaneously establishing a sensible balance between the obtained benefits and the incurred costs.

Electroplating possesses advantages over traditional electroless plating, since they can provide a higher deposition rate from simpler electrolytes and show the added benefit of controlling the deposit composition and microstructure by changing the applied current waveform and operational conditions [[4](#page58), [5](#page58), [31](#page60)]. Thick deposits (<1 mm) are easily achieved through electroplating although most applications call for a coating thickness of 10-25 m. Amorphous Ni-P alloys can be electroplated up to mm thickness on widely differing substrates [[17](#page59)]. However, it is still necessary to work on improving the electroplated deposit uniformity and on maximising the process efficiency, compared to electroless plating. The electroless process must be autocatalytic at the surface of the workpiece to ensure continuing deposition. Electroless plating is characterised by solution instability, a relatively slow deposition rate (generally around 10 µm h 1, acidic electroless baths can plate at about 25 µm h 1), high temperatures of operation (often >85 oC to achieve an acceptable deposition rate), difficulties with barrel plating of small parts and high cost, which is approximately 5 to 10 times higher than for electrodeposition [[32](#page60)].

Nevertheless, electroless plating enjoys excellent throwing power and the advantage of producing deposits of uniform thickness particularly on components of complex shape [[33](#page60)]. In order to achieve the latter by electroplating, an intricate system of internal anodes and/or shielding may be necessary, due to the non-uniform current distribution characterising this process. Ni-P deposits fabricated by electroless deposition are also reported to be harder and to possess better corrosion resistance than those obtained through electrodeposition [[17](#page59)]. An overview of key benefits and limitations of the alloys and composites electroplating process is given in Table [1](#page79).

Electroplating is a mature surface finishing technique which has been widely applied in industry since the end of the 19th century. According to several global market studies, electroplating is set to witness an expansion, predominantly in the Asia-Pacific excluding Japan region (APEJ). In the market report titled “Electroplating Market: Global Industry Analysis and Opportunity Assessment, 2016–2026” [[34](#page60)], Future Market Insights foresee that the global electroplating market is expected to expand at a compound annual growth rate of 3.7% by the end of 2026 reaching worth of US$ 21 Bn. APEJ will be according to them the fastest growing region and the Automotive and Electrical & Electronics sectors are estimated to collectively hold about 65% of the total value share of the global electroplating market. On the basis of metal type, owing to the growth of the Electrical & Electronics sectors of industry, copper and nickel are expected to gain significant ground. Future Market insights identify applications across a diverse set of industries and anticipated growth in the Asia Pacific region, while challenges are likely to come from stricter legislation and stringent environmental regulations, decelerated economic growth in mature markets and the growing popularity of electroless nickel plating.

**3. Ni-P alloy electroplating**

**3.1 Electrode reactions**

The principles of nickel electroplating are shown as a schematic in Figure 2. Normally, an undivided cell is used with a soluble nickel anode in an uncomplexed acidic electrolyte. The figure highlights some of the important aspects involved in choice of electrolyte and control of operational conditions.

In the usual case of a soluble anode, nickel ions are formed:

Ni – 2e- = Ni2+ (1)

When an insoluble anode, such as platinised titanium is used, oxygen is evolved:

2H2O - 4e- = O2 + 4H+ (2)

At the cathode workpiece, the main reaction is nickel deposition:

Ni2+ + 2e- = Ni (3)

Which is accompanied by deposition of phosphorus, This can take place directly via reduction of an oxyanion such as hypophosphite, a simplified reaction being:

H2PO3- + 4H+ + 3e- = P + 3H2O (4)

An indirect reaction is also possible via surface adsorption of hydrogen atoms:

6H+ + 6e- = 6Hads (5)

and *in-situ* generation of phosphine as an intermediate:

H2PO3- + H+ + 6Hads = PH3 + 3H2O (6)

followed by rapid decomposition of phosphine:

2PH3 + 3Ni2+ = 3Ni + 2P + 6H+ (7)

Hydrogen evolution takes place as a secondary reaction at the cathode surface:

2H+ + 2e- = H2 (8)

This reaction not only lowers current efficiency and decreases local pH but can result in deposit porosity due to hydrogen gas bubbles sticking to the surface, if the electrolyte/electrode movement is limited or a surfactant is not present in the bath.

**3.2 The mechanism of** **phosphorus codeposition**

Ni-P electroplating is predominantly performed in an aqueous electrolytic bath that contains Ni+2 ions as a source of nickel and a phosphorus oxyacid (or its salt) which acts as a source of phosphorus. Electrodeposition is driven by the electric current passing between the anode and the cathode (plating substrate) [[33](#page60)]. Standard reduction potentials for Ni (-0.25 V) and P (-0.28 V) are near to each other facilitating their codeposition. Earlier reviews that consider the electrodeposition of Ni-P alloys and their composites have been contributed by Berkh and Zahavi [[18](#page59)] and Daly and Barry [[17](#page59)]. The 1996 review [18] considers NiP alloys and their composites containing solid inclusions of SiC, Al2O3, ZrO2, etc. The coating properties, including microhardness, ductility, internal stress, porosity, wear and corrosion resistance are discussed in terms of coating composition and structure. With a view to use as wear-resistant and anticorrosive coatings. The 2003 contribution [17] considers the importance of bath pH, mechanisms of Ni-P deposition and the crystallinity of deposits. Despite both being significant surveys of the topic, a need for a full critical review containing an overview of more recent advances that highlights important aspects, including alloy preparation, composition control, its properties and emerging trends is important.

Two mechanisms are generally proposed in order to elucidate the process of phosphorus incorporation during Ni-P alloy electrodeposition, namely: direct and indirect mechanism. In the direct mechanism, it is proposed that Ni2+ ions and phosphorus oxyacid are directly reduced to Ni and P atoms which then form a NixP solid solution. According to Brenner [[27](#page60)] who first suggested this mechanism, the hypophosphite anion is reduced to phosphorus and phosphorus is codeposited with nickel owing to the polarisation involved in the deposition of nickel assisting the deposition of phosphorus (induced codeposition). The main argument against the direct deposition mechanism is the claimed impossibility of obtaining phosphorus in aqueous solutions through electrochemical methods in the absence of metal ions [[35](#page60)].

According to the indirect mechanism, which was first proposed by Fedotev and Vyacheslavov [[36](#page60)] then by Ratzker et al. [[37](#page60)], hypophosphite ion is initially reduced to phosphine (PH3) in the presence of H+ ions, PH3 is then oxidised to P in the presence of Ni2+ ions, while Ni2 is simultaneously reduced to metallic Ni. Zeller and Landau [[38](#page60)] supported the hypothesis of PH3 formation and suggested its subsequent reaction with Ni2+ to produce Ni-P, H+ and a series of phosphorous oxyanions.

The indirect mechanism has been corroborated by authors who have reported the detection of phosphine [[39](#page60)–[41](#page61)]. Harris and Dang [[39](#page60)] quantified phosphine by its chemical analysis during Ni-P electrodeposition. PH3 was also identified by Crousier et al. [[35](#page60)] who performed a cyclic voltammetry study. Zeng and Zhou [[42](#page61)] obtained Raman spectra during Ni-P electrodeposition that indicated the formation of Ni(PH3)n intermediate species. According to the authors, this intermediate was then oxidised by Ni2+ with consequent formation of the alloy. Saitou et al. [[40](#page60)] generated analytical solutions of kinetic equations for the reactions. The results predicted a dependence of the phosphorous content in Ni-P electrodeposits on current density (Figure [3](#page73)). Phosphorous content, as measured by the electron probe microanalyser (EPMA), was found to decrease with the increase in current density which was in agreement with the solution of kinetic equations corresponding to the indirect mechanism of phosphorus codeposition.

Morikawa and colleagues [[43](#page61)] studied the electrodeposition of Ni-P from a citrate bath. Binding energy data obtained from X-ray photoelectron spectroscopy (XPS) indicated the direct reduction of H2PHO3 to P, implying direct deposition of nickel-phosphide. Detection of phosphine in previous studies include Morikawa et al., who explained the possibility of partial reaction of phosphorus atoms on the electrode surface with hydrogen at low pH values, which in their case was negligible owing to high pH value of the employed citrate bath.

Ordine and coworkers [[41](#page61)] found kinetics of phosphorus incorporation to be strongly affected by the electrolytic solution pH value. They employed interfacial pH measurements, cathodic polarisation curves and electrochemical impedance spectroscopy and observed different mechanisms of Ni and Ni-P electrodeposition at different degrees of solution acidity in the presence of NaH2PO2.H2O in the electroplating bath.

Sotskaya and Dolgikh [[44](#page61)] carried out electrochemical studies of the cathodic kinetics of hypophosphite anion reduction. Their results indicated that phosphorus formation proceeds via parallel electrochemical and chemical routes, depending on the catalytic nature of the metal surface. According to the authors, atomic phosphorus is formed as a result of the cathodic reduction of hypophosphite ion. They observed also that the Ni-P alloy electrosynthesis takes place in the region of potential region which does not correspond to the electroreduction of hypophosphite anion. They concluded that a chemical disproportionation of hypophosphite occurs in this case [[45](#page61)].

Bredael et al. [[46](#page61)] proposed that two mechanisms are involved in the formation of Ni-P electrodeposits, one that is active at low current efficiency and leads to formation of amorphous deposits and the other dominating at high current efficiencies and leading to formation of crystalline ones. Such a claim was corroborated by polarisation measurements in which a change of slope of the polarisation curve was observed, this at the average current density corresponding to the transition from amorphous to crystalline structure.

There is disagreement on whether a direct or indirect mechanism can be assumed, with most of the authors supporting the latter. Phosphorus formation and incorporation into the nickel lattice are both complex and several different mechanisms can operate to control codeposition, depending on the electrolyte composition and process conditions.

**3.3 The overall rate of deposition**

The overall rate of an electrode process can be described by Faraday’s laws of electrolysis, where the electrical charge, *q* flowing through a cell due to the movement of *z* electrons is:

*q* = *n*.*z*.*F* (9)

where the electrical charge, *q* in the time interval *t2* - *t1*, is:

(10)

If *t2* = 0, the overall charge is involved; otherwise, the charge in the time interval (*t2-t1*) is involved.

It is common to electroplate at constant current, when the expression for the mean rate of deposit thickness development becomes:

 (11)

where *j* is the current density [A cm-2], i.e., the current, I per unit electrode area, :

*j* = *I* / *A* (12)

 is the deposit thickness [cm],is the density of the deposit [g cm-3], is the number of electrons in the electrode process [dimensionless], *F* is the Faraday constant [96 485 C mol-1], is the time [s], (which is <1) is the current efficiency for metal deposition [dimensionless] and M is the molar mass of deposited metal [g mol-1]. In the case of pure nickel deposition at a current efficiency of 95%, a current density of 2 A dm-2 (i.e., 20 mA cm-2) is expected to produce a uniform deposition rate of approx. 23 m h-1.

The percentage current efficiency (charge yield), the fraction of total current used in the primary reaction, i.e., Ni-Co-P alloy deposition, is defined as:

%** = 100 (*INi* + *ICo* + *IH2PO2-*) / I (X)

Where the total current has contributions from nickel and cobalt deposition, hypophosphite ion reduction to phosphorus and hydrogen evolution, i.e.

*I* = *INi* + + *ICo* + *IH2PO2-*+ *IH2* (X)

**3.4 Electrolyte composition**

The properties of the electrodeposited Ni-P coatings depend greatly on the composition of the employed electrolytic bath. The majority of nickel plating solutions are based on the ‘Watts’ formulation developed by Professor Oliver P. Watts in 1916 [[24](#page59)] owing to its simplicity and moderate costs. Modified Watts electrolyte for Ni-P plating combines the traditional nickel sulfate, nickel chloride and boric acid with a phosphorus oxyacid which is a source of phosphorus. Modified Watts bath containing sodium hypophosphite as a phosphorus source has also been reported in many works [[41](#page61), [42](#page61), [47](#page61)–[49](#page61)]. Other than sulfate electrolyte, several other kinds of Ni-P aqueous electroplating baths exist, contingent on the nickel source nature mostly used are based on sulfamate and sulfonate anions.

Most of the studies dedicated to nickel and nickel alloys electrodeposition have been restricted to simple sulfate or Watts baths. A wide range of coatings can be deposited from these versatile and stable electrolytes, thus they still remain a basis for electroplating Ni-based coatings [[25](#page59)].

Sulfamate baths are employed primarily for the purposes of high speed plating and electroforming. Nickel sulfamate has a high solubility in aqueous solutions, so higher nickel concentration can be achieved compared to other nickel electrolytes which facilitates higher plating rates [[50](#page61), [51](#page61)]. Ni-P deposits obtained from sulfamate baths exhibit lower internal stress, good ductility and enable higher current efficiency [[4](#page58), [51](#page61), [52](#page61)]. Stress values of electrodeposits fabricated from sulfamate, sulfate and Watts baths have been reported to be approximately 30, 180 and 250 MPa, respectively [[52](#page61)] although values are dependent on bath additives and operational conditions. Several issues need to be addressed when a nickel sulfamate bath is used.

The sulfamate ion is stable in neutral or slightly alkaline solutions, however because of the nickel hydroxide precipitation these solutions are not used at pH values greater than 5. Sulfamate hydrolysis reaction has been found to proceed at an increased rate at lower pH values and at higher temperatures, thus sulfamate baths need to be operated at lower temperatures and higher pH values than Watts-type nickel plating solutions. pH values below 3.0 and temperatures above 70 oC should be avoided as nickel sulfamate can hydrolyse to the less soluble nickel ammonium sulfate [[50](#page61), [51](#page61)]. Incorporation of ammonium and sulfate ions in the deposit can lead to increases in the internal tensile stress. Sulfamate ion additionally tends to decompose at the anode; at insoluble anodes such as platinum and at passive nickel oxide electrodes, and its decomposition can result in intermediate species which may affect the quality of the electrodeposited coatings [[50](#page61), [51](#page61)]. However, nickel sulfamate solutions are preferred in some cases over nickel sulfate solutions due to the superior mechanical properties of the coatings, higher rates of deposition and lower influence of variations in pH and current density on the deposit quality [[53](#page61)]. Figure [4](#page74) shows a comparison of phosphorus content, current efficiency and internal stress in the obtained Ni-P deposits as a function of phosphorous acid concentration, for the sulfate and sulfamate electrolytes.

Another interesting electrolyte for Ni-P alloy electroplating is the one containing methanesulfonate or methanesulfonic acid. Sknar et al. [[54](#page62)] found the effect of reducing kinetic difficulties of the Ni-P alloy electrodeposition to be more pronounced when using methanesulfonate than when employing sulfate electrolyte. This is owing to weaker buffering properties and lower stability of nickel complexes of methanesulfonate which contribute to the increase of concentration of the present electroactive species.

Alloys obtained from sulfate baths possess higher phosphorus content which is explained by the elevated acidity in the near electrode layer due to stronger buffering properties of the sulfate electrolyte [[45](#page61)]. Methanesulfonic acid has good electrolytic conductivity and is capable of dissolving many metals as well as acting as a useful medium for dispersion of solids prior to electrophoretic coating. A diverse range of surface coatings and films are available from methanesulfonic acid electrolytes [[55](#page62)]. Compared with known nickel plating baths, such as the Watts bath, methanesulfonate bath can be considered to enable higher current density and result in higher throwing power. Maximum nickel deposition rates can be achieved with deposits having low porosity, low internal stress and high ductility [[55](#page62)]. This organic acid may be considered as a ‘green’ electrolyte since it possesses few environmental, storage, transport or disposal problems being readily biodegradable. Additionally, methanesulfonic acid offers a high solubility for metal salts such as those of Pb and Ag, which are soluble only in a limited number of acid electrolytes [[56](#page62)].

The source of phosphorus in the Ni-P electroplating bath is typically a phosphorus oxyacid or its salt. The main types of bath for Ni-P electroplating contain phosphorous acid or hypophosphite anions. Generally, the quality of Ni-P deposits electroplated from electrolyte containing hypophosphite ions is changeable since the deposits darken at longer times or at higher current density, while Ni-P deposits electroplated from baths containing phosphorous acid are often smooth and optically reflective [[5](#page58)]. Phosphine is more readily produced from hypophosphite than from phosphorous acid owing to the rate of reduction of H3PO3 being the limiting factor in the phosphorous codeposition in this case [[18](#page59)].

When used as a contributing source of Ni in the bath, nickel chloride has two major functions. It appreciably increases solution conductivity, reducing cell voltage requirements and it promotes active dissolution of nickel anodes [[57](#page62), [58](#page62)]. Due to the increase in solution conductivity, plating thickness and cathodic current efficiency are reported to increase with the increase of chloride concentration [[49](#page61)]. In the chloride electrolytes activity of Ni2+ ions is higher than in sulfate electrolyte and metal deposition potential is lower [[59](#page62), [60](#page62)]. However, deposits obtained from chloride electrolytes with high chloride concentrations are reported to possess different texture and higher internal stress compared to those obtained from sulfate ones [[60](#page62)]. It is possible to operate with zero chloride in the bath if sulfur activated nickel anodes are used under appropriate operating conditions, nonetheless a low concentration of nickel chloride (min 5 g L 1) is generally recommended [61]. Most authors agree that boric acid limits the effects on the solution pH value resulting from the discharge of hydrogen ions and simplifies pH control [[62](#page62)]. However, many studies show that the beneficial influence of boric acid on Ni electrodeposition is complicated and affects the deposit’s crystallographic phase, structure and morphology, brightness, adhesion, etc. [[60](#page62)].

The presence of boron in the bath waste is reported to be harmful to the environment. Since the enforcement of Water Pollution Control Act in Japan [[63](#page62)], the imposed national minimum effluent standards have greatly influenced the electroplating industry. Thus, it became necessary to find more environmentally friendly solutions for the electrodeposition of nickel and its alloys.

One of the possible alternatives proposed is the substitution of boric acid by citric acid. This species can complex free nickel ions in the solution influencing the deposition rate but also acts as a buffering agent [[64](#page62)]. Doi et al. [[65](#page62)] found that the properties of Ni electrodeposits and resulting cathode current efficiency depend on the employed citrate bath pH. Electroplating resulted in a high cathode current efficiency and hard deposits exhibiting crystal structure of nearly random orientation in case of the bath pH value being between 4 and 6, while when the pH value was 3.5 or less current efficiency was lower and hardness of the obtained deposits decreased. Dadvand and colleagues [[49](#page61)] reported electrodeposition of Ni-P from a citrate bath containing sodium chloride, citric acid, nickel sulfate, ammonia and sodium hypophosphite. They found cathode current efficiency in low current density regions to be twice higher compared to the one achieved when employing modified Watts bath. Additionally, obtained deposits exhibited more uniform plating thickness. Even though complexes form between nickel and citrate ions and citrate ions as such can adsorb on the cathode surface, block active sights for Ni+2 discharge process and thus decrease the plating thickness, authors of the mentioned work estimated that this effect was small for citric acid concentrations below 20 g dm-3. Morikawa and colleagues [[43](#page61)] employed a Ni-citrate bath and obtained uniform and bright Ni-P electrodeposits with high throwing power. H3PO3 was added in excess so as to generate a large amount of P atoms on the Ni electrode. According to these authors, the bath composition was such that it satisfied the requirement necessary to form nickel phosphide with a stoichiometric composition equivalent to Ni3P over a wide range of current densities. Phosphorus content in the deposits was found to be approx. constant at 25 at.% over a wide range of plating conditions. When it comes to the environmental impact exerted by the electroplating process from either of the two baths: the one containing boric or the other containing citric acid, reported findings are contradictory.

Takuma et al. [[63](#page62)] applied a life cycle assessment method to demarcate the extent of their influence in terms of human toxicity and ecotoxicity. Results indicated that the newly developed citrate plating bath exerts higher environmental impact compared to the traditional Watts electrolyte, this owing to the release of nickel chelated with citric acid whose harmful influence overshadows the benefit of reduced boron emissions achieved by substituting boric acid in the electroplating bath.

In the Brenner sulfate bath [[27](#page60), [28](#page60)], pH buffering is achieved generally by employing phosphoric acid (H3PO4) whose slight excess can moreover aid in the prevention of H3PO3

oxidation [[66](#page62)]. Pillai and colleagues [[66](#page62)] investigated electrodeposition of Ni-P alloy from a Brenner type bath containing both phosphorous and phosphoric acid. Their observation was that a 100% nickel coating without any phosphorous incorporation was obtained when the plating was carried out in the absence of H3PO3, indicating that phosphorous acid is the only electrochemically active phosphorousspecies which acts as a phosphorous source in the given solution.

Electroplating baths containing phosphorus and/or phosphoric acid can be very acidic, hence typically partial neutralisation is necessary in order to increase the pH value of the bath up to an optimum value [[28](#page60)]. For this purpose different alkaline compounds can be employed, i.e.: potassium or sodium carbonate, potassium or sodium hydroxide, ammonia. Dadvand et al. [[49](#page61)] advocated the benefits of using ammonia for bath neutralisation, as carbonate salts decrease the solution conductivity and alkali metal hydroxides promote the formation of nickel hydroxide complexes.

Electrolyte additives are another crucial factor in the Ni-P electroplating process. They can be incorporated in the electrolytic solution in order to influence grain growth and crystallite orientation, to suppress undesirable secondary reactions, to promote the codeposition of alloys, dissolution of metals, etc. Additives can be grouped according to their main purpose as: carriers, surface wetters, inhibitors or levellers, auxiliary brighteners, buffers, conductive electrolytes and chemical complex-ants [[67](#page63)]. It is important to keep in mind that these species are also incorporated in the coating during its deposition and they may produce various adverse effects on the deposit’s properties. For example, they can lead to a decrease in corrosion resistance and exacerbate mechanical properties of deposits. As such, their use should be carefully optimised.

Grain refiners are usually aromatic organic compounds that contain sulfur whose codeposition with nickel inhibits grain growth. Most commonly employed grain refiner in Ni-P electrodeposition is saccharin. This species is reported to effectively reduce the internal stress of the fabricated deposits [[68](#page63)]. However, there are concerns related to deterioration of the corrosion resistance due to incorporation of sulfur in the growing deposit [[69](#page63)]. Saccharin is reported to decrease the phosphorus content in the coating and to bring an improvement in current efficiency [[70](#page63), [71](#page63)]. This is related to occupation of cathode surface active centres by adsorption of saccharin molecules and their conversion which consumes available hydrogen, restricting codeposition of phosphorous [[71](#page63)].

The properties of Ni electrodeposits depend on their crystallographic structure. Ni (100) soft-mode texture is associated with deposits that possess maximum ductility, minimum hardness and internal stress [[72](#page63)]. Textural modifications of this matrix can be induced by the introduction of certain additives [[71](#page63)]. Mixed crystal orientation can be achieved allowing to fabricate deposits with controlled properties.

Table [2](#page80) provides an overview of the proposed composition of the aqueous baths for Ni-P alloy electroplating. Applied deposition conditions and achieved phosphorus content where this information was available are stated along with some basic observations.

Traditional Ni-P electroplating baths are corrosive and their use generates toxic effluents. As an alternative to conventional electroplating solutions, You and colleagues [[73](#page63)] have proposed Ni-P electrodeposition from a bath containing choline chloride: ethylene glycol (1:2 molar ratio) deep eutectic solvent (DES) and NiCl2·6H2O and NaH2PO2·H2O as nickel and phosphorous sources, respectively. DESs are formed from mixtures of Lewis or Brønsted acids and bases and can contain a variety of anionic and/or cationic species. Employing ionic liquids in electroplating is beneficial owing to their lower corrosivity and wider potential window, exhibiting less hydrogen evolution than aqueous baths. As such, they can present a suitable alternative for traditional plating solutions [[74](#page63)]. Disadvantages of DESs however include their lower electrical conductivity, metal salts solubility and higher viscosity in comparison with aqueous electrolytes.

It has been proposed that environmental issues related to the use of aqueous baths in nickel electroplating can be mitigated also by performing electrodeposition in a supercritical CO2 fluid [[75](#page63), [76](#page63)]. Chuang and colleagues [[77](#page63)] studied the properties and the electrodeposition behaviour of Ni-P coatings in emulsified supercritical CO2 in the presence of suitable surfactants. They observed improved hardness, wear resistance and surface quality of the obtained coatings compared to deposits fabricated from conventional aqueous electroplating solutions. However, current efficiency from a supercritical CO2 bath was lower.

**3.5** **Cathode current efficiency**

In accordance with both direct and indirect phosphorus incorporation mechanisms, concurrent reduction of protons at the surface of the growing deposit layer is necessary for the codeposition of phosphorus with nickel. However, subsequent recombination of Hads limits the amount of phosphorus that can be deposited. Surface H+ concentration affects both the phosphorus content and the cathode current efficiency whose magnitude can never reach values close to 100% as long as the phosphorus is codeposited with nickel.

The cathode current efficiency during Ni-P electroplating is primarily affected by the elec-trolytic bath composition, plating regime, applied current density, temperature, bath pH and agitation rate. Ross et al. [[78](#page64)] found that the current efficiency decreases as the deposit’s phosphorus content increases and that it depends on the rotation speed of the cathode. In the case of rotating-disc electrode (RDE), maximum efficiency was attained for low phosphorus plating solutions and low rotation speeds. In general, electrodeposition of high phosphorus Ni-P coatings proceeds at a lower current efficiency than the electrodeposition of low phosphorus ones [[4](#page58), [46](#page61)]. Naryan and Mungole [[79](#page64)] found that the current efficiency decreases with increasing H3PO3 concentration and decreasing temperature of the sulfate electroplating bath. Similarly, Seo and col-leagues [[52](#page61)] observed that with increasing H3PO3 concentration in the sulfamate bath, phosphorus content in the deposit increases, current efficiency decreases and stress in the obtained deposits augments. Morikawa [[43](#page61)] observed that in citrate bath current efficiency exhibits a maximum at intermediate H3PO3 concentrations.

The cathode current efficiency in Ni-P electroplating is generally found to increase with the increase of current density [[32](#page60), [80](#page64), [81](#page64)], bath temperature [[18](#page59)] and pH [[18](#page59), [82](#page64)]. Luke [[32](#page60)] found that the cathode current efficiency does not vary appreciably with current density in the higher range (above 20 A dm 2) but increases with the increase of current density at its lower values. Similar trend was observed by Toth-Kadar et al. [[81](#page64)]. Li et al. [[83](#page64)] found cathode current efficiency to be lower for a larger overall current density, due to the discharge of H+ ions, resulting in the evolution of hydrogen gas bubbles. This reaction shares a larger portion of the electrodeposition current at higher total current densities.

In general, reactions involved in the conversion of phosphorus in the solution into phosphorus in the deposit can be interpreted differently and thus the discrepancies in elaborating cathode current efficiency behaviour may arise.

Cathode current efficiency of Ni-P alloy electrodeposition can be significantly improved by employing pulse instead of direct current plating [[4](#page58)]. Benefits of using pulse plating for Ni-P deposits fabrication are explored in Section [6](#page44).

As mentioned in the previous section, additives such as saccharin are found to improve the current efficiency of Ni-P electrodeposition [[71](#page63)].

In Ni-P electroplating, anodes are usually made of nickel and current efficiency of nickel dissolution in additive free solution is approximately 100% (small percentage of the current is consumed on the discharge of hydrogen ions from water). Hence there exists a difference in cathode and anode efficiency which leads to nickel ions build up in the solution and its pH value increase. This problem can be solved by solution drag-out [[84](#page64)] and the use of soluble and inert anodes connected to different power supplies, while the current to each is controlled in order to compensate for the low cathode efficiency and incurred drag-out losses [[7](#page58), [32](#page60)].

**3.6 The crystallographic structure of deposits**

The crystallographic structure of deposits is strongly influenced by their phosphorus content and the deposition conditions. Incorporation of even small amounts of phosphorous in the nickel lattice substantially refines the nickel grain structure. In the case of low-phosphorus Ni-P electrodeposits, XRD patterns reveal a set of diffraction peaks corresponding to face-centred cubic (f.c.c.) nickel, i.e.: (111), (200), (220), (311), (222) [[85](#page64)]. Presence of these textures is an indication of crystallinity of the low-phosphorus coatings in which case a material is a supersaturated solution of phosphorus in f.c.c. nickel [[78](#page64)]. As the phosphorus content in Ni-P deposits increases, the (111) reflection becomes broader while others disappear, as seen in Figure [5](#page74). This is indicative of nickel crystalline structure losing its long-range order due to the increased difficulty of more phosphorus atoms accommodating into the nickel lattice. Codeposition of phosphorus in octahedral interstital sites of f.c.c. nickel inhibits the sur-face diffusion of Ni atoms and the subsequent crystal growth [[17](#page59)]. As the phosphorus content in the deposit increases the nucleation becomes dominant over nucleus growth and when the critical phosphorus content is exceeded amorphous structure, characterised by a short range order of only few atomic distances, is obtained. A more colony-like morphology is achieved where each colony consists of numerous grains with smaller grain size thereby making the coating brighter and smoother in appearance [[66](#page62)]. Figure [6](#page75) shows SEM micrographs of Ni-P deposits containing varying phosphorus contents.

At high-phosphorus content, the XRD pattern of a Ni-P electrodeposit exhibits only a diffuse broad peak. Hence, an increase in phosphorus content converts the microstructure of Ni-P alloys from crystalline to amorphous, which results in the decreased ductility and the increased corrosion resistance. It has been suggested that adsorbed hydrogen blocks the surface and prevents regular crystal growth, hence playing a crucial factor in obtaining N-P deposits with amorphous structure, however amorphous deposits can be fabricated with high current efficiencies and low hydrogen evolution thus indicating that the adsorbed hydrogen does not play a major role [[17](#page59)].

Bredael et al. [[86](#page64)] observed significant broadening of the (111) XRD peak for Ni-P deposits containing more than 9 wt.% of phosphorus. However they stated that the observed effect, other than being a sign of the structure becoming amorphous, can also originate from a crystalline material with very fine grains (ca. 1 nm in size) and may be due to non-uniform internal stresses and stacking faults. Hence, as they asserted, it is not possible to exactly distinguish between amorphous and microcrystalline structure based only on XRD patterns. Nonetheless, conventionally Ni-P deposits with more than 9 wt.% of phosphorus are entitled X-ray amorphous.

Owing to variations in the pH at the electrode-solution interface inherent in the Ni-P electroplating process, phosphorus content varies across Ni-P deposit thickness, hence its composition and microstructure are not homogeneous (Section [7](#page49)). Alkaline solutions are more influenced by the pH variations compared to acidic ones, thus electrodeposits produced in this environment are often characterized by a lamellar structure [[87](#page64)].

Ni-P electrodeposits can be grouped in three categories, alloys with: low (1-5 wt.%), medium (5-8 wt.%) and high (above 9 wt.%) phosphorus content [[17](#page59)]. Microstructure-wise, it is possible to fabricate polycrystalline, microcrystalline, nanocrystalline or fully amorphous Ni-P deposits through electroplating.

Pillai et al. [[66](#page62)] found the structure of Ni-P alloy to undergo transition from crystalline to nanocrystalline and become amorphous at phosphorus contents above 9.14 wt.%. Bredael and coworkers [[46](#page61)] fabricated Ni-P electrodeposits with phosphorus contents ranging from 0 to 18.0 wt.% and a uniform composition profile across the samples. They observed that for phosphorus contents above 12 wt.% the as-plated Ni-P coatings were amorphous, whereas below this threshold value, which was independent of the plating parameters, crystalline Ni-P coatings were obtained. In a subsequent work Bredael and colleagues [[86](#page64)] conducted a study with the goal to exactly identify the percentage of phosphorus at which the transition from crystalline to amorphous structure takes place. They found that the border between these two states can be found at phosphorus contents between 11.6 and 13.1 wt.% P, with the structure being fully amorphous at a P content of 13.1 wt.%. Although there is no consensus, many authors agree that the phase transition of Ni-P happens over a wide range of P composition, rather than at an abrupt phosphorus content [[66](#page62)]. Lin et al. [[4](#page58)] found that not only phosphorus content influences the crystallographic structure of Ni-P electrodeposits. At the same phosphorus percentage, pulse current plating can preserve crystalline structure even at phosphorus contents above the critical value using smooth direct current. In contrast,, the phosphorus content at which transition from crystalline to amorphous structure occurs has been reported to decrease in the presence of certain additives, such as saccharin [[17](#page59)].

Discrepancies which exist in the literature related to the structural transitions of Ni-P electrodeposits can be attributed to the lack of appropriate techniques that would allow to make a proper differentiation between different crystallographic structures. Additionally, Ni-P alloys are neither completely amorphous nor crystalline; they represent a mixture of several phases. This can be attributed to the low solubility of phosphorus into the nickel lattice. Often Ni-P deposits contain more of the alloying element (P) than what the f.c.c. Ni matrix can dissolve, thus the surplus must separate out resulting in regions that have a different concentration of phosphorus, different lattice parameters and different crystallite sizes. Vafaei-Makhsoos et al. [[88](#page64)] found alloys with 3.8 and 6.7 wt.% of P to be solid solutions composed of micrometer-sized grains. However, amorphous alloys (11.7 and 13 wt.% P) were not homogeneous on a microscale and films contained microcrystalline regions. Ni-P electrodeposits displaying a structure that represents a mixture of solid Ni(P) solutions and amorphous or nanocrystalline phases have been reported [[87](#page64)].

The microstructure of Ni-P electrodeposits undergoes a transformation following subsequent thermal treatment. This aspect is considered further in Section [5](#page42). A suitable structure of the electroplated Ni-P alloy depends on the desired features of the fabricated deposit. Crystalline materials are traditionally interesting on account of their exceptional mechanical properties. Amorphous materials are very appealing owing to the isotropy of their properties and them lacking disadvantages characteristic for crystalline ones, namely the presence of crystal boundaries, lattice defects, segregation, etc. [[89](#page64)]. Amorphous Ni-P electrodeposits are reported to possess better corrosion resistance when compared to crystalline deposits. However, transition to amorphous structure and consequent decrease of the grain size causes deterioration in mechanical properties which is termed an inverse Hall-Petch effect [[90](#page64)]. Its onset is related to the increase of the volume fraction of the triple junctions relative to the volume fraction of the grain boundaries which exerts a detrimental effect on coating hardness [[91](#page65)]

Jeong et al. [[92](#page65)] produced Ni-P electrodeposits with grain size of less than 10 nm, achieving hardness values that fall into the range of the inverse Hall–Petch behaviour. Recently reported results claim even better mechanical properties of nanocrystalline materials (Figure [10](#page76)). compared to both coarse-grained and amorphous ones [[10](#page58), [67](#page63), [93](#page65), [94](#page65)]. The main feature, which makes nanocrystalline materials distinct from the other two mentioned groups, is the existence of a larger number of atoms disposed at interfaces, as grain boundaries and triple junctions. These interfaces are considered to be involved in the deformation mechanism occurring in the material. It is postulated that for nanocrystalline materials dislocations inside the grains hardly occur and that other plastic deformation mechanisms, such as grain boundary diffusion and sliding, grain rotation and a viscous flow takes place [[85](#page64)].

**3.7 Variables influencing the phosphorus content of deposits**

The phosphorus content of Ni-P electrodeposits reportedly depends on many factors, predominantly on the concentration of the phosphorus donor in the bath, temperature, pH, current density, waveform in the case of pulse current deposition, agitation rate and the presence of additives. Thus, phosphorus quantity can be controlled by altering the electroplating bath composition and the employed deposition conditions.

In the 1950s, Brenner [[27](#page60)] found that the amount of phosphorus incorporated in the Ni-P alloy increases with the increase of phosphorus acid content in the bath and with the decrease of the current density. However, too high H3PO3 concentration leads to deterioration of the current efficiency owing to more cathodic charges being spent on the reduction of protons. Additionally, proton reduction results in the atomic and molecular forms of hydrogen, both of which can be incorporated in the deposit imposing inauspicious effects on its properties and increasing its internal stress [[95](#page65)]. Chang et al. [[96](#page65)] found that for the same content of H3PO3, phosphorous content can be increased by decreasing electrolytic bath pH value on account of the consequent increase of the concentration of non-dissociated phosphorous acid molecules in the electrolyte. This effect is however weakened at very low phosphorus acid concentrations on account of diffusion becoming the rate-controlling process.

Yuan and coworkers [[5](#page58)] conducted a study on the preparation of amorphous-nanocrystalline Ni-P electrodeposits from a Brenner type plating bath. Their goal was to interrogate the key electroplating factors and their influence on the deposit’s phosphorus content. Effects of: temperature, current density, pH, H3PO3 concentration and agitation rate were investigated in the orthogonal experimental design study. The findings indicated that only pH value and H3PO3 concentration and their interaction are the major variables affecting phosphorus content in the deposit. Figure [7](#page75) shows contour plots for the constant phosphorus content versus Ni-P electroplating pH and H3PO3 concentration.

Hu and Bai [[47](#page61)] employed modified Watts Ni bath and similarly investigated the influence of the main electroplating variables, namely: temperature, current density, pH, NaH2PO2·H2O concentration and agitation rate on the phosphorus content in the Ni-P deposits. By using experimental strategies such as: fractional factorial design, path of steepest ascent and central composite design coupled with response surface methodology they came to the conclusion that the predominant factors affecting phosphorus content are temperature and current density of the electroplating with strong interactive effect between current density and pH. Figure [8](#page76) shows contour plots for the constant phosphorus content versus Ni-P electroplating temperature and current. A recurring trend of gradual decrease of phosphorous content with the increase of the applied current density is observed in the work of many authors, however a large scatter between the data points of different authors can be perceived (Figure [9](#page76)) [[46](#page61)]. In their study of Ni-P electrodeposition on a rotating-disc electrode, Bredael and coworkers [[46](#page61)] observed a steep transition from high to low phosphorus content with increasing local current density, while the literature data according to them do not show such a steep transition owing to the general approach where average current densities are used. In the bath where phosphorous acid is the only electrochemically active phosphorus species, dependence of the phosphorus content on the current density can be explained in terms of slow diffusivity of the large phosphorus acid ions compared with Ni2+ions [[46](#page61)]. Pillai et al. [66] found that at higher H3PO3 concentration in the bath (15 g L 1), the phosphorus content in the coating was independent of current density. However, at low phosphorous acid amounts in the bath, the decreasing trend of phosphorus con-tent in the coating with increasing current density was evident. Thus, they concluded that the observed scatter in the results presented by different authors, regarding the influence of current density on phosphorus content can be mainly attributed to the different bath compositions used. In their study, an increase in the concentration of H3PO4 resulted in no significant effect on the phosphorus content in the coating although the rate of deposition decreased continuously. An increase in the plating temperature from 50 oC to 80 oC resulted in the decrease of the amount of phosphorous incorporated in the coating and in the increase of the deposition rate. Naryan and Mungole [[79](#page64)] observed contrary to the previously mentioned study a slight increase of the phosphorus content of the coating up to H3PO4 concentrations of 125 g L 1 and a slight decrease with further increase in H3PO4 concentration, all at the bath temperature of 80 C. At 90 oC an increase in the H3PO4 concentration generally produced a slight decrease in the phosphorus content in the coating. Naryan and Mungole also found that, at low H3PO3 concentrations, more phosphorus was deposited at 90 oC than at 80 oC. At H3PO3 contents in excess of 25 g dm-3 more phosphorus was deposited at lower temperature.

Sadeghi [[21](#page59)] employed hypophosphite as a phosphorous source and found that increasing its concentration and decreasing the current density (1-4 A dm-2) caused higher phosphorous contents in the fabricated Ni-P deposits. However, the content of phosphorus in the deposits electroplated from the baths containing very low phosphorus source amounts did not vary appreciably with the current density. Deposits obtained from the baths containing up to 10 g dm-3 of NaH2PO2 exhibited a decrease in the content of phosphorus as the current density was raiseAn increase in temperature has been observed to cause a decrease in phosphorus content in general. However, too low temperature leads to unsatisfactory current efficiency and plating rate, so a compromise is needed. Temperatures from around 50 to 70 oC are generally adopted as acceptable for optimal feasibility of the Ni-P electroplating process.

The phosphorus content of the deposit has been reported to be dependent on the presence of certain additives in the electroplating bath. Increase of the saccharin concentration was found to induce the decrease of phosphorus content [[17](#page59), [70](#page63), [71](#page63)].

The influence of pulse plating on Ni-P deposit alloy structure and composition will be considered further in Section [6](#page44).

**4**. **Properties of electroplated Ni-P alloy deposits**

**4.1** **Mechanical, tribological and corrosion properties**

Alloying nickel with phosphorus via electroplating effectuates many improvements in deposit

properties: increased hardness (&500 HV as-plated Ni-P), wear and corrosion resistance, decreased coefficient of friction (0.4-0.7 as-plated Ni-P), but also transition towards paramagnetic features. Overall, properties and functional behaviour of Ni-P electrodeposits depend on their composition and microstructure. Ni-P coatings with low phosphorus content demonstrate high hardness and good wear resistance, while coatings with higher phosphorus content exhibit good corrosion resistance but poor mechanical properties owing to the transition towards amorphous structure. Amorphous Ni-P deposits are generally brittle and possess low ductility. At the same phosphorus content, microstructure of the deposit can be modified by altering the deposition conditions. Applying pulse plating instead of direct current plating can help to preserve Ni-P crystalline structure even at higher incorporated phosphorus quantities, thus good mechanical properties characteristic for low-phosphorus deposits can be maintained [[4](#page58)].

Initially, microhardness of the alloy increases with at higher phosphorus content, while further enhancement of phosphorous quantity leads to hardness deterioration [[18](#page59)]. Figure [10](#page76) shows the evolution of the hardness with the change in its grain size. Nava et al. [[20](#page59)] found that the wear volume of Ni-P electrodeposits is inversely proportional to the microhardness of the deposits. They perceived also that nanocrystalline Ni-P coatings, with a phosphorus content of 2-8%, exhibit significantly higher wear resistance compared to coatings with higher phosphorus content. Pillai et al. [[66](#page62)] observed that Ni-P electrodeposits with phosphorus content in the range of 4-7 wt.% exhibit good microhardness (7.74–8.57 GPa) and the microhardness of these alloys increases up to 12 GPa by annealing a 400 oC for 1 h. Yuan and colleagues [[5](#page58)] reported that nanocrystalline composites with phosphorus content 5-9 wt.% demonstrate better corrosion resistance than that of microcrystalline Ni-P deposits, and better abrasion resistance than that of amorphous Ni-P deposits. Therefore, under certain work conditions, when a compromise is needed in terms of obtaining both corrosion resistance and favourable mechanical properties, nanocrystalline deposits could present an optimal choice.

Another way to ensure good mechanical and electrochemical properties is to design multilayered or gradient coatings. For example, a duplex coating that consists of an inner layer having a high phosphorus content and an outer layer with low phosphorus content presents a structure that combines advantageous features characteristic for each of the two compositions [[14](#page59), [15](#page59), [97](#page65)]. Fabricating graded structures can also help to improve coating‘s adhesion on the substrate owing to the gradual structure evolution across layer thickness and the lack of abrupt interfaces (Section [7](#page49)).

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Adhesion of the coating on the substrate’s surface is critical for engineering applications. Ni-P electrodeposits exhibit good adhesion on a range of widely differing substrates (brass, soft steel, copper, etc.). However, stainless steel for example can be problematic owing to the formation of a passive oxide layer which prevents Ni-P coating from sticking to its surface. Conventional way of addressing this issue is to apply on the substrate surface a Wood’s nickel strike before Ni-P electroplating [[98](#page65)]. Being highly acidic it dissolves the oxide and concurrently forms a thin layer of nickel on the stainless steel surface.

Published data offer diverse information regarding corrosion characteristics of Ni-P alloy, particularly about the nature of its anodic dissolution, ability to passivate and pitting susceptibility. Corrosion resistance of Ni-P coatings is much better than in the case of pure Ni [[18](#page59)]. In chloride containing and slightly acidic environments Ni-P electrodeposits demonstrate lower corrosion resistance when compared to neutral or slightly alkaline settings [[99](#page65)].

Amorphous and crystalline deposits have been found to exhibit different corrosion behaviour [[17](#page59)]. Generally, the weight loss of Ni-P deposits in corrosive solutions de-creases with the increase of their phosphorus content [[100](#page65)]. Splinter and coworkers [[101](#page65)] reported the preferential dissolution of Ni on the surface of the Ni-P coating and the surface with the enriched P content after corrosion. They asserted that the formation of Ni3(PO4)2 film on the surface impedes the speed of corrosion. Additionally, their study demonstrated that the corrosion behaviour of nanocrystalline Ni-P alloys with lower phosphorus contents (1.4 wt.% and 1.9 wt.%) in 0.1M H2SO4 approaches that of amorphous Ni-P electrodeposits (6.2 wt.% P). X-ray photoelectron spectroscopy revealed that neither the nanocrystalline (1.9 wt.% P, grain size 8.4 nm) nor the amorphous (6.2 wt.% P) Ni-P alloys formed a passive layer in this environment. Diegle et al. [[102](#page65)] reported that the addition of phosphorus improves the corrosion resistance of nickel owing to the reaction with water in which hypophosphite ions are formed. These ions prevent further dissolution of nickel through chemical passivation. Krolikovski and Butkiewicz [[103](#page66)] determined that the behaviour of Ni-P alloys is similar in neutral solutions under open circuit potential. However, under anodic polarisation, amorphous alloys.

**4.2** **Internal stress**

A well-controlled internal stress is a very important to successful fabrication and use of protective Ni-P coatings. Compressive stresses are advantageous in mechanical structures under load, since they tend to inhibit crack formation and growth, they rise strength and hardness of the coating [[21](#page59)]. Many factors influence stress [[51](#page61)], especially the electroplating bath composition and operating conditions. Baudrand [[51](#page61)] fabricated electrodeposits from a sulfamate bath without the presence of additives with stress value of approximately 30 MPa, while the minimal value of stress for deposits obtained from a Watts bath was 180 MPa.

The amount of phosphorus, hence crystallographic structure, of the Ni-P electrode-posit influences its stress value. Lin et al. [[95](#page65)] studied Ni-P electrodeposition from a sulfamate bath containing no additives. They observed that amorphous Ni-P deposits exhibit lower internal stresses compared to crystalline ones. The internal stress and the amount of adsorbed hydrogen exhibited a maximum at intermediate phosphorus contents suggesting that hydrogen incorporation and subsequent escape play an important role when it comes to the internal stress of the Ni-P electrodeposits. Nonetheless, high phosphorus content characteristic for amorphous Ni-P alloys comes with lower cathode current efficiency, thus conditions must be carefully optimized in order to secure optimal feasibility of the process along with desired properties of the deposits.

Certain organic additives are known to induce a reduction of the internal stress of the Ni-P deposits. A grain refiner saccharin is typically employed for this purpose, inducing compressive internal stress [[10](#page58), [17](#page59), [50](#page61), [104](#page66)]. Nevertheless, additives containing sulfur can cause deterioration in the corrosion resistance of the fabricated coatings hence their application must be carefully optimized [[69](#page63)].

Another possibility to reduce stress of a Ni-P electrodeposit is to apply a low temperature heat treatment that would help to desorb hydrogen present in the coating [17]. Employing pulse current instead of direct current deposition is reported to be beneficial for stress reduction. Chen et al. [[68](#page63)] fabricated Ni-P deposits with high phosphorus contents and low internal stresses, ranging from tensile to compressive, with high current efficiency by using pulse current.

**4.3** **Magnetic properties**

Nickel is a typical ferromagnetic material, while magnetic properties of the Ni-P alloy present a function of its composition and preparation technique [[105](#page66)]. Magnetic mo-ment and Curie temperature are found to decrease with the introduction of phosphorus into Ni matrix [[106](#page66)]. According to Weiss theory, nickel exhibits ferromagnetic properties owing to quantum-mechanical exchange forces which cause the spins of vicinal Ni atoms to be parallel [[107](#page66)]. The introduction of phosphorus into nickel matrix enlarges the separation between Ni atoms and with the increase of interatomic distance ex-change forces decrease rapidly. Stated effect renders the transition from ferromagnetic to paramagnetic properties [[108](#page66)].

Bakonyi et al. [[105](#page66)] performed a study of the magnetic properties of Ni100-xPx alloys fabricated by employing various techniques. For electrodeposited alloys the composition range studied was 11 and 23at.%. Throughout the concentration range, magnetic inhomogeneities were observed. Hu and Bai [[109](#page66)] observed that the ferromagnetic in Ni was transformed into paramagnetism at a phosphorus content of 17 at.%. They confirmed that the magnetic properties of Ni-P alloys are a function of their phosphorus content. In a subsequent study [[110](#page66)], they demonstrated that the paramagnetic Ni-P deposits become ferromagnetic after thermal treatment.

Knyazev and colleagues [[6](#page58)] performed magnetisation and differential scanning calorimetry analysis of the Ni-P alloys obtained via electrodeposition. Their results indicated that the untreated alloys with phosphorus contents exceeding 12 at.% were paramagnetic, owing to the lack of exchange interactions due to fluctuations in chemical composition and the formation of a network of phosphorus rich paramagnetic domains. Amorphous Ni-P alloys that were originally paramagnetic were rendered fer-romagnetic through thermal treatment that also led to their devitrification. Dhanapal et al. [[108](#page66)] studied the influence of phosphorus content, employed duty cycle and current density on the magnetic properties of Ni-P alloy fabricated by pulse current deposition. They observed saturation magnetization dependence on the phosphorus content. At low phosphorus amounts saturation magnetization value of the obtained deposits was high. Increasing the duty cycle resulted in the increase of soft ferromagnetic nature of the Ni-P alloy and decrease of the coercivity.

**4.4** **Catalytic activity**

Ni-P alloy is known to exhibit catalytic activity foremost in water splitting reaction. This presents a very important feature especially in the light of today’s rapidly increasing energy demands and progressive exhaustion of fossil fuels resources. Catalysts (platinum and ruthenium) conventionally employed to reduce the large overpotentials for hydrogen and oxygen evolution reactions (HER and OER respectively) are fairly scarce and their use not feasible when it comes to incurred costs, thus suitable alternatives are in high demand.

Nickel is a popular electrode material due to its reasonably high hydrogen generation activity, availability, acceptable cost and ease of production [[111](#page66)]. Although Ni does not perform as well as steel from the viewpoint of its electrocatalytic activity, it shows an excellent resistance to corrosion in hot concentrated alkaline solutions [[112](#page66)]. Issues encountered when employing this metal as cathode material are its low catalytic activity or low resistance to intermittent electrolysis, however alloying nickel with other elements (P, Mo, etc.) can aid in mitigating these issues [[112](#page66), [113](#page66)]. According to Paseka [[114](#page66)], the reason for the improvement of nickel activity in HER achieved through alloying it with phosphorus is the augmentation of the amount of amorphous phase surrounding the Ni crystals. Alloys containing amorphous phase which is able to dissolve large amounts of hydrogen possess high internal stress which contributes to their good electro-catalytic activity.

Hu and Bai [[115](#page66)] conducted a study in order to interrogate the effects of key electroplating variables on the hydrogen evolution activity of Ni-P deposits. By employing fractional factorial design, path of steepest ascent and central composite design, they found that the key factors influencing catalytic activity of Ni-P electrodeposits include: temperature, pH and NaH2PO2·H2O concentration and their interactions. The models developed indicated that the alloy containing 7 at.% of P should exhibit maximal electro-catalytic activity. In the subsequent study [[109](#page66)], they experimentally found the deposit with 8 at.% of P to be the best electrode material for HER. They attributed this deposit’s highest specific activity to its largest true surface area and hence its maximum roughness. Wei et al. [[116](#page67)] investigated catalytic activity of Ni-P in HER both experimentally and theoretically. Alloys that contain 10,8 at.% P were found to perform best. In order to elaborate the influence of phosphorus content in Ni-P amorphous alloys on their catalytic activity they employed density-functional theory and front molecular orbital theory. Obtained results indicated that alloys with phosphorus content anywhere from 9.1 at.% to 14.3 at.% should exhibit optimal activity for the HER. Paseka [[114](#page66)] found that the alloy deposited at 65 oC demonstrates worse atalytic activity than alloys deposited at a temperature of 53 oC. He asserted that this was due to the presence of larger amounts of adsorbed hydrogen in alloys fabricated at lower temperatures, which contributes to their higher internal stresses. According to Paseka, catalytic activity also depends on the deposit’s thickness and exhibits an increase as deposit grows. Thick deposits possess great catalytic activity owing to their high internal stress. However, mechanical instability presents a problem and thickness increase will be beneficial only up to a critical width of coating at which it will suffer a final failure. In the study by Li et al. [[83](#page64)] it was determined that at low bath temperatures high NH4Cl content in combination with low NaH2PO2 concentration can contribute to creating thick films (6-8 at.% of phosphorus) with optimum catalytic activity, even at high current densities. However, ammonia concentration must be chosen carefully because exceeding the ammonia concentration above the certain limit can negatively affect the cathode current efficiency, hence decrease the plating rate [[49](#page61)].

Bai and Hu [[110](#page66)] observed that for Ni-P electrodeposits with P content from 0 to 28 at.% the ability of catalysing hydrogen evolution decreases with increasing annealing temperature, concluding that annealed deposits are not suitable for HER.

Elias et al. [[117](#page67)] studied the efficiency of electrodeposited Ni-P for both HER and OER in alkaline media. They found that the alloy thin films with 9.0 wt.% of P and 4.2 wt.% of P were preferred electrode materials for HER and OER. Recently Tang and coworkers [[118](#page67)] reported a room-temperature electrodeposition of Ni-P nanoparticle film on Ni foam which acts as a bifunctional water-splitting catalyst in strongly alkaline media, achieving very small overpotentials of 80 mV and 309 mV for HER and OER, respectively.

As an alternative to alkaline media in which water electrolysis systems are simple but demonstrate low efficiency and high energy consumption, Lu et al. [[119](#page67)] inter-rogated electrocatalytic activity of Ni based alloys in acidic media. They observed a decrease of catalytic activity with the increase of phosphorus content which they attributed to moving away from the optimal electronic configuration with phosphorus incorporation but additionally to the decrease of the number of grain boundaries which present active sites for HER. In contrast, the authors of [[120](#page67)] claimed that increasing the phosphorus content, even past contents that can be achieved through conventional electrodeposition would impart exceptional catalytic properties to these systems for applications in acidic media and very high phosphorus contents ought to be beneficial.

**5.** **Thermal treatment of electroplated Ni-P alloys**

Following heat treatment, the hardness of Ni-P electrodeposits increases substantially, due to the precipitation crystalline phases. Most studies report detecting a mixture of Ni3P and f.c.c. nickel as a final product of thermal treatment [[20](#page59)]. The annealing temperature under which crystallisation occurs depends on the phosphorous content in the deposit as well as on the heating rate [[121](#page67)]. Phase transformation temperatures of the deposits increase with increasing heating rate and decreasing phosphorus content [[110](#page66), [121](#page67)]. Continued heating at temperatures higher than the transition temperature leads to a decrease of hardness owing to the subsequent recrystallisation and grain coarsening [[18](#page59), [122](#page67), [123](#page67)]. The degree of loss of hardness is higher for deposits having lower phosphorus content on account of more pronounced grain growth and coarsening of Ni phase compared to Ni3P phase [[122](#page67)]. Transition from an amorphous to a crystalline state is followed by a thermal contraction phenomena due to a higher density of crystalline structure when compared to amorphous one, the amplitude of contraction being higher at higher phosphorus contents [[104](#page66)].

Nava et al. [[20](#page59)] fabricated Ni-P electrodeposits containing 10.6 at.% of P which exhibited maximum hardness (990 HV) after thermal treatment at 500 C (comparable to the hardness of hard Cr coatings 1000 HV). The deposits demonstrated the lowest wear rate, as indicated by SEM images of their wear track patterns exhibiting the narrowest width and most shallow plough lines (Figure [11](#page77)). A linear relationship between the hardness and the wear resistance of the heat treated Ni-P alloy coatings was seen. The corrosion resistance of the deposits deteriorated upon annealing owing to the formation of cracked structure in the thermally treated coatings, which promoted localised corrosion. Bai and Hu [[110](#page66)] found crystallisation for Ni-P deposits containing 24 at.% of P to occur at 400 oC, while deposits with 28 at.% demonstrated a phase transformation at 200 oC. The phosphorus content of the deposits decreased at higher annealing temperature, owing to the replacement of phosphorus by the oxygen from the atmosphere.

Habazaki et al. [[124](#page67)] conducted a study in order to interrogate the effect of annealing on the microstructure and the corrosion behaviour of the electrodeposited amorphous Ni-P alloys. Obtained results indicated that Ni-P alloys with 19.2 at.% phosphorus crystallise directly to f.c.c. Ni and Ni3P phases. High phosphorus alloys (24.6 at.% P) were first crystallised to a metastable single phase and then decomposed to Ni3P. Crystallisation of alloys with an intermediate P content (19.2 at.% < P < 24.6 at.%) resulted first in a mixture of f.c.c. Ni, Ni3P and the metastable phase. The precipitation of f.c.c. Ni in the amorphous phase occurred for Ni-16.7P alloy before complete crystallisation. Annealing decreased corrosion resistance for alloys containing 22.7 at.% P owing to the formation of phosphorus deficient f.c.c. Ni phase. Keong et al. [[121](#page67)] also reported that amorphous coatings with high phosphorus content follow a sequence of transformations during annealing and form metastable phases, such as Ni2P and Ni12P5 before forming stable Ni3P and f.c.c. Ni phases. Zoikis et al. [[125](#page67)] observed crystallization of the amorphous Ni-P electrodeposit into Ni and Ni3P phases after annealing at 400 oC. The presence of the Ni2P phase after thermal treatment above 330 oC was detected. Ni2P phase formation was also reported in [[48](#page61)].

Jeong et al. [[126](#page67)] reported the increase of hardness and abrasive wear resistance after heat treatment for nanocrystalline Ni-P coatings, with Taber abrasive wear resistance being linearly proportional to the hardness of the coatings. Heat treatment causes also the elastic modulus of the deposit to increase significantly according to the authors of [[66](#page62)]. When maximum hardness is achieved upon annealing fracture toughness exhibits the lowest value [[127](#page67)].

Chang et al. [[128](#page68)] argued that significant strengthening by annealing for electrode-posited Ni-P alloys with low phosphorus content and nanocrystalline grains is not induced by the precipitation of Ni3P phase. The increase in hardness upon annealing was attributed to grain boundary relaxation, phosphorus segregation and reduction of interior defects with possible contributions from the increase of density owing to degassing of hydrogen.

Opting for subsequent Ni-P alloy thermal treatment and accordingly choosing the suitable heat treatment temperature, finally depend very much on the employed substrate nature and the intended process complexity.

**6**. **The application of pulse plating to Ni-P alloy deposition**

Constant direct current is the most commonly applied regime in which metallic coatings are electrodeposited. In recent years, however, the application of pulsed, alternating current has seen a renaissance. This is due to the demonstration that pulse current (PC) exerts a beneficial influence on the structure and properties of the fabricated deposits. Comprehensive reviews on pulse and pulse reversed plating have been contributed by, e.g., Devaraj and Seshadri [[129](#page68)] as well as Chandrasekar and Pushpavanam [[130](#page68)].

Development of modern electronics has offered great flexibility in available modulated current waveforms, with trains of pulses that can be programmed to have complex sequences and forms. Figure [12](#page77) shows a typical pulse-current waveform.

Rectangular waves are the easiest waveforms to produce [[131](#page68)]. They have been demonstrated to produce a higher nucleation rate of the grains compared to a triangular waveform [[132](#page68)]. Typical waveforms employed in pulse plating include: cathodic pulse followed by a period without current (or an anodic pulse), direct current (DC) with superimposed modulations, duplex pulse, pulse-on-pulse, cathodic pulses followed by anodic pulses (pulse reverse current-PRC), superimposing periodic reverse on high frequency pulse, modified sine and square wave pulses [[130](#page68)].

During electroplating, a negatively charged layer is formed around the cathode as the process advances. During DC deposition, this layer charges to a definite thickness and prevents ions from reaching the substrate. In a simple form of PC electrodeposition, where cathodic pulse is alternatively switched on and off, when the output is turned off this layer discharges which allows easier transport of ions from the bulk of the solution [[130](#page68)]. During plating, high current density areas in the bath become more depleted of ions compared to low current density areas. During time when the current is off ions migrate to the depleted areas and when subsequent current pulse occurs more evenly distributed ions are available for deposition onto the part [[130](#page68)]. In the absence of current, small grains are recrystallised owing to their higher surface energy which makes them less thermodynamically stable than large grains, hydrogen is also desorbed decreasing the internal stress of the obtained deposits. In general, PC plating results in finer grain deposits exhibiting improved properties, including hardness, roughness, porosity, wear resistance, etc. Pulse plating can reduce additive requirements substantially [[129](#page68), [130](#page68)].

Pulsed current results in metal deposition at the same rate as direct current provided that the average pulse current is equal to the mean direct current of DC electrodeposition [[67](#page63), [130](#page68)]. In PC plating, the choice of the applied waveform is critical and care must be taken to optimise all parameters (peak current, duty cycle, frequency, pulse shape, etc.). In his work Pearson [[131](#page68)] explored the benefits and the limits of the PC electrodeposition technique. He asserted that very low duty cycles were not feasible; in order to produce the same average deposition rate as for DC, as duty cycle is reduced the pulse peak current needs to be increased. In practical applications, too high peak current densities are seldom viable due to limitations of rectifier capacity. On the other hand, as duty cycle is increased the process begins to approach direct current deposition, thus a compromise must be made. When it comes to the frequency, practical maximum frequency which can be applied is limited by the capacitance of the double layer at the interface between the plating electrolyte and the article being plated. If the frequency is very high, the double layer does not have enough time to fully charge during the pulse and the process begins to resemble DC deposition [[131](#page68)]. Maximum useful frequency is around 500 Hz for most applications. However, higher frequencies can be used where very high peak current densities are employed because the double layer charge and discharge times become shorter as the peak current density is increased.

In the pulse reversed current technique (PRC) anodic pulse is introduced into the plating cycle. PRC has the same effect of replenishing the diffusion layer as PC does. It results in dissolution of the protrusions on the metal surface ensuring a more uniform deposition through elimination of the discrepancies between high and low current density areas and increases coating thickness uniformity [[130](#page68)]. PRC plated amorphous Ni-P deposits are reported to exhibit better ductility owing to the absence of voids and to consist of layers with different amorphous structures [[133](#page68)].

It has been reported that the application of PC deposition results in the increase in limiting current density [[130](#page68)]. However according to Pearson [[131](#page68)], the total thickness of the diffusion layer is equivalent to that obtained when plating in DC regime, since use of PC has very little effect on the limiting current density.

In Ni electrodeposition, pulse plating is extensively employed and studied [[134](#page68)–[136](#page68)]. Pavlatou et al. [[72](#page63)] investigated the use of pulse current in order to interrupt the columnar growth of the In Ni-P electroplating, pulse plating also possesses several advantages over DC plating. Lin and coworkers [[4](#page58)] studied Ni-P alloy deposition in a PC regime from a sulfamate bath. They established that compared with DC plating, current efficiency associated with high phosphorus content deposits can be improved by applying pulse current having low duty cycle, high frequency, and peak current density (Figure [13](#page77)). It was demonstrated that after applying the same total charge associated with DC and PC waveforms of different duty cycles, a more uniform concentration profile is maintained for PC than for DC deposition, particularly with the PC having small duty cycles. By employing 0.1 duty cycle with frequencies exceeding 100 Hz deposits with 14 wt.% of P were plated with an efficiency of around 80%. Figure [14](#page78) shows phosphorus content of the fabricated deposits as a function of the peak current density, pulse frequency, and duty cycle. Low duty cycles and high frequencies were beneficial in terms of maintaining more stable surface proton concentration distribution inhibiting alloy composition modulations induced by pH value variations. Unlike DC-plated Ni-P deposits that might become amorphous when their phosphorus content exceeds a critical value, pulse-plated deposit with 14 wt.% phosphorus still consisted of equiaxed crystalline grains. This is in agreement with the study done by Chen et al. [[68](#page63)] who concluded that a reduction in duty cycle from 0.5 to 0.1 simultaneously increases phosphorus content and grain size of the deposits. They found that Ni-P deposits with high P content can be achieved with high current efficiencies by employing pulse plating and that the obtained deposits exhibit lower internal stress than the DC-plated coatings. Pulse-plated deposits were also consistently harder than the DC-plated ones.

**7.** **Compositionally modulated Ni-P electrodeposits**

In DC plating, methods for improving deposit properties include microstructure manipulation by varying deposition conditions or alloying in which case a two-component deposit is formulated by employing an appropriate bath formulation. However, technological development imposes the demand for coatings that combine favourable properties of different metals, a task unachievable solely by employing individual components neither their resultant alloys. In this case compositionally modulated (functionally graded or multi-layered) coatings present a remarkable opportunity owing to the possibility of tailoring engineering coatings to suit a wide range of applications requiring specific functional properties.

In nickel electroplating, production of multilayer coatings consisting of films of bright and semi bright nickel (60-75% of the total nickel thickness) is traditionally employed to improve deposits’ corrosion resistance. Preferential corrosion in the electrochemically more active upper bright nickel layer and propagation of the corrosion in the lamellar direction protects the columnar lower layer of semi-bright nickel through retarded pitting [[61](#page62)].

In a number of applications including the use of coatings for thermal, wear or corrosion protection and microelectronics, the mismatch in properties at the interface between the coating and the substrate can cause stress concentration that could result in the failure of the interface. Employing functionally graded materials (FGMs) [[137](#page68)–[139](#page68)] which are characterised by a position-dependent chemical composition, microstructure or atomic order [[15](#page59)] and by a subtle gradient of their properties along the coating thickness is reported to help in reducing the stress usually incurred due to the abrupt composition change when going from substrate toward A non-uniform, graded [[14](#page59)] or layered distribution [[140](#page68), [141](#page69)] relative to the phosphorus content along the coating thickness or a grain size gradient [[142](#page69), [143](#page69)] are considered to impart favourable properties to Ni-P deposits. Phosphorus content in Ni-P electrodeposits inherently varies with layer thickness. pH at the electrode-solution interface rises concomitantly with the discharge of hydro-gen. After escape of a cohort of hydrogen bubbles from the cathode resultant enhanced convection increases the interfacial proton concentration. Interfacial pH variations cause the variations in the deposit phosphorus content as electroplating continues [[95](#page65)]. Crousier et al. [[35](#page60), [144](#page69)] confirmed that Ni-P electrodeposits consist alternately of layers having varying phosphorus contents. Sadeghi [[21](#page59)] observed that the formation of layers with different phosphorus amounts occurs more readily for alloys with low or medium phosphorus content and at higher current densities. A homogeneous deposit can be fab-ricated and stratification avoided by enhancing the rate of mass transport to the cathode surface or by employing pulse plating [[95](#page65)]. Oscillations in pH are damped out as the coating grows in thickness as electroplating continues [[17](#page59)]. However, variations in phosphorus content can be sometimes intentionally induced in order to produce composition modulation in fabricated Ni-P electrodeposits. With careful optimisation, this approach can result in a significant improvement of features, compared to conventional homogeneous Ni-P electrodeposits.

Layered crystalline/amorphous Ni-P alloys are for example reported to exhibit higher tensile strength, moduli of elasticity and improved corrosion resistance [[144](#page69)]. It is known that Ni-P deposits with low phosphorus content exhibit high hardness and good wear resistance but poor corrosion resistance, conversely high phosphorus coatings exhibit good corrosion resistance but poor mechanical properties. Developing multilayer coatings can be an effective way to obtain deposits characterized by both optimal mechanical and electrochemical properties. For example, a duplex coating with an outer layer having a low phosphorus content and an inner layer with high phosphorus content is a good way to ensure corrosion stability in the contact with surrounding environment and in the same time favourable mechanical properties [[97](#page65)].

Techniques used to produce layered Ni-P electrodeposits include either using two baths with different phosphorus source contents or a single electroplating bath, when electrochemical methods can be used to achieve composition modulation (changing cathodic current or potential). In the dual-bath electrodeposition technique, the item to be electroplated is moved between two plating baths of arbitrary composition and a layer is plated from each electrolyte in cycles. First multilayer deposition by employing dual bath technique was reported by Blum for Ni (24 µm)/Cu (24 µm) as early as 1921 [[145](#page69)]. This approach is mechanically complex compared to the single-bath method and carries a risk of contamination during the substrate transfer [[78](#page64)]. Historically, the first realisation of single-bath multilayered coatings of CuBi( µm)/BiCu( µm) was made by alternately switching the deposition current between low and high value [[146](#page69)]. Single bath method is efficient, versatile and technologically simple. A review of both dual-bath and single-bath electrodeposition methods is compiled by Ross [[147](#page69)].

When employing single bath deposition method pulsed current is a useful tool to achieve the desired composition modulation. Early attempt with two-pulse plating was reported by Girard [[148](#page69)] for the electrodeposition of permalloy films with a compo-sition as close as possible to the zero-magnetostriction (Ni81Fe19) ensuring the smallest magnetic coercivity.

For compositionally modulated Ni-P electrodeposits, Goldman and coworkers [[82](#page64)] demonstrated a method to fabricate Ni/Ni-P films, with wavelengths between 2.1 and 4.0 nm and an average phosphorus content around 12 at.%, by alternating electrodeposition in two baths of different composition. Ross et al. [[78](#page64)] revealed a dual bath electrodeposition technique for the production of thin-film metal multilayers in which substrate was suspended above nozzles of electrolyte and rotated by a motor. Specific steps were taken, including washing and drying the substrate with N2, in order to mitigate problems related to cross-contamination between electrolytes. Multilayered films of Ni/NiPx, NiPx/NiPy, Cu/Ni, and Co/NiPx were fabricated with a range of repeated lengths. Ni/NiPx and NiPx/NiPy multilayers exhibited the highest quality, with repeat lengths as low as 19 Å and up to three orders of reflection in low angle X-ray scans. NiPx/NiPy multilayers were fabricated over a wide range of compositions and with crystalline or amorphous structure. Problems were encountered with other compositions, in the case of Cu/Ni and Cu/Co systems, due to galvanic coupling as well as contamin and in case of Co/Ni-P owing to non-uniformity of Co nucleation.

Wang et al. [[14](#page59)] described electrodeposition and investigated properties of Ni-P deposits having a varying phosphorus content in the direction of the coating thickness. Single bath method was applied and composition gradient was achieved using a range of current density (5-30 A dm 2). The wear resistance of the fabricated Ni-P electrodeposits was approximately two times greater than that of the ungraded Ni-P deposits. Beneficial wear properties of the obtained deposits were attributed to the inhibition of formation and propagation of through-thickness cracks during the wear process owing to their graded structure. Heat treated coatings exhibited low friction coefficient and hardness that was close to the one of hard Cr coatings.

In another study, Wang and colleagues [[15](#page59)] examined corrosion resistance of the developed Ni-P gradient deposits and their tribological behaviour under the oil-lubricated conditions. Deposits heat treated at 400 oC exhibited two orders of magnitude better corrosion resistance than hard Cr coatings (Figure [16](#page78)). The best corrosion resistance was found for deposits heat-treated at 200 oC, which was attributed to the preserved amorphous structure and the stress relaxation at this temperature. Heat-treated coatings exhibited relatively higher wear rate and friction coefficients than hard Cr deposits under oil-lubricated wear conditions.

Elias et al. [[149](#page69)] fabricated multilayer Ni-P alloy coatings for better corrosion protection of mild steel by employing cyclic modulation of the cathode current density. Achieved improvement in the corrosion protection of fabricated multilayer Ni-P alloy coatings was attributed to the large number of interfaces between layers of alloys having different composition and phase structures, at which corrosion propagates laterally until the interface breaks down (Figure [15](#page78)). This mechanism systematically slows down corrosion and improves the coatings stability. Corrosion protection efficiency of multilayer coatings was found to increase with the number of layers, however only up to a certain point (300 layers). At very high layer numbers corrosion resistance deteriorated owing to the lack of distinct interfaces between individual films (approaching a monolayer structure). Both the number of layers and their composition determined the performance of fabricated deposits.

Multilayers of Ni-P with other metals or alloys can be engineered also in order to ensure optimal functional performance in demanding environments. Improved corrosion properties of multilayers of Ni-P/Zn-Ni, when compared to pure Ni-P and Zn-Ni alloys, was detected by Liu and colleagues [[150](#page69)]. According to them, this was due to the corrosion of the sacrificial sublayers of Zn-Ni which extends in the direction parallel to the substrate surface. Continued corrosion generation through the subsequent sublayers overall slows down the corrosion reaching the substrate and an eventual material brake down. Bahadormanesh and Ghorbani [[151](#page69)] recently devised a single bath deposition method for electrodeposition of Ni-P/Zn-Ni compositionally modulated multilayer coatings. At low current densities Ni–P was deposited, while at higher current densities Zn–Ni alloy containing 3.2 wt.% P was obtained. It was observed that the Ni–P/Zn–Ni compositionally modulated multilayer coatings were sacrificial to the steel substrate.

Bozzini and colleagues [[99](#page65)] fabricated Ni-P and Sn multilayer amorphous deposits (layer thickness 0.1 µm to 0.5 µm) by employing a dual bath electrodeposition technique to explore the possibility of improving the Ni-P deposits passivation behaviour. They investigated anodic behaviour of obtained coatings in acidic chloride solution. Current densities at the passivation plateau were in the range of 2-5 µA cm 2 for Ni-P/Sn multi layers, in comparison to a passivation current density of 45 µA cm 2 for Ni-P coatings with similar phosphorus content. They found that the present interfaces improve considerably the passivation behaviour provided that the incorporated Sn layers were sufficiently thin.

**8**. **Areas needing further research and development**

As Figure 17 indicates, there is considerable interaction between the substrate surface, electrolyte composition, process conditions and properties of Ni-P electrodeposits. Process simplicity along with the combined variability of designed solutions for surface modification of various substrates drive the techno-logical and research efforts forward in this field [[22](#page59), [152](#page69)]. Major driving forces are requirements for coatings adapted to progressively more aggressive, possibly variable environments and harsh working conditions, more and more stringent environmental regulations and exploration of amelioration of industrial practices and approaches in terms of large scale production.

In Ni-P electroplating, many areas also require further attention and research. Clarification of the phosphorus codeposition mechanism is still a matter of difficulty and further research efforts are needed in order to improve our knowledge of process mechanism. Electrolyte formulations generating less toxic effluents in combination with preserved quality of the fabricated deposits but not imposing additional process cost are also a focus of attention. Establishing a better connection between process variables influencing phosphorus content in the coatings and their properties in general is necessary. Improved definition of certain process variables such as current density could aid in ameliorating approaches for process optimisation. Practical technological solutions (especially on a large scale) allowing complex coating deposition, such as composition-ally modulated and composite coatings are paramount if wanting to make the necessary steps forward in terms of bridging the ever increasing gap between research advances and applied industrial practices. Exploration of solutions for practical applications of hybrid techniques could result in the fabrication of deposits possessing formally inaccessible combination of the characteristic features allowing to profit from the unique advantages offered by the each specific technique (e.g. uniformity of electroless plating and low cost and simplicity of metals and alloys electroplating [[153](#page69)]).

**9** **Conclusions**

Ni-P protective coatings can be electrodeposited to have a wide range of crystallographic structures. Deposits extending from fully crystalline to amorphous ones can be easily fabricated. Properties of the obtained coatings very much depend on the deposition conditions and their phosphorous content. Post treatment, such as heating, can bring significant improvement of its overall mechanical, tribological and electrochemical properties. Designing unconventional structures, such as graded or multilayered ones, can also with proper optimization give rise to substantial deposits’ characteristics amelioration.

Despite the maturity of Ni-P electroplating, there are still many unknowns and numerous issues still remain to be addressed. Phosphorus incorporation mechanism is still a matter of great disagreement. Factors influencing phosphorus content of the deposit are many and with the plethora of variables characterising Ni-P electroplating process and poor definition of certain process parameters it is not easy to establish clearly the key influencers, manner and the extent of their impact. Up-scaling of the electroplating procedure induces new process variables and more attention in research needs to be bestowed on feasibility study of method transferral to larger scales and its robustness. Current density distribution is a parameter that is often poorly defined. Ageing of the electrolytic baths is not addressed in many of the research works. Additionally, distinguishing between different Ni-P microstructures and establishing a point of transition from one state to another is still a matter of some difficulty.

**Acknowledgements**

This work was supported by the European Union’s Horizon 2020 research and innovation programme SOLUTION, under grant agreement No. 721642.

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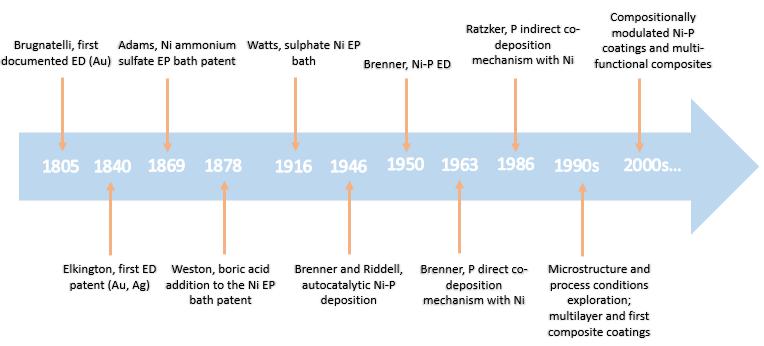
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Fig. 17 Interactive aspects during the electrodeposition of Ni-P coatings divided into substrate properties, electrolyte characteristics, process conditions and properties of the electrodeposits.

**Figures**

****

**Figure 1**

**Deposit**

*- composition*

*- P content*

*- phase composition*

*- thickness*

*- uniformity*

*- porosity*

*- surface roughness*

*- hardness*

*- internal stress*

*- wear resistance*

*- corrosion resistance*

*- adhesion*

*- optical reflectivity*

*- tribology*

**Electrolyte**

*- pH*

*- composition*

*- additives and their level*

*- single or multiple phase*

*- static or flowing*

*- temperature*

**Cathode**

*- 2-or 3-D structure*

*- porous or smooth*

*- current density*

*- current efficiency*

*- static or moving*

**Anode**

*- 2-or 3-D structure*

*- soluble (Ni) or insoluble, O2 evolving (e.g., Pt/Ti)*

anions

cations

Current, *I* and electrons, *e-*

**Operational conditions**

*- temperature, T*

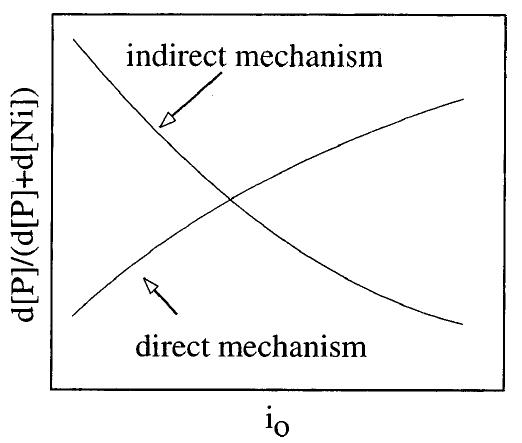
*- current density, j*

*- electrical waveform*

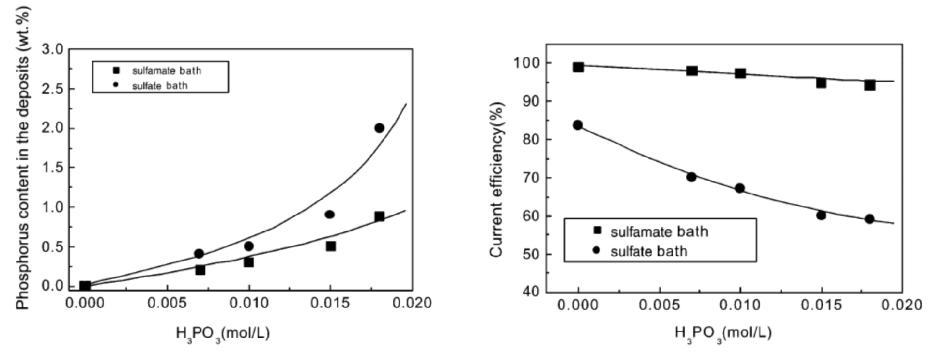
*- current efficiency, *

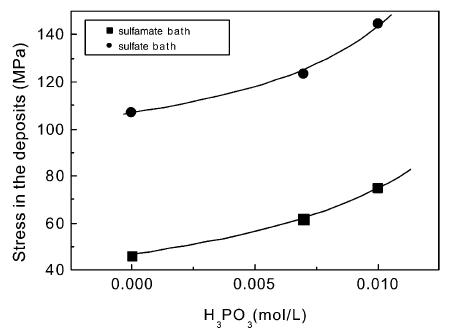
*- static or moving cathode*

**Figure 2**



**Figure 3**



1. (b)

(c)

**Figure 4**

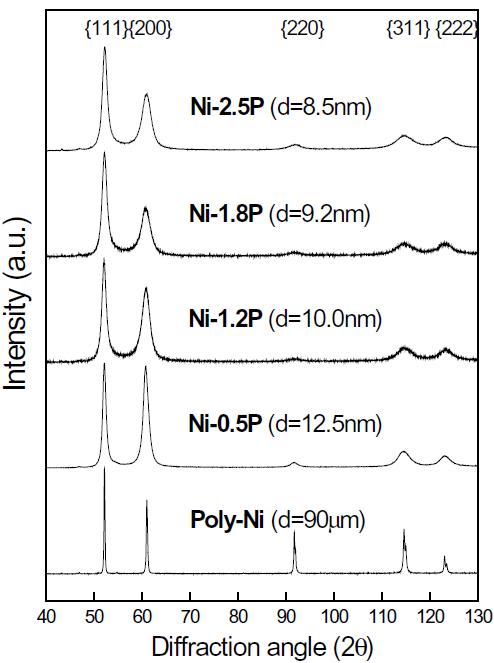
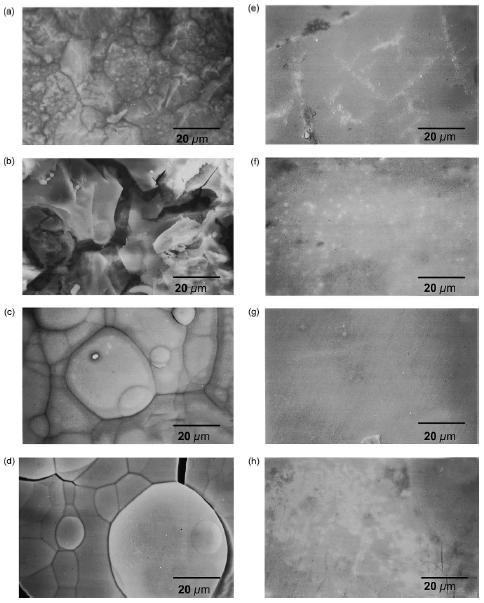
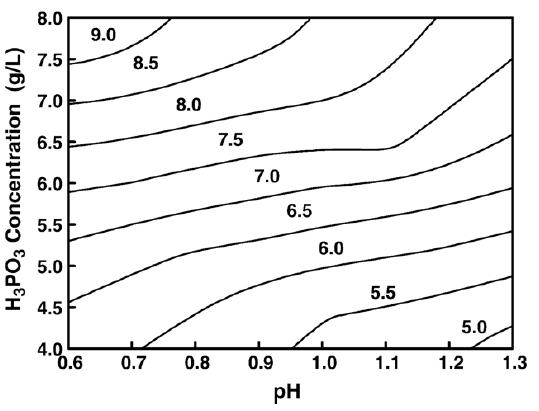


Figure 5

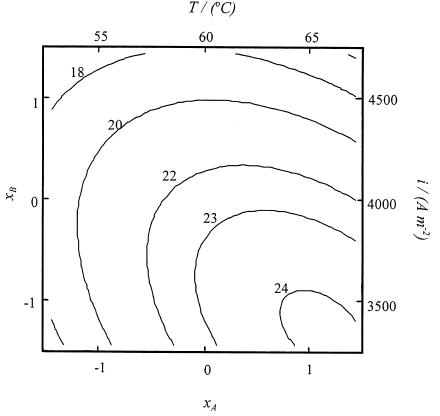
**Figure 5**



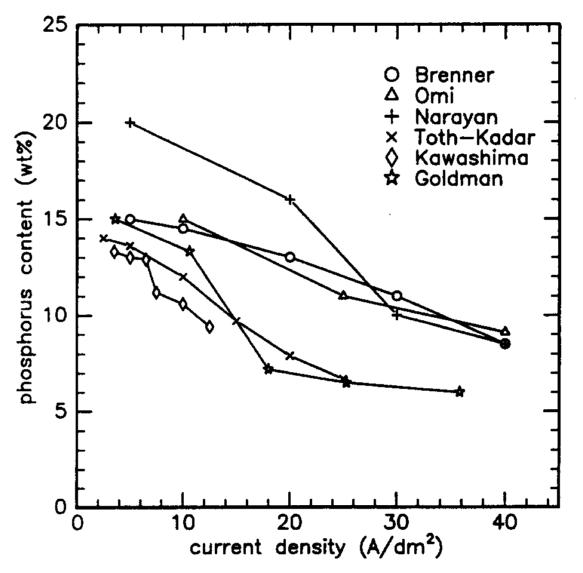
**Figure 6**



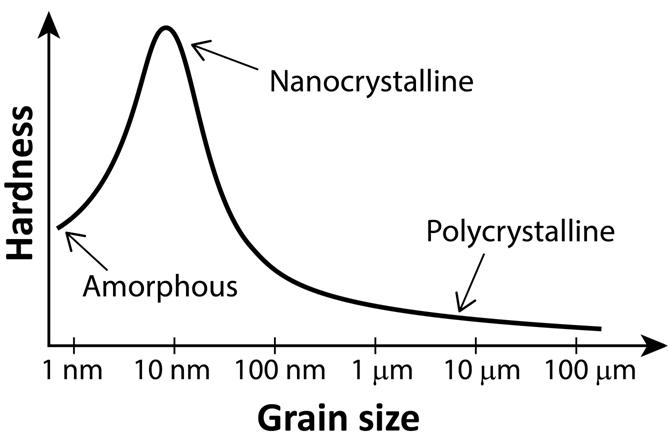
**Figure 7**



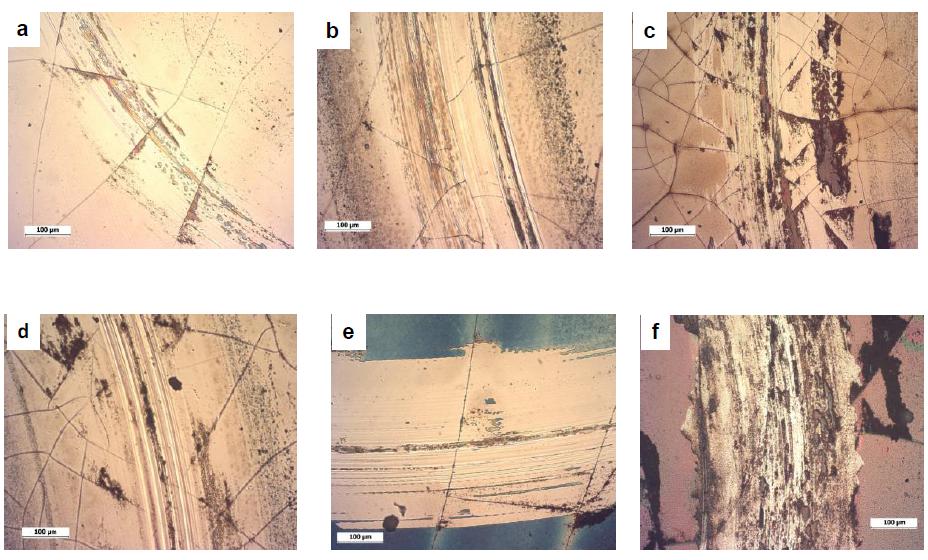
**Figure 8**



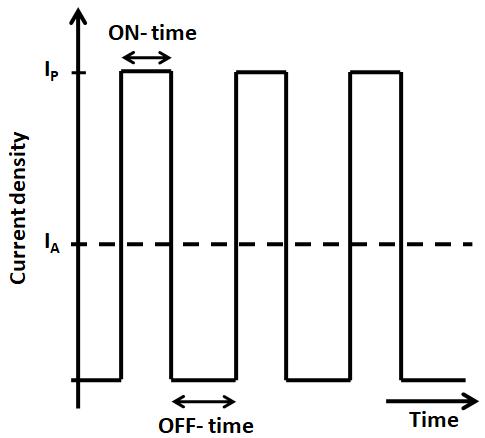
**Figure 9**



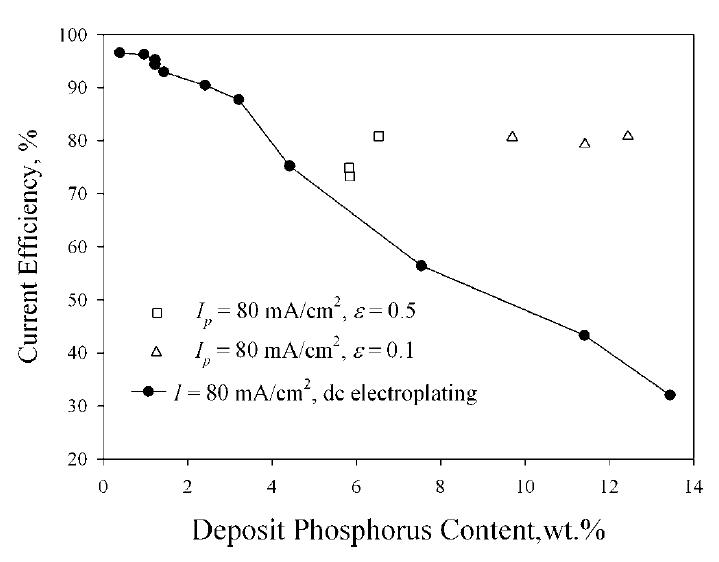
**Figure 10**



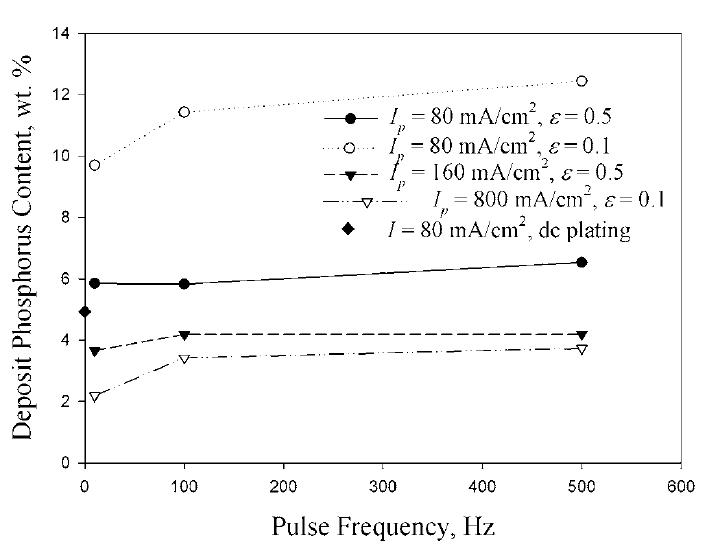
**Figure 11**



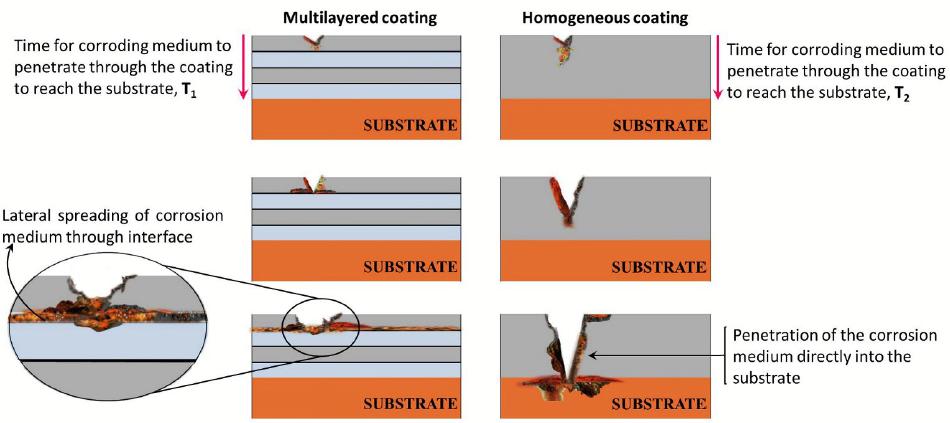
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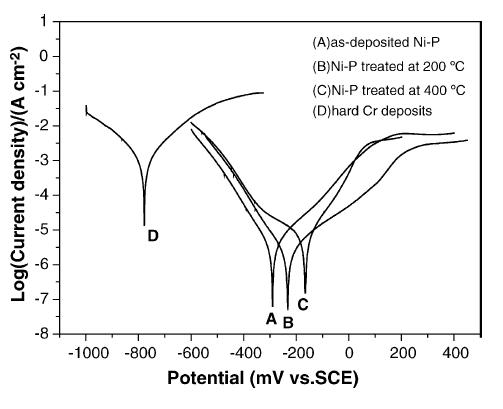
**Figure 13**



**Figure 14**



**Figure 15**



**Potential vs SCE/V**

**Figure 16**

**Figure 17**

Table 1: Benefits and limitations of the alloy and composite coatings electroplating process.

*Benefits Limitations*

Mild operating conditions: temperatures generally lie in the range 2-70 ◦C, normal pressures

Simple low-cost process, scaling-up and/or automation possible

High deposition rates attainable

Even thin electrolytic coatings bring significant improvement in terms of materials engineering performance

Possibility to design multi-functional composite

coatings possessing combination of properties not easily accessible in the realm of pure alloy coatings

Toxic bath constituents, progressively more stringent environmental regulations

Non-uniform current distribution imposing problems with coating extremely complex shapes substrates such as for example high aspect ratio structures

Low current efficiencies for certain compositions and substrate adhesion issues

Gap between the research advances in the field of alloy and composite plating and industrial practices-technological innovations

Poor definition of certain process parameters and mechanisms and complicated process optimization especially in the case of composites plating

Non-pitting agent 0.15 g L−1

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *Reference* | *Bath composition* | *Deposition conditions* | *Phosphorus content* | *Additional information* |
|  | I: NiSO4·6H2O 330 g L−1 | pH 1.7-3.0 |  |  |
|  | NiCl2·6H2O 45 g L−1 | 63 ◦C |  |  |
|  | H3BO3 30 g L−1 | 2-5 A dm−2 | 2-3 %P |  |
| Durney, 1984 [[154](#_bookmark153)] | H3PO3 0.225-2.25 g L−1 |  |  |  |
|  | II: NiSO4·6H2O 150 g L−1 | pH 0.5-1.0 |  | |
|  | NiCl2·6H2O 45 g L−1 | 85 ◦C |  | |
|  | H3PO4 50 g L−1 | 2-5 A dm−2 | 12-15%P | |
|  | H3PO3 40 g L−1 |  |  | |
|  | NiSO4·6H2O 150 g L−1 |  | Maximum P content from baths | |
|  | NiCl2·6H2O 45 g L−1 and: |  | I,II,III and IV is achieved for | |
|  |  |  | following conditions: | |
|  | I: H3PO4 50 g L−1 | 80 and 90 ◦C | I:35 wt.%P for 40 g L−1 | |
|  | H3PO3 0-40 g L−1 | *<*10 A dm−2 | H3PO3 and 80 ◦C (CE∼25%) | |
| Narayan and | II: H3PO4 0-200 g L−1 | 80 and 90 ◦C | up to 35 wt.%P II:≈20 wt.%P for 125 g L−1 | |
| Mungole, 1985 [[79](#_bookmark80)] | H3PO3 20 g L−1 | *<*10 A dm−2 | H3PO4 and 80 ◦C (CE∼50%) | |
|  | III: H3PO4 50 g L−1 | 90 ◦C | III:≈30 wt.%P for 12 g L−1 | |
|  | H3PO3 20 g L−1 | *<*10 A dm−2 | carbonate (CE∼70%) | |
|  | NiCO3·NiOH2·4H2O 0-15 g L−1 |  |  | |
|  | IV: H3PO4 50 g L−1 | 70-90 ◦C | IV:30 wt.%P for 5 A dm−2 | |
|  | H3PO3 20 g L−1 | 5-40 A dm−2 | and 70 ◦C (CE∼25%) | |
|  | NiSO4·6H2O 150 g L−1 | pH 0.43-1.0 | Transition to amorphous | |
| Bredael et al., 1993 [[46](#_bookmark47)] | NiCl2·6H2O 50 g L−1 | 60 ◦C | up to 20 wt.%P structure at ≥12 wt.% P | |
|  | H3PO4 42.5 g L−1 | 2-150 A dm−2 |  | |
|  | H3PO3 3-70 g L−1 | RDE 750 rev/min |  | |

NiSO4 0.38M pH 1.5-4.5 Maximum P content 25 at.%

NiCl2 0.13M 30-90 ◦C

∼

Morikawa et al., 1996 [[43](#_bookmark44)] H3BO3 0.49M 1-30 A dm−2

0-25 at.%P for ≈ 0.5M H3PO3, at 60 ◦C,

3 A dm−2 and pH 3.5

Citric acid 0.5M (CE 25%);

Table 2: Proposed bath compositions and deposition conditions for Ni-P alloy electroplating from sulfate, sulfamate and sulfonate baths according to various literature sources. Obtained phosphorus content is stated where applicable and some basic observations are noted. (jd-current density, t-temperature, *ε*-duty cycle, f-frequency, CE-cathode current efficiency)

∼

H3PO3 0-2M for H3PO3 *>*0.5M P levels off

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *Reference* | *Bath composition* | *Deposition conditions* | *Phosphorus content* | *Additional information* |
| Hu and Bai, 2001 [[47](#_bookmark48)] | NiSO4·6H2O 330 g L−1  NiCl2 45 g L−1 | pH 1.0 and 4.0  20 and 50 ◦C | 13-28 at.%P (pH 1.0  , NaH2PO2·H2O 1M) | Composition control by  simultaneous change |
| Hu and Bai, 2003 [[109](#_bookmark110)] | H3BO3 37 g L−1 | 5 and 25 A dm−2 | 4-12 at.%P (pH 4.0 | of t and jd; Amorphous |
| NaH2PO2·H2O 0.5 and 1M 200 and 400 rev/min , NaH2PO2·H2O 0.5M) structure for ≥12 at.%P NiSO4·6H2O 150 g L−1 pH 1.8 Primary nucleation of Ni | | | | |
| Kurowski et al., 2002 [[155](#_bookmark154)] | NiCl2·6H2O 45 g L−1  H3PO4 50 g L−1 NiCO3 40 g L−1 H3PO3 40 g L−1 | 55 ◦C  -420 mV (SHE) | 27 at.%P | followed by Ni-P formation;  Growth driven by surface diffusion of Ni and P species |
| Li et al., 2003 [[83](#_bookmark84)] | NiCl2·6H2O 0.2M NaH2PO2·H2 0.1M  NH4Cl 0.5-4M | pH 3.3 25 ◦C  5-50 A dm−2 | 2-10 at.%P | 10 at.%P for 4M NH4Cl (CE ≈ 60%) |
|  | NiSO4·6H2O 137 g L−1 | pH 1.5 |  | Nanocrystalline deposit; |
|  | NiCO3 36.5 g L−1 | 70 ◦C | 0.5-2.5 wt.%P | Maximum hardness (990 HV) |
| Jeong et al., 2003 [[126](#_bookmark127)] | H3PO3 2-3 g L−1 | 1-3 A dm−2 |  | and wear resistance after |
|  | Saccharin 5 g L−1  SLS 0.1 g L−1 | Magnetic stirring |  | heat treatment at 370 ◦C |
|  | Ni(SO3NH2)2·4H2O | pH 1.0-2.5 |  | Maximum P content 14 wt.% |
| Lin et al., 2006 [[4](#_bookmark6)]  Chen et al., 2010 [[68](#_bookmark69)] | (Ni+2 90 g L−1)  NiCl2·6H2O 3 g L−1 H3BO3 40 g L−1  H3PO3 10 g L−1 SDS 0.4 g L−1 | 50 ◦C  jp 8 A dm−2 10-500 Hz  *ε* 0.1-0.5  Air bubbling | 2-12 wt.%P | for *ε*=0.1 and f*>*100Hz (CE ≈ 80%);  Deposit still crystalline; Compressive internal stress  (-40 MPa) |
|  | NiSO4·6H2O 240 g L−1  NiCl2·6H2O 28 g L−1 | pH 0.8-1.8  45 and 75 ◦C | up to 10 wt.%P | Maximum P content  for higher H3PO3 |
| Yuan et al., 2007 [[5](#_bookmark7)] | H3BO3 30 g L−1  H3PO3 2 and 8 g L−1 | 4 and 10 A dm−2  Magnetic stirring 150 and 550 rev/min |  | concentration and lower pH values |
| Chang et al., 2008 [[96](#_bookmark97)] | Ni(SO3NH2)2·4H2O (Ni+2 96 g L−1) NiCl2·6H2O 4 g L−1 H3BO3 32 g L−1  H3PO3 0-4 g L−1  Wetting agent 0.3 mL L−1 | pH 1.5-3.5 45 ◦C  2 A dm−2 Air bubbling | 1-4.5 wt.%P | Maximum P content for higher H3PO3 concentration and lower pH values (CE ≈ 70%) |

H3BO3 0.005M 70 ◦C ≈ 8-12 at.%P plating conditions dependent; Alleg et al., 2016 [[87](#_bookmark88)] NaH2PO2·H2O 0.1M -1.3 to -1 V across depth: Deposits mixtures of

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| *Reference* | *Bath composition* | *Deposition conditions* | *Phosphorus content* | *Additional information* |
| Schlesinger and | NiSO4·6H2O 170 or 330 g L−1  NiCl2·6H2O 35-55 g L−1 | pH 0.5-3.0  60-95 ◦C |  |  |
| Paunovic, 2010 [[7](#_bookmark9)] | H3BO3 0 or 40 g L−1  H3PO4 50 or 0 g L−1 H3PO3 2-40 g L−1 | 2-5 A dm−2 |  |  |
| Pillai et al.,2012 [[66](#_bookmark67)] | NiSO4·7H2O 150 g L−1  NiCl2·6H2O 45 g L−1 H3PO4 0-40 g L−1  H3PO3 0-20 g L−1 SLS 0.25 g L−1 | pH∼1.5 50-80 ◦C  5-30 A dm−2 | 0-20 wt.%P | P content decreases with  H3PO3 concentration decrease and increase of jd and t  (up to 15 g L−1H3PO3);  Deposit amorphous for ≥9 wt.%P; Hardness 8.57 GPa (4-7 wt.%P), after annealing at 400 ◦C  maximal hardness (12 GPa) |
|  | NiSO4·6H2O 0.65M | pH 1.5 |  | Transformation to crystalline |
| Nava et al., 2013 [[20](#_bookmark21)] | NiCl2·6H2O 0.75M  H3BO3 0.15M | 3 A dm−2 | 10.6 at.%P | at 500-600 ◦C;  Annealed deposit hardness |
|  | NaCl 2M |  |  | 990 HV |
|  | H3PO3 0.1M |  |  |  |
|  | NiSO4·6H2O 0.2M | pH 3.0-4.0 | at surface: | Soft magnetic character, |

Saccharin 0.005M ≈ 4-6 at.%P Ni(P) solid solutions and NaCl 0.7M amorphous or Ni2P phase

I: Ni(CH3SO2)2 1M pH 3.0 Max P content for 0.12M

NaCl 0.3M 60 ◦C NaH2PO2 and 2 A dm−2:

NaH2PO2 0.03-0.12M 2-7 A dm−2 ≈ 8 (I) and ≈ 13 wt.%P (II);

Sknar et al., 2017 [[54](#_bookmark55)] up to 13 wt.%P

II: NiSO4 1M P content is higher from

NaCl 0.3M a sulfate bath;

H3BO3 0.7M Internal stress and hardness

NaH2PO2 0.03-0.12M are better from sulfamate