Ni-P coatings electroplating — A review
Part II: Ni-P composites

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Abstract
Ni-P coatings produced by electrodeposition are characterized by good mechanical, tribological and electrochemical properties, they exhibit catalytic activity and beneficial magnetic behaviour. With subsequent thermal treatment hardness of this binary metal-metalloid system can approach or be even higher than that of hard Cr coatings. Electrochemical co-deposition of homogeneously dispersed second phase particles within the Ni-P metal matrix can result in the enhancement of alloy’s favourable properties and in the possibility of completely new engineering applications. The purpose of this paper is to provide a general overview of the research work regarding the electrodeposition of Ni-P matrix based composite coatings. Advances in the research of Ni-P composites reinforced by: SiC, B₄C, WC, Al₂O₃, SiO₂, TiO₂, CeO₂, MWCNT, MoS₂, WS₂, TiN, hBN, PTFE and their combinations are covered, with the consideration of the main models proposed for the co-deposition of particles, influence of the system hydrodynamics and other process factors.

1 Introduction

Among binary alloy coatings fabricated through electroplating, Ni-P has attracted a lot of attention. Alloying nickel with phosphorus brings improvement of its mechanical properties, wear and corrosion resistance, magnetic features, results in a higher fatigue limit and lower macroscopic deformation [1]. Vast number of studies have been conducted which prove that coatings based on Ni-P with careful tailoring of the composition and structure can offer smart and adaptive solutions to a wide range of environmental and working conditions [2, 3]. By applying subsequent thermal treatment the hardness of Ni-P electrodeposits can approach or surpass that of hard Cr coatings [4]. However, the brittleness and the reduced integrity of Ni-P electrodeposits upon heat treatment restricts their applications for the replacement of Cr. This is especially notable for anti-wear applications involving high thickness deposits in a progressive environment, such as under the conditions of high speed and heavy load [5]. Electroplated Ni-P is also characterized by higher internal stress when compared to pure Ni electrodeposits [1].

It has been corroborated by many studies that electrolytic co-deposition of inert particles within the metallic matrix, with proper optimization, can contribute significantly to the improvement of mechanical, tribological and electrochemical features inherent to the matrix [6–9]. Composite materials fabricated in such a way possess basic properties that originate from the matrix while the incorporated particles enhance and/or add particular features or functionalities. Achieved attributes enhancement, being mainly derived from the presence of the particles dispersed within the metal matrix, depends on their content and nature. Until today, two types of reinforcements have been employed to produce Ni-P composites through electro-
plating, namely solid lubricant particles and hard and softer ceramic particles but without lubricating properties.

Regarding the first type of reinforcement, this paper covers the research work concerning the co-deposition of: MoS$_2$, WS$_2$, CNT, carbon black, PTFE and hBN; while from the latter group Ni-P composites containing: SiC, B$_4$C, WC, Al$_2$O$_3$, CeO$_2$, SiO$_2$, TiO$_2$, TiN are considered. Review composed by Berk and Zahavi [3] provides more information on the findings concerning electrodeposition of Ni-P composites containing also: B, TiC, CaF$_2$, Si$_3$N$_4$, ZrO$_2$, Fe$_{80}$B$_{20}$, HfB$_2$, with particle sizes ranging from 0.2 to 7 µm.

2 Composites electroplating

Benefits of incorporating inert particles into a metallic matrix via electroplating are many. Inclusion and uniform distribution of nano or micron size second phase particles can lead to improvement of inherent mechanical, tribological, electro-chemical properties of the material and sometimes even open pathways into completely new realms of material application. Table 1 gives an overview of the type of reinforcement used for fabrication of several Ni-P composites through electroplating, with the employed particle sizes, proposed bath loads and achieved deposits dominant functional property.

A number of studies have demonstrated that the use of nano-sized particles rather than the sub-micron or micron-size ones can give rise to more substantial improvement of the deposit’s properties [9]. Uniformly dispersed nano-particles in the deposit contribute to significant strengthening of the material (dispersion strengthening) which can be preserved even at higher temperatures owing to thermal stability of the reinforcing particles. According to Zhang and Chen [10] the strengthening effects in particulate-reinforced metal matrix nanocomposites arise from: Orowan strengthening mechanism, enhanced dislocation density generated by the difference in the coefficient of thermal expansion between the matrix and the particles and load-bearing effect. Particles contribute to significant grain refinement as their presence provides more sites for nucleation and retards the growth of crystals producing a smaller grain size [11]. With increasing availability of nanoparticles the interest in electroplating nano-composites is continuously growing. Big challenges are however achieving high co-deposition rates of particles, their homogeneous distribution in the metal matrix and being able to produce deposits with high levels of consistency, controlled composition and properties.

Different types of reinforcement bring various improvements of features. Hard ceramic particles inclusion can contribute to the improvement of coating’s mechanical properties primarily and soft lubricant particles can prove favourable when it comes to the tribological performance. Metallic matrix based coatings comprising both hard and lubricant particles can be engineered also. In such case, lubricant/soft phase provides lubrication to a surface, hard ceramic phase provides structural integrity and wear resistance of the coating and a ductile metal phase ensures ductility and matrix support. A non-line-of-sight (“NLOS”) process for electroplating lubricant-hard-ductile nano-composite coatings has been demonstrated in [12].

Co-deposition of particles within metallic matrix during electroplating occurs through a number of stages. These can be said to include: formation of ionic clouds around the particles in the bulk electrolyte, convection towards the cathode, diffusion through a hydrodynamic boundary layer, diffusion through a concentration boundary layer and finally adsorption at the cathode surface where particles are entrapped within the metal deposit (Figure 1) [13]. Co-deposition of particles within the deposit is dependent on many process parameters including: characteristics of the particles (e.g. concentration, surface charge, type, shape, size), electrolyte composition (e.g. electrolyte concentration, additives, temperature, pH, surfactant type and its concentration), applied current density (e.g. direct current, pulsed current, pulse time, duty cycle, potentiostatic versus galvanostatic control), flow environment inside the electroplating tank (e.g. laminar, mixed, turbulent regime) and shape/size of electroplating tank and electrode geometry (rotating disk electrode, rotating cylinder electrode, plate-in-tanks, parallel plate electrodes and many variations of electroplating tanks) [13, 14].

Process modelling–A number of models were proposed in order to describe and rationalize the process of particles co-electrodeposition within a metal matrix and several review papers offer surveys of the main ideas of these models [6, 9, 13, 15, 16].

Guglielmi [17] devised the first comprehensive model for the co-deposition of particles. Model assumed two adsorption steps (one physical and other electro-chemical in nature) and elaborated current density and particle loading effect on par-
particles’ co-deposition rate. Guglielmi’s model presented a kernel for many subsequently proposed models and its validity has been verified in many studies by employing different deposit compositions. However, the main drawback of the Guglielmi’s paradigm was that it neglected the influence of the particle size and hydrodynamics on the particle incorporation process. Modifications of this model have been proposed by several other research groups. Bercot et al. [18] additionally considered hydrodynamic conditions and the effects of adsorption and flow. They devised a corrective factor for Guglielmi’s model allowing to study the incorporation of PTFE particles into nickel electrolytic coatings performed under the conditions of magnetic stirring. Bahadormanesh and colleagues [19] modified Guglielmi’s model in order to study the deposition of high volume percentages of the second phase particles. Formulated model was employed to describe the effects of current density, particle load and stirring rate of the electrolytic bath on the kinetics of the particles co-deposition process.

Alternative models have also been proposed. Celis et al. [20] hypothesized that the particle will only be embedded in the growing deposit if a certain amount of adsorbed ions on its surface is reduced. They derived an equation allowing to predict the degree of co-deposition at a given current density for a system of defined hydrodynamics (e.g. rotating disc electrode). In the Trajectory model devised by Fransaer and colleagues [21], the co-deposition rate is determined via considering the fluid flow, taking into the account all forces acting on the particle and assuming that particles will be incorporated in the matrix once the contact with the electrode surface occurs. Bozzini et al. [22] studied the effect of varying the concentration of suspended particles on the volume fraction and the size distribution of the embedded particles under constant hydrodynamic conditions.

Inherent complexity of the composites’ electroplating process complicates any attempt to elaborate and establish the operating interdependences, hence obtaining robust generalized models applicable to large scale plating conditions represents a great challenge. General drawbacks of the presently advocated models are that they are specific to certain electrodeposition conditions, ignore the impact of significant process influencers with the occurring discrepancies in definition of certain process parameters [9].

Particles co-deposition—The majority of recent investigations indicate that three global factors can be identified as influencing the particles co-deposition process, namely: the applied current density, bath agitation or electrode movement and particle type, concentration and size [13].

Choice of the employed particles and their properties play a pivotal role in the process. Ehrhardt [23] found conductive SiC to demonstrate larger co-deposition within the Ni matrix when compared with non-conductive Al2O3. In general, it has been observed that in the case of highly wettable particles larger weight fraction in the deposit is obtained for conductive particles when compared to the case of co-deposition of non-conductive species, while in the case of low wettability particles lower particle content is obtained than in the event of employing wettable ones [3]. When it comes to employed particles size, Surviliene et al. [24] studied the co-deposition of MoO3 and TiO2 particles with chromium. They found that the particle type bears more influence on coating’s morphology when compared to the particle size. Such finding is corroborated by the study of Chen et al. [25] who also observed that particle type exerts greater impact on the co-deposition process. They found α-Al2O3 particles to be more easily co-deposited with copper when compared to γ-Al2O3. Recently Sadeghi in his doctoral dissertation [1] summarized findings on the effects of employing various particle types and sizes in Ni and Ni-P composites plating. Particle type effect was explored by employing Al2O3, TiO2 and SiC nanoparticles having the same nominal grain size. Particle incorporation amount, coating’s morphology, microstructure, residual stress, etc., were all very much different in the case of different reinforcement type. For Ni-P co-deposition of TiO2 resulted in the highest incorporation amount and the highest decline in residual stress upon annealing. In terms of particle size, Sadeghi investigated the co-deposition of Al2O3 particles of nano and sub-micron size. Ni crystallographic structure, its hardness, Ni-P composites phosphorus content and their internal stress were significantly different when employing particles of different size. In the case of Ni-P, the presence of sub-micron size particles more substantially reduced phosphorus content in the deposit when compared to nano size ones. This was associated with the higher hydrogen adsorption on these particles, hence higher restriction of the phosphorus production in this case. Additionally, for compos-
ites containing sub-micron particles the internal stress was even 5 times smaller than that of Ni-P electrodeposits with no reinforcement. Structurally different particles (e.g. fullerenes, nanotubes) in a single metal deposit may also exhibit different behaviour during the incorporation process [13]. These matters are not extensively interrogated as most of the research works focus on only one type of reinforcement possessing specific features.

In general particle content in the deposit can be increased by applying appropriate agitation approach, by the addition of metal cationic accelerants [26] and organic surfactants [27], but also by changing the type of the applied current [28, 29].

Figure 1: Particle co-deposition into a metal deposit. Reprinted with permission from [13]. Copyright (2006) Elsevier.

Dispersing the reinforcing particles in the electroplating solution and obtaining a stable suspension are of crucial significance for obtaining deposits with optimal incorporation and uniform distribution of the particles. Methods for improving the particles dispersion include mechanical (agitation, ultrasonication, etc.) or chemical (altering pH value of the solution to values higher or lower than the one of particle isoelectric point) treatment of their suspension, addition of appropriate surfactants or in some cases even chemical modification of the sole particles.

Electrolytic bath agitation—Controlled agitation in the electrolytic bath is one of the prerequisites for achieving uniform, high quality composite coatings. In the electroplating process agitation serves many purposes: to disperse bath constituents, to keep the particles suspended in the electrolyte, to enhance the transport of particles toward the cathode surface, to increase the deposition rate, to disperse gases and overall to maintain general solution uniformity and thermal equilibrium.

Agitation can be directed primarily at electrolyte mixing or it can aim at interface agitation when the goal is to reduce the thickness of the diffusion layer at the electrode/electrolyte interface. In the former case it is mechanical agitation and air bubbling that are quite effective. Air bubbling however decreases solution conductivity, hence increasing the process power consumption. Mechanical stirring is driven by electrical energy and even though widely applied, it must be carefully optimized in order to ensure satisfactory level of internal and interfacial mixing. In the case of rotating electrodes (e.g. RDE, RCE), their spinning produces both effect of bath stirring and interface agitation, the latter resulting in the decrease of thickness of the diffusion layer [30]. Diminishing the width of the diffusion layer helps ions diffuse from the bulk solution towards the electrode surface, increases the limiting current density and the deposition rate.

In many investigations it has been found that increased agitation generally enhances the amount of particles in the metal deposit. However, excessive agitation resulting in turbulent flow regime may lead to a lower quantity of particles in the metal deposit. This can be explained by the existence of the vigorous hydrodynamic forces in the electrolyte which remove the particles from the cathode surface before they can be entrapped in the metal deposit [13]. Different flow regimes affect particles of micron or nano size in a different way [9, 13]. Strategies for bath agitation depend on the dimensions of the electroplating cell and the scale at which the electrodeposition is being carried out. For laboratory investigations magnetic stirring, rotating disk or cylinder electrodes and parallel plate channel flow are commonly employed while in industrial processes popular methods used in open tanks include the overhead blade stirrer, the reciprocating plate plunger or a pumped recycle loop of the electrolyte [9, 13]. Among all methods employed at the laboratory scale for dispersing nanoparticles, magnetic stirring is the easiest. However, it is characterized by poor reproducibility and inducing complex and eddy-prone flow. The shortcoming of this method is also the re-aggregation of nanoparticles that occurs owing to the acting of van der Waals forces once the stirring is suspended [31].

When performing composites plating, strict control of hydrodynamics in the electroplating bath is vital for obtaining coatings with high and homo-
geneous volume fraction of the co-deposited particles and its microstructure control \[32, 33\]. This problem is especially pronounced in the large scale plating where complex hydrodynamics distribution can generate numerous problems especially in terms of the particle incorporation and the uniformity of their distribution. Many studies have been performed in order to estimate the extent of hydrodynamics influence and to mitigate concomitant problems \[32, 34–36\]. Fransaer et al. \[21\] devised a particle co-deposition model that took into consideration the forces affecting the particles, hence taking into the account the fluid flow. Bozzini and colleagues \[32\] investigated the entrapment mechanism of particles on a rotating disc electrode with the approximation of steady laminar flow past solid wall of a Newtonian incompressible fluid in which rigid spheres are dispersed. Entrapment of particles and their diameter selection have been looked at in terms of balance of the forces acting on the particle, namely: viscous drag, Magnus and centrifugal forces, resulting in mass transport being identified as the key factor influencing the incorporation of particles.

Figure 2: Cross-sectional view of the non-traditional plating cell geometry utilizing parallel solution flow with respect to the substrate surface. Parallel flow is achieved through orienting the eductors below each anode chamber and directing flow to the substrate surface with the dampening element, distinct flow channels are formed between the substrate and the anode chambers. Reprinted with permission from \[35\]. Copyright (2016) Electrochemical Society, Inc.

Many solutions have been proposed, involving particular geometry and electroplating cell design in order to achieve uniform flow conditions relative to the work piece \[2\]. Gebhart and Taylor \[34, 35\] introduced a patent in which electroplating cell was engineered so as to provide a uniform boundary layer thickness and to dampen uneven localized current distribution. Design involved coupled flow channels and dampening elements which were employed to direct the eductor flow in a parallel fashion across the substrate surface. Basic scheme of the design is shown on Figure 2.

Application of the external magnetic field, according to many studies, helps to improve the quality of fabricated composite coatings owing to a strong, localized convection arising from the micromagnetohydrodynamic effect which enhances the mass transfer toward the coating’s surface \[31\]. Additionally, magnetic field enhances desorption of hydrogen and diminishes the fractional bubble coverage by reducing the mean bubble size and changing their distribution which decreases the formation of holes in the coating \[37\]. Magnetic field breaks down the dendrites formed on the coating’s surface and increase the nucleation resulting in a coating with finer grains. Wang et al. \[38\] studied the effect of the external high parallel magnetic field on the Ni/nano-Al₂O₃ composites co-deposition process. They found that the distribution of nanoparticles displays a network shape when applying a magnetic field and that the average diameter of single network increases with increasing the current density. High content of nanoparticles was obtained at low current density with a magnetic field applied, while high current density was necessary to realize the same when no magnetic field was employed. Hu et al. \[39\] found that the application of an external magnetic field can significantly improve the mass transport process, causing an increased SiC content in the nickel matrix and modifying the obtained composite’s surface morphology. Bund and coworkers \[40\] corroborated findings on the benefits of magnetic field application in the electrodeposition process. They observed an augmentation of the alumina particle content in electrodeposited nickel layer, the effect being induced by the application of a perpendicular magnetic field.

Ultrasonic irradiation (UI) implementation in surface treatments involving nanoparticles can also bring numerous benefits, not only as a tool to enhance the dispersion of nanoparticles in the treatment bath, but also to improve the incorporation of dispersed nanoparticles into the coating. Cavitation bubbles which form due to UI produce instantaneous high pressure and strong shock waves, which weaken the interactions between the nanoparticles, resulting in an effective and even dispersion. Nano-composite coatings produced under UI exhibit an enhancement in corrosion and
wear resistance and improved hardness [31]. Zhu et al. [41] reported that owing to the intensity of ultrasonic agitation being much higher than that of electromagnetic stirring, the hydrogen produced concurrently with the reduction of Ni ions can be taken away from the cathode surface in time, reducing the effect of hydrogen embrittlement in the fabricated Ni matrix composites. Nishira et al. [42] studied the effects of agitation methods on the particle size distribution of PTFE aggregates in the electroless plating solution. Their findings indicated that employing ultrasonic homogenizer is more effective than plain mechanical agitation of the bath.

Additives—Employing appropriate surfactants to ensure a stable dispersion of particles in the electroplating solution is another factor of crucial significance in the composite electrodeposition process. Colloidal and nanosuspensions are thermodynamically unstable owing to the large surface energy of the particles, thus keeping them un-agglomerated by the means of agitation and addition of surfactants is vital. In the absence of such additives quality of the dispersion of particles tends to be low and the influence of purely physical parameters such as the geometry and the position of the work piece becomes more important [9]. Cationic (e.g. cetyl-trimethyl-ammonium bromide), anionic (e.g. sodium dodecyl sulphate) and non-ionic (e.g. octylphenol ethoxylate, polyethylene glycol) surfactants and the combinations thereof can be used to control surface charge of particles. High values of zeta potentials of like sign maximize electrostatic repulsion between the particles minimizing their aggregation, thus helping to ensure a stable particle suspension. However, excessive amounts of surfactants ought to be avoided as they can reduce the active cathode area and increase the deposit brittleness [43].

Up-scaling—Most of the published studies which employ techniques for coatings deposition are applied only at the laboratory scale. Up-scaling of these processes, especially in the case of more complicated compositions and structures of coatings (nanostructured, gradient, nanolattice films), larger pieces or more complicated shapes presents a huge technical and economical challenge. This is due to the introduction of many new variables which induce many modifications to the process but also owing to the difficulties related to maintaining particles in the dispersed state when using large volumes [44, 45]. Deposit properties can be significantly different for different deposition scales and specific level process conditions must be carefully optimized and very well defined. Hence more attention needs to be bestowed to method transfer and feasibility investigation on a commercial level.

Ageing—It is a common practice, especially in industrial applications, that the same electrolytic bath is employed for fabrication of number of deposits over time. In such conditions bath components become depleted or enriched, hence their concentrations change. Keeping track of the extent and nature of the bath composition evolving, electrolyte degradation and ageing under the specific deposition conditions is vital for obtaining deposits with uniform and consistent quality. As in the case of electroplating process up-scaling, not many studies have been devoted to Ni-P electrolytic baths ageing investigation.

3 Ni-P electrodeposits reinforced by ceramic particles

Mitigating problems related to corrosion and wear of materials is the subject of major focus in the modern world. In the 1970s MIT professor Rabinowicz conducted a large study of US-based industry in order to determine the key causes of premature machine failures. In his “loss of usefulness” study [53] he later pointed out that 50% of all failures of machine parts are being caused by wear and can be traced back to inadequate lubrication strategies and 20% by corrosion which in total can account for up to 6-7% of GNP. It is estimated that the world’s economy looses billions of dollars every year due to energy losses caused by machinery depreciation and eventual failure. In the light of these facts it is easy to appreciate the immense significance of exploring and adopting the most effective surface engineering practices.

Hard and wear resistant coatings are commonly deposited on tools which are used for severe cutting, forming and casting applications, where the conditions typically result in high temperatures, mechanical loads and pronounced wear [54]. Hard Cr coatings are renown for their exceptional hardness, wear and corrosion resistance but also materials such as nitrides, carbides, oxides, borides and carbon-based ones are extensively used in hard coatings technology owing to their outstanding mechanical and tribological properties [55]. Excellent chemical stability and oxidation resistance in severe environments are also their recurring features.
Table 1: Different types of reinforcement particles and their recommended bath loads for optimal enhancement of Ni-P composite functional properties (DC-direct current, PC-pulse current, WCA-water contact angle, COF-coefficient of friction, d-diameter, l-length).

| Reference | Reinforcement type | Particle size | Bath load | Substrate | Content in deposit (wt.%) | As-plated deposit properties |
|-----------|--------------------|---------------|-----------|-----------|--------------------------|-------------------------------|
| [29]      | SiC                | 300 nm        | 20 g L\(^{-1}\) | mild steel | 1.5 (PC)                 | hard coating (∼700 HV); ∼50 µm |
| [29]      | SiC                | 1 µm          | 20 g L\(^{-1}\) | brass      | 22 (PC)                  | hard coating (∼730 HV); ∼50 µm |
| [46]      | WC                 | 200 nm        | 10 g L\(^{-1}\) | brass      | 30 (PC)                  | hard coating (∼780 HV); ∼40 µm |
| [47]      | B\(_4\)C           | 1.2 µm        | 5 g L\(^{-1}\) | gold; iron | / (PC)                   | hard coating (∼800 HV); ∼50 µm |
| [48]      | TiO\(_2\)          | 5-15 µm       | 100 g L\(^{-1}\) | copper     | 24.2 (DC)                | electroactive material; ∼25 µm |
| [49]      | CoO\(_2\)          | 1-200 nm      | 50 g L\(^{-1}\) | iron       | 2.3 (PC)                 | hard coating (∼575 HV); 50 µm |
| [50]      | MoS\(_2\)          | 1-4 µm        | 10 g L\(^{-1}\) | mild steel | 7.9 (DC)                 | self-lubricating (COF 0.05) |
| [11]      | WS\(_2\)           | 100-300 nm    | 15 g L\(^{-1}\) | mild steel | 4.8 (DC)                 | hydrophobic (WCA 157°); COF 0.17; <40 µm |
| [51]      | MWCNT              | d=100-200 nm | ~20 µm     | copper, stainless steel | 0.7 (DC) | self-lubricating (COF 0.1-0.2); ∼200 µm |
| [52]      | TiN                | 20 nm         | 5 g L\(^{-1}\) | Mg alloy   | ~0.5 (DC)                | corrosion resistant (-0.4 V vs SCE >1600 h); ∼10 µm |

For mentioned materials functional properties are directly related to their structure and present their intrinsic features. However, multi-component materials containing these phases can extrinsically adopt similar properties owing to their presence and induced structural and compositional modifications. This observation is heavily exploited in fabrication of Ni-P composites containing different reinforcement phases and several examples are reviewed in the following text.

3.1 Ni-P electrodeposits reinforced by SiC

The most amply studied Ni-P based composites produced by electrodeposition are the ones containing SiC particles. SiC is employed in a wide range of industrial applications owing to its superior physical and chemical properties, including excellent room and high temperature hardness, wear resistance and chemical durability [56]. Many findings corroborate that the addition of homogeneously dispersed SiC nano or micron size particles to the Ni-P alloy matrix leads to achievement of though, dispersion hardened coatings with improved properties [57–59]. Additionally, employing this type of reinforcement results in the most sensible balance between the amelioration of performance characteristics and the process cost effectiveness.

Majority of studies demonstrate that increasing the SiC particles concentration in the electrolytic bath results in the increase of the SiC content and decrease of the phosphorus content in the fabricated Ni-P based composites [28, 29, 60]. Latter was attributed to the restriction of phosphorus production owing to the enhanced adsorption of H\(^+\) ions on the surface of SiC particles [28]. Increasing particle bath load is beneficial in terms of increasing SiC content in the deposit, however only up to a certain level. Too high SiC amount in the electrolyte leads to saturation, particle agglomeration and subsequent decrease of SiC quantity in the coating [61]. Yuan et al. [58] studied the codeposition of 50 nm SiC particles within the Ni-P matrix. Already upon increase of SiC concentration in the bath up to 10 g L\(^{-1}\) they observed significant agglomeration.

In general the smaller the particles, the more arduous to co-deposit they are [63]. Nano-size particles exhibit higher tendency towards agglomeration in the electroplating solution which can be detrimental in terms of obtained deposit properties. Garcia et al. [64] demonstrated the highest achieved particle volume fraction in the case of 5 µm SiC particles co-deposition, when compared to 0.7 or 0.3 µm particles. Similarly, Wang et al. [65]
demonstrated that the ultra-fine SiC was more difficult to co-deposit than the coarse SiC, and that the rate determining step was controlled by the transfer process of weak adsorption to strong adsorption (in accordance with Guglielmi model). Lee et al. [66] demonstrated that nano-size SiC particles are more difficult to co-deposit in the Ni matrix compared to micron size particles. Furthermore, they observed that the co-deposition of α-SiC particles is easier than β-SiC owing to the more negative Zeta potential of α-SiC. Powders with high zeta potential (absolute value) usually exhibit higher stability in slurries than powders with low zeta potential [67]. Accordingly, the stability of slurries can be interrogated by the zeta potential measurement [68]. Malfatti and coworkers [62] investigated the co-deposition of SiC particles with large granulometric distribution within the Ni-P matrix. They found however that even though volumetric fraction of incorporated particles reaches a plateau when increasing particle load, the incorporated particle number per unit area continues to increase accompanied by the reduction in the incorporated particle size, demonstrating the selective nature of the process (Figure 3). According to them, this was owing to higher probability of mechanical interactions between larger particles and their subsequent ejection, which reduces the likelihood of large particles incorporation in the Ni-P deposit. This finding highlights the significance of taking into the account both volume fraction and number of particles per area when interrogating deposit properties.

Application of suitable additives is very important when dealing with SiC particles electrolytic co-deposition. Narasimman et al. [27] studied the effect of the presence of several different surfactants (TX, DDS, SAC, CTAB, TMAI, TMAH) on the obtained volume fraction of incorporated β-SiC particles in the Ni matrix. Their findings indicated that TMAH performs the best in terms of obtaining deposits with highest volume percentage of incorporated particles and their most homogeneous distribution. In the case of Ni-P matrix, Hou et al. [69] found that the addition of surfactant CTAB can decrease the agglomeration of inherently hydrophobic SiC particles in the aqueous solution. They observed a trend of increasing sub-micron SiC particles content in the deposited layer with increasing concentration of the surfactant in the electrolyte. Malfatti et al. [70] investigated co-electrodeposition of SiC particles possessing a large granulometric distribution (average diameter 600 nm) within the Ni-P matrix. They found that the addition of anionic (SDS) and cationic (CTAH) surfactants decreases the amount of co-deposited SiC particles coupled with the increase in size of the embedded particles. Obtained results suggested that the particle incorporation was practically independent of the surfactant's charge.

Saccharin is commonly used grain refiner in the Ni-P alloy electroplating. Addition of saccharin significantly improves cathode current efficiency of the Ni-P electrodeposition [63, 71] and decreases deposit’s internal stress [72]. This compound however can lead to composite coatings having lower contents of SiC particles and of phosphorus, compared to deposits obtained from saccharin free baths [73]. Co-depositing SiC particles within the Ni-P matrix, with proper optimization, results in the increase of hardness, corrosion and wear resistance and improved coefficient of friction of the alloy [57, 58, 74]. Reduced residual stress and eliminated surface cracking were also reported, so is the increased ductility [29, 60, 75]. Ni-P/SiC composites however exhibit larger surface roughness compared to the pure Ni-P alloy electrodeposits [76].

As in the case of pure Ni-P electrodeposits, owing to precipitation hardening, annealing improves hardness of Ni-P/SiC composites substantially. Martinez-Hernandez et al. [74] studied the incorporation of 100 nm SiC particles in the Ni-P matrix via electrodeposition. Obtained Ni-P/SiC composites (~0.5 at.% SiC) exhibited higher hardness (600 HV) when compared to pure Ni-P alloy fabricated under the same electroplating conditions (430 HV). After annealing at 500 °C deposits attained very high hardness (1453,4 HV), which was greater then the hardness of a typical hard Cr coating. With further thermal treatment above 500 °C hardness decreased sharply. Annealing led to a significant decrease of SiC content in the coating. This was owing to the particle detachment from the upper and middle layers of the coating during the thermal treatment. Vaillant et al. [77] similarly observed that Ni-P/SiC electrodeposits containing >15 at.% of P upon heat treatment at 420 °C exhibit hardness (1100 HV) and mass loss on par with those obtained for hard Cr.

Wang and coworkers [57] investigated post-deposition heat treatment influence on structural, mechanical and tribological properties of Ni-P/SiC nano-composite coatings. SiC particles with a bath concentration of 5 g L$^{-1}$ and average size 45-55 nm
were employed. Obtained results indicated the formation of Ni$_3$P phase in the annealed coatings regardless of the treatment temperature. Gradual augmentation of deposits hardness was observed upon annealing at temperatures up to 400°C while further increase of annealing temperature caused hardness deterioration. Nevertheless, all annealed coatings exhibited higher hardness when compared to as-plated deposits. Improved tribological properties were however observed for composite coatings annealed at temperatures ≥ 400°C. This was associated with the tribo-chemical reaction of formed P$_2$O$_5$ oxide with water from the surrounding environment and the formation of H$_2$PO$_4$ which tends to exhibit a lubricating effect. In spite of the lower hardness compared to other coatings, Ni-P/SiC composite annealed at 500°C exhibited the lowest friction coefficient (0.51) and wear rate ($7.8 \times 10^{-9}$ mm$^3$ N$^{-1}$ m$^{-1}$) owing to a sufficient formation of H$_2$PO$_4$ and its better surface quality. Ni-P/SiC deposits annealed at 350°C exhibiting the highest hardness (∼830 HV) demonstrated the worst tribological properties due to their rough surface morphology and scarce formation of the solid lubricant phase.

Martinez-Hernandez et al. [74] detected a decrease in the wear volume of Ni-P matrix upon addition of 100 nm SiC particles and a very low coefficient of friction comparable to the one of hard Cr coatings. In the case of Ni, Cheng et al. [78] established that the weight loss of friction of Ni/SiC composite coatings decreases with increasing SiC content in the coating, exhibiting a minimum at the optimum value of second phase particle content. Further increase in SiC content beyond the optimum amount caused a deterioration in tribological properties. This effect was attributed to the excessive quantity of SiC particles that formed a soft constituent. Garcia et al. [64] reported that a decrease in size of SiC particles improves the wear resistance of the Ni/SiC composite coatings owing to the resultant particle number density increase in the deposit rather than their volume fraction augmentation. Hou et al. [69] however stated subsequently that the assumption used in the previously mentioned work of SiC particles being monodisperse and spherical can cause significant discrepancies and oversimplifies the co-deposition process interpretation as it ignores the possibility of particle agglomeration in the plating bath which would influence the vol% of SiC in the deposition layer. They employed surfactant CTAB to prevent the agglomeration of SiC sub-micron particles and found that the wear resistance of Ni/SiC electrodeposit increases with increasing SiC vol% in the deposit layer. Aslanyan et al. [76] observed in the case of Ni-P matrix, that the wear rate exhibits a growth when content of SiC increases in the composite coatings. They detected a lower wear rate for annealed pure Ni-P coatings when compared to composites, even though composites exhibit higher hardness [59, 76, 79]. This was justified with the increased sensitivity towards crack formation around SiC particles in the case of composites. Aslanyan and colleagues [59, 76, 80] found that, in spite of the admixtures of SiC and the heat treatment, the wear of the electrolytic Ni-P coatings is of abrasion-oxidizing nature. Wear properties of Ni-P/SiC composite coatings were shown to depend on the type of the sliding test. In the case of the unidirectional sliding test abrasive wear was noticed, whereas in the bi-directional sliding test oxidative wear was revealed [80].

Corrosion resistance is another crucial aspect when it comes to the application of the fabricated coatings. Yuan et al. [58] observed that the addition of nano-SiC particles improves the corrosion resistance of the Ni-P electrodeposits. This was justified by the assumption of the SiC particles presence decreasing the exposed area of the deposit and increasing the density of boundaries between the nanoparticles and the matrix. The best corrosion resistance was obtained for the deposits having an intermediate SiC content (3.07 wt.%). Further increase of SiC amount caused corrosion resistance deterioration owing to particle agglomerates occurrence which led to uneven surface and hence increased corrosion susceptibility. However, all composites exhibited better corrosion resistance when compared to as-plated amorphous Ni-P deposits.

Malfatti and coworkers [62] observed also that the presence of SiC particles in the Ni-P matrix improves its electrochemical behaviour. However, they found that, in the case of electrodeposits possessing the same volumetric fraction of SiC particles, the ones containing particles of smaller size exhibit higher corrosion current densities which was associated with the increased matrix/particle interface area in this instance. Further deterioration of corrosion resistance for composites was observed upon thermal treatment due to concurrent shrinkage of the metallic matrix.

Concerning the applied current density in the electrodeposition process, general observation is that its increase influences the co-deposition of SiC
particles in a positive way. Figures 4 (b) and (c) show the increase of SiC content in the deposit with increasing the current density [60].

Figure 4: SEM micrographs of the polished cross-section of the Ni-P-SiC deposits at various current densities and SiC concentrations (×2KX): (a) 20 A dm\(^{-2}\), SiC 1 g L\(^{-1}\); (b) 20 A dm\(^{-2}\), SiC 10 g L\(^{-1}\); (c) 5 A dm\(^{-2}\), SiC 10 g L\(^{-1}\). Reprinted with permission from [60]. Copyright (2005) Elsevier.

Employing pulse plating instead of direct current deposition at the same average current density leads to composite coatings with higher incorporation rate of SiC particles and more uniform particle distribution [28, 29], the effect being more significant at higher SiC concentrations in the bath [29].

Pulse current electrodeposition results in deposits possessing overall better properties: reduced porosity, surface roughness, improved ductility, hardness, wear resistance. This is owing to the numerous beneficial effects of this plating regime: replenishing of the depleted diffusion layer during the time when the current is suspended, recrystallization of thermodynamically unstable small grains, hydrogen bubbles desorption and many others [81]. Spyrellis et al. [82] studied the co-deposition of 1 µm SiC particles in the Ni-P matrix. They observed that in the PC regime the amount of co-deposited SiC particles (5-8 wt.%) is twice higher when compared with the one obtained by DC plating. Low duty cycle values and high frequencies tend to favour embedment of SiC particles according to the authors of [28], while others find low frequencies in combination with low duty cycles to be beneficial [63].

Zoikis-Karathanasis and coworkers [28] observed that in the electrodeposition of 1 µm SiC particles from an additive-free bath pulse plating leads to a higher percentage of the co-deposited SiC particles regardless of the rotation velocity of the employed RDE. SiC content exhibited a maximum value at the optimum rotation velocity which increases the convective flow towards the disc electrode. The highest percentage of incorporated SiC particles (for 20 g L\(^{-1}\) particle load) was observed for the coating produced under duty cycle 10%, frequency 100 Hz and 700 rpm RDE velocity, reaching ~22 wt.%. Annealing of the obtained composite coatings resulted in the improvement of mechanical properties. Deposits with low phosphorus content exhibited XRD patterns containing main diffraction peaks of Ni, those with intermediate phosphorus content revealed peaks of Ni\(_3\)P (Figure 5), while deposits with phosphorus content higher than 11,5 wt.% demonstrated the presence of Ni\(_2\)P phase additionally (Figure 6). At certain conditions of pulse plating regime, as-plated deposits contained Ni\(_{12}\)P\(_5\) crystalline phase which was maintained after annealing.

Hansal et al. [63] investigated the influence of pulse reverse plating on the incorporation of micron and sub-micron SiC particles in the Ni-P matrix. Their results demonstrated that the particle incorporation rate decreases with increasing current density and shows no significant dependency from the pH value in the investigated range (pH 1-2). A decrease in frequency below 5 Hz with duty cycle of 20% resulted in a higher particle incorporation rate
(150 g L\(^{-1}\) bath load) reaching \(~\sim\)3 wt.%. However, even though incorporation of the particles seemed to be hindered at short pulse times, higher frequencies were beneficial in terms of obtaining deposits with optimal hardness and wear resistance owing to low phosphorus content and intermediate particle amount. Applying unipolar pulses led to improved hardness and wear resistance, while bipolar pulses generated higher amount of phosphorus in the deposit causing a deterioration in mechanical properties and cathode current efficiency. Columnar growth was observed in the case of unipolar deposition, while the application of bipolar pulses induced a change of the structure to a lamellar type.

According to several studies [28, 63], deposits obtained under PC conditions exhibit higher microhardness owing to the higher SiC content when compared to those obtained by DC deposition. According to others [29], hardness of composites produced under PC regime is lower even though SiC co-deposition rate is higher. Phosphorus content in the coating has a secondary effect on hardness according to the authors of [28]. Others find that phosphorus amount in the deposit is the main factor influencing hardness while SiC exhibits an indirect effect through the influence on the composite microstructure [60]. The latter applies in the case of deposits with low SiC incorporation rate. When the SiC concentration in the bath is low the fall in microhardness with the increase of SiC content in the deposit is caused by the decrease of phosphorus content in the deposit. At higher bath loads the effect of the increase of SiC quantity in the coating becomes more significant than the effect of phosphorus content decrease and the microhardness exhibits an augmentation [29].

Figure 5: XRD patterns (a) before and (b) after thermal treatment of Ni-P/SiC deposit with P and SiC content 4.35 and 9.6 wt.%, respectively, produced under PC conditions (10% duty cycle and 0.1 Hz frequency). Reprinted with permission from [28]. Copyright (2010) Elsevier.

3.2 Ni-P electrodeposits reinforced by B\(_4\)C

Fields of interest for Ni-P/B\(_4\)C composite coatings are those in which highly corrosion and wear resistant deposits are required. B\(_4\)C possesses high hardness (38 GPa Vickers), elastic modulus (460 GPa) and fracture toughness (3.5 MPa m\(^{-1}\)), low specific gravity and the ability of neutron absorption.

Bozzini et al. [83] investigated corrosion and erosion-corrosion behaviour of fabricated Ni-P/B\(_4\)C electrodeposits. The presence of 70 µm B\(_4\)C particles was correlated with higher crystallinity of the matrix at a specific phosphorus content, increase in microhardness (\(~\sim\)615 HV), more noble breakdown potentials and lower plateau current densities for the composites. In general composites displayed improved corrosion and erosion-corrosion resistance in aerated slightly acidic chloride solutions. Positive correlation between B\(_4\)C volume fraction and current density was observed.

Bernasconi et al. [47] studied the co-deposition of 2 µm B\(_4\)C particles within the Ni-P matrix. Two compositions of Ni-P, one with a low phosphorus content in the order of 4 wt.% and another with a high phosphorus content of about 12 wt.%, were deposited from a modified Watts nickel electrolyte using both direct and pulse current plating regimes. PC plating was found to induce a significant augmentation of both phosphorus content and the quantity of co-deposited particles. Phosphorus content exhibited a decreasing tendency as particle content increased, the effect being more evident when the high phosphorus formulation was consid-
ered (Figure 7). Hardness reached a maximum of about 830 HV in the case of PC plating from the low phosphorus bath containing 5 g L\(^{-1}\) of reinforcing particles. PC regime proved to exhibit a more substantial beneficial effect on mechanical properties in the case of HP composition.

**Figure 7**: Phosphorus content as a function of particles concentration in the bath and of the form of deposition, DC or PC. Reprinted with permission from [47]. Copyright (2017) Taylor & Francis.

### 3.3 Ni-P electrodeposits reinforced by WC

WC is extremely hard ceramic material that possesses high thermal and chemical stability. Deposition of electrically non-conductive tungsten carbide is very much alleviated through co-deposition with a transition group metal such as Ni.

Spyrellis and colleagues [82] investigated the effects of electrolysis parameters on the structure and morphology of Ni and Ni-P matrix composite coatings reinforced by 200 nm WC particles in DC and PC electrodeposition conditions. Ni-P/WC coatings were characterized by the highest phosphorus content when compared to studied pure Ni-P and Ni-P/SiC composite coatings. Employing PC plating led to an increase of the percentage of incorporated particles. 30 wt.% of WC particles was achieved, while in the case of Ni-P/SiC composites percentage of embedded SiC particles was 5-8 wt.%. In both cases percentages of co-deposited reinforcing particles obtained with PC plating were more than twice higher than those achieved by DC plating. Additionally, embedding of ceramic particles modified in various ways Ni electro-crystallization process, while Ni-P amorphous matrix was not affected by the occlusion of the particles having also greater amount of non-agglomerated particles of the solid phase that were embedded as compared to the polycrystalline Ni matrix. Hardness of as-plated composites was \(\sim 6.9\) GPa which presented a significant improvement when compared to the hardness of pure Ni-P deposits \((\sim 4.8\) GPa\) obtained under the same conditions. Annealing of PC plated Ni-P/WC composite coatings at 400°C resulted in complete crystallization revealing Ni, Ni\(_2\)P and Ni\(_3\)P phases and was accompanied by a significant increase in microhardness [46]. Maximum value of hardness obtained after heat treatment was 18.6±1 GPa.

Xu and colleagues [84] performed electro-brush plating of Ni-P/WC composite coatings. Obtained deposits were reinforced by the electric contact strengthening (ECS). ECS is a surface treatment method which is based on electric contact resistive heating localized at the surface of the work piece, with the aim of improving the coating properties and bonding strength. Results obtained indicated that the application of ECS reduces the number of defects and results in a denser microstructure. Hardness and wear resistance of the coatings were also significantly improved.

### 3.4 Ni-P electrodeposits reinforced by TiN

Zhou et al. [52] performed the co-electrodeposition of TiN nano particles within the Ni-P metal matrix. Fabricated Ni-P/TiN composites demonstrated good adhesion on the magnesium substrate owing to the series of applied pretreatments. Figure 8 shows the cross-section morphology of the obtained deposit. Sequence of layers enables good adhesion and fabrication of a compact and pore free Ni-P/TiN electrodeposit. Hardness of the composite was higher when compared to the hardness of pure Ni-P alloy. Upon annealing at 400°C during 1 h hardness of the Ni-P alloy and Ni-P/TiN composite were 653 HV and 855 HV, respectively. Electrodeposition of composite induced a significant improvement of the long term corrosion resistance of a magnesium substrate. Pure Ni-P electrodeposits performed better in terms of short term corrosion protection owing to the phosphorous rich layer formation, however in the long term the presence of TiN nano-particles contributed to the inhibition of pitting attack penetration and brought more lasting corrosion stability of the substrate. Corrosion potential during immersion of the composite in a 3.5% NaCl solution was stable at approximately (-0.4) V vs SCE after more than 1600 h of test, contrary
to pure Ni-P alloy that demonstrated significant decrease of corrosion resistance already after 170 h.

Ma et al. [85] fabricated Ni-P/TiN nanocomposites on steel sheets through magnetic electrodeposition technique. Magnetic field application resulted in improved microstructure and decreased grain size owing to the combination of magneto-hydrodynamic effect that reduced the viscosity of the plating bath and increased movement rates of Ni$^{2+}$ ions and TiN particles which promoted the co-deposition. Thermal treatment brought a significant amelioration of mechanical and electrochemical properties. Composites heat treated on 500 °C during 10 min demonstrated the highest microhardness value ($\sim$918.6 HV) and maximum impedance value.

### 3.5 Ni-P electrodeposits reinforced by TiO$_2$

Titanium oxides are used as activating agents for cathodic electrode materials in numerous electrochemical processes [86].

In most studies Ni-P/TiO$_2$ composites fabrication was achieved through electroless deposition. Lee et al. [87] established that in auto-catalytic deposition addition of TiO$_2$ nanoparticles slightly decreases deposit’s phosphorus content.

Losiewicz and coworkers [88] asserted that the introduction of TiO$_2$ to the amorphous Ni-P through electrodeposition results in the increase of the rate of the hydrogen evolution in comparison with conventional Ni-P layers in both acid and alkaline environments. According to them, this effect can be associated with the presence of TiO$_2$, its protonated states and/or redox forms which exert an electro-catalytic effect on the hydrogen evolution reaction (HER) but also with the resultant increase in the real surface area.

Gierlotka et al. [48] found that the heat treatment does not bear an appreciable influence on the rate of hydrogen evolution of a Ni-P electrode however induces a slight inhibition of hydrogen evolution of a Ni-P/TiO$_2$ electrode in the acidic environment. Heat treatment was found to be beneficial by the authors of [89]. They observed the increase in catalytic activity occurring after heating of Ni-P + TiO$_2$ + Ti layers which is according to them related to TiO$_2$ reduction and formation of non-stoichiometric Ti oxides.

Losiewicz and colleagues [90] made an attempt to elaborate the relationship between the obtained particle content in the electrodeposited Ni-P/TiO$_2$ composite coatings and the key electrodeposition parameters, such as cathodic current density, bath temperature as well as the content of TiO$_2$ powder suspended in the electrolytic bath. They employed the Hartley’s polyselective quasi D optimum plan of experiments and found within the limits of their study that the porous composite Ni-P/TiO$_2$ coating with the maximal TiO$_2$ content of about 28.7 at.% can be obtained from the suspension bath containing 99 g L$^{-1}$ of TiO$_2$ at 40 °C using the cathodic current density of 5 A dm$^{-2}$.

Sadeghi [1] found TiO$_2$ nanoparticles incorporation in the Ni-P electrodeposits to be greater when compared to incorporation of SiC and Al$_2$O$_3$ particles having the same nominal size, electrodeposition being carried out under the same working conditions. Addition of this type of reinforcement...
led also to the highest decline in the deposit’s internal stress.

3.6 Ni-P electrodeposits reinforced by SiO$_2$

SiO$_2$ particles are mostly incorporated in the Ni-P metallic matrix by the means of electroless deposition [87, 91–95]. Electro-codeposition of SiO$_2$ particles from an aqueous solution into the metal matrix is somewhat limited. This is owing to the inherent hydrophilicity of the SiO$_2$ particles which makes the co-deposition of SiO$_2$ into metal matrix from an aqueous solvent extremely difficult. It is reported that the maximum content of micron-sized SiO$_2$ particles in Ni matrix composite coating obtained from aqueous electrolytes is less than 6 wt.% and that the content of co-deposited particles decreases to 1 wt.% or less (without additives) when the particle size changes from micron dimension to nano dimensions [96]. Nowak and colleagues [97] made an attempt to elaborate why the co-deposition of SiO$_2$ particles is more difficult when compared to SiC. Electrochemical impedance spectroscopy measurements demonstrated that the presence of SiO$_2$ increases while the presence of SiC decreases the electrode capacitance. Positive influence of the SiO$_2$ particles on the cathode surface roughness, hence increase of the surface area, was the only effect detected for this type of particles while SiC particles also block the cathode surface demonstrating the balance effect of the two phenomena.

As an alternative to classical aqueous and organic electrolytes Li and colleagues [96] employed a new type of ionic liquid: a deep eutectic solvent (DES) as an electrolyte in order to produce Ni matrix composite coatings containing SiO$_2$ nano particles (15-30 nm) by employing pulse current electrodeposition. Effective and stable dispersion of SiO$_2$ nano particles in DES was achieved without any stabilizing additives due to its higher viscosity and ionic strength when compared to aqueous solutions. Incorporation of SiO$_2$ nanoparticles in this environment almost reached the level of incorporated SiO$_2$ micron size particles from an aqueous electrolyte (4.69%). Authors determined that the presence of SiO$_2$ particles bears influence on the nucleation/growth process, microstructure and composition of Ni coating. Ni/SiO$_2$ composite coatings exhibited much better corrosion resistance compared to pure Ni, which increased with increasing SiO$_2$ content in the coatings.

The research works regarding co-electrodeposition of these particles with the Ni-P matrix are sparse. Xu and colleagues [98] co-deposited nano SiO$_2$ and CeO$_2$ particles in the Ni-W-P based matrix. Maximum microhardness of Ni-W-P-SiO$_2$-CeO$_2$ composite coatings was obtained after heat treatment at 400°C (1338 HV) and it was higher for composites containing both kinds of particles when compared to composites containing each individual type of reinforcement. Abrasion resistance of the composites also presented a significant improvement. These deposits exhibited amorphous structure in the as-plated state and a transition to crystalline state after thermal treatment. More favourable high temperature oxidation resistance of these films was also established [99].

3.7 Ni-P electrodeposits reinforced by Al$_2$O$_3$

Al$_2$O$_3$ particles possess numerous superior properties such as: low price, chemical stability, good microhardness and wear resistance [5]. Al$_2$O$_3$ nanoparticles are however very ardours to disperse [100]. Work done by Kuo et al. [101] demonstrated that applying ultrasonic oscillation to the electrolytic bath could more efficiently improve the dispersion of nano Al$_2$O$_3$ than applying a surfactant. However, a higher volume content of Al$_2$O$_3$ particles in the deposit is obtained when employing a cationic surfactant CTAB, owing to its chemical adsorption on the particles and resultant increased attractive force between the positively charged agglomerates and the cathode.

Composites of Ni-P containing Al$_2$O$_3$ particles are mostly produced by electroless deposition technique. Sheu and colleagues [5] investigated the influence of employing PC plating for the co-deposition of Al$_2$O$_3$ nano particles in the Ni-P matrix without the presence of surfactants. They concluded that the percentage of Al$_2$O$_3$ in the deposit increases with increasing its content in the electrolytic bath (Figure 9) and with increasing the current density, indicating that process is adsorption controlled in the used current density range. PC plating led to a higher percentage of embedded particles and their more uniform distribution in the matrix when compared to DC plating. High duty cycles (0.7), corresponding to smaller peak current densities and high frequencies (1000 Hz) were found to be beneficial when it comes to the particle incorporation percentage and composites'
microhardness. Maximum amount of Al$_2$O$_3$ was found to be 24.6 vol% and maximum microhardness of the as-plated deposits was 690.3 HV. The increase in particle incorporation with decreasing peak current density they asserted is in line with the model proposed by Celis et al. [20]. They asserted that the increase in peak current density leads to preferential reduction of free metal ions from the solution on the cathode owing to their higher mobility when compared to particles with the ions adsorbed on them, the effect which was observed essentially substantiating the proposed model adoption.

Figure 9: Volume percentage of co-deposited nano-Al$_2$O$_3$ particles in the coatings prepared by direct plating at a current density of 5 A dm$^{-2}$ as a function of Al$_2$O$_3$ concentration in the plating bath. Reprinted with permission from [5]. Copyright (2013) Elsevier.

Sadeghi [1] performed the co-deposition of Al$_2$O$_3$ particles of nano and sub-micron size within the Ni-P metallic matrix. He observed the reduction in phosphorous co-deposition and crack formation upon addition of the reinforcement particles. Phosphorous content decline was higher in the case of sub-micron particles and their co-deposition volume grater when compared to nano particles. Addition of both types of particles induced a decrease in deposits’ internal stress. Internal stress reduction was greater in the case of sub-micron size Al$_2$O$_3$. Lower hardness was observed for composites when compared to pure Ni-P alloy. Upon annealing however hardness of the composites was greater.

3.8 Ni-P electrodeposits reinforced by CeO$_2$

CeO$_2$ is characterized by good corrosion and wear resistance and excellent oxidation performance. Its inclusion in the metal matrix is determined to bring an improvement of deposit’s mechanical properties, moreover to result in the crystal refinement and a denser structure of the coating.

Jin et al. [102] found Ni-P/CeO$_2$ composites prepared by auto-catalytic deposition to possess compact microstructure and good corrosion resistance. Zhou et al. [49] fabricated Ni-P composite coatings containing nano size CeO$_2$ particles by employing PC electrodeposition under ultrasonic field. Composite coating synthesized by PC plating with 15 g L$^{-1}$ CeO$_2$ in the electrolytic bath exhibited fine-grain structure and improvement in microhardness (575 HV) compared to pure Ni-P coatings (425 HV) fabricated in the absence of CeO$_2$ particles under the same deposition conditions. Hardness of the composites was further improved up to 780 HV by annealing at 600 °C during 2 h.

4 Ni-P electrodeposits reinforced by solid lubricant particles

It was estimated that 23% of the world’s total primary energy consumption originates from tribological contacts [103]. Out of that 20% is on account of overcoming friction and 3% is used to remanufacture worn parts and equipment. Responsible energy management is particularly important in the today’s world, where concerns of global warming grow more important every day and increase in the production of green house gases and of the carbon footprint accelerates. This imposes ever-increasing need to improve the energy consumption efficiency and this is where sustainable tribology could create a huge impact with the design of new smart solutions which will increase the performance and reduce the systematic energy losses.

Solid lubricant coatings are in high demand owing to the rapid industrial progress where tribological applications involve progressively more extreme settings that imply vacuum, high temperatures, radiation, oxidative environment, etc. [104, 105]. In these kinds of variable and complex operating conditions liquid and grease based lubricants by their nature cannot provide adequate operation and protection anymore [106, 107]. However, solid lubricant coatings allow to overcome many of the issues related to the use of liquids. They exhibit self-lubricating properties, can sustain harsh environments and have the ability to improve machine efficiency and decrease the energy consumption [108]. It has been demonstrated by many authors that the
addition of phases possessing lubricant properties (solid lubricants), such as: MoS$_2$, WS$_2$, graphite, hBN, etc. to a metallic matrix such as Ni-P can result in a significant improvement of material’s tribological properties and in fabrication of coatings that can be characterized as self-lubricating.

There are several marked classes of solid lubricant materials: carbon-based materials (graphite, CNT, DLC, nanocrystalline diamond), lamellar solids (TMDs, hBN), polymers (PTFE), soft metals (Au, Ag, Sn, In), halides and sulfates of alkaline earth metals and finally oxides (TiO$_2$, B$_2$O$_3$) [105, 109].

4.1 Ni-P electrodeposits reinforced by PTFE

PTFE has numerous appealing properties, out of which some are: non-stickiness, dry lubricity, low coefficient of friction due to its low intermolecular cohesion, good corrosion resistance, low surface energy, chemical inertness [105, 110, 111]. However, PTFE is characterized by low thermal conductivity (which can cause failure owing to melting) and poor wear properties [105]. PTFE particles are intrinsically hydrophobic and they aggregate easily in the electroplating solution owing to what it is very difficult to obtain their stable dispersion [111, 112].

Not many studies are performed on the inclusion of PTFE particles in the Ni-P metal matrix through electroplating, this composition is dominantly fabricated by the means of auto-catalytic deposition. Losiewicz et al. [113] studied the structure and surface morphology of Ni-P/TiO$_2$-PTFE electrodeposits. They fabricated amorphous Ni-P composites with embedded second phase particles that exhibited a tendency of co-agglomeration. Presence of PTFE was established to cause the reduction of the embedded TiO$_2$ particle mean area and to change coatings surface morphology. In the case of Ni-P/TiO$_2$-PTFE composites greater number of microcracks was observed.

4.2 Ni-P electrodeposits reinforced by TMDs

Transition metal dichalcogenides (TMDs) [114–118] have attracted a lot of attention as a second phase in composite coatings designated to efficiently mitigate friction. Good tribological properties of TMDs are associated with their intrinsic structural anisotropy characterized by weak interlayer bonds that allow easy shearing and creation of tribolayer on the counter surface [119]. Upon shearing basal plains are determined to reorient parallel to the sliding direction facilitating sliding friction [105, 109]. This class of solid lubricants is however restricted to use in vacuum or dry nitrogen environment (same friction coefficient however better wear life in dry N$_2$). This is owing to their easy oxidation in the humid atmosphere attributed to the existence of surface irregularities and unsaturated, dangling bonds [120, 121]. For instance, when the test environment is switched from dry nitrogen to humid air, the friction coefficient of a typical WS$_2$ film can rise from 0.03-0.04 to 0.15-0.20, decreasing its wear life by several orders of magnitude [121]. However, studies of Colas et al. [122] have demonstrated that the wear life of MoS$_2$ can be extended if a reasonable amount of contaminants is present in both the coatings and the environment. Chemical reaction with water, carbon and oxygen contamination can help friction and offset the loss of ductile properties of the 3rd body film, hence better wear properties of MoS$_2$ under mild vacuum compared to high vacuum. Additionally, N$_2$ environment is not neutral. Velocity accommodation mechanism is modified through N$_2$ adsorption resulting in better wear life of MoS$_2$ under dry N$_2$.

It was reported by Tenne and coworkers [123, 124] that nanoparticles of organic compounds like TMDs possessing layered structure become unstable in the planar form and are prone to form closed-cage and hollow core nanostructures termed inorganic fullerene-like nanoparticles (IF) and multi-wall nanotubes (inorganic nanotubes-INT). These kinds of structures [125, 126] are proved to be less prone to oxidation owing to the lack of reactive sights and to be in general more chemically inert [127] compared to conventional 2H-MoS$_2$ and 2H-WS$_2$ hexagonal structures.

Many researchers have postulated that incorporating conventional forms of TMDs or embedding them in a metallic matrix could contribute to their protection against oxidation and could allow to exploit their beneficial tribological properties even in humid atmosphere conditions [50]. In the case of IF structures, the main mechanisms of favourable friction behaviour attributed to metallic matrix composites containing IF materials are postulated to be: rolling friction of the IF nanoparticles which are gradually furnished to the surface from the network of pores of the matrix, IF particles
are confined in nanoscopic cavities providing the spacing effect and preventing contact between the asperities and third body material transfer [128]. Due to above mentioned, they are deemed to have even greater potential for solid lubrication applications when compared to conventional structures [129, 130].

Incorporation of TMDs in the Ni-P matrix has been mostly achieved through electroless deposition [131, 132]. However, He and coworkers have recently reported successful cases of co-deposition of WS\(_2\) [11] and MoS\(_2\) [50] within the Ni-P matrix through electroplating. Obtained composites demonstrated improved tribological properties and other beneficial features.

In their first study, He et al. [50] fabricated Ni-P/MoS\(_2\) composite coatings by electrodeposition. Micron size MoS\(_2\) particles were co-deposited within the metallic matrix. Friction coefficient (COF) of the coating containing 7.9 wt.% MoS\(_2\) during sliding against steel in air exhibited a steady-state value of 0.05 during 1 h reciprocating test. Obtained COF value was almost one order of magnitude lower than one of the Ni-P coating without MoS\(_2\) inclusion (0.45). Ni-P/MoS\(_2\) coatings were characterized by rough surface with nodules. This was, according to the authors, owing to the preferential deposition of Ni atoms on the conductive surfaces of the MoS\(_2\) particles once these were attached to the cathode surface. However, with the increase of the MoS\(_2\) incorporation composite coatings exhibited much smoother surfaces characterized by the growth of smaller crystals which indicated that the increasing number of incorporated MoS\(_2\) particles have provided the increased number of sites for the nucleation of nickel growth. Linear relationship was observed between the particle amount incorporated in the coating and the particle concentration in the bath up to a certain level above which saturation occurred. Even in the case of addition of soft particles such as MoS\(_2\) increase in hardness of obtained deposits was observed (∼600 HV). This was associated with the fact that adsorbed reinforcement particles act as nucleation sights on the cathode, hence they increase charge transfer resistance of the electroplating process resulting in more negative cathode potential and enhance the crystal refinement. Resultant increased number of grain boundaries inhibits the dislocation movement, as per Hall-Petch mechanism.

In the subsequent study, He et al. [11] demonstrated successful incorporation of sub-micron size WS\(_2\) particles in the Ni-P matrix via electroplating. According to them, even though surface of pure Ni-P alloy coatings is intrinsically hydrophilic with a water contact angle of 87°, hydrophobic properties can be obtained through the addition of WS\(_2\) particles which additionally impart lubricating properties to the coatings. Sufficient WS\(_2\) content in the composite coatings ensured the formation of a uniform tribofilm and provided a very low coefficient of friction (as low as 0.17). Water contact angle for the composite containing 4.8 wt.% WS\(_2\) was 157°. As in the previous case, the incorporation of WS\(_2\) particles into Ni-P metal matrix was found to cause significant changes of surface morphology from: a planar smooth surface, to a nodular rough surface and eventually to a hierarchical rough surface.

Modification of microstructure, surface morphology and improvement of tribological properties, all induced by the inclusion of nano or micron size MoS\(_2\) particles have been observed also in the case of other binary alloys with nickel, such as Ni-Co [134] and Ni-W [135].

4.3 Ni-P electrodeposits reinforced by carbon based lubricant particles

Graphite [114] is similarly to TMDs characterized by a layered structure, however for graphite to function properly presence of water vapour or other gases is necessary (≥100 ppm) resulting in poor tribological properties of graphite in vacuum or dry atmosphere. It has been postulated that these compounds introduce an intercalation or chemisorption effect which weakens the binding force between basal planes near the surface owing to the increase in interlayer spacing, thereby allowing graphite’s planes to shear easily. Yen et al. [136] investigated the origin of low-friction behaviour in graphite by surface X-ray diffraction. They demonstrated, within the limits of experimental error, that there was no change in the interlayer spacing of graphite’s basal planes near the surface of the outgassed graphite sample exposed to ambient and humid air environments. Such finding supported the alternative explanation for the good tribological properties of graphite, namely that molecules are required to saturate dangling covalent bonds at edge sites of the basal planes for graphite to maintain its low friction behaviour.

Suzuki et al. [137] studied the microstructure and properties of Ni-P matrix composite films with the inclusion of nano size carbon black particles,
produced by electrodeposition. Carbon black content in the deposits increased with increasing its concentration in the bath up to an optimal value reaching a maximum of 0.77 wt. %, while phosphorus content was approximately constant. Obtained composites exhibited higher hardness and better tribological behaviour both before and after heat treatment when compared to pure Ni-P alloy.

Since their discovery by Iijima in 1991 [138], carbon nano tubes have attracted a lot of attention, owing to their beneficial properties which include: good mechanical characteristics (high tensile strength (60 GPa) and high elastic modulus (1 TPa)), thermal and electrical conductivity, favourable chemical and optical properties.

Most studies regarding the tribological properties of the metal-CNT composite coatings have been focused on the electroless nickel plating technique, however several authors have reported the fabrication of Ni-CNT composites through electrodeposition [139–141]. Arai and coworkers [140] fabricated Ni/MWCNT composite electrodeposits having excellent thermal conductivity and improved tribological properties [139]. Friction coefficient of Ni/MWCNT composite films additionally decreased with increasing MWCNT content, minimum value obtained being 0.13 under dry lubrication conditions.

In another study, Suzuki and colleagues [51] investigated microstructure, mechanical and tribo-
logical properties of Ni-P/MWCNT electrodeposits. They fabricated composite films containing 20-22 at.% of P and 0.7-1.2 wt.% of MWCNT. Obtained deposits exhibited higher hardness both before and after heat treatment and lower friction coefficient when compared with pure Ni-P alloy films. The friction coefficient of the Ni-P alloy film gradually increased with increasing cycle number. In contrast, the friction coefficient of the Ni-P/MWCNT composite films decreased rapidly at an early stage and reached a steady value, indicating solid lubricity caused by the intrinsic solid lubricity of the MWCNTs. At 50 cycles, the friction coefficient of the Ni-P/MWCNT composite film was approximately 0.1-0.2, both before and after heat-treatment.

Wang et al. [142] investigated structural, mechanical and tribological properties of Ni-P/MWCNT coatings annealed at temperatures from 350 °C to 500 °C. MWCNT incorporation amount was low (1.9 wt.%). Results indicated that the annealed coatings comprised a hard Ni₃P phase and consequently presented a higher hardness ~(7-8) GPa than the as-plated samples ~6 GPa. Maximum hardness was obtained after annealing at 350 °C. Annealed samples exhibited lower friction coefficients (0.71-0.86) compared to as-plated coatings (0.87). This effect was attributed to the formation of H₃PO₄ in the course of the tribochemical reaction of Ni₃P with ambient environment. Lower wear rate was obtained after annealing at temperatures <380 °C owing to the decomposition of the amorphous carbon in MWCNT above this temperature.

4.4 Ni-P electrodeposits reinforced by hBN

Boron nitride with its hexagonal close-packed structure (hBN) possesses the same crystalline organization as graphite having the same total number of electrons available for bonding [114]. However, adsorption of atmospheric gases in the case of hBN does not produce an amelioration of its lubricating properties. This is attributed to the lack of unpaired electrons present in graphite and their pairing in p orbitals in hBN.

Data published on the incorporation of hBN in the Ni-P matrix refer to the deposition of composite coatings mostly by electroless technique [143, 144]. Findings corroborate improvement in wear resistance and coefficient of friction for the fabricated composites. Peng and coworkers [145] studied the effect of incorporation of 2 µm hBN particles in the Ni-P matrix through PC electrodeposition. Obtained composite coatings were characterized by an amorphous structure and demonstrated a significant improvement in friction coefficient and wear resistance with a slight decrease in hardness compared to Ni-P coatings. Minimum coefficient of friction obtained was 0.08 in the case of the bath containing the highest content of hBN (20 g L⁻¹). There is no investigation of the influence of hBN inclusion on corrosion properties of Ni-P alloy, studies on Ni [146] indicate however increased microwear, refined surface morphology and improvement in corrosion behaviour.

5 Conclusion

It can be generally observed that the study of Ni-P composites produced by electrodeposition is still lagging much behind the advances made on the investigation of composites produced by electroless deposition, even though research demonstrates that the co-deposition of particles in the Ni-P matrix by the means of electroplating can be optimized to meet the increasing requirements on process simplicity and obtained deposits multi-functionality. Lack of attention in research is given to investigation of bath ageing, incorporation of particles of different shapes and forms, up-scaling, combining/sequencing different deposition techniques. It is important to iterate that obtaining a stable dispersion of non-agglomerated reinforcement particles is of critical significance and further investigations of the possibilities and approaches to interrogate and control this aspect are necessary. Influence of hydrodynamics and mass transport need to be further investigated especially at the larger scale when the influence of the variability of all relevant conditions and parameters is even more pronounced and produces a complex combination effect on deposit structure and properties. Current distribution is also vital but often its influence is poorly defined. Despite small advances, modelling of the composite electrodeposition remains unsatisfactory. Finally, there exists a significant discrepancy between industry and scientific research and efforts need to be made in the future to bridge this gap and establish a sustainable relationship between the two worlds.
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