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**Electrodeposited Ni-Co alloy-particle composite coatings:**

**A comprehensive review**

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**Abstract**

Electrodeposited composite and nanocomposite layers have attracted considerable attention as engineering coatings, due to their favourable tribological properties and corrosion resistance. Ni-Co alloy matrix composite coatings are particularly significant due to their extensive and developing industrial applications. Ceramic nanoparticles are commonly incorporated into the Ni-Co alloy matrix to further improve their properties, opening new windows for industrial applications. This review aims to comprehensively assess the influence of operating parameters (including the type of current control, plating bath conditions, particle loading and size) on the deposit properties. Developments in this field are summarized. Fundamental and technological aspects requiring further R & D are identified.

**Keywords:** composite; corrosion; electroplating, Ni-Co; operating parameters; tribology.

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**List of Symbols**

|  |  |  |
| --- | --- | --- |
| **Symbol** | **Meaning** | **Units** |
| *A* | Surface area of the electrode | m2 |
| *cw* | Mass concentration of solids suspended in the electrolyte | kg m-3 |
| *%d* | Percentage duty cyclefor pulsed current | s-1 |
| *dE/dx* | Potential field gradient | V m-1 |
|  | Percentage duty cycle of pulse reverse current | s-1 |
| *E* | Potential | V |
| ** | An efficiency factor | dimensionless |
| *f* | Pulse frequency | dimensionless |
| *F* | Faraday constant | 96485 C mol-1 |
| I | Relative intensity in XRD patterns | dimensionless |
| *j* | Current density | A cm-2 |
| *M* | Molar mass of deposited metal | g mol-1 |
| *Rct* | Charge transfer resistance | ohm |
| *t* | Time | s |
| *toff* | Off time | s |
| *ton* | On time | s |
| *x* | Deposit thickness | cm |
| *x* | Distance in the interelectrode direction | m |
| *z* | Stoichiometric electron number | Dimensionless |
| **Greek** | **Meaning** | **Units** |
| **  *µ* | An efficiency factor  Electrophoretic mobility of a charged species | Dimensionless  m2 V-1 s-1 |
| *ρ* | Density | g cm-3 |

**Abbreviations**

CNT: Carbon nanotube

CTAB: Cetyltrimethylammonium bromide

DC: (Smooth) direct current

EIS: Electrochemical impedance spectroscopy

fcc: Face centered cubic

FSP: Friction stir processing

hcp: Hexagonal close packed

LC50: Lethal concentration 50

LSE: Laser surface engineering

MWCNT: Multiwalled carbon nanotube

PC: Pulsed current

PRC: Pulse reverse current

PZC: point of zero charge

SCD: Sedimentation codeposition

SDS: Sodium dodecyl sulfate

SEM: Scanning electron microscopy

TEM: Transmission electron microscopy

XRD: X-ray diffraction

1. **Introduction**

The interface between workpiece and its environment is critical to engineering performance, as it governs duty cycle and service lifetime. The mechanical, thermal, chemical, and electrochemical interactions of a material in an environment are all important. Surface modification of engineering components using coatings plays a crucial role in achieving the desired properties including improved microstructural and mechanical properties leading to enhanced tribological and corrosion behaviour [1-4]. Laser surface engineering (LSE) [5], plasma spray [6], friction stir processing (FSP) [1], physical and chemical vapour deposition and electrochemical treatment [7, 8] are well-known surface finishing techniques.

Electrodeposition can produce a deposit having a tailored structure. In addition to its low cost, convenience, near-ambient working conditions and reproducibility, a wide variety of materials can be electroplated, including pure metals, alloys, and composites on various substrates. The early use of electrodeposition can be traced back almost 2000 years, when single or multi-component layers were realised [9, 10]. The science and technology of electrodeposition has matured into an outstanding level of surface modification and materials finishing, which can satisfy the diverse demands for specialized applications. The electrodeposited layers can usually provide a sufficient capability to enhance the solderability, lubrication properties, electrical conductivity, resistance to both corrosion and wear, as well as thermal activity of the surface via offering versatile coatings [11]. The proficiency of this method in producing coatings with controlled thickness, ranging from extremely thick films to ultra-thin protective ones, even on complex geometries with reasonable deposition rate as well as scaling up availability, distinguishes the method from common coating technologies [12]. Due to facile operation at atmospheric pressure and ambient temperature together with its ease of control, electrodeposition can be considered with other cost-effective and energy-saving methods [13, 14].

It is possible to produce nanostructure coatings with via electrodeposition process. Many attempts have been made to synthesize nanostructured coatings having improved mechanical properties. Many factors govern the generation of nanostructured coatings, including the crystalline structure of the substrate, surface and adhesion energy, lattice orientation, and lattice mismatch with the interface. The mechanism of how such coatings exhibit superior properties over conventional coarse-grained ones is not completely understood. Moreover, the final structure and crystallite size of the electrodeposited layer is affected by the kinetics of nucleation and growth. There are significant differences between the properties of microstructured and nanostructured Ni coatings [15].

Pure Ni coatings have gained much attention due to its great corrosion resistance associated with the superior resistance to thermal oxidation [16]. However, alloying of Ni with Co can considerably affect the crystalline structure, morphology, and physical properties of the coating. Codeposition of Ni with Co during fabrication of Ni-Co alloy coatings is an anomalous codeposition process, where the less noble component, Co, occupies cathode surface deposition sites in preference to Ni [17]. Common approaches for inclusion of Co into a growing Ni deposit to produce Ni-Co alloy coating are (i) incorporation of cobalt salts into the electrolyte and (ii) use of soluble cobalt anodes. Ni-Co alloy coatings have several advantages over pure Ni and Co deposits, such as improved tribological, mechanical and corrosion properties, favourable magnetic features, and enhanced electrocatalytic activity. The possibility of achieving Ni-Co solid solutions over a wide range of Ni:Co concentration ratios provides versatility in depositing alloy coatings with a wide range of composition [3, 12, 18-22]. Ni-Co alloy deposits have been the subject of many publications due to their magnetic properties [23], catalytic nature and electrochemical energy storage capability [24-26], resistance to high temperature oxidation [27, 28], resistance to wear and corrosion, and favourable mechanical properties [29-34]. Accordingly, such coatings are used in sensors, automobiles, actuators, inductors, aerospace, and supercapacitors [33].

In order to exploit the full benefits of these coatings, an incorporation of insoluble metallic and non-metallic materials into the Ni-Co electrolyte has become a promising option. Various types of included particles including oxides, carbides, nitrides, different forms of carbon, polymers, and metallic compounds can be incorporated into the microstructure of coatings [35]. The concentration, size and shape of these particles may alter the final properties [36-38]. While the presence of these particles through the coating can give rise to desired physicomechanical properties, several critical, interrelated parameters such as electrolyte temperature, electrolyte pH, current type, applied current density, plating duration, incorporation of surfactants and additives, which determine the deposit properties. Incorporation of nanoparticles into the alloy coatings results in improved tribomechanical and corrosion properties. Increased costs have restricted the use of these nanocomposites in industry. When economic aspects of producing a coating become more important, it will be necessary to improve the final properties Ni-Co alloy coatings by changing the operational parameters such as current type and plating bath conditios, rather than incorporating high-cost particles. If the dominant issue is high hardness or wear resistance, other coatings, including heat treated Ni-P having lower costs, can be employed [15, 39].

Early use of composite coatings dates back to the 1920s. By the 1970s, SiC particles were introduced into a Ni matrix to promote the wear resistance of the Ni coating, which is still a major industrial application [40, 41]. During the advent of Ni-based composite coatings, there are two central aims of studies: (i) designing the optimum electrolyte including the chemical composition and size of incorporated particles and additives; (ii) realizing the capability of such coatings as engineering components. Further studies in the field of electrodeposited Ni matrix composite coatings have revealed that adding an alloying element to Ni matrix, e.g. Co, P and W, can dramatically improve the mechanical, tribological and corrosion properties of coatings [19, 36, 42-44].

The final properties of the electrodeposited composite coating are greatly affected by chemical composition, concentration, and size of the included particles. Nevertheless, incorporation of desired loading of particles into the microstructure of the coating and their uniform distribution throughout the matrix still remain two potential challenges to be overcome [45]. The use of a magnetic field coupled with ultrasonic agitation and inclusion of bath additives are recommended to overcome such challenges [46-52].

Despite the benefits and widening applications of composite coatings, the vast majority of reported studies are carried out on a small, laboratory bench scale; the scale-up of composite/nanocomposite electrodeposition has received very little attention. Nevertheless, the industrial scale production of electrodeposited composite coatings and their use have proven the satisfactorily corrosion resistance of these deposits. Changes in corrosion resistance of laboratory-scale and industrial-scale deposits, due to variations in thickness or porosity have been mentioned [53-56]. It is unfortunate that few studies appreciate the importance of measuring through porosity of coatings in corrosion protection, especially in the case of thin (e.g., <10 m) deposits.

This comprehensive review considers the influence of current control, operating parameters, type of included particles and post treatments on the final properties of Ni-Co alloy matrix composite coatings. The ways in which the above factors affect coating properties is addressed.

1. **Environmental, health & safety concerns**

Hard chromium coatings have traditionally been used for their unique tribological and mechanical properties. The use of chromic acid electrolytes, which can release toxic hexavalent Cr ions has restricted worldwide use of such deposits and raised serious environmental concerns. Many research studies have aimed to find competitive, greener, coatings. Ni-Co based coatings have provided a potential alternative for some applications. However, electrodeposition of these coatings can also result in the release of toxic Ni and Co ions into the environment. At the concentrations encountered in electroplating baths, nickel ions can also result in skin allergies among some operators, so protective gloves should routinely be used. To minimize the harmful effects of Ni and Co ions on human and environmental health, appropriate waste water treatment should be applied. For example, advanced electrodeposition techniques and cation exchange resins can be used to eliminate metal ions from electroplating industry wastewaters [57, 58].

Nanoparticle inclusions and surfactants may also be considered as a possible threat to environmental health, since they can be released into the environment through wastewaters from composite electroplating. Regarding surfactants, some of them are highly toxic while others are biodegradable. Non-toxic surfactants show negligible risk to human and environmental health and can be rinsed away by water dilution, while others may cause environmental concern. In general, most of non-ionic such as dodecyl dimethylamine oxide and anionic surfactants such as sodium linear alkylbenzene sulphonate are non-toxic. For example, the anionic surfactants exhibit toxic behaviour for an LC50 between 10-100 mg L-1. Since the discharge of highly polluted wastewaters with surfactants is dangerous for environmental health, application of adequate recycling and effluent treatment is important [59, 60].

Environmental and health concerns over nanoparticles can arise from their high surface activity. Studies have demonstrated that the nanoparticles may not positively affect the environment. In order to diminish the harmful influences of the nanoparticles on human and environmental health, a more complete understanding of the ways in which nanoparticles affect the environment [61] is of rising concern.

1. **Proposed Mechanisms of Ni-Co Electrodeposition**

The codeposition of the iron group metals including Ni, Co, and Fe is considered to be an anomalous deposition, wherethe volume fraction of the less noble one in the deposit exceeds its concentration in the plating bath.This interesting behaviour ascribed to the evolution of hydrogen leads to enhancing the local concentration of hydroxyl ions, thereby providing a strong adsorption force for metal hydroxide ions, e.g., M(OH)+, to settle on the substrate. Co incorporates into the Ni matrix with the aid of these hydroxide ions. The proposed mechanism for such codeposition is [62]:

|  |  |
| --- | --- |
|  | (Eq. 1) |
|  | (Eq. 2) |
|  | (Eq. 3) |
|  | (Eq. 4) |

where M is Fe, Ni or Co.

1. **Types of Current Control**
   1. **Overview**

Ni-Co based composite coatings can be electrodeposited using three different current types including pulse reverse current (PRC), pulsed current (PC), and direct current (DC). The applied current is constant during DC electroplating. Advantages of this method include low cost, simplicity and well-established background knowledge [63-66]. PC involves a periodic current in which the current changes between zero and positive values. There are on-time and off-time periods; ion transport between the anode and cathode stops during the off-time period. Percentage duty cycle (*%d*) and pulse frequency (*f*) are two predominant factors which may alter the final properties of the electrodeposit using PC. The following equations are commonly used to obtain these factors [9]:

|  |  |
| --- | --- |
|  | (Eq. 5) |
|  | (Eq. 6) |

During PRC, the applied current has a zero or negative value; during the *toff* period and changes to positive values at *ton*. Unlike PC, it can change between positive and negative values [67].

The electrodeposited coatings using PRC claims multiple advantages over those produced via DC and PC, such as low internal stress, the ability to eliminate passive layers and better control over the chemical composition of the coating. The duty cycle in PRC, is calculated from:

|  |  |
| --- | --- |
|  | (Eq. 7) |
|  |  |

where, *d'*, *tC*, and, *tAA* show the duty cycle of PRC, cathodic time, and anodic time, respectively [9]. Despite the stated advantages, PRC and PC methods suffer from drawbacks, such as a prolonged process time, the need for a roadmap to achieve the required results, a higher cost than DC and a decreased need for additives which is an unfavorable situation to chemical suppliers [68].

* 1. **Surface Morphology**

The surface morphology of electrodeposited coatings is strongly affected by the type of current control, so it is possible to precisely control the surface features of the coating via changing the current type. For instance, PRC and PC provide a more compact and smooth surface than DC. This is attributed to the alternative transformation of the current direction in PRC which enhances the cathode polarization. This can noticeably increase the nucleation energy of the present metallic grains, thereby increasing the nuclei numbers. Practical studies have demonstrated that a more homogenous microstructure may be formed by application of PRC rather than PC and DC [7, 69-71].

The application of PC can result in a more compact microstructure than in DC electrodeposition due to a more dense, finer-grained morphology.

**4.3. Chemical Composition**

According to the literature, changing the current type can profoundly alter the amount of codeposited particles/nanoparticles as well as the volume fraction of the existing constituent elements, namely Ni and Co. In general, the application of PRC and PC leads to an increase in the volume fraction of codeposited particles compared to DC [70-72]. The mechanism behind this improvement is periodic alternation of current between zero and positive or positive and negative values during electrodeposition via PC and PRC, respectively. This can satisfactorily discharge the generated electric double layer and promotes the infiltration of the particles toward the cathode due to the higher reduction rate of ions adsorbed on the particle surface of the electrical double layer during discharge [72].

Co content, as a substantial factor in determining the final properties of Ni-Co based composite coatings, can be varied by using different current types, wherein Karslioglu et al. [72] have indicated that using PRC and PC rather than DC may slightly increase the Co content of the synthesized coatings. The exact mechanism of this enhancement is unclear.

**4.4. Phase Composition**

Generally, the intensity of the X-ray diffraction peaks assigned to the incorporated particle and peak width may be varied by changing the current type. However, the current type cannot affect the position of the diffraction peaks [70, 73].

Studies have shown that the application of PC provides a stronger peak corresponded to embedded particle than DC. This means that better codeposition can be achieved through PC [70]. Ranjith et al. [73] showed that the growth orientation of emerged peaks by changing the current mode from PC to PRC remained unchanged, however, the peaks assigned to all crystal faces have been broadened. In other words, the coatings electrodeposited through PRC exhibit more refined microstructure than PC. The main reasons for this refinement is not fully addressed in the literature and it is important to consider surface adsorption, mass transfer and electrocrystallisation effects.

**4.5. Mechanical Properties**

Parameters such as weight percent of incorporated particle, mean particle size, and predominant growth orientation determine the mechanical properties of electrodeposited coatings. Since the application of different current types may alter these parameters, they can dramatically affect the microhardness of the coatings [70-73].

A higher content of particles content in the deposit can be achieved using PC and PRC rather than DC control. Unlike DC, a long time is provided for Ni2+ and Co2+ cations to adsorb on embedded particles during the off-time periods in PC. The deposition process stops during the off-time period, so a higher co-depositing rate is obtained. Moreover, PC and PRC provide a more refined microstructure than DC. It can be concluded that the coatings electrodeposited via PC and PRC exhibit promising mechanical properties. In comparison to the PC method, PRC deposited coatings can achieve a higher microhardness due to the greater loading of codeposited particles [71-73].

**4.6. Corrosion Resistance**

The type of applied current can determine the corrosion behaviour of Ni-Co based composite coatings by (i) refining the microstructure of coatings, (ii) changing the volume fraction of codeposited particles, and (iii) morphological changes [70, 71, 73]. For instance, Ghazanlou et al. [70] have reported that the Ni-Co-SiO2 composite coatings electrodeposited by PC method exhibit higher corrosion resistance than the others which electrodeposited by the DC route. This improved behaviour is attributable to the higher loading of SiO2 nanoparticles when applying PC control. The mechanisms which explain how particles can contribute to corrosion resistance enhancement will be discussed in section 5.8.

Studies on the effect of grain size on corrosion behaviour are limited and contradictory. In environments where a passive film can be formed on the alloy surface, the high density of grain boundaries promotes the formation of a more protective passive film and reduces the corrosion rate. Conversely, when a metal is not passivated, the reactive nature of the fine-grained materials leads to accelerated corrosion. Regardless of the environment, there is agreement that the fine-grained alloys are less susceptible to localized corrosion of grain boundaries in comparison to course-grained ones [74].

**4.7. Tribological Properties**

Generally, the application of PRC and PC, rather than DC noticeably improves the wear resistance of the coatings. This is related to the generation of the rougher surface when using DC, which can also leads to a higher coefficient of friction [70-72]. Literature suffers from a lack of deep analysis concerning the relation between various current types and tribological properties, in the case of Ni-Co alloy matrix composite coatings.

**5. The Importance of Operational Parameters**

**5.1. pH**

pH can govern the various properties of the electrodeposited Ni-Co based composite coatings. Morphological features, mechanical properties, and even thickness of these coatings can be varied by changes in the electrolyte pH. It is to be noted that acidic electrolytes are the most frequently used electrolytes for fabrication of Ni-Co coatings [64, 75, 76].

Generally, altering the volume fraction of the codeposited particles can be considered as the most influence of electrolyte pH. A given suspended particle has a characteristic point of zero charge (PZC) in a particular bath. If the pH of electrolyte is higher than the PZC, codeposition will progress easily due to the negative charge of the included particle. More heterogeneous nucleation sites result and a finer microstructure is expected. On the other hand, practical results confirm that, if electrolyte pH exceeds the optimum value, agglomerated particles can appear due to inadequate absorption of surfactants [70, 76]. For instance, Ghazanlou et al. [70] have reported an optimum pH value of 4.6 for Ni-Co-SiO2 nanocomposite coatings; higher pH values result in a poorer dispersion, resulting in agglomerated particles. Furthermore, they indicated that lower pH values can generate agglomerated particles owing to the excessive surface adsorption of surfactants is due to an increased zeta potential.

Electrolyte pH can affect the mechanical properties of the coatings by changing the (i) volume fraction of codeposited particles and (ii) amount of produced hydrogen. In other words, lower the bath pH, higher the hydrogen production which shows up by internal pores in the film structure. The generated pores may degrade the fracture strength and elongation. A further increase in pH can result in a brittle deposit [77, 78].

**5.2. Bath Temperature**

The bath temperature can determine the morphological, tribomechanical, and corrosion properties of the composite coatings by controlling the loading of codeposited particles. Albeit an overwhelming of studies have reported that there is an optimum bath temperature for obtaining the maximum particle codeposition [70, 79-81], Pushpavanam et al. [76] showed an inverse relationship between the bath temperature and the content of embedded particles. The content of codeposited particles strongly depends on the temperature range. At low temperatures, for instance below 60 oC [79], at 35 oC [81], and at 50 oC [70], the activity of included particles markedly increases at higher bath temperatures, resulting in improved codeposition. However, a further rise in the bath temperature can noticeably contribute to the ionic mobility, which lowers adsorption of particles, in accordance with Langmuir adsorption [81, 82].

Empirical results demonstrate that the microhardness and resistance to both wear and corrosion of the coatings can be drastically improved with temperature rise to the optimum amount and degrades with further increase in the bath temperature [70, 76, 79].

**5.3. Surfactants**

Two types of surfactants have been commonly used in the electrodeposition of the Ni-Co based composite coatings: Cationic surfactants, such as cetyltrimethylammonium bromide (CTAB) can result a positive surface charge on the particles suspended in the electrolyte helping their migration to the cathode surface. Anionic surfactants, such as sodium dodecyl sulfate (SDS) can adsorb on the existing cations in the electrolyte, e.g. Co2+ and Ni2+ and hinder the formation of agglomerated particles [70, 83]. Contradictory results have been reported concerning the effect of SDS on the zeta potential of included particles. It was shown that an increase in the surfactant concentration in the electrolyte decreases the zeta potential of SiO2 particles, while it increases the zeta potential of SiC ones [70, 80]. Such a shift in the zeta potential toward more positive or negative values can strongly affect the degree of adhesion between existing particles and promote the loading of codeposited particles. As a concise summary, (i) decreasing the volume fraction of the agglomerated particles and (ii) increasing the volume fraction of embedded particles are the major roles of surfactants in the composite coatings. It is well known that the more the embedded particles, the superior the mechanical properties is. In order to exploit the full benefits of surfactants in the deposition of composite coatings, selecting an optimum surfactant concentration in the bath is essential [70, 80, 83]. An inclusion of an excessive concentration of surfactants may result in the formation of agglomerated particles due to the enhanced ionic strength of electrolyte which degrades the physical and mechanical properties of the composite coatings. On the other hand, surfactants may lose their efficiency in the way that they cause the formation of agglomerated particles if the low concentration is added to the plating bath [70, 84]. It is possible to use a mixed surfactant, nonionic surfactant or mixtures but the effects on dispersion and surface charge are rarely considered.

**5.4. Other Additives**

In addition to surfactants, other additives that can be incorporated to improve the final properties of the composite coatings [64, 75]. Saccharin (C7H5NO3S) and cerium (III) sulfate Ce2(SO4) are frequently used in the case of Ni-Co alloy composite coatings. Saccharin is an organic compound that widely used to form a smooth surface for Ni-based coatings as it can slow down the growth rate of pyramidal crystals by surface adsorption. They can also alter the preferred growth orientation and the crystallite size, acting as grain refiners. Interestingly, saccharin has been shown to have a greater influence on crystallite size refinement than that of included particles. Furthermore, cathodic overpotential becomes more negative on addition of saccharin to the bath, which results in the generation of the finer crystallites. As a concise summary, saccharin can reduce the crystallite size via (i) slowing down the growth rate and (ii) making the cathode overpotential for metal deposition more negative. It should be expected that the incorporation of saccharin into the microstructure of the composite coatings dramatically improves microhardness through the Hall-Petch relation [85-89]. Bakhit et al. [48] have reported conflicting results, where the microhardness of Ni-Co-SiC composite coatings degrades with the inclusion of saccharin due to overcoming the grain boundaries on the dislocations during the plastic deformation of the coating, in so-called inverse Hall-Petch behaviour. Also, the corrosion resistance of the composite coatings can be promoted by adding saccharin originated from the microstructure refinement [48].

In a similar fashion to saccharin, incorporation of Ce2(SO4) in the electrolyte not only reduces the particle size but also gives rise to the improved particle codeposition. Fig. 1 shows the influence of Ce2(SO4) bath additions on the particle size of an Ni-Co-Al2O3 composite coating [66].

**Insert Fig. 1**

A compact coating with finer particles can be obtained when using Ce2(SO4) as an additive. Nevertheless, adding excessive amounts of Ce2(SO4) to the plating bath may lead to the generation of defects due to the low solubility of Ce2(SO4) in aqueous solutions. The reason for enhanced codeposition of particles with the incorporation of Ce2(SO4) is ascribed to the fact that Ce3+ can strongly adsorb on the present particles in the electrolyte and shift their zeta potential toward positive values. Generally, adding Ce2(SO4) can improve the mechanical properties of the composite coating through three ways, as (i) grain size refinement, (ii) generation of more compact microstructure, and (iii) increase in the volume fraction of the codeposited particles. Moreover, Ce2(SO4) can diminish the residual macrostress of the composite coatings. The mechanism has been related to the substitution of adsorbed Ce3+ with H+, which restricts H2 evolution, producing a coating with low residual internal stress [66].

**5.5. Bath Agitation Conditions**

Generally, it is possible to tune the codeposition content and tribomechanical properties of the Ni-Co based composite coatings with controlling the agitation speed [35, 71, 78, 81, 90, 91]. Before discussing the influence of stirring rate on the above features, it should be noted that there are five primary goals behind the application of bath agitation, as: (i) giving rise to uniformity of the coatings from the viewpoint of thickness, (ii) keeping the present particles suspended in the plating bath, thereby improving its homogeneity, (iii) decreasing the width of hydrodynamic and concentration boundary layers, (iv) contributing to the hydrogen release from the surface of the cathode and (v) increasing in the particles transport toward the cathode [35, 78, 81]. In order to take the full advantages of bath agitation, it is necessary to employ the optimum stirrer geometry and agitation rate. Almost all studies confirm that the codeposition of the incorporated particles increases with increasing the stirring rate until it reaches an optimum value. The volume fraction of the codeposited particles then decreases with a further increase in the stirring rate [35, 90]. For instance, Bakhit et al. [35] indicated that the degree of codeposited SiC nanoparticles enhances with at higher stirring rats up to to 350 rpm, followed by a significant decrement at the faster rates. The reported optimum rate for obtaining the highest codeposited particle content are as follows: 350 rpm [35], 480 rpm [91], and 120 rpm [90]. The decreased codeposition amount at fast stirring speeds is attributed to the two main factors: (i) an increased collision factor and (ii) detachment of the loosely adsorbed particles from the surface of the cathode as a result of intense agitation [90, 92]. Additionally, the type of agitation can alter the content of included particles. Bakhit et al. [35] have introduced pulsed agitation involving *ton*/*toff* periods in which stirring continues and stops during *ton*and *toff* periods, respectively. They confirmed that the volume fraction of the incorporated particles noticeably decreased by increasing the *ton*/*toff*ratio. It is unfortunate that authors do not apply chemical engineering principles to appreciate the importance of electrolyte hydrodynamics, mass transport and electrophoresis to the cathode. The geometry, location and diameter of stirrers are important, not just their rotation speed.

Literature results have confirmed that the highest microhardness can obtain when using the optimum stirring rate. This is ascribed to the highest amount of the included particles at such rates [35, 71, 78]. However, the microhardness value of the coatings stirred using the pulsed agitation technique can be slightly higher than those agitated without stopping the stirring process, due to the enhanced amount of the embedded particles during the *toff* period [35]. As with mechanical properties, the wear resistance of the Ni-Co alloy matrix coatings can be improved by the use of an optimum stirring rate [78].

Most studies neglect the importance of flow regime, electrode geometry and mass transfer in composite electrodeposition, despite their critical importance. Indeed, many studies use the convenient but ill-defined hydrodynamics and mass transfer in a magnetically stirred beaker.

**5.6. Ultrasonication of the Electrolyte**

Ultrasonication has been employed to improve electrodeposition since the 1960s. Current efficiency, diffusion, conversion, exchange current density may be greatly enhanced with the application of ultrasonic waves. Also, they can lower cathode polarization and influence reaction mechanism [93-96].

Ni-Co based composite coatings electrodeposited under the ultrasonic waves exhibit more compact microstructure accompanied by the finer grains with uniform dispersion compared to the free-ultrasonic electrodeposited coatings. The main mechanism of grain refinement is related to the domination of the nucleation rate over the growth rate with the application of the waves. The waves can successfully hinder the growth of the previously nucleated crystals through cavitation and microstreaming. The high pressure induced by cavitation may reduce the critical radius of the nucleus, generating finer grains [97].

There is an inverse relationship between the volume fraction of the codeposited particles and the ultrasonic power. Application of an intense, focused ultrasonic wave may detach the adsorbed particles on the cathode and return them to the plating bath [97].

The effect of the ultrasonic waves on the microhardness of the composite coatings deeply depends on which parameter is the predominant one, namely the amount of codeposited particles or quality of particles dispersion. At low ultrasonic power, microhardness will increase with increasing the power because there is a favourable dispersion of particles, despite the descending trend of the codeposition amount. Therefore, the quality of particles dispersion is predominant when there is low ultrasonic power. On the other hand, at higher ultrasonic power, there is a lower amount of codeposited particles associated with the poor dispersion and formation of agglomerated particles, lowering the microhardness [97].

**5.7. Current Density**

As a facile control parameter, the current density can govern the morphological, microstructural, tribological and corrosion properties of Ni-Co based composite coatings. This fact that a small change in the current density can vary the volume fraction of the incorporated particles as well as Co amount, emphasizes its importance. In order to tailor the final properties of the Ni-Co based composite coatings, the current density during the electrodeposition process needs to be closely controlled [35, 75, 76, 98, 99].

The main influence of the applied current density is to alter the loading of codeposited particles. The available data in the literature are contradictory. Three types of relationship between codeposition and current density can be seen: (i) inverse [76], (ii) direct [75, 91], and (iii) mixed inverse and direct, i.e. ascending followed by descending [35, 39, 79, 98, 99]. Pushpavanam et al. [76] have suggested that with increasing the current density the conditions become more favourable for deposition of metallic ions, e.g. Ni, than the ceramic included particles. Hence, codeposition of the particles is decreased. On the other hand, the authors reported the direct relationship between the amount of codeposited particles and current density have proposed two mechanisms to confirm their claim, as follows: (i) enhanced chance of loosely adsorbed particles to strongly adsorb on the cathode as a result of the generation of more reductive circumstance originated from the increased current density [91]; (ii) accelerated electrophoretic movement of the included particles, along with an increased columbic force between present metallic ions which have formed clouds on the incorporated particles according to the Guglielmi mechanism, where such particles move faster to the cathode [75]. The majority of the studies have demonstrated that the volume fraction of the embedded particles increases at higher current density. Then, the volume fraction starts to decrease after the applied current density surpasses an optimal amount. The reported optimum varies in different studies (for example, 50 mA cm-2 [79], 3 A dm-2 [35, 39, 98], and 4 A dm-2 [99]). This concept is based on the premise that metallic ions are more favourable to deposit on the cathode at low current densities, however, the required energy for convection and diffusion of these agents and can be supplied with increasing the current density [79, 99]. Furthermore, Ghazanlou et al. [7] have suggested that the increasing the current density up to an optimal value may promote the attractive force between surface of cathode and particles which are surrounded by charged clouds and there is a higher loading of codeposited particles. A further increase in applied current density may result in a high rate of metal deposition, resulting to a lower particle volume fraction in the deposit.

An increase in current density may also promote the surface roughness of Ni-Co based composite coatings owing to the enhanced hydrogen evolution on the surface [100]. Moreover, it can govern the amount of agglomerated particles. For instance, if the volume fraction of embedded particles increased with current density, application of higher current densities may give rise to the formation of more agglomerated particles [98]. The phase structure of such coatings may vary with varying the current density. For example, Shetty et al. [100] have reported that the intensity of the peaks assigned to the face centered cubic (fcc) structure enhanced at higher current density.

Fig. 2 indicates the microhardness of Ni-Co alloy matrix composite coatings containing various included particles versus current density. It is clear that there is no simple trend between the variations of microhardness with current density in these coatings. The influence of the applied current density on the mechanical properties of these coatings is highly related to the way that they alter the particle loading in the deposits [7, 75, 79]. Nevertheless, grain refinement arising from a more negative overpotential at higher current density is another factor affecting mechanical properties [89, 101].

**Insert Fig. 2**

.

Finally, the applied current density alters the corrosion and tribological properties of these coatings through similar mechanisms to those affecting the mechanical properties [79, 98].

**5.8. Pulse Frequency and Duty Cycle**

Pulse frequency and duty cycle are two critical parameters in PC electrodeposition of the coatings so that they can significantly determine the final properties of the coating [29, 102]. Concerning the morphological and microstructural characteristics of the coatings, results illustrated that the surface morphology, crystallite size, and amount of the codeposited particles greatly change with variation in pulse frequency and duty cycle. In general, to guarantee the improvement in the final properties of the coatings, these parameters should be adjusted by their optimum amount [7, 103].

The surface morphology changes from nodular to acicular with an increase in pulse frequency or decrease in the duty cycle [65]. An increase in both parameters lowers the degree of porosity in the deposit and provides an opportunity to achieve a smooth and compact surface [29]. Enhanced pulse frequency may reduce the thickness of the diffusion layer and diminish the loss of electrolyte near the cathode, thereby improving the homogeneity of the deposited coating. Furthermore, prolonged pulse-on time originated from an increased duty cycle contributes to the structure uniformity due to the enhanced Faradaic current and larger cathode overpotential [29, 104]. Fig. 3 shows changing the surface morphology from nodular with several short fibres to acicular with increasing the pulse frequency from 0.1 to 10 Hz in a PC-electrodeposited Ni-Co-SiC coating.

**Insert Fig. 3**

There are contradictory results concerning the influence of pulse frequency and duty cycle on the content of codeposited particles. Jiang et al. [29] reported that an increase in both parameters to their optimum amount increases the volume fraction of the embedded ZrO2 particles. However, a further increase in the pulse frequency and duty cycle decreases the codeposition amount due to shortening the duration of each pulse and concentration polarization, respectively. On the other hand, Yang et al. [65] indicated that more SiC particles may be incorporated into the coatings with an increase in pulse frequency or decrease in the duty cycle. They have confirmed that the longer toff duration arises from the low duty cycle provides a more suitable platform for the particles to adsorb on the surface of the cathode. A higher pulse frequency results in a more negative overpotential during PC electrodeposition. A higher loading of included particles has been expected to adsorb on the cathode because of such high energy.

Although variations in pulse frequency and duty cycle did not result in emerging new peaks in X-ray diffraction patterns, the relative intensity of the peaks can be altered, wherein it was shown that the relative intensity I(200)/I(111) is lower with an increase in both parameters [29]. Yang et al. [65] have reported the formation of more refined grains with an increase in pulse frequency or decrease in duty cycle, due to (i) increasing the volume fraction of the embedded particles, consequently more nucleation sites and (i) enhancing the nucleation rate.

The pulse frequency and duty cycle can affect mechanical and corrosion properties of the coatings through altering the amount of the incorporated particles [7, 29, 65, 103]. As a general rule, the highest microhardness and corrosion resistance will be achieved if optimum parameters are applied. Besides, it is well known that the mechanical properties of the polycrystalline materials deeply depend on the mean size of the crystallites. In order to achieve the superior mechanical properties, the pulse frequency and duty cycle should be modulated in a way that more refined grains generate [65]. In summary, the influence of pulse electrodeposition parameters on the mechanical and corrosion properties of Ni-Co based composite coatings is principally associated with the volume fraction of the embedded particles. Fig. 4a) and b) show the charge transfer resistance of Ni-Co alloy matrix composite coatings containing various particles as a function of a duty cycle and pulse frequency, respectively.

**Insert Fig. 4**

Few studies have evaluated the effects of duty cycle and pulse frequency on the corrosion performance of resultant Ni-Co based composite coatings. Furthermore, there is a large variation in the range of reported results. Further research is needed to clarify the exact influence of duty cycle and pulse frequency on the morphology and corrosion behaviour of these coatings. Fig. 5a) and b) show the microhardness of Ni-Co alloy matrix composite coatings versus duty cycle and pulse frequency, respectively.

**Insert Fig. 5**

**5.9. Arrangement of Electrodes**

In general, electrodes are vertically placed inside the electrodeposition bath [16, 105, 106]. A different, but less practical arrangement was used by Bakhit et al. [107] to encourage a maximum incorporation of particles into the growing deposit. They placed the electrodes horizontally at the bottom of the bath, called sediment codeposition (SCD) technique. Fig. 6 shows a schematic representation of the SCD technique.

**Insert Fig. 6**

It was concluded that a higher particle loading was achieved in deposits owing to the positive effects of gravity [108]. It is to be noted that the larger the embedded particles, the more the codeposition due to the larger gravity force originated from their higher weight. This may greatly enhance the mechanical and corrosion properties of the coatings arise from the higher content of the embedded particles. However, the agglomeration of the particles can be a problem with this technique. Moreover, sedimentation approaches can only be used with high density particles, in the absence of aggregation, and have no generality.

**6. The Importance of Included Particles**

**6.1. Overview**

Generally, codeposition of the insoluble ceramic and polymeric particles with a pure metal or alloy matrix is found to be a reliable approach to improve the final properties of the coatings. The method includes the inclusion of micron and nano-sized particles into the plating bath. There are several models proposed to describe the mechanism of codeposition of the embedded particles, which are discussed elsewhere [82]. Among the suggested models, the most widely appreciated model during recent years is the one which has been suggested by Guglielmi et al. [109]. According to the model, the incorporated particles into the electrolyte can be codeposited through five successive steps, as (i) generation of ionic cloud around the embedded particles; (ii) movement of the charged particles to the cathode due to the electrophoresis; (iii) propagation via a hydrodynamic boundary layer; (iv) propagation via a concentration boundary layer; and eventually (v) absorption on the substrate along with the pure metal or alloy deposit [110-112]. Models due to Celis et al., Fransaer et al., and Hwang et al. have been comprehensively discussed in the literature [82]. Fig. 7 shows a schematic illustration of the codeposition process in Ni-Co based composite coatings.

**Insert Fig. 7**

Particles are transported to the cathode by both electrophoresis and convective-diffusion mass transfer. Further studies are required to quantify how electrode/electrolyte motion, particle size and particle charge affect mass transfer [82]. It is also critical that incorporation of particles into the deposit, rather than glancing off the cathode surface due to excess momentum is considered. The relative rates of metal deposition and particle inclusion are important hut seldom considered in an integrated approach to composite electrodeposition.

**6.2 The rate of deposition**

The overall rate of metal deposition is given by Faraday’s laws:

|  |  |
| --- | --- |
|  | (Eq. 8) |

where *j* is the current density (A cm-2), *x* is the deposit thickness (cm), *ρ* is the density of the metal deposit, *z* is the number of electrons in the electrode process (dimensionless), *F* is the Faraday constant (96485 C mol-1), *t* is the time (s), ** (which is <1 or =1) is the current efficiency for metal deposition (dimensionless) and *M* is the molar mass of deposited metal.

For instance, for uniform deposition of Ni, assuming a current efficiency of 95%, and coating density of 8.91 g cm-3, a current density of approx. 2-10 A dm-2 would result in a typical thickness development rate of 6.5- 32.5 m h-1.

The overall kinetics of electrophoresis can be related to operational conditions by the empirical Hamaker law, which describes the rate of coating mass, *w* deposition with time due to movement of dispersed particles in colloidal solution:

|  |  |
| --- | --- |
| = | (Eq. 9) |

or

|  |  |
| --- | --- |
| = | (Eq. 10) |

where *µ* is the electrophoretic mobility of a charged species (m2 V-1 s-1),  *t* the time (s), *dE/dx* the potential field gradient (V m-1), *E* isthepotential (V), *x* thedistance in the interelectrode direction (m), *A* the surface area of the electrode (m2), *cw* the mass concentration of solids suspended in the electrolyte (kg m-3) and ** an efficiency factor (<1) which allows for the fact that not all solids arriving at the electrode are deposited on the surface of the workpiece [33, 113].

**6.3. Thickness**

Table 1 lists the thickness of Ni-Co alloy matrix composite coatings electrodeposited using various types of current control. The thickness of an electrodeposited coating plays a crucial role in determining satisfactorily use in a given application. It is necessary to tailor the electrodeposition parameters in a way that the thickness of the fabricated coating reaches to favourable value. As Ni-Co based coatings are employed in a wide variety of the industrial application, care should be taken to synthesis the coatings with suitable thickness. For Ni-Co based coatings used as erosion protection layers, the minimum thickness is typically 50 µm. Thicker deposits can improve the performance and durability at increased cost and deposition time. On the other hand, the coatings employed in electronic chips should have a typical thickness in the range 1-20 µm.

**Table 1. The typical thickness of Ni-Co alloy matrix composite coatings electrodeposited under different types of current control**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Chemical composition of Coating | Type of applied current\* | Electrodeposition duration (min) | Thickness /µm | Ref. |
| Ni-Co-CNT | PC | 30 | 30-50 | [72] |
| Ni-Co-fly ash | DC | 30 | 30 | [114] |
| Ni-Co-Al2O3 | DC+PRC | 180 | 60 | [69] |
| Ni-Co-Al2O3 | DC+PRC | 180 | 60 | [115] |
| Ni-Co-BN (h) | PC | 20 | 13-37 | [116] |
| Ni-Co-CNT | DC | 30 | 8-10 | [117] |
| Ni-Co-Fe2O3 | DC | 120 | 80-100 | [118] |
| Ni-Co-GO | PC | 240 | 150 | [101] |
| Ni-Co-MoS2 | DC | --- | 80 | [119] |
| Ni-Co-Si3N4 | DC | --- | 20 | [13] |
| Ni-Co-SiC | DC | --- | 90 | [32] |
| Ni-Co-SiC | DC | --- | 8 | [99] |
| Ni-Co-TiO2 | DC | 60 | 5-25 | [75] |
| Ni-Co-TiO2 | DC | 30 | 8 | [120] |
| Ni-Co-YZA | DC | --- | 50 | [121] |
| Ni-Co-ZrO2 | PC | 20 | 40 | [29] |

\* DC: smooth direct current; PC: pulsed current; PRC: periodic reverse current.

Included particles may alter the thickness of the alloy coatings by altering the volume of the deposit or by protruding from the surface. Karslioglu et al. [72] have demonstrated a decrease in the thickness of the alloy deposits with CNT nanoparticles inclusion, since these particles hinders the grain growth and results in the formation of thinner layers. In contrast with this result, Panagopoulos et al. [114] have reported that introduction of fly ash particles can slightly increase the thickness of the alloy coatings due to codeposition of large particles.

**6.4. Polarization Behaviour**

An overwhelming majority of studies have demonstrated that the reduction potential of the alloy coatings shifts toward more negative values with the inclusion of the particles. However, they indicate that the slope of the reduction curve in cathodic polarization curves remains unchanged. The introduced particles dominate the shift by decreasing (i) active surface area of the cathode and (ii) ionic transport [13, 90, 119, 122]. On the other hand, contradictory results have been reported by Bahadormanesh et al. [91], where a positive shift in the reduction potential takes place with the addition of SiC particles into the electrolyte. They have related this increment to an increase in both cathode surface area and ionic transfer [91]. It is unfortunate that much of the literature on corrosion of composite electrodeposits does not state the type of corrosion (uniform or localized), its location, the half-cell reactions or their rate control. It is not always appreciated that the cathodic half-cell reaction in corrosion is oxygen reduction, which is dependent on dissolved oxygen concentration in the electrolyte and solution agitation.

**6.5. Surface Morphology**

The surface morphology of Ni-Co based coatings significantly depends on their Co content, wherein the surface morphology of the coatings with less than 24 wt.% is pyramidal, while the others with higher Co content, i.e., 24-66 wt.%, exhibit spherical/nodular morphology. Further increase in Co content, namely more than 66 wt.% changes the structure to branched-like one [20, 39]. Fig. 8 clearly shows the change in the morphology of the DC-electrodeposited Ni-Co-SiC coatings changing from pyramidal to nodular with the Co amount varying from 24 to 65 wt.%.

**Insert Fig. 8**

Empirical results demonstrated that the (i) morphology of the constituent particles as well as (ii) surface condition of the alloy coatings can also be altered with the codeposition of the particles. The way these incorporated particles alter the surface morphology strongly depends on their influence on the Co content of the coatings. In other words, to change the particles morphology, it is necessary to vary the Co content of the coatings from the amount which belongs to a given morphology to the other with different morphology [26, 72, 80, 90]. Otherwise, the incorporated particles cannot affect the surface morphology [106, 107]. In such cases, the embedded particles can alter the size of generated particles of the alloy deposits. Results confirmed that the inclusion of particles drastically refines the size of formed nodules [35, 48, 107]. For instance, Rasooli et al. [106] have indicated that the morphology of the particles remains unchanged with the inclusion of even 20 g/L Cr2O3 particles into the electrolyte. It was attributed to the negligible change in Co content in the range of 40-50 wt.%.

Due to their small size and low density, it can be difficult to distinguish the embedded particles from the alloy matrix. Nevertheless, some investigations have revealed the exact location of the embedded particles. Ma et al. [45] found that some of the incorporated TiO2 particles were positioned inside the formed spheroidal metal nodules. Table 2 summarizes the morphological changes of Ni-Co alloy coatings after particle inclusion.

**Table 2. Morphological changes in Ni-Co alloy coatings following inclusion of particles**

|  |  |  |
| --- | --- | --- |
| Morphology of Ni-Co alloy coating | Morphology of Ni-Co alloy coatings containing included particles | Ref. |
| Polyhedron | Spherical | [72] |
| Regular fibril | Nodular | [26] |
| Needle-like | Particulate | [119] |
| Needle-like | Particulate | [13] |
| Smooth, spherical | Rough, nodular | [67] |
| Irregular, spherical | Cauliflower-like | [91] |
| Pyramidal | Global | [31] |

The incorporation of particles may vary the number and size of the generated nuclei during the electrodeposition process. Yang et al. [123] have reported that the inclusion of SiC particles into the Ni-Co coating can decrease the number and size of formed nuclei. Moreover, the incorporated particles prevent the metallic atoms to deposit, thereby decreasing the grain size. On the other hand, some studies have shown that the grain size of alloy coatings remains unchanged with particles embedment [100, 107].

Improving the surface condition of the alloy coatings is one of the other benefits of inclusion of the particle particles. According to the vast majority of results, incorporation of the particles into the alloy coatings can lead to a reduction or even elimination of porosities, cracks, flaws, and defects, thereby generating a continuous and compact microstructure [13, 31, 75, 79, 81, 90, 117, 124-129]. It arises from the uniform dispersion of the particles throughout the alloy matrix [81]. In contrast to these studies, a few investigations have reported an increased porosity following the particle inclusion [72, 100]. The only proposed mechanism for porosity enhancement is that the incorporated particles adsorbing OH- ions in the electrolyte followed by NiOOH formation on the the cathode surface, which gives rise to porosity [100].

To enhance the physicomechanical and corrosion properties of the given matrix particle inclusion, a uniform dispersion of particles is important [130]. Two major factors affect the uniform distribution of particles in the bath, hence the deposit, namely application of ultrasonic waves and incorporation of surfactants such as sodium dodecyl sulfate (SDS) in the bath [107, 119, 122].

While the above factors can lead to the formation of a homogenous composite deposit, the most critical factor to achieve a homogenous layer is the particles concentration in the electrolyte. It was found that increasing the particles concentration in the electrolyte beyond the optimum amount may result in the formation of agglomerated particles with a nonuniform dispersion, lowering homogeneity in the deposit microstructure [13, 45, 76, 90, 106]. Fig. 9a) and b) show TEM images of Ni-Co alloy and Ni-Co-TiO2 composite coatings.

**Insert Fig. 9**

**6.6. Chemical Composition**

In general, the effects of concentration of particles in the electrolyte on the chemical composition of Ni-Co based coatings are not limited to volume fraction of the embedded particles and Co content variation should also be taken to account since these particles can provide heterogeneous nucleation sites for Co. As a summary, the influences of particles concentration in the plating bath on the chemical composition of such coatings is evaluated as a function of (i) embedded particle content and (ii) Co content. These two factors deeply affect the final properties of the deposited coatings. The deposition mechanisms of Ni and Co as well as the codeposition process are discussed in sections 3 and 6.1, respectively. The effects of included particles on the volume fraction of Co in the coatings has been assessed [45, 72, 76, 81, 114, 131].

The particle loading in the deposit can be strongly influenced by two major factors: (i) the concentration of particles in the electrolyte and (ii) operating conditions, such as current density, pulse frequency, duty cycle, electrolyte pH and temperature. [35, 103, 106]. The reported volumetric and gravimetric particle content of selected Ni-Co based deposits is summarized in Table 3.

**Table 3. Reported volumetric and gravimetric particle content of the Ni-Co based deposits**

|  |  |  |  |
| --- | --- | --- | --- |
| Composite coating | Concentration of particles in the electrolyte (g L-1) | Particle content  in deposit | Ref. |
| Ni-Co-Cr2O3 | 5-20 | 3-9 wt.% | [106] |
| Ni-Co-diamond | 1-15 | 10-45 vol.% | [76] |
| Ni-Co-Fe2O3 | 10-90 | 2-11 wt.% | [45] |
| Ni-Co-SiC | 1-20 | 1-6 wt.% | [90] |
| Ni-Co-SiC | 25-75 | 5.8-17.8 vol.% | [80] |
| Ni-Co-SiC | 10-50 | 8-21 wt.% | [79] |
| Ni-Co-WC | 2-8 | 8-36 wt.% | [31] |

At higher particle concentrations in the electrolyte, the volume fraction of particles in the coating increases [26, 31, 45, 75, 79-81, 91, 132]. Guglielmi's two-step adsorption model rationalises such a trend. According to this model, the particles should transfer from loose adsorption step to strong adsorption step in order to incorporate into the microstructure of the coating. The presence of a higher amount of particle enhances the chance of these particles to strongly adsorb on the cathode and as a result raise the amount of codeposited particles [79, 81, 91, 133].

In some studies, this trend is not evident and the loading of included particles may decrease after reaching an optimal value. Several parameters are involved in such a fall off, such as (i) agglomeration of the embedded particles [35, 90] or (ii) the blocking effect of the incorporated powders, leading to a lower surface area for deposition [76]. The agglomerated particles suffer from low wettability and can separate from the substrate surface [106]. In contrast most literature results, Bakhit et al. [98] have reported that the loading of codeposited particles decreases at higher particle concentrations in the plating bath.

The results of studies by Bakhit [39] showed that the amount of Co2+ cations could also be effective in controlling loading of codeposited particles, so that with increase in cation concentration in the electrolyte results in more particles becoming positively charged. This may facilitate the movement of the positively charged particles toward the cathode and raise their content within the coating. Note that Co2+ cations adsorb more easily than Ni2+ ones on the particles.

The trend for Co content to vary with particle concentration in the bath is similar to that for the particle loading, except that there is no increment in Co content with increase in particle concentration. Studies have reported (i) descending [72, 114] and (ii) ascending followed by descending trend [35, 106] in Co content with increase in particles concentration in the electrolyte. To pay close attention to the Co variation in these coatings versus particle concentration in the electrolyte, anomalous codeposition process should be explained in detail. This process can be described via various mechanisms, such as depletion of the diffusion layer owing to the preferential deposition of Co2+. Karslioglu et al. [72] have shown that the Co content decreases with inclusion of MWCNT particles due to the preferential nucleation of Ni on the defect surfaces of present MWCNT particles in the plating bath. They also proposed a model to illustrate the deposition of Ni-Co on the MWCNT particles (Fig. 10). This model offer a two-step mechanism for deposition of Ni-Co wherein Ni-Co initially deposits on the existing MWCNTs followed by sedimentation on the cathode.

**Insert Fig. 10**

**6.7. Phase Structure**

There are four effects of particle incorporation on the phase structure of the coatings: (i) changing crystal lattice, (ii) altering peak intensity, width, and position, (iii) emerging new peaks corresponded to particles and intermetallics, and (iv) varying the growth orientation [69, 105].

Generally, XRD patterns of Ni-Co alloy matrix composite coatings, regardless of the type of used reinforcing agents, show Ni-Co solid solution and/or Ni single-phase peaks with face centered cubic (fcc) crystal structure. However, there are some exceptions. For example, Bakhit [39] has illustrated the change in crystal lattice from fcc in Ni-55wt.% Co/SiC to mixed structure of fcc and hcp in Ni-65wt.% Co/SiC, or Wu et al. [26] have reported that the fcc Ni and fcc Co peaks can distinctly emerge in XRD patterns. Usually, Co present in the microstructure of the coatings substitutes with part of the Ni, generating a Ni-Co solid solution. Both Ni and Co follow Hume-Rothery rules[114] and Co peaks cannot always be demonstrated in XRD spectra [31, 45, 66, 90, 101, 106, 114, 118, 119, 131].

Often, peaks assigned to included particles are not obvious in XRD spectra due to their low loading in the coating and their high dispersion [16, 35, 39, 45, 48, 69, 73, 103, 106, 114, 119, 121, 134]. However, several studies have reported that these peaks can emerged with very low intensities [26, 31, 67, 78, 100, 118, 131, 135].

Incorporation of particles into the coatings can strongly affect the crystallite size. An overwhelming majority of the research works proved a decrease in crystallite size with the inclusion of the particles. In other words, the peak width becomes broader with the incorporation of the particles. Two major factors as: (i) providing more suitable nucleation sites and (ii) preventing the movement of grain boundaries are responsible for such crystallite refinement [39, 45, 67, 73, 90, 106, 119, 122, 125, 136]. It should be noted that there is an optimal amount for this particles and further inclusion may lead to an increase in the crystallite size due to the saturation of the existing nucleation places as well as the generation of agglomerated particles [106]. Srivastava et al. [121] have acknowledged that the way incorporated particles affect the crystallite size of the coatings greatly depends on the lattice structure of the coatings, wherein crystallite size decreases with inclusion of the particles if the crystal structure of the Ni-Co based coating is fcc whereas an increase in crystallite size is predictable provided the particles incorporate into the hcp-structured coating.

The main growth orientation observed in XRD patterns of Ni-Co alloy matrix composite coatings are: (111), (200), (222), and (311). In accordance with texture coefficient (TC) observations, (200) is the main growth orientation of Ni-Co alloy coatings [114]. Chang et al. [69] have confirmed that the growth orientation of Ni-Co alloy coatings changes from (200) to (111) with particle inclusion. They also indicated that the relative intensity of (111) plane increases after the incorporation of the particles. This behaviour is highlighted when using the PRC technique which originated from the application of anodic pulses after a sequence of cathodic current pulses. Similar results have been reported in many studies, e.g. [16, 66, 67, 72, 122]. Nevertheless, few studies showed either a change in relative intensity or peak width [120]. Fig. 11 schematically indicates the growth structures in Ni-Co alloy and Ni-Co alloy matrix deposits.

**Insert Fig. 11**

Another change in the XRD patterns of Ni-Co alloy coatings with the inclusion of the particles is shifting the reflected peaks (Ni-Co solid solution regardless of their crystal face) to higher 2*θ* values which is common when employing PC and PRC. This can be also recognized as a sign of grain refinement [72, 73].

Although XRD has been used by most researchers to study the phase structure of the composite coatings, its use can be limited by the low level of included particles. This technique can be satisfactorily employed to assess the influences of alloying element, i.e. Co, on the phase structure; to provide detailed, local information on phase composition, TEM and ED are sometimes required.

**6.8. Mechanical Properties**

Microhardness, elastic modulus, micro-strain, failure strength, and plastic deformation are of the well-studied mechanical properties of the Ni-Co based composite coatings. Altogether, all of the studies carried out to evaluate the microhardness of the coatings have demonstrated that the microhardness of the alloy coatings extremely improves with inclusion of the particles [13, 16, 35, 48, 69, 72, 73, 75, 76, 78-81, 90, 91, 106, 107, 114, 122, 131, 134, 136, 137], except one reported by Srivastava et al. [67] in which the microhardness remained unchanged with an incorporation of the particles. They have related this manner to deviation from Hall-Petch behaviour. Hereon, the phrase "incorporation" varies from "incorporation for any amount", since there is an optimum value for the concentration of the particles in the electrolyte so that the inclusion of the excessive amount of particles may degrade the microhardness. However, the reported optimal concentrations are different. In general, the microhardness improvement mechanism of the coatings through adding the particles is associated with five factors: (i) dispersion hardening, i.e. Orowan mechanism which refers to the presence of small and closely-spaced particles throughout the matrix. In Orowan strengthening, hard and non-shearable particles hinder the movement of the present dislocations. This strengthening mechanism is more highlighted for nano-scale particles [13, 16, 48, 69, 75, 76, 79-81, 90, 91, 114, 121, 122, 134, 136-138], (ii) hard nature of ceramic reinforcing particles [66, 69, 114, 131], (iii) an increase in the integrity of coatings, e.g. diminishing porosity [66, 73, 106], (iv) grain refinement of the matrix through providing nucleation sites, namely the Hall-Petch effect [13, 31, 66, 79, 90, 106, 114, 136], and (v) strengthening the grain boundaries through embedding the particles at the interface of particle/matrix which may form stronger barriers to restrict the movement of the boundaries [91, 107]. As mentioned above, the microhardness of such coatings may decrease if an excessive particle concentration is used into the plating bath due to the agglomeration of the present particles and formation of porous structure [16, 78, 106, 137].

The microhardness of such coatings is not only depended on the particle type or concentration. The features of the alloy matrix including phase structure and Co content can also play a vital role in determining their microhardness. It can be easily realized that changing the lattice structure from fcc to mixed fcc+hcp degrades the microhardness [39, 121]. The main mechanism governing such behaviour is not clarified so far. Moreover, the more the Co content, the higher the microhardness if the structure is fcc [106, 121]. In this connection, Rasooli et al. [106] have illustrated that the Co content of Ni-Co-Cr2O3 is the primary factor in determining the microhardness of coatings, which can be even more important than Cr2O3 content. Incorporated particles can also contribute to an improved microhardness by providing more nucleation sites for Co particles. Fig. 12 exhibits the microhardness of the Ni-Co based composite coatings as a function of wt.% of the embedded particles.

**Insert Fig. 12**

As for other mechanical properties including elastic modulus, fracture strength, and micro-strain, these features can also be enhanced with the incorporation of the reinforcing particles [101, 122]. Wang et al. [101] have confirmed that the fracture strength and strain of Ni-Co alloy coatings can be noticeably improved with the inclusion of graphene oxide (GO) particles. This is ascribed to the decreased grain size originated from covering the GO particles on the alloy matrix grains as well as high Young's modulus and fracture strength of these particles. Furthermore, plastic deformation of the composite coatings is lower than in alloy ones due to their higher microhardness [91].

**6.9. Corrosion Behaviour**

The corrosion performance of Ni-Co based coatings has attracted considerable attention. Table 4 summarizes the reported corrosion parameters for Ni-Co alloy coatings.

**Table 4. A summary of the most favourable reported corrosion parameters for Ni-Co alloy coatings in aqueous solutions**.

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| **Corrosive medium** | **Highest reported *Rct*** | **lowest reported *jcorr*** /µA cm-2 | **Highest reported *Ecorr*** / mV | **Ref.** |
| 3.5% NaCl, 25oC | 324 Ω | 5.309 | -552 | [73] |
| 3.5% NaCl, 25oC | Not reported | 7.064 | -488 | [120] |
| 3.5% NaCl, 25oC | Not reported | 6.57 | -354 | [107] |
| 3.5% NaCl, 25oC | Not reported | 8.33 | -372 | [98] |
| 3.5% NaCl, 25oC | Not reported | 6.57 | -354 | [39] |
| Aerated 3.5% NaCl | Not reported | 15.01 | -470 | [117] |

Ni-Co alloy coatings exhibit desirable corrosion performance, an inclusion of reinforcing agent may enhance such performance and open the window to new applications across industrial sectors. An improvement in the corrosion properties of these coatings can be obtained if an optimum particle loading is achieved in the deposit [70, 78, 90, 106, 131, 136, 139]. Unlike the majority of the studies, Panagopoulos et al. [114] have reported that the corrosion behaviour of the alloy coatings drops slightly with introduction of the reinforcing particles. The degraded quality of deposit/substrate interface as a result of fly-ash particles embedment is responsible for such a drop. (i) Matrix characteristics, (ii) features of the embedded particles, and (iii) quality of coating/substrate interface are three major parameters determining the corrosion properties of Ni-Co alloy matrix composite coatings. The way that these factors affect the corrosion behaviour the coatings will be discussed comprehensively below.

Grain size, Co content, presence of the surface-related defects such as pores, voids, cracks, crevices, and etc. in the microstructure of the coating, crystal structure, and growth orientation are of the notable characteristics of the Ni-Co matrix which can significantly affect the corrosion resistance [90, 106]. Practical results reported the inconsistent influences of Co content of deposits with fcc lattice on the corrosion performance of the coatings, as: (i) increase in Co content may degrade the corrosion performance originated from its higher activity than Ni and (ii) increase in Co content may promote the codeposition of particles, thereby improving the corrosion behaviour [91, 107]. It was mentioned before that an increase in Co content may change the lattice from fcc to hcp which may alter the corrosion resistance via different pathways. This can also be recognized as the effects of the phase structure. Therefore, care should be taken to compare the effects of Co content on the corrosion performance of the coatings in the same lattice [140]. An increase in corrosion resistance of the composite coatings can be obtained with grain size enlargement. This is not always correct as considered in section 4.6. A smaller grain size leads to more grain boundaries. On the other hand, as the grain boundaries possess high energy they may give rise to corrosion and degrade the corrosion resistance of the coatings. Thus, refined grains accelerate corrosion to progress. In this connection, an increase in Co content makes the grains smaller which can be listed as harmful effects of Co content increment on the corrosion behaviour of Ni-Co based composite coatings. The influence of crystal structure on the corrosion performance of the coatings should not be neglected so that the more compact crystal structures exhibit superior performance. Additionally, two-phase structures are more prone to corrosion damages than single phase ones [107, 141].

The size, shape, and chemical composition of the embedded particles has a crucial influence on the corrosion resistance enhancement of the alloy coatings. Also, the uniformity of the embedded particles may have the almost the same importance. As the microgalvanic cells form at the interfaces of embedded particles and the alloy matrix, it is predictable that the type of corrosion can vary from localized to uniform providing the particles disperse uniformly along the alloy matrix. Such a change in the corrosion mechanism may promote the corrosion resistance. An inclusion of ceramic particles with anti-corrosive properties, such as SiC and Cr2O3, gives rise to corrosion behaviour since these particles can serve as physical barriers against the corrosive medium. Furthermore, an introduction of the particles may vary the volume fraction of the Co as well as grain size of the matrix. It also contributes to diminishing the amount and size of the present surface-related defects as potential factors decreasing the corrosion resistance, through filling the micro-pores and micro-cracks. Moreover, the embedded particles may hinder the further propagation of the pits. In this connection, nanoscale particles show superior efficiency than the micro-scale ones [39, 48, 78-80, 98, 106, 131, 136, 142]. However, generation of agglomerated nano-particles resulted from the inclusion of excessive amounts of particles may degrade the corrosion properties [79].

The open circuit potential of Ni-Co alloy coatings was found to alter after particle inclusion, although such effects are rarely explained. Bakhit et al. [98] have shown the superior electrochemical stability of SiC-reinforced Ni-Co deposits than the alloy ones, as their open circuit potential shift to more positive values. Table 5 provides a summary of reported corrosion parameters for Ni-Co alloy matrix composite coatings.

**Table 5. A summary of the most favourable reported corrosion parameters for Ni-Co alloy composite coatings in aqueous solutions.**

|  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- |
| **Composite coating** | **Corrosive medium** | **Highest reported *Rct*** | **lowest reported *jcorr*** /µA cm-2 | **Highest reported *Ecorr*** / mV | **Ref.** |
| Ni-Co-Cr2O3 | 3.5% NaCl, 25oC | 46082 Ω cm2 | 1.006 | -711 | [106] |
| Ni-Co-TiO2 | 3.5% NaCl, 25oC | 436 Ω | 3.869 | -291 | [73] |
| Ni-Co-TiO2 | 3.5% NaCl, 25oC | Not reported | 5.244 | -403 | [134] |
| Ni-Co-WC | Aerated 0.5 mol L-1 H2SO4, 25oC | 580 Ω | 32.20 | -322 | [31] |
| Ni-Co-CNT | 1M KOH, 25oC | Not reported | -2300 | -1160 | [100] |
| Ni-Co-CNT | Aerated 3.5% NaCl | Not reported | 3.36 | -385 | [117] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 0.49 | -240 | [127] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 0.01 | -67 | [91] |
| Ni-Co-SiC | Non-aerated 3.5% NaCl | Not reported | 0.050 | -199 | [107] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 0.050 | -199 | [48] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 0.050 | -199 | [98] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 0.050 | -199 | [39] |
| Ni-Co-SiC | 3.5% NaCl and 5% HCl, 25oC | Not reported | 5.962 | -442 | [136] |
| Ni-Co-SiC | 3.5% NaCl, 25oC | Not reported | 4.768 | -391 | [139] |
| Ni-Co-SiO2 | 3.5% NaCl, 25oC | Not reported | 4.529 | -354 | [70] |
| Ni-Co-BN (h) | 3.5% NaCl, 25oC | Not reported | 0.77 | -476 | [116] |
| Ni-Co-ZnO | 3.5% NaCl, 25oC | Not reported | 3.283 | -349 | [103] |

The passivation behaviour of Ni-Co-WC coatings has been examined by Elkhoshkhany et al. [31]. They related the origin of such behaviour to oxidation of cobalt and tungsten on the surface. The oxidation of WC may proceed as follows:

|  |  |
| --- | --- |
|  | (Eq. 11) |

CoO and CoO.H2O are the major passive oxide films formed on cobalt, according to [31]:

|  |  |
| --- | --- |
|  | (Eq. 12) |
|  | (Eq. 13) |

Unfortunately, authors rarely state the assumption of uniform corrosion (rather than, e.g., localized pitting attack). Often, it is unclear if it is the coating or the substrate which is corroding and how through-porous the coating is. Simple Tafel extrapolation or linear polarization resistance techniques are invalid unless reactions are clearly defined and under complete charge transfer (activation) control. The determination of the corrosion current density is based on the Butler - Volmer equation, and this equation is valid only when the corrosive process is controlled by charge transfer. Often, it is unclear whether oxygen reduction or hydrogen evolution is the cathodic half-cell process; if oxygen is involved, then the dissolved oxygen concentration in the electrolyte needs measuring and mass transfer, hence electrode/electrolyte movement, is important. For future studies of Ni-Co based composite coatings, studies should evaluate the location of corrosion, its products and determine whether corrosion path alters with incorporation of the reinforcing particles, as in studies by Arghavanian et al. [143]. They used EIS to investigate the corrosion behaviour of the coatings. EIS is a reliable and non-destructive method to study the corrosion behaviour of different materials. This powerful technique is capable of providing important information on corrosion mechanisms for the coatings, as well as the surface layers that tend to form during service. The advantages of this technique over potentiodynamic polarization, include easy recognition of the circuit elements via data fitting and interpretation of EIS spectra with the help of equivalent circuit models. In the case of composite coatings, the EIS method has been used in a few studies due to complications in data modelling and limited understanding of corrosion mechanisms. The study of corrosion paths is a helpful way to understand the corrosion mechanism, but few detailed studies have been carried out on composite coatings [143, 144].

In the case of Ni-ZrO2 composite coatings, the authors showed that the introduction of ZrO2 particles led to a change in the corrosion path from grain boundary attack to corrosion at the particle-matrix interface [143].

**6.10. Tribological Properties**

Generally, incorporation of particles into Ni-Co alloy coatings improves the wear resistance of the coatings through various mechanisms. The main parameters involved in the improvement of wear resistance are outlined below:

1. **Obtaining finer microstructure. A** finer grain structure due to nucleation and growth changes caused by included particles can noticeably restrict the movement of the present dislocations, hindering plastic deformation of deposits [69, 70, 79, 90, 124].
2. **Protrusion of the embedded hard particles during the wear test.** Most included particles in composite electrodeposits are hard, ceramic materials, the counterbody will not be able to cut/break these particles. Particles protruding during sliding can come into contact with the counterbody. Therefore, the real contact area between the surface of the coating and the counterbody, but the effect diminishes with particle inclusion [76, 78, 80, 115, 120, 131].
3. **Increasing the hardness of the coatings.** Harder deposits can provide improved wear resistance, in agreement with Archard's law [16, 76, 81, 120, 121] but the actual relationship can be far more complex than this classical law suggests.
4. **Transferring the particles to improve contact area between the counterbody and the coating surface.** If the carbon materials such as graphene, graphite, and CNT as well as MoS2 particles employ as the reinforcing phase, they can facilitate the sliding and decrease the wear rate with forming a lubricating tribolayer between the counterbody and the coating surface [119, 122].Karslioglu et al. [72] have ascribed the improved wear resistance of Ni-Co-CNT coating compared to Ni-Co one, to raised temperature at the contact area between the counterbody and deposit which may cause the generation of the oxides.
5. **Formation of *in-situ* compounds;** Shi et al. [13] have demonstrated the formation of hydroxylated silicon oxide via the tribochemical reaction between embedded Si3N4 nanoparticles and present water vapor in the atmosphere of wear tests. These compounds may serve as a solid lubricant, thereby enhancing the wear resistance.

Besides the abovementioned parameters, the crystal structure of the Ni-Co deposit may affect their wear resistance, e.g., deposits with an hcp lattice tend to exhibit superior wear resistance than those of fcc lattice structure. However, further studies are required to exactly find out why the wear resistance of such coatings improves by changing the structure from fcc to hcp. Consideration should be given to the importance of using optimum particle concentrations in the electrodeposition bath. Otherwise, particles may adversely influence the wear resistance of deposits, due to the agglomerated particles and porosity [67, 76, 120, 121, 145]. The most favourable reported wear properties of Ni-Co based composite coatings are provided in Table 6.

**Table 6. The most favourable reported wear properties of Ni-Co based composite coatings**

|  |  |  |  |  |
| --- | --- | --- | --- | --- |
| Ref. | Lowest reported weight loss due to wear | Lowest reported volume  wear rate | Wear test condition | Coating Type |
| [124] | --- | 1.5 mm3/N m | a load of 5 N and 15 N, at 37-300 oC | Ni-Co-SiO2 |
| [69] | 1.25 ×10-5 g m-1 | --- | a load of 9.8 N, sliding speed of 0.48 m s-1 | Ni-Co-Al2O3 |
| [115] | 0.75 ×10-5 g/m | --- | a load of 9.8 N, sliding speed of 0.48 m s-1 | Ni-Co-Al2O3 |
| [72] | --- | 1.5 ×10-4 mm3/N m | a load of 1.0 N, sliding speed of 0.05-0.15 m s-1 | Ni-Co-CNT |
| [76] | --- | 0.6 ×10-5 mm3/N m | a load of 7.5 N | Ni-Co-diamond |
| [119] | --- | 1.5 ×10-7 mm3/N m | a load of 1.0-4.0 N at 25oC | Ni-Co-MoS2 |
| [13] | --- | 2.1 ×10-6 mm3/N m | a load of 1.0 N at 25oC | Ni-Co-Si3N4 |
| [90] | --- | 2.2 ×10-6 mm3/N m | a load of 1.0 N at 25oC | Ni-Co-SiC |
| [145] | (0.05 ×10-4 mm3 m-1) | --- | a load of 10 N, sliding speed of 0.628 m s-1 at 25oC | Ni-Co-SiC |
| [70] | 5 mg | --- | a load of 50 N | Ni-Co-SiO2 |
| [78] | 6 mg | --- | a load of 50 N at 25oC | Ni-Co-SiO2 |
| [137] | 2.3 ×10-4 mm3 | --- | a load of 5 N at 25oC | Ni-Co-TiO2 |
| [120] | 1.5 ×10-4 mm3 | --- | a load of 5 N, sliding speed of 0.033 m/s at 25oC | Ni-Co-TiO2 |
| [146] | 5 ×10-3 mm3 | --- | a load of 5 N at 25oC | Ni-Co-WS2 |
| [121] | 0.1388×10-5 mm3/m | --- | a load of 9.8 N, sliding speed of 0.628 m/s at 25oC | Ni-Co-YZA |
| [103] | 6 mg | --- | a load of 50 N at 25oC | Ni-Co-ZnO |
| [16] | 2.06 ×10-4 mm3 | --- | a load of 7 N at 25oC | Ni-Co-ZrO2 |

The influence of the incorporated particles on tribological properties of the Ni-Co coatings is not limited to a variation in the wear loss. The friction coefficient, wear mechanism, and post-wear morphology can be altered with the introduction of these particles. There are inconsistent results on the effects of the particles on the friction coefficient of the Ni-Co based coatings, where the present literature can be divided into the two groups. The first group reported that the friction coefficient increases with particles embedment. They ascribed such behaviour to (i) generation of abrasive wear owing to the formation of the agglomerated particles [72] and (ii) enhanced shear and lateral forces [67, 72]. Others has demonstrated the lowering of friction coefficient of deposits containing included particles, arising from pulling out of the particle, e.g. CNT, MoS2, SiO2, WS2, and TiO2 which facilitates the sliding between the counter ball and deposit through formation of a lubricating layer [13, 70, 78, 119, 120, 122, 146].

Karslioglu et al. [72] have observed that the wear mechanism of Ni-Co alloy coatings can be altered from delamination to abrasive with CNT particles introduction. They have attributed such a change to the diminished real contact area during the wear test. Comparison between the worn surface morphology of the alloy and composite deposits shows a remarkable abate in adhesion with particles inclusion which can be corresponded to wear resistance improvement [13, 122]. The presence of the solid lubricant particles can also decrease the damage of the counterbody. The generation of a smooth wear track on the counterbody as a result of WS2 particles inclusion has been reported by He et al. [146], which can be recognized as an indication of the lubricating effect of WS2 particles. SEM micrographs of wear surfaces of Ni-Co and Ni-Co-WS2 deposits are presented in Fig. 13.

**Insert Fig. 13**

**6.11. Internal Stress**

In general, the large number of interrelated factors in electrodeposition and the complex nature of the coatings, are considered as the major sources for internal stress generation in composite coatings. It is well accepted that the macrostress can be generated as a result of shrinking and/or expansion when the existing atoms in an electrodeposited layer fit on the substrate. The deposited layer may grow in a way that generates compression or tension [66].

The reported results associated with the effects of incorporation of the reinforcing agents on the internal stress of the Ni-Co alloy coatings show that the stress increases with increasing the content of incorporated particles [69, 115].

A practical approach to diminish internal stress is electrodeposition of functionally graded and multilayer structures. Deposition of an interlayer can satisfactorily facilitates the diffusion and transition of the present atoms, thereby significantly reduce the internal stress [147, 148].

**7. Effect of Included Particle Size**

While the size of the incorporated particles is critically important, this factor has not been evaluated as extensively as that of loading and concentration of embedded particles. The studies dealt with assessment of influences of the reinforcing particles size so far have reported more or less same results, wherein usually the smaller the incorporated particles the higher the final properties are. Morphological, tribomechanical, and corrosion properties of these coatings may be greatly affected by the size of embedded particles [70, 80, 145].

**Morphological Features**

Although an inclusion of nanoscale particles provide more uniform distribution of particles throughout the matrix than micro-scale ones, more agglomerated particles may be formed in this situation. Moreover, smoother surface may be achieved through introduction of nanoscale particles as they are able to provide more heterogeneous nucleation sites. The generation of more nucleation sites is consistent with smaller crystallite size [70, 103].

**Codeposition of Included Particles**

Altogether, the volume fraction of codeposited particles increase when using nanoscale particles mainly originated from diminished dislodging force which controls the satisfactorily incorporation of the particles into the deposits [70, 80, 103, 145]. Unlike the previous results, Bakhit et al. [107] have showed the higher amount of codeposited micro-scale SiC particles than nano-scale ones due to the more rapid inclusion of micro-scale particles than reduction of existing metallic ions.

**Mechanical Properties**

Almost all of the performed investigations have demonstrated the superior mechanical properties of the coatings reinforced by nanoscale particles than the micro-scale reinforced ones. The factors involved in improved microhardness when incorporating nanoscale particles are as: (i) higher amount of embedded particles accompanied by more uniform distribution [103] and (ii) Providing stronger barriers to plastic deformation [70, 107]. Srivastava et al. [145] proved that the micro strain of Ni-Co coatings can be more improved when incorporating nano-scale SiC particles rather than micro-scale ones owing to higher amount of embedded particles as well as formation of more refined grains.

**Corrosion Resistance**

The corrosion resistance of Ni-Co alloy deposits reinforced by nanoscale particles is higher than those reinforced by micro-sized particles. This can be attributed to this fact that since introducing nano-scale particles leads to a higher degree of particle codeposition, these particles can remarkably hinder the initiation and even extension of corrosion defects such as pits and pores [70, 103, 107].

**Tribological Features**

Inclusion of nanoscale particles results in better wear resistance than micro-scale ones since they may uniformly dispersed along the matrix giving rise to dispersion hardening and grain refinement. Much more decrement in friction coefficient of Ni-Co deposits is shown through inclusion of nanoscale particles [70, 103]. It was found that the wear mechanism may vary with decrease in the size of embedded particles, where the Ni-Co-micro ZnO and Ni-Co deposits containing ZnO nanoparticles show abrasive and adhesive wear mechanisms, respectively [103]. However, Srivastava et al. [145] have reported no obvious changes in the friction coefficient of Ni-Co-SiC coatings electrodeposited by micro- and nano- scale SiC particles.

**8. The Effect of Post Treating Deposits**

It cannot be claimed that heat treatment always leads to enhanced properties in Ni-based coatings and the deposit microstructure is critical. In contrast to Ni-P systems (where a variety of Ni-P alloys form), application of heat treatment is not recognized as a favourable route to enhance the final properties of Ni-Co and Ni-Fe deposits. It is usually attributed to softening. This is why few studies have been carried out in this field [42, 149]. Atuanya et al. [124] have demonstrated that an application of post heat treatment at 300 oC may lead to an increment in wear resistance of Ni-Co-SiO2 deposits highly due to the generation of precipitations which markedly contribute to strain hardening of the deposits. They also mentioned the inverse influence of heat treatment at lower temperatures, e.g. 100 oC on the tribological properties of the coatings. On the other hand, a noticeable lowering of microhardness in Ni-Co-diamond coatings has been reported by Sofer et al. [150] following heat treatment of the deposits.

**9. Conclusions and Future Outlook**

This contribution has aimed to provide a comprehensive overview of the effects of current type, processing parameters and features of embedded particles, e.g. volume fraction and size, on the final properties of the Ni-Co alloy matrix coatings. It has clearly highlighted that inclusion of (mainly ceramic) particles, into the microstructure of Ni-Co alloy coatings improves the tribomechanical and corrosion properties of deposits. Among various particles, BN(h), SiC, and Cr2O3 showed the greatest improvement in corrosion protection of Ni-Co. The composite coatings containing Al2O3, SiC, and MoS2 exhibit the highest wear resistance. The greater influence of particles on the corrosion resistance of the deposits can be related to their easier co-deposition along with their significant impact on coating morphology. The marked effect of Al2O3 and SiC on wear resistance is due to their high hardness; MoS2 acts as a solid lubricant and reduces the friction coefficient and weight loss of the Ni-Co matrix composite coatings. Most studies in this field have confirmed that there is an optimum loading of included particles to yield optimum deposit properties; it should not be expected that the more incorporated particles always leads to improved properties.

Aspects of Ni-Co electrodeposition deserving further study are highlighted in Figure 14 and are considered in detail, elsewhere [33]. While a division into fundamental and technological aspects is offered, it should be realized that there is a considerable overlap. Future studies should focus on the influence of operating conditions on deposit properties and elucidating the exact mechanisms involved in altering the deposit characteristics by tailoring these parameters. It is essential for authors to utilise a suitable experimental design and data analysis to weight the number of critical variables and their weighting. In the absence of detailed models, empirical relationships between operating conditions and deposit characteristics are important. Unfortunately, it is common for plots in the literature to contain insufficient data points to establish a meaningful regression line; accuracy and precision deserve much more detail. In view of the identification of key parameters, insufficient attention is paid to the factorial design of experiments and the quantitative analysis of data.

In the case of corrosion protection by the coatings, it is important to:

a) specify the type of corrosion and its location.

b) state the half-cell electrode reactions and consider how the reactants and products affect reaction rate.

c) consider the factors controlling the rate of corrosion.

d) validate rapid, indirect corrosion measurements from polarization data gained using software suites against weight loss and solution analysis over extended times.

Regarding tribological evaluation of coatings, it essential to:

a) state the shape, size, composition and position of the counterbody.

b) quantify the load on the component under test and its time dependence.

c) consider various types of environment and load to evaluate tribological performance.

d) evaluate the importance of time, stop-start and cycling on results.

In both types of testing, the temperature, composition and flow velocity of the environment is critical.

**Insert Fig. 14**

The possibility of incorporating hybrid particles, effects of bath additives on electrocrystallisation hence deposit properties, and the influence of particle size are also critical areas for research. Finally, employing novel deposition techniques following appropriate substrate pre-treatment and deposit post-treatment can also be recognized as important in achieving deposits showing improved service lifetime and tribological characteristics.

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