A review of electrodeposited Ni-Co alloy and composite coatings: Microstructure, properties and applications

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ARTICLE INFO

Keywords:
Cobalt
Corrosion
Electrodeposition
Microstructure
Nickel
Tribology

ABSTRACT

Ni–Co alloy electrodeposits have been widely employed in industry due to their good corrosion and wear resistance, high mechanical strength, moderate thermal conductivity and outstanding electrocatalytic and magnetic properties. This review aims to provide an insight into the mechanism of electrodeposition and effect of operational parameters and deposit microstructure, together with the mechanical, electrochemical and tribological characteristics of Ni–Co alloys and included particle, composite deposits. Potential applications of the coatings have also been considered in applications as diverse as additive manufacturing, micro-tools, micro-sensors, electronic imaging and electrochemical energy conversion.

1. Introduction

Most failures in metallic components originate from the interaction of their surface with the environment. Problems can include wear, abrasion, fatigue, fretting, corrosion, oxidation, stress corrosion cracking (SCC). The practical use of engineering components is severely limited by these failures. The surface of the component plays an essential role and can restrict its uses. Appropriate attention to surface engineering can help to transform the microstructure, chemical composition and the resultant properties of materials. Coating is an effective method of improving the service life of the components [1]. Electrodeposited Ni–Co alloys and nanocomposite coatings provide a good example of such coatings. Ni–Co alloys possess great practical importance due to their protective and decorative properties. Among the production methods of Ni–Co coatings, electrodeposition is commonly used because of its moderate costs, flexibility (single layer or multilayer deposition as intermittent or gradient), high efficiency and simple mass production procedure with little need for high temperatures and high pressures, compared to other production processes, such as chemical vapour deposition (CVD), sputtering and flame spraying [2–4].

While the electrodeposition of Co or Ni–Co alloys is more expensive than Ni, due to the higher price of Co and its salts, significant benefits can be achieved due to the improved engineering properties of the alloy deposit. The electrodeposition of Ni and Co single metals has been considered in classical texts and reviews. The benefits of electrodepositing nickel and cobalt single metals, their binary alloys and ternary composites in a nanostructured form was highlighted in a series of three reviews [4A–4C] [5–7]. The often superior corrosion and tribological characteristics of Co–Ni compared to Ni are accompanied by higher costs; the specific cost of cobalt metal is often more than twice that of nickel.

Many coating techniques are available, such as chemical vapour deposition, CVD, high velocity oxygen fuel (HVOF) flame spraying, plasma spraying and laser cladding. The advantages of electroplating include versatility, an acceptable rate of deposition and moderate costs together with the ability to control the thickness and structure of the deposits, even on complex shapes. In the case of Ni–Co alloy electrodeposits, A review [6] considered that there was a need for continued developments in several areas:

1. A clarification of the role of tribofilms and wear debris on the tribological behavior of Ni–Co deposits.
2. Developing techniques, such as compositionally graded coatings and application of pulsed current have limitations including complex equipment and high cost.
3. The deposit microhardness needs to be increased further and direct nanostructured alloy deposition needs to be achieved by optimizing bath additives and plating conditions.
4. Despite many studies on coarse-grained deposits, there have been relatively few investigations of nanocrystalline Ni–Co coatings.

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https://doi.org/10.1016/j.surfcoat.2019.04.079
Received 5 March 2019; Received in revised form 20 April 2019; Accepted 25 April 2019
Available online 29 April 2019
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These aspects are considered in this review, which highlights the continuing importance of Ni–Co electrodeposited coatings, including bath composition, deposition mechanism, types of controlled current deposition, the effect of key operational parameters on microstructure and chemical composition as well as the physical, mechanical, magnetic, corrosion, high temperature oxidation resistance and thermal stability of Ni–Co deposits. Special highlights during the development of Ni–Co electrodeposits are shown in Fig. 1. Several aspects deserve attention:

1. The sulfate based Watts bath, introduced in 1916, remains the most popular electrolyte. This and other bath compositions are considered in Section 4.
2. The benefits of modern baths, such as the use of ionic liquids [8] in avoiding hydrogen evolution as a secondary cathode reaction, are also seen in Section 4.

3. The introduction of P as an alloying element in Ni–Co electrodeposits [9] is mentioned in Section 16.
4. Ni–Co composite deposits containing included particles are treated in Section 17.
5. Special cases of Ni–Co electrodeposition have included ultrasonically assisted jet plating [10].
6. Traditionally, Ni–Co deposits have offered better corrosion and wear resistance than Ni deposits and have seen increasing use in specialized tribological engineering applications since the 1960s; they have been one of the possible replacements for high chromium over the last twenty years.
7. Over the last decade, Ni–Co electrodeposits have found diverse uses in electronics and as electrocatalysts in electrochemical energy conversion.

The types of Ni–Co electrodeposits considered in this review are...
1.1. Characteristics of Ni, Co, and Ni–Co alloys

Ni belongs to the transition group with a molar mass of 58.69 g mol⁻¹ and density of 8.90 g cm⁻³ at 25 °C. It has a face-centered cubic (fcc) crystal structure in the solid state. It melts at 1453 °C and is resistant to corrosion and oxidation at moderate to high temperatures. The electrical resistivity of Ni is negligible at low temperatures, having a value as low as 68.44 nΩ m at 20 °C. It is chemically inactive and its corrosion resistance decreases in oxidizing conditions. Ni is extremely versatile and will readily form an alloy with most of the metals. Cobalt is positioned between Fe and Ni in the periodic table. The molar mass and density of Co are close to that of Ni, at 58.93 g mol⁻¹ and 8.85 g cm⁻³, respectively. As in the case of Ni, Co is a ferromagnetic metal. Depending on the temperature, Co can take two different crystalline structures; hexagonal closed packed (hcp; γ-Co) at \( T < 417 ^\circ C \), and fcc; α-Co) at \( 417 ^\circ C < T < 1493 ^\circ C \) (melting point). Alloying Co with Ni results in lowered corrosion and wear rate [17]. The physical, mechanical and magnetic properties of nickel and cobalt are shown in Table 1.

Ni and Co-based alloys have been studied as prominent engineering coatings due to their enhanced properties compared to pure Ni or Co. They possess higher strength, better wear and corrosion resistance, suitable electrocatalytic activity and special magnetic properties [18]. An important aspect of the Ni–Co alloy system is that these two

indicated in Fig. 2.

![Diagram](image1)

**Fig. 1.** Selected highlights relevant to the development of Ni–Co electrodeposits [6,11–16].

![Diagram](image2)

**Fig. 2.** Types of Ni–Co electrodeposits.
The incorporation of Co ions into such baths is readily achieved by the use of soluble cobalt anodes or addition of cobalt salts to the bath. The resultant Ni–Co deposits have become prominent engineering materials and coatings due to their attractive mechanical properties (high tensile strength and high hardness), good tribological properties and suitable heat resistance and anti-corrosion properties. Such properties have allowed these coatings to develop as anti-wear resistant and corrosion coatings [22–24]. It has also been reported that Ni–Co deposits have good electrocatalytic properties, rendering them competitive catalysts for the cathodic hydrogen evolution reaction (HER) and anodic oxygen revolution reaction (OER) during electrolysis of water in alkaline solutions [25–27]. The electrocatalytic activity of the coating is generally increased at higher Co levels in the alloy [28].

One of the important properties of Ni–Co alloys is their unusual magnetic properties. Much attention has been given to magnetic properties of these alloys for their potential applications in electronics and computer industry, including discs, memory cards, drums and microelectromechanical systems (MEMS). The physical and mechanical properties of coatings largely depend on their microstructure and chemical composition. It has been reported that a higher Co content can improve the magnetic properties of Ni–Co coatings [2,29].

These alloys can also be used for high-temperature applications. Golodnitsky et al. [30] have investigated the impact of Co content on the mechanical properties and high-temperature oxidation of these coatings. However, Chang et al. [31] have shown that the corrosion rate of Ni–Co coatings was accelerated in the presence of salt deposits such as NiCl₂ at 800°C.

Ni–Co alloys have several specialized applications. In some cases, these coatings are used in the electronic industry such as Ni–Co coated chips [32,33], guide blocks and microprobes [34–36], micro-connectors [37] and cantilever type micro-connectors [38]. Recently, Ni–Co films have been employed in the fabrication of micro-lenses. In fact, the Ni–Co electrodeposition process was used for the creation of metallic mold with micro-lens arrays, resulting in enhanced brightness and scattering [39].

The diverse application areas of Ni–Co electrodeposits are summarised in Fig. 4.

2. Environmental and health concerns

Electroplating is commonly used in industry for a variety of purposes, such as improvement of the properties of the material. However, electroplating process of Ni and Co produces hazardous wastewater containing various metallic and nonmetal ions, which are highly effective on the environment and human health (both Ni and Co give rise to selective skin irritations as well as being toxic metals, etc.) [40]. Many important issues hinder the application of Ni, Co, and Ni–Co coatings, including (1) health and environmental problems, and (2) the price of raw materials, especially cobalt salts. However, these coatings have lesser health problems than chromium coatings. According to the (EPA), Cr, Ni and their compounds are classified as extremely hazardous substances [41]. At present, replacement of hard chromium with low-cost materials is unrealistic and Ni and Co can be considered as acceptable choices until they can be satisfactorily replaced with non-hazardous coatings. As mentioned above, they possess unique properties that have attracted a great deal of industrial attention. Ni–Co coatings possess such great importance that the ASTM B994 standard is fully dedicated to these coatings. These coatings are deposited on the majority of the substrates without limitation, and owing to the negligible friction coefficient, they provide a dry lubricant on the surfaces.

### Table 1

<table>
<thead>
<tr>
<th>Properties</th>
<th>Nickel</th>
<th>Coalt</th>
</tr>
</thead>
<tbody>
<tr>
<td>Atomic number</td>
<td>28</td>
<td>27</td>
</tr>
<tr>
<td>Molar mass (g/mol⋅3)</td>
<td>58.69</td>
<td>58.93</td>
</tr>
<tr>
<td>Electron configuration</td>
<td>[Ar] 3d⁸ 4s² or [Ar] 3d⁹ 4s²</td>
<td>[Ar] 3d⁷ 4s²</td>
</tr>
<tr>
<td>Melting point (°C)</td>
<td>1455</td>
<td>1495</td>
</tr>
<tr>
<td>Boiling point (°C)</td>
<td>4946</td>
<td>2927</td>
</tr>
<tr>
<td>Density (g cm⁻³)</td>
<td>8.9</td>
<td>8.9</td>
</tr>
<tr>
<td>Crystal structure</td>
<td>fcc</td>
<td>hcp</td>
</tr>
<tr>
<td>Electrical resistivity (nΩ m)</td>
<td>69.1</td>
<td>62.4</td>
</tr>
<tr>
<td>Magnetic ordering</td>
<td>Ferromagnetic</td>
<td>Ferromagnetic</td>
</tr>
<tr>
<td>Young’s modulus (GPa)</td>
<td>200</td>
<td>209</td>
</tr>
<tr>
<td>Vickers-Hardness (MPa)</td>
<td>638</td>
<td>1043</td>
</tr>
<tr>
<td>Thermal conductivity (W/(m⋅K))</td>
<td>90.9</td>
<td>100</td>
</tr>
<tr>
<td>Thermal expansion (µm (K⁻¹))</td>
<td>13.4</td>
<td>13.0</td>
</tr>
</tbody>
</table>

Fig. 3. Ni–Co equilibrium phase diagram [20].
that are in contact with each other. Thus, there is no need for various harmful lubricants. In addition, the easy fabrication of three-dimensional morphologies with high surface area provides high potential for usage of Ni–Co coatings as an electrocatalyst for energy conversion in fuel cells and water electrolysers.

Efforts have been made to reduce the environmental impact of Ni–Co electroplating baths. Replacement of some of the raw bath materials has been regarded as an effective way of reducing the risks of usage of Ni–Co coatings as an electrocatalyst for energy conversion in fuel cells and water electrolysers.

Ni-Co coatings (50-100 μm) provide resistance to SCC, hydrogen embrittlement and corrosion

Ni-Co coatings having 1-5 μm thickness with modified surface morphologies of nanocone, nanoshit or nanopore are suitable for water splitting electrodes.

Thickneses can range from 5 μm in mildly corrosive environments to >25 μm for highly corrosive environments.

Ni-Co alloy has moderately high thermal conductivity for heat sinks.

A 5-1000 nm Ni-Co film exhibits induced anisotropy as a magnetic layer.

Mild steel pipes and pumps suffer from erosion in oil-sand transport systems. They can be improved by a 50-200 μm Ni-Co composite coating.

Fig. 4. Applications of Ni–Co coatings.
other methods of recovering or removing Ni from wastewaters are discussed further in ref. [53]. It is very difficult to replace Ni, Co and Ni–Co coatings due to their attractive engineering properties. By optimizing the methods used to treat wastewater and used baths from Ni–Co electroplating, harmful effects on the environment and human health can be mitigated by lowering Ni and Co levels in electroplating effluents and wastes.

3. Electrode reactions

The principles of Ni–Co electroplating are shown in Fig. 5. Normally, an undivided cell is used with soluble Ni and Co anodes are used in an acidic electrolyte although the Ni and Co concentrations can also be maintained by periodic addition of their soluble salts. In the case of soluble anodes (in the form of foil, plate or rounds) a microporous polymer bag is often used to retain anode slime (e.g., fine metal oxide/hydroxide particles) to prevent bath contamination. The figure highlights some of the important aspects involved in choice of electrolyte and control of operational conditions.

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

\[
\text{Ni} + 2e^- = \text{Ni}^{2+} \quad (1)
\]

\[
\text{Co} + 2e^- = \text{Co}^{2+} \quad (2)
\]

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

\[
2\text{H}_2\text{O} + 4e^- = \text{O}_2 + 4\text{H}^+ \quad (3)
\]

At the cathode workpiece, the main reaction is Ni and Co deposition, as described by reactions (1) and (2). In some cases, these are accompanied by deposition of phosphorus, boron or tungsten (see Section 17).

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

\[
2\text{H}^+ + 2e^- = \text{H}_2 \quad (4)
\]

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

4. The overall rate of deposition

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

\[
q = \Delta n \cdot z \cdot F \quad (5)
\]

where the electrical charge, \(q\) in the time interval \(t_2 - t_1\), is:

\[
q = \int_{t_1}^{t_2} Idt \quad (6)
\]

If \(t_2 = 0\), the overall charge is involved; otherwise, the charge in the time interval \((t_2-t_1)\) is involved.

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

\[
\frac{x}{t} = \frac{jM}{\rho zF} \quad (7)
\]

where \(j\) is the current density \([\text{A cm}^{-2}]\), i.e., the current, \(I\) per unit electrode area, \(A\):

\[
j = I/A \quad (8)
\]

\(x\) is the deposit thickness \([\text{cm}]\), \(\rho\) is the density of the deposit \([\text{g cm}^{-3}]\), \(z\) is the number of electrons in the electrode process \([\text{dimensionless}]\), \(F\) is the Faraday constant \([96,485\text{C mol}^{-1}]\), \(t\) is the time \([\text{s}]\), \(\phi\) (which is < 1) is the current efficiency for metal deposition \([\text{dimensionless}]\) and \(M\) is the molar mass of deposited metal \([\text{g mol}^{-1}]\). In the case of pure nickel deposition at a current efficiency of 95%, a current density of 0.5 A cm\(^{-2}\) and an electrode area of 1 cm\(^2\), the overall rate of deposition is 0.46 μm hr\(^{-1}\).
of 2 A dm$^{-2}$ (i.e., 20 mA cm$^{-2}$) is expected to produce a uniform deposition rate of approx. 23 μm h$^{-1}$.

The current efficiency (charge yield), the fraction of total current used in the primary reaction, i.e., metal deposition, is defined as a percentage by:

$$\% \psi = 100 \left( \frac{I_{Ni} + I_{Co}}{I} \right)$$

(9)

where the total current has contributions from Ni–Co deposition and hydrogen evolution, i.e.

$$I = I_{Ni} + I_{Co} + I_{H2}$$

(10)

5. Electrolytes used in Ni–Co electrodeposited coatings

Various baths are used for electrodeposition of Ni–Co coatings. Three different electrolytes that are commonly employed in the production of Ni–Co alloys consist of sulfate (Watts type), sulfamate and chloride baths. In this section, the classification of baths is based on the source of Ni and Co. Recently, ionic liquids have been introduced as possible electrolytes. Other baths with special additives such as pyrophosphate, gluconate, and glycine baths have been developed which are considered further in Section 7.4. Advantages and disadvantages of three common baths are listed in Table 2.

5.1. Chloride bath

The Ni–Co coatings obtained from chloride baths have been studied in previous research [54–58]. This bath consists of nickel chloride and cobalt chloride. Sodium chloride and ammonium chloride are often utilised as supporting agents to enhance the cathodic current efficiency, and trisodium citrate is sometimes employed as a complexing agent for Ni and Co ions [55,56]. Chloride baths have disadvantages such as expensive make-up chemicals, corrosivity, a greater tendency to pit formation compared to the other baths [55]) and higher internal stress in the deposits [59]. However, the deposits from this bath can realize a higher microhardness [54,59].

5.2. Watts-type (sulfate) bath

This bath is a modified Watts (sulfate-chloride) bath in which the Ni–Co alloy is electrodeposited from simple ions [60]. Nickel sulfate and cobalt sulfate are the primary sources of Ni and Co ions, respectively. Chloride ions provide good solution conductivity, reducing cell voltage requirements, and are vital to achieve satisfactory dissolution of nickel anodes [61]. Abd elRehim et al. [60] have shown that sound, smooth and bright coatings are obtained from this bath and that the properties are improved by the increment of Ni content in the bath. Watts-type bath exhibits a strong ability for passive film formation, so good corrosion resistance is a characteristic of the deposits resulting from sulfate bath [55]. Established and developing sulfate baths [9A] have multiple advantages such as low cost, low risk of equipment corrosion, simplicity of use and maintenance, and also the fact that its deposits have lower internal stress and larger grain sizes compared to chloride bath [59]. The presence of boric acid as a buffering agent is necessary in order to attain high current efficiencies [19].

5.3. Sulfamate bath

Usage of sulfamate baths in the electrodeposition of Ni–Co coatings has been reported in numerous studies [62–64]. Nickel sulfamate and cobalt sulfamate act as the sources of the Ni and Co ions in the bath. These salts are extremely soluble, and using chloride instead of sulfamate helps dissolve the anodes more uniformly while preventing anode polarisation [65]. The internal stress of deposits from a sulfamate bath can be lower but this is very sensitive to impurities and the bath is more expensive [59]. Sulfamate baths have higher solubility, which enables

<table>
<thead>
<tr>
<th>Table 2</th>
<th>Comparison and condition of common baths used in Ni–Co electrodeposition.</th>
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<tbody>
<tr>
<td>Bath type</td>
<td>Chemicals</td>
</tr>
<tr>
<td>Sulfamate bath</td>
<td>Ni(NH$_2$SO$_3$)$_2$.4H$_2$O, NiCl$_2$.6H$_2$O, Co(NH$_2$SO$_3$)$_2$, CoCl$_2$.6H$_2$O, H$_3$BO$_3$</td>
</tr>
<tr>
<td>Sulfamate bath</td>
<td>Ni(NH$_2$SO$_3$)$_2$.4H$_2$O, NiCl$_2$.6H$_2$O, Co(NH$_2$SO$_3$)$_2$, CoCl$_2$.6H$_2$O, H$_3$BO$_3$</td>
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</tr>
</tbody>
</table>
high current densities in the production units [65]. Excellent stability for different ranges of pH from 2 to 4 and for temperatures by up to 60 °C is another advantage of this bath [66–68]. There is a local pH increment close to the surface of the electrode in alloy electrodeposition of iron group metals. Hydroxides may precipitate and partially block the cathode surface. The pH increase close to the cathode is also observed in the sulfamate bath [69]. Addition of boric acid buffers the pH [70]. Ni–Co alloys electrodeposited from sulfamate baths can exhibit good mechanical properties at deposition rates of 7–20 μm min⁻¹ (decreased for chloride and sulfamate baths. The cobalt content of Ni₆Co increases the yield and ultimate strength but fracture resistance may decrease [62].

Goldbach et al. [71] have shown that the presence of cobalt in sulfamate bath does not affect the deposition of Ni, however the presence of Ni in the electrolyte prevents the deposition of Co. Tury et al. [72] have reported that the coatings deposited from the sulfamate and Watts type Ni–Co baths exhibit uniform chemical composition and microstructure throughout the entire of cross-section, but had lower microhardness compared to those produced from chloride electrolytes. The hydrogen evolution potential is low for the Watts bath, and is increased for chloride and sulfamate baths. The cobalt content of Ni–Co coatings largely depends on the utilised electroplating bath. Due to the anomalous deposition of Ni–Co alloys, it can be expected that percentage of Ni in the deposited layer is raised by increasing the current density of deposition. For the aforementioned baths, the deposit Co content showed a near linear decrease with applied current. According to this behaviour, Ni deposition likely to be activation-controlled [55].

5.4. Acetate bath

A survey of the literature reveals that there are very few studies available for Ni–Co electrodeposition in acetate-based baths. These baths are greatly attractive owing to their inherent low toxicity, low biodegradability [73] and eco-friendly properties [74]. Singh et al. [75] have used acetate-based baths for the electrochemical deposition of Ni–Co and Ni-Co-Fe films. The sources of Ni and Co in the electrolyte were nickel acetate (Ni(CH₃CO₂)₂·4H₂O) and cobalt acetate (Co(CH₃CO₂)₂·4H₂O), respectively. The mechanism of electrodeposition (for iron-group metals such as Ni, Co, Fe) in an acetate bath is anomalous codeposition similar to the other baths. The amount of Co acetate in the electrolyte is lower than Ni acetate [76,77]. Buffering capacity is another advantage of this bath. To avoid passivation and improve the dissolution of Ni anodes, Cl⁻ ions are added to the electrolyte [76,78]. The cathode current efficiency of the bath can be increased to about 99% by the use of additives [78].

5.5. Ionic liquid baths

Electrolytes based on ionic liquids can be suitable alternative electroplating baths (as they may provide green electrolytes) [79] although their cost and stability must be scrutinised. Recently, ionic liquids such as deep eutectic solvents (DES), have attracted a great deal of attention in electrodeposition of Ni, Zn, Cr, Cu and Co. Electrodeposition of nickel based alloys from DES baths has been studied in previous research [80–83]. You et al. [80] have investigated the electrodeposition of pure Ni and Ni–Co coatings from choline chloride/ethylene glycol DES (the most common DES [84]). The DES contained dissolved by Ni chloride and Co chloride. Co content in the Ni–Co coatings was lower than the Co ions in the electrolyte. This hints at the absence of an anomalous codeposition mechanism for non-aqueous baths, unlike the anomalous codeposition for aqueous baths.

6. Mechanism of Ni–Co electrodeposition

Ni–Co codeposition behaviour is recognised as abnormal (anomalous) codeposition according to the Brenner classification [21]. This type of codeposition is often observed in codeposition of iron group elements (including Ni, Fe, or Co) [85,86], and also in codeposition of one of the elements of the iron group with zinc [87] or cadmium [88]. In fact, in the electrochemical deposition of iron group alloy systems, the composition of the coatings is clearly different from the composition of components in the electrolyte since Co is deposited preferentially to the more noble element (Ni) under many conditions.

The Co content in the coating is higher when the ion fraction of noble element is higher [21,56,89]. For instance, in a Watts type bath with a cobalt sulfate to nickel sulfate ratio of 1:10 in the bath, the deposit yield was 40 wt% cobalt [64]. The cyclic voltammograms of Ni, Co, and Ni–Co alloys are presented in Fig. 6. In Fig. 6a), the current during Ni–Co deposition is higher than that for pure Ni and Co deposition. Thus, both Ni and Co determine the charge reduction in the positive scan. Fig. 6b) shows that the partial current of Co is improved in comparison to Ni in electrolytes with lower Ni(II)/Co(II) ratios (curves 1 and 2), indicating that anomalous codeposition is preferred at lower Ni(II)/Co(II) ratios in the bath. By increasing the Ni(II) ion concentration in the electrolyte, the reduction peaks shift towards more negative potentials and give higher currents.

The results of cyclic voltammetry are in agreement with linear sweep voltammetry results (Fig. 7). Comparison of Ni–Co coatings
fabricated in solutions with different Ni(II)/Co(II) ratios reveals that by increasing the ratio, scans shift towards the positive direction. This demonstrates that the kinetics of Ni(II) reduction are faster at a higher Ni(II) ion concentration in the bath. Scanning in the bath with lower ratio led to lesser polarisation. According to Fig. 7, the current density after the potential of about −0.5 V is measurable for all the deposits. The low overpotential of region I is related to H⁺ reduction. Region II appears only for the bath containing higher amounts of NiSO₄ in the potential of −0.7, which is due to the starting of Ni(II) reduction. In the bath containing 0.1, 0.3 and 0.4 mol dm⁻³ NiSO₄, the reduction of Ni(II) is inhibited due to the presence of Co(II) ions.

Recently, various models including experimental and mathematical ones, have been developed which try to explain this behaviour [85,86,91–98]. Among the iron group binary systems, Ni–Fe is studied the most and owing to the mechanism of codeposition in this system and Ni–Co exhibiting similar behaviour (anomalous codeposition), some explanation of the mechanism is based on Ni–Fe system. An early investigation of iron group codeposition was conducted by Vagramyan and Fatueva [99]. They found retardation in the cathode current density on the surface prior to the reduction and reduction of Ni is prohibited as a result of surface hydroxides. Measuring the surface pH indicated that it was insufficient to precipitate metal hydroxide [100,101] although true surface pH measurements are difficult to realize. Many studies have proposed that monohydroxyl (MOH⁺) metal ions discharge at the electrode [96,102,103]. Such models suggest that hydrolysis of metal ions plays an important role in the electrodeposition of iron group metals. Hesami et al. [96] and Grande et al. [103] suggested a model based on one-dimensional diffusion, conversion, and hydrolysis of Fe ions, Ni ions, and H₂O. According to this model, the cathode current density consists of a partial current density for reduction of H⁺ and H₂O as well as the reduction of NiOH⁺, FeOH⁺, Ni²⁺ and Fe³⁺ ions. Sasaki and et al. [94,95,104] later extended the formation of MOH⁺ (Grande and Talbot model [103]) to other iron group systems (Ni–Co and Fe–Co).

Equilibrium constants for the Ni–Co alloy compared less favorably with experimental results. The models were then revised and surface hydroxide adsorption blockage was added to competitive adsorption of monohydroxyl intermediates of metals [94,95]. The model proposed by Matlosz was based on the competition between the Fe(Ⅰ)ads and Ni(Ⅰ)ads which were adsorbed on the surface. These monovalent intermediates were formed during the reduction of the dissolved Fe and Ni [97]. In fact, the model was proposed as a two-step reaction mechanism: reduction and adsorption of metal cation on the surface as a monovalent intermediate ion (first step), and reduction of the intermediate to metal (second step). Baker and West [98,105] used EIS to examine this model with experimental data in agreement with the Matlosz model. Zech et al. [85,86,91] developed a model which measured partial current densities of metal co-reduction during electrodeposition compared to electrodeposition of pure metal individually. Their investigations indicated that in the electrodeposition of Ni–Fe and Ni–Co, deposition of Ni is inhibited in presence of Fe and Co ions, whereas the deposition is accelerated by the presence of Ni ions active metal (Fe and Co). According to these results, Arenas and Pritzker [106] suggested that 3 reactions occur simultaneously during codeposition of Ni and Co.

Reduction of the noble and active species (Ni²⁺ and Co²⁺) can be shown as:

\[
\begin{align*}
Ni(II) + e^- &\rightarrow Ni(I)_{ads} \quad (11) \\
Ni(I)_{ads} + e^- &\rightarrow Ni^0 \quad (12) \\
Co(II) + e^- &\rightarrow Co(I)_{ads} \quad (13) \\
Co(I)_{ads} + e^- &\rightarrow Co^0 \quad (14) \\
Ni(II) + Co(II) &\rightarrow NiCo(III)_{ads} \quad (15) \\
NiCo(III)_{ads} + e^- &\rightarrow Co^0 + Ni(II) \quad (16)
\end{align*}
\]

Reactions (11) to (14) are mutually independent. (15) and (16) are reductions in which Ni(II) and Co(II) ions interact (as assumed by Podlaha and Landolt [107,108] for induced behaviour during Mo–Ni codeposition). These act as catalytic reactions for reduction of Co(II) ions and are secondary pathways for cobalt deposition, having an accelerating effect on codeposition of components. However, the NiCo(II) ads intermediate is capable of covering the surface, effectively inhibiting the deposition of Ni. NiCo(II) ads and blocking other valid sites for Co(II) ads and Ni(II) ads [85,86]. Reduction of the intermediate CoNi(II) ads can then be considered:

\[
CoNi(III)_{ads} + e^- \rightarrow NP^+ + Co(II) \quad (17)
\]

All studies show that only the active metal is brought up in the anomalous codeposition of iron group metals and this reaction is not possible [86]. During electrodeposition, reduction of H⁺ ions takes place simultaneously with metal adsorption on the electrode surface. Increasing the pH at the surface during the electrodeposition process (due to the consumption of H⁺) and formation of hydroxide ions is the...
other hydroxide mechanism [109]:

\[ \text{H}^+ + 2e^- \rightarrow \text{H}_2 \]  

(18)

\[ 2\text{H}_2\text{O} + 2e^- \rightarrow \text{H}_2 + 2\text{OH}^- \]  

(19)

In these circumstances, the pH at the surface is sufficiently high for hydrolysis of metal ions with OH\(^-\). Precipitation of Co hydroxide (Co(OH)\(^+\)^+) on the cathode hinders the deposition of Ni [109]. According to the previous studies [19,98,110–114] based on the deposition of pure Co, Fe, and Ni metals, hydrogen evolution reaction consists of adsorbed species (such as H\(_{ads}\)). This is a weakness in the model proposed by Zech et al. [86] which does not consider such adsorbed species:

\[ \text{H}^+ + e^- \rightarrow \text{H}_{ads} \]  

(20)

\[ 2\text{H}_{ads} \rightarrow \text{H}_2 \]  

(21)

The active sites on the electrode surface can be obstructed by H\(_{ads}\), otherwise Co(I)\(_{ads}\), Ni(I)\(_{ads}\), and NiCo(III)\(_{ads}\) will occupy these sites. Regarding the competition between the adsorbed species, their interaction is vital and therefore its effects need to be considered. Reaction (10) may be stopped at higher overpotentials [111,115], leading to [111]:

\[ 2\text{H}_2\text{O} + e^- \rightarrow \text{H}_{ads} + \text{OH}^- \]  

(22)

Studies have shown the impact of H\(_2\)O reduction on the deposition of iron group metals [85,86,91]. It has been indicated that Co content in the electrodeposited Ni–Co alloy is lower at more negative overpotentials. This result is, however, contrary to the behaviour shown in Fe–Ni systems [93,103,124,125].

There is some disagreement regarding the mutual impact of bath constituents. So far, all models have been based on the inhibiting effect on the codeposition of the active metal in anomalous codeposition. Indeed, the majority of studies indicate that the presence of Fe(II) or Co (II) inhibits the deposition of Ni [56,58,71,89,95,117], despite the fact that it was revealed that Co(II) did not have a strong effect on the Ni deposition in some cases [71,95]. Moreover, the fact that the reduction of Co(II) is considered an improvement in the electrolyte containing Ni (II) is not yet fully elucidated. Some researchers [85,86,95,117,120] have shown that Co(II) reduction is accelerated in presence of Ni(II), while others have claimed that it is unaffected in this condition [96–98,103,125]. It has even been claimed that the reduction of Co(II) can be completely prevented [71]. Most recently, Vazquez et al. [126] studied the competitive adsorption of Ni(II) and observed that Co(II) and the desirable Co(II) adsorption energies were achieved instead of Ni (II). In the last study [127], however, anomalous codeposition is related to the hcp phase structure formed during deposition. Ni solubility is limited in the hcp structure and thus the deposition of Ni atoms in the hcp lattice structure is hindered. In contrary, normal deposition is related to the deposition with fcc phase structure, resulting in full Ni solubility in this phase. According to the arguments above, it can be concluded that the mechanism of anomalous codeposition is still challenged, however, the schematic of this codeposition behaviour deduced from the models (the most common hypothesis, hydroxide suppression [128,129], is illustrated in Fig. 8.

In contrast to the anomalous nature of codeposition of Ni–Co alloy deposition, attempts have been made to limit anomalous Co–Ni deposition. In the laboratory, this may be achieved using techniques such as cyclic voltammetry and pulse reversed electrodeposition in chloride electrolytes [57,130,131]. The inhibition of the anomalous codeposition in cyclic voltammetry is ascribed to dissolution of the newly formed alloys and co-dissolution of the adsorbed hydroxide layer in the anodic dissolution region [130]. Grill et al. [132,133] have shown, by electrodeposition of Co–Ni in a modified 3D-printed Hull cell and sulfate baths including trisodium citrate or glycine, that a transition to normal codeposition is occurred. Fan and Piron [58] have revealed that the anomalous behaviour in Ni–Co system is different from the Ni–Fe system, and that electroplating in high current densities leads to a transition from anomalous to the normal codeposition. Hu et al. [127] have observed a deviation from anomalous behaviour of electrodeposited Co–Ni nanowires in some conditions. Electrodeposition of Ni–Co alloys in non-aqueous electrolytes, despite the aqueous electrolytes, displays no anomalous codeposition process [80].

7. Effect of electrodeposition parameters

In this section, the effect of various parameters such as the composition of electrolyte, temperature, current density, agitation of the electrolyte and additives are considered. The effect of current type (direct current (Section 6.1), pulsed current (Section 6.2) and pulsed current reversal (Section 6.3) on the deposition of Ni–Co coatings is considered further in Section 7.

7.1. Electrolyte composition (metal ratio of the bath)

Nickel and cobalt form solid solutions in any concentration range, and therefore Ni–Co alloys with any composition can be electrodeposited [134]. In fact, this phenomenon enables deposition of Ni–Co alloys with a wider range of composition. However, electrodeposition of alloys with a high Ni content (Ni-rich alloys) is difficult due to the anomalous behaviour of this system [21] and the Co percentage in the alloys is usually higher than the electrolyte [6]. However, Ni–Co alloys containing low Co (Ni-rich alloys) have been electrodeposited from a very low Co\(^2+\)/Ni\(^2+\) ratio in the bath [135,136]. Based on previous studies [2,136–139], the relationship between Co percentage in the alloy deposit and Co\(^2+\)/Ni\(^2+\) ratio in the bath is non-linear, as shown in Fig. 9. However, the linear relationship was observed in some rare cases [140]. Tian et al. [2] employed cyclic voltammetry to study the electrodeposition behaviour of Ni–Co films. They observed that the deposition current is increased at a higher Co\(^2+\)/Ni\(^2+\) ratio. In addition, the contributions of the partial current for Co, compared to Ni deposition, is much higher even at low Co ion content in the electrolyte (anomalous codeposition). The anomalous codeposition degree defined as M\(_{\text{Film}}\)\(/c_0\) (M\(_{\text{Film}}\) is the molar fraction of Co in the alloy and c\(_0\) is the molar cobalt ion concentration in the bath) is increased by decreasing Co\(^2+\) percentage in the electrolyte [90]. Studies have proven that the impact of operational factors, including temperature, pH and current density on the anomalous codeposition degree of Ni–Co alloys is significant.
density, on properties is influenced by the composition of the bath. Abd El-Rehim et al. [60] have shown that the bath composition affects the cathodic current efficiency but it has a greater impact on cathodic polarisation and Ni–Co alloy composition.

7.2. Electrolyte pH

The literature reveals that bath pH during the electrodeposition of Ni–Co alloys is in the acidic range. pH is a critical parameter for anomalous codeposition of iron group metals because of two reasons [58,103,141]: (1) adsorption of metal hydroxides, mono-hydroxides or the active metal (Co) on the surface which are caused by the local increase of pH, thus if pH value on the cathode surface is lower than the formation of the hydroxide, codeposition occurs; (2) hydrogen evolution reaction occurs simultaneously which depends on pH. In addition, it affects the coating composition and morphology [131,142]. Fig. 10 indicates the impact of pH on alloy composition of Ni–Co system. In the case that Co content is increased by increasing the pH at low pH values, formation and adsorption of hydroxides are hindered and normal deposition is predominant. Therefore, a deposit with lower Co content is formed. This is in agreement with the results obtained by Orinakova et al. [142]. There is no general consensus about the effects of ions concentration and pH in the electrolyte. According to some researchers [131,137,142,143], by increasing the pH, the amount of Co in the deposit is increased while others [64,144] have demonstrated that it is decreased instead. Vazquez-Arenas et al. [19] studied the effect of pH (bath containing 0.018 M CoSO4, 0.2 M NiSO4, and 0.5 M H3BO3) on the current efficiency. They observed that current efficiency was raised by increasing pH from 2 to 4. The current efficiencies at pH values of 2, 3 and 4 were 82%, 72 and only 42%, respectively. The usual range of pH in electrodeposition of Ni–Co coatings is acidic in the range of 2–6. In some cases, such as pyrophosphate baths, pH values up to 10 were examined [145].

7.3. Temperature

Correct control of the operating temperature in the electrodeposition process is a vital factor for the suitable performance of the electrolyte [147]. Different and inconsistent reports have been provided regarding the impact of temperature on Co content and properties of Ni–Co deposits in the literature. Przyluski et al. [148] have investigated the effects of bath temperature (30–60 °C) on Co deposition. They observed that by increasing the temperature of a Ni–Co Watts type bath, the cobalt content of Co–Ni coatings is lowered from about 80 to 60 wt%. This is in agreement with the results obtained by Qiao et al. [10]. However, Bai and Hu [131] have demonstrated that the impact of raising temperature from 25 to 50 is negligible. Fernisne and Coddet [149] showed that by increasing the temperature from 10 to 80 °C, both current efficiency and hardness are decreased. Coatings formed at a lower temperatures (< 40 °C) tend to be brighter and smoother than those deposited at higher temperatures (40–80 °C). The results of different studies related to the effect of temperature on Co content in the coating in different studies are summarised in Fig. 11. These differences mainly depend on both the composition and the deposition current density.

7.4. Current density

Fig. 12 demonstrates the impact of applied current density on the composition of the coatings in baths having different Ni2+/Co2+ ratios. Current density is a major control parameter in electrodeposition since it controls the rate of deposition, the electrode kinetics, deposit composition, texture, surface morphology and coating properties. It is unfortunate that electrode potential is not always monitored and related to current density by steady state polarisation curves. Burzynska and Rudnik [151] observed that by decreasing the current density, the amount of Co was raised in accordance to the previously obtained results [19,109,152]. However, Kamel [89] has reported the contradictory influence of current density on the alloy composition in gluconate baths. Chung et al. [109] have also shown that the effect of direct current and pulse deposition techniques on the composition is insignificant. A number of researchers [60,95,116,118] have studied the dependence of efficiency on current density for iron group alloy systems, and concluded that current efficiency is increased by raising current density (current density range was up to 6 A dm⁻²). Arenas et al. [19] demonstrated that the current efficiency was lowered in the current densities values above 6 A dm⁻², falling to 0% current efficiency at 8 A dm⁻². On increasing the current density, metal ions are quickly consumed; the concentration and diffusion of the metal ions are decreased with deposition time, so anomalous behaviour is hindered (in this situation the effect of mass transport is enhanced [19]). As mentioned, on decreasing the current density, Co content in the deposit is increased, so Ni peaks in XRD patterns will be more intense [109]. It was demonstrated that increasing the current density in the range (0.5–5 A dm⁻²) resulted in more compact and smoother deposits [3].

Fig. 9. Co content in the deposit as a function of Co²⁺/Ni²⁺ ratio in the bath [2,29,136,138,139].

Fig. 10. the Co content in the Ni–Co coating as a function of bath pH. [29,146].
at the deposit surface, respectively and \( \delta \) is the Nernst diffusion layer thickness. Qiao et al. [10] observed that by increasing the agitation of the bath, Ni–Co grain size became finer. The relationship between the probability of nucleation (\( W \)) and overpotential (\( \eta \)) can be described by:

\[
W = B \exp \left( -\frac{b}{\eta} \right)
\]

where \( B \) and \( b \) are constants. Bath agitation decreases the diffusion layer thickness, effectively increasing the maximum current density that can be used. According to Eq. (25), the deposit grain size is reduced.

In electrolytes containing nanoparticles, bath agitation and electrode movement serve two purposes: (1) to suspend the particles in the electrolyte and (2) to transfer them to the electrode surface. RDE, RCE and parallel plates in channel flow are suitable laboratory techniques for quantitative characterisation of these electrolytes. Bahadoranesh and Dolati [161] reported that by choosing a stirring rate between 120 and 770 rpm, SiC particle content in Ni-Co-SiC nanocomposite coating with 480 rpm is the highest. This result is in agreement with Ni–Co nanocomposite coatings maintaining different nanoparticles [139,162]. In fact, by increasing agitation, the particle content in the deposit is enhanced in general. Excessive stirring can cause a lower degree of particle in the coating due to the strong hydrodynamic forces in the bath. Excessive tangential force can remove the nanoparticles from the surface before they become entrapped in the deposit.

### 7.6. Electrolyte additives

Additives can be added to the electrodeposition baths of Ni–Co alloys to alter the electro-crystallization process for various purposes, such as mirror-like surfaces and improvement of properties [78]. The added additives to Ni–Co electrolytes are listed in Table 3. Among various additives, saccharin as a grain refiner and ammonium/sodium chloride as a support for increasing the conductivity are most the commonly used. The effects of additives on the alloy content, grain size, microstructure and mechanical properties of the coatings have been investigated. The influence of H\(_3\)BO\(_3\) on anomalous codeposition of iron group deposits has been focused on Fe–Ni coatings [102,103,124]. However, Lupi and Pilone [163] have reported that increasing boric acid to 20 g dm\(^{-3}\) causes the current efficiency to increase. Arenas et al. [19] showed that the boric acid had a negligible effect on the Ni–Co alloy composition, in contrast to the claims of the past studies [93,103,124] on iron group codeposits. H\(_3\)BO\(_3\) is a buffering agent and its main function is to control bath pH. H\(_3\)BO\(_3\) is added to the bath to avoid precipitation of metal hydroxides and oxides at the cathode surface [164,165]. The buffering effect of boric acid is attributable to the hydrolysis:

\[
3\text{H}_3\text{BO}_3 \leftrightarrow \text{B}_3\text{O}_5(\text{OH})_4^{-} + \text{H}^+ + 2\text{H}_2\text{O}
\]

In acidic conditions, pH < 6, boric acid dissociates and remains stable. At high pH levels (7.5–9.5), B\(_3\)O\(_5\)(OH)\(_4\) is stabilised [106,110]. The effect of boric acid in the water reduction region is important:

\[
\text{H}_2\text{O} + e^- \rightarrow \text{H}_3\text{O}^+ + \text{OH}^{-}
\]

SDS is an anionic surfactant which promotes the uniform distribution of particles and prevents the agglomeration of ceramic particles [166–168]. Lari baghal et al. [169] have proven that adsorption of Ni\(^{2+}\) and Co\(^{2+}\) ions on SiC nanoparticles is enhanced by increasing the SDS concentration from 0 to 0.75 g dm\(^{-3}\) in the Ni–Co bath. They reported that, at SDS concentrations higher than 0.5 g dm\(^{-3}\), the number of nanoparticles was decreased. SDS content higher than 0.25 g dm\(^{-3}\) had a negative impact on the ductility of Ni–Co deposits. 2-butin, 1,4-dioll (BD) is another additive that reacts with adsorbed hydrogen (H\(_{ads}\)) and lowers the growth rate of the crystal. BD can promote the formation of

---

**Fig. 11.** Co content in the Ni–Co deposit as a function of bath temperature. [10,89,148,150].

**Fig. 12.** The effect of current density on the Co content of the deposit in electrolytes containing different concentration of NiSO\(_4\) and CoSO\(_4\) [19].

### 7.5. Agitation of electrolyte or cathode rotation

In general, bath agitation and cathode rotation enhance the homogeneity and thickness of the deposits [153]. Air agitation, impeller [61], magnetic stirrer [154], high speed jet [155,156] and peristaltic pump [151] are common methods of electrolyte agitation. In agreement with all studies on Ni–Co alloys electrodeposition [10,91,157–160], intensifying the agitation leads to higher cobalt percent in the Ni–Co alloys, since the thickness of diffusion layer (\( \delta \)) is reduced by increasing the metal ions contained within [10]. In the laboratory, electrolyte agitation may be achieved by a rotating cylinder electrode (RCE) in turbulent flow or a rotating disk electrode (RDE) in laminar flow. For the RDE, the Nernst diffusion layer thickness, \( \delta \) is decreased, i.e., mass transport of metal ions towards the cathode surface is enhanced, by increasing the angular speed of rotation according to the Levich equation [147]:

\[
\delta = \frac{1.61D^{1/2} \nu^{1/3}}{w} \sim \frac{1}{\omega^{1/2}}
\]

where \( D \) is the diffusion coefficient of metal ions; \( \nu \) is kinematic viscosity and \( \omega \) is the rotation speed of RDE. The limiting current density (\( j_l \)) can be increased using agitating the electrolyte according to [155]:

\[
j_l = zFD \frac{C_b - C_i}{\delta}
\]

where \( F \) is the Faraday constant, \( D \) is the diffusion coefficient of the metal ions, \( C_b \) and \( C_i \) are the concentration of metal ions in the bulk and at the deposit surface, respectively and \( \delta \) is the Nernst diffusion layer thickness. Qiao et al. [10] observed that by increasing the agitation of the bath, Ni–Co grain size became finer. The relationship between the probability of nucleation (\( W \)) and overpotential (\( \eta \)) can be described by:

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Table 3

<table>
<thead>
<tr>
<th>Additive</th>
<th>Formula</th>
<th>Performance</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boric acid</td>
<td>H₃BO₃</td>
<td>Buffer</td>
<td>[163]</td>
</tr>
<tr>
<td>Ammonium sulfate</td>
<td>(NH₄)₂SO₄</td>
<td>Buffer</td>
<td>[163]</td>
</tr>
<tr>
<td>Sodium dodecyl sulfate (SDS)</td>
<td>C₁₂H₂₅Na₂S₄O₄</td>
<td>Surfactant</td>
<td>[163]</td>
</tr>
<tr>
<td>Thiosalicyclicarhydrochloride</td>
<td>C₂H₆Cl₂S</td>
<td>Surfactant</td>
<td>[180]</td>
</tr>
<tr>
<td>Thiourea</td>
<td>C₂H₄N₂S</td>
<td>Surfactant, brightener</td>
<td>[180–182]</td>
</tr>
<tr>
<td>Sodium saccharin</td>
<td>C₁₂H₂₅Na₂S₄O₄</td>
<td>Stress reducing, grain refinement, surface roughness reducing, brightener</td>
<td>[180, 183, 184]</td>
</tr>
<tr>
<td>Saccharin</td>
<td>C₆H₁₂O₆</td>
<td>Improving the brightness and quality of coatings</td>
<td>[135, 162, 185, 186]</td>
</tr>
<tr>
<td>Dextrin</td>
<td>(C₆H₁₂O₆)ₙ</td>
<td>Surface smoother</td>
<td>[187]</td>
</tr>
<tr>
<td>Gum Arabic</td>
<td>–</td>
<td>Surfactant</td>
<td>[187]</td>
</tr>
<tr>
<td>Gelatin</td>
<td>–</td>
<td>Surfactant</td>
<td>[187]</td>
</tr>
<tr>
<td>Sodium acetate</td>
<td>C₂H₄Na₂O₂</td>
<td>Internal stress reducer, complesxant, stabilising the structure and properties</td>
<td>[63, 64]</td>
</tr>
<tr>
<td>Citric acid</td>
<td>C₆H₈O₇</td>
<td>Internal stress reducer, stablising the structure and properties</td>
<td>[63]</td>
</tr>
<tr>
<td>t-Ascorbic acid</td>
<td>C₆H₈O₇</td>
<td>Surface smoother</td>
<td>[140]</td>
</tr>
<tr>
<td>Triton X-100</td>
<td>C₁₇H₂₄O₆(OH)₉₋₁₀</td>
<td>Anti-pitting agent</td>
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</tr>
<tr>
<td>1,4-Butyne diol</td>
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<td>Brightener</td>
<td>[78]</td>
</tr>
<tr>
<td>Coumarin</td>
<td>C₆H₄O₂</td>
<td>Reducing the current efficiency</td>
<td>[78, 189]</td>
</tr>
<tr>
<td>1,3-Naphthalene sulfonic acid</td>
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<td>[78]</td>
</tr>
<tr>
<td>Formaldehyde</td>
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<td>[78]</td>
</tr>
<tr>
<td>Glycine</td>
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<td>Crotonaldehyde</td>
<td>C₅H₈O</td>
<td>Complexant</td>
<td>[64]</td>
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<tr>
<td>Glycolic acid</td>
<td>C₅H₈O</td>
<td>Complexant</td>
<td>[64]</td>
</tr>
<tr>
<td>Oxalic acid</td>
<td>C₅H₈O</td>
<td>Complexant</td>
<td>[64]</td>
</tr>
<tr>
<td>2-Butin-1,4-diol (BD)</td>
<td>C₆H₁₀O₂</td>
<td>To control the internal stress; and grain size and texture</td>
<td>[14]</td>
</tr>
<tr>
<td>FC 95TM</td>
<td>a blend of sodium salts of unroalkylsilonate</td>
<td>Wetting agent</td>
<td>[71]</td>
</tr>
<tr>
<td>Sodium gluconate</td>
<td>C₆H₁₂O₆Na</td>
<td>Complexing agent</td>
<td>[89]</td>
</tr>
<tr>
<td>Dodecyltrimethylammonium chloride (DTAC)</td>
<td>CH₂(CH₂)₂(N(CH₃)₂Cl)</td>
<td>Cationic surfactant</td>
<td>[190]</td>
</tr>
</tbody>
</table>

(10T0)hcp fibre texture in Co-rich coatings. It has been demonstrated that the impact of saccharin at concentrations as low as 0.1 g dm⁻³ is insignificant. Absorption of saccharin is accomplished by formation of coordinate bonds through filling its non-sharing lone pair electrons with the 3d electrons of Ni and Co atoms. In higher amount of saccharin (0.5 g dm⁻³), it was adsorbed by close-packed planes of (0002)hcp/(111)fcc. 2 g dm⁻³ saccharin and 0.5 g dm⁻³ BD result in higher inhibition effect greater XRD peaks of (0002)hcp/(111)fcc. With the addition of saccharin and BD, the texture was changed from (200)fcc to (0002)hcp [14]. Li et al. [135] studied the relationship between saccharin content (3–5 g dm⁻³) and physical-mechanical properties of Ni–Co deposits. The results indicated that saccharin leads to inhibition of Co deposition (because of increasing the overpotential [10]) and deterioration of microhardness due to grain refinement. However, Bakhit and Akbari [162] have reported that hardness was changed slightly in the presence of 4 g dm⁻³ saccharin. Saccharin can lead to some sulfur and carbon impurities in the coatings, causing embrittlement, lower ductility [170–172] and poor corrosion resistance [173]. Marikkannu et al. [78] demonstrated that the addition of various additives such as saccharin, dextrin, coumarin, formaldehyde, glycine, and crotonaldehyde to acetate baths result in a lower corrosion rate of the deposits, together with a higher hardness and mirror-bright surface in some cases. Gomez et al. investigated the effect of dodecyl trimethylammonium chloride (DTAC) on Co–Ni electrodeposition. The process was modified in the bath containing DTAC surfactant, and increased the Co content in the coating. Even the magnetic properties of the deposit were affected, due to a phase transformation from fcc to hcp structure.

Glucanone is another additive which is often added to electrodeposition bath of Ni–Co coatings. Such electrolytes are not only inexpensive, but also non-toxic and eco-friendly similar to the acetate baths. This bath contains 0.02–0.12 mol dm⁻³ cobalt sulfate, 0.8–0.18 mol dm⁻³ nickel sulfate, mol dm⁻³ sodium sulfate and 0.20–0.5 mol dm⁻³ sodium gluconate. The pH of the electrolyte was adjusted to 5 [89]. Boric acid can be added as a buffer to control the pH [174]. Sodium gluconate is used as a supporting electrolyte [175]; its addition to the bath lowers cathode polarisation due to the enhanced stability of Ni²⁺-gluconate complex species [89].

A few studies have investigated the formation and properties of Ni–Co alloys in glycine-containing electrolytes [78, 176–178]. Glycine is a complexing agent which eases the electrodeposition of rare-earth elements from aqueous electrolytes. In addition, it possesses remarkable buffering properties, so it stabilises the pH of the electrolyte [179]. In another study [178] it was indicated that the addition of glycine to the bath affects the alloy composition of the Ni-Co-Mo coatings, enhancing the deposition rate of Ni and Mo, while having a negligible impact on current efficiency at high current densities.

8. Current control during Ni–Co electrodeposition

Various methods have been employed for the production of Ni–Co coatings. Among them, electrodeposition is commonly used due to its low cost, flexibility (coatings with different structure and patterns), high efficiency and simple mass production procedure with little necessity for high temperatures and high pressures compared to other production techniques. Three techniques have been commonly used for Ni–Co films: (1) direct current (DC), (2) pulsed current (PC) and (3) pulsed reversal current (PRC). Fig. 13 shows the current modes for electroplating of Ni–Co deposits.

8.1. Direct current deposition

In DC electrodeposition procedure, a constant and continuous current is applied throughout the process. Only current density (or voltage) is effective in this method. DC electrodeposition has several advantages including low cost and ease of operation. In many studies [57, 64, 114, 131, 135, 191] on the morphology, microstructure, corrosion behaviour, microhardness, internal stress, and magnetic properties of Ni–Co alloy depositions fabricated by the DC technique, PC, RPC and cyclic voltammetry have also been investigated. Some researchers have studied the effect of different currents and their intensity on anomalous...
Under DC deposition, the codeposition behaviour of Ni–Co deposits in sulfate baths is always anomalous. The deposition current efficiency in PC and RPC methods have been higher than that of DC deposition [114].

8.2. Pulsed current deposition

Pulse or unipolar plating is a recent and attractive choice for improving the properties of electrodeposited coatings in comparison to DC electrodeposition. In this process, the current/potential alternatives between two values. Thus, there are series of pulses having the same amplitude, time period and polarity. During electrodeposition, metal ions are reduced when they reach the cathode surface. There is a zero concentration of metallic ions at the cathode surface and the transport rate of ions to the cathode surface controls the deposition rate. Application of a current (greater than limiting current density) results in a more negative charge on the double layer [61]. In DC electroplating, this layer is thick and inhibits the ions from reaching the surface. Throughout the PC process, the off-time period allows the layer to discharge, so the ions can easily pass the layer and arrive at the cathode surface [192]. PC electrodeposition has various advantages in comparison to DC electrodeposition [192–194]: (1) in PC electrodeposition, the grain growth is inhibited and nucleation rate is boosted on the surface, resulting in a more compact structure; (2) this method introduces lower internal stresses compared to the DC plated coatings; (3) chemical composition, structure and properties can be controlled by modifying the DC parameters; the need for additives in PC plating can be approx. 50% lower than in DC plating and (4) incorporated ceramic nanoparticles content in PC are more numerous than the DC method. PC can be interpreted by many parameters including average current density ($I_a$), peak current density ($I_p$), on time ($t_{\text{on}}$), off time ($t_{\text{off}}$), duty cycle ($\phi$) and pulse frequency ($f$) as shown in Fig. 13b). $I_a$, $t_{\text{on}}$ and $t_{\text{off}}$ are independent variables [195]. The microstructure and properties on Ni–Co coatings are affected by changing PC parameters ($I_p$, $\phi$ and $f$) which are defined in the next section:

### Duty cycle

The duty cycle, which is in the range of 1–100%, is defined as the ratio of on time to total time ($t = t_{\text{on}} + t_{\text{off}}$) [192]:

$$\phi = \frac{t_{\text{on}}}{t_{\text{on}} + t_{\text{off}}} \times 100$$  (28)

In a PC process, at very low duty cycles (like 5%), a high $I_p$ is necessary for deposition rate to be equal to DC plating. At very high duty cycles, PC is similar to DC [192]. Arenas et al. [114] have shown that the Ni–Co alloy composition strongly depends on the duty cycle (Fig. 14) but it does not affect anomalous behaviour. Indeed, the decrease in duty cycle leads to a shorter on-time duration and a slower depletion rate of Co$^{2+}$. At longer $t_{\text{off}}$ values, Co$^{2+}$ is enriched in the boundary layer and consequently, the Co content in the deposit will be higher. A study of the Co-Ni-Fe pulse electrodeposition from a sulfate bath demonstrated that by decreasing duty cycle and pulse current density, current efficiency is reduced [196]. By raising duty cycle, the brightness and smoothness of Ni–Co deposits will be increased and the grain size of coatings will be reduced [114], in accordance with the results obtained by Yang and Cheng [197].

Duty cycle has a significant role in determination of the number of ceramic nanoparticles in composite coatings. In a study, it was reported that with decreasing duty cycle from 80% to 20%, the difference in volume fraction of SiC nanoparticles in Ni-Co-SiC composite coatings was 4 vol%. According to the early Guglielmi model (which focuses on charge transfer, neglecting mass transfer) [198] the adsorption of ceramic nanoparticles takes place in two continuous steps: (1) weak
adsorption on the cathode surface along a high coverage of cations and (2) electrophoretic transfer and attraction of charged nanoparticles to the surface and thus adsorption on the surface due to the Coulomb force between the nanoparticles and metal cations which were adsorbed. In short off-time duration at a high duty cycle, there is no chance of transferring nanoparticles to the surface. Thus, the amount of SiC nanoparticles in the Ni-Co coating is decreased.

8.2.2. Pulse frequency

Frequency is the rate of pulsing expressed as Hz (s\(^{-1}\)) unit, and defined as the inverse of the total cycle time \(t = t_{\text{on}} + t_{\text{off}}\) according to the following equation [192]:

\[
f = \frac{1}{t_{\text{on}} + t_{\text{off}}}
\]

(29)

At high frequencies, \(t_{\text{on}}\) and \(t_{\text{off}}\) are very short and the double layer cannot completely charge or discharge during \(t_{\text{on}}\) and \(t_{\text{off}}\) durations, respectively. Alloys with a uniform composition are often electrodeposited at high frequencies [192]. Fig. 14 shows the impact of pulse frequency on composition of the coating. As can be observed, by increasing the frequency, Co content of the coating is slightly changed. However, the composition is affected by the bath composition. Chung and Chang [109] have shown that changing pulse frequency in the range of 10–100 Hz had a negligible effect on the Co content. Ni-Co coating with smoother morphology and finer grain structure was obtained using increased frequency [109,114,199], which is due to the formation of more nuclei on the substrate [200].

Pulse frequency has a significant effect on the properties of Ni-Co coatings. It is reported that the hardness of Ni-Co coatings at 10–100 Hz and a constant current density of 3 A dm\(^{-2}\) was between 6.67 and 6.82 GPa, whereas under DC conditions, it was measured to be 8.45 GPa [109]. This difference can be ascribed to the finer grain size, smoother surface or lower internal stress under higher frequencies. The effect of pulse frequency in Ni-Co nanocomposite coatings is stronger than the alloy deposits. Yang and Cheng [197] have stated that by increasing the peak current density, the amount of Co in the coating was decreased. This is in agreement with the results obtained by other researchers [10,72,193]. Ni deposition in deposits is controlled by activation. Increasing the current density leads to higher overpotential, resulting in higher activation. Under these conditions, the Ni content is enhanced in the deposit.

8.2.3. Pulsed current

Metal deposition rate in PC is the same as in DC, which is the average (mean) current density. The average (mean) current density \(j_{\text{ave}}\) is calculated from the peak current density \(j_p\), according to [192]:

\[
j_{\text{ave}} = j_p \cdot \phi
\]

(30)

This parameter can affect chemical composition, structure, morphology and properties of the coatings. Several studies [72,109,114,192] have revealed that Ni-Co coatings with a compact structure, smoother morphology, and finer grain size were formed at lower pulse current densities. Li et al. [135] have shown that by increasing the peak current density, the amount of Co in the coating was decreased. This is in agreement with the results obtained by other researchers [10,72,193]. Ni deposition in deposits is controlled by activation. Increasing the current density leads to higher overpotential, resulting in higher activation. Under these conditions, the Ni content is enhanced in the deposit.

8.3. Pulsed current reversal electrodeposition

PRC electrodeposition is a bipolar process. In this technique, the polarity of a direct current (including anodic and cathodic currents) is continually reversed. PRC parameters include [201]: (1) cathodic current density \(j_{\text{C}}\); (2) anodic current density \(j_{\text{AA}}\); (3) anodic (reverse) time \(t_{\text{AA}}\), and (4) cathodic (forward) time \(t_{\text{C}}\). The average current density \(j_{\text{A}}\) and duty cycle \(\phi\) are defined below [192]:

\[
j_{\text{A}} = \frac{j_{\text{C}} \cdot t_{\text{C}} - j_{\text{AA}} \cdot t_{\text{AA}}}{t_{\text{AA}} + t_{\text{C}}}
\]

(31)

\[
\phi = \frac{t_{\text{C}}}{t_{\text{AA}} + t_{\text{C}}}
\]

(32)

Not all of the current is used for deposition. During reverse
polarisation, a small part of the coating is dissolved [201]. In general, the current efficiency in PRC electrodeposition is lower than that of PC electrodeposition [202] and higher than DC plating [114]. According to the formation mechanism of iron group metals, M(OH)\textsuperscript{ads} ions are produced in pulse period and dissolved in reverse period. Thus, the anomalous codeposition of Co–Ni can be improved by PRC, which is a powerful technique for easy control of composition [57]. However, depending on the bath type, the deposited layer can be passivated [55]. Arenas et al. [114] observed that PCR is unable to efficiently reduce the anomalous behaviour of Ni–Co alloys in sulfate baths and different frequencies, duty cycles or current densities, whereas Bai and Hu [57,130,131] were successful in overcoming the anomalous behaviour of Ni–Co deposits in chloride baths. The increase in anodic current density and frequency and the decrease in duty cycle lead to higher Co content in the alloy. Numerous studies [57,149] have reported similar results. Examination of the microstructure has revealed that anodic current during the electrodeposition promoted a crack-free Ni–Co coating [203] due to the diminishing hydrogen reduction and lowering the internal stresses in the deposit (Fig. 15a) [204,205]. PRC results in the enhancement of the ceramic nanoparticles content in Ni [206–208] and Ni–Co [204,205,209] nanocomposite coatings (in comparison with DC and PC). Chang et al. [205] have shown that the microhardness of Ni-Co-Al\textsubscript{2}O\textsubscript{3} coatings prepared by PRC was higher than the DC plating (Fig. 15b). Higher hardness in PRC electrodeposition can be due to a better distribution of Al\textsubscript{2}O\textsubscript{3} nanoparticles in the coating.

8.4. Other controlled current techniques

In addition to the square shape of current, various other shapes such as triangular can be used for electrodeposition of Ni–Co alloys. Cyclic voltammetry (CV) is an electrochemical technique which is conducted through cycling the potential of a working electrode and measuring the obtained current. In this method, the working electrode is scanned linearly by an applied voltage in a forward and reverse direction, and in repetitive cycles. The current is the response of the applied potential, and the differences between scans yield information about the reaction mechanisms [210]. The potential range and number of cycles are important parameters of CV [131]. This technique has been employed in the previous research [56,57,114,130,131,211,212] for electrodeposition of iron-group alloys such as Ni–Co and Ni–Fe films. However, potential cycling is not a common method for electroplating of metals and alloys. In fact, the only valid reason for employing this method is to survey the anomalous codeposition mechanisms of iron-group metals [130]. CV is commonly used as a laboratory technique in which the potential of the electrode is swept at a relatively fast, rate between set potential limits [57]. However, CV is not feasible on an industrial scale involving large cathodes, since double layer capacitative charging becomes excessive and it is difficult to design fast, large current potentiostats. Hu et al. [130] have shown that anomalous codeposition of alloys such as Co–Ni, Fe–Co, Zn–Fe, Fe–Ni, and Zn–Ni was prevented using CV electrodeposition method, which is in agreement with the previously obtained results [131,211,212]. They have suggested that the inhibition of anomalous codeposition by CV is because of the following steps: (1) dissolution of the deposited alloys, (2) removal of the M(OH)\textsuperscript{ads} layer by anodic dissolution, (3) so the less noble metals dissolve slowly, and (4) finally the anomalous behaviour is prevented. Bai et al. [131] have investigated the effect of bath pH, temperature, number of cycles and the potential range of CV on the composition of Ni–Co coatings. The results indicate that the anomalous behaviour of deposits is increased at higher pH values. Morphologies of Ni–Co coatings were affected by CV potential range. Moreover, finer grain Ni–Co deposits were obtained by decreasing the temperature and number of CV cycles.

9. Microstructural characteristics

Numerous Ni–Co electrodeposition studies [56,63,119] have stated that different properties, microstructure, and phase structure of these

Fig. 16. (a–f) XRD patterns of Ni–Co alloys containing 0–81 wt% Co [6,154], (g) TEM image of the selected area diffraction (SAD) patterns for Ni-49 wt% Co alloy [215] and (h) the percentage of relative texture coefficient for (111), (200) and (220) in Ni–Co alloys with different Co content [220].
alloys are a function of the Co content of the coating, which is controlled by process variables such as pH, temperature, electrolyte composition and deposit current. According to the phase diagram for the Ni–Co binary system (Fig. 3), Ni and Co can form two different phases, consisting of a face-centered cubic (fcc) phase and a hexagonally close-packed (hcp) phase, depending on alloy chemical composition [213]. Wang et al. [154] have investigated the phase structure and composition of Ni–Co deposits by XRD. The results indicated that the pure Ni coating has fcc phase grown in the preferred orientation of (200). By adding cobalt ions to the Ni electroplating bath, the solid solution of Ni–Co is deposited. As can be seen in Fig. 16a)–e), for alloys consisting Co < 49 wt% (Ni-rich alloys), the alloy structure is completely fcc (XRD peaks location at $2\theta = 44.5$ deg., 51.8 deg., 76.4 deg., and 93.1 deg., in agreement with previous studies [63,214]. TEM micrograph of selected area diffraction (SAD) confirms the fcc single-phase structure of Ni-49 wt% Co alloy [215] (Fig. 16g). Myung and Nobe [216] have reported that in Ni-rich alloys, by increasing the alloy content from pure Ni to 50 wt% Co, the grain size remains constant and is equal to about 140 nm. By increasing the Co content, the growth orientation of (111) will be predominant. In addition, according to Vegard’s law [10], higher Co content in the alloy can increase the lattice constant. Based on this law, the relationship between the lattice constant and Co content is linear [10,217]. Fig. 16g) shows that the relative texture coefficient (RTC) is changed depending on the Co content. In addition, at 66 wt% Co, the hcp lattice begins to form in accordance to (100) peak at XRD pattern (Fig. 16h). At this point, the structure of Ni–Co alloy is a mixture of both fcc (major phase) and hcp (minor phase), as suggested in other studies [139,218]. Based on nanostructured materials, a mixed structure of fcc + hcp can be formed [219]. In this structure, a cluster of hcp-Co includes an fcc-Ni (structure (a) in Fig. 16), or there is a hcp-Co in the fcc-Ni in Fig. 16b) [72]. The smallest grain size of the alloys belongs to the mixed phase region [216]. In Co-rich coatings (alloys containing > 80 wt% Co), a vigorous texture of (002), (100) and (110) peaks is observed which belongs to hcp structure, as shown in Fig. 16f). By gradually increasing the Co content, the structure is transformed from fcc to hcp.

As mentioned in Section 4, the alloy composition of Ni–Co deposits is altered by operational parameters, which can also affect the structure and phase of the coatings. Park et al. [146] have studied the impact of pH and additives such as saccharin on the XRD patterns. The results indicated that Ni–Co coatings obtained from a bath containing saccharin exhibited the same peaks with lower intensity in comparison to the coatings from baths without saccharin. The dominant phases at low current densities (5 and 10 A dm$^{-2}$) are similar to Fig. 16b)–e). By increasing the current density to 20 and 25 A dm$^{-2}$, the dominant phases are changed to fcc (220) and hcp (110). However, Chung and Chang [109] have stated that the dominant phases remain unchanged by changing the current density. Bath pH has no influence on XRD patterns [146]. Pulse parameters such as frequency do not change the peaks [109]. Hu et al. [127] have studied the impact of deposition potential. There is a prominent peak at $2\theta = 41.2$ deg. (related to the (100) plane of hcp) and a small peak at $2\theta = 76.0$ deg. (related to the fcc planes of Ni–Co) for Ni–Co alloys coated at $-0.9$, $-1.3$ and $-1.6$ V. However, the alloy deposited at $-3.0$ V showed a dominant peak at $2\theta = 76.0$ deg.

According to the discussion above, the study of microstructure and texture of the top surface using XRD is limited to the deposit surface that is in contact with electrodeposition bath. Thus, it is not useful for investigating the microstructure, phases or texture on the cross-section of the electrodeposited coating. Fig. 17 represents the microstructure of the coating/substrate interface, free surface and FIB image of the cross-section. It can be observed that the grains of coating/substrate interface have a smaller size than that of the free surface. FIB image (Fig. 17d) reveals a columnar grain structure. The majority of the grains are situated along the direction of grain growth. However, several smaller grains form clusters as indicated in Fig. 17d). It can be concluded that

![Fig. 17. The microstructure of a Ni–80Co coating: (a) schematic cross-section, (b) coating/substrate interface, (c) top surface and (d) FIB image of cross-section [221].](image-url)
the microstructure includes a bimodal distribution of grain size.

Electron backscatter diffraction (EBSD) and forced ion beam (FIB) microscopy are powerful techniques for determining the microstructure, crystallographic properties, texture and phases in the cross-section and interface of Ni–Co electrodeposited films. Bastos and et al. [221] investigated the microstructure and texture of Ni-80 at.% Co coating by FIB and EBSD. According to the XRD pattern, Ni-80 at.% Co coating is a single phase alloy (hcp structure) [186]. However, EBSD results revealed that this coating contains two phases (a mixture of hcp and fcc structures) consisting of about 6% fcc phase in the coating/substrate interface, and 3% at the top surface [221] (Fig. 18). This value in cross section depends on the thickness of the coating. By increasing the thickness, the amount of the fcc phase is reduced.

Grain boundaries have a significant effect on physical and mechanical properties, and therefore the determination of their characteristics is of great importance. Researchers have used 3D EBSD to demonstrate that the formation of Ni–Co columnar grains is because of triple junctions with low energy [222]. In some cases, the grains are not columnar [223]. According to cross-sectional studies, <1120> is the prominent growth direction.

10. Mechanical characteristics

10.1. Microhardness

The hardness of coatings depends on various factors including chemical composition, microstructure, the strength of coatings, etc. All these factors are influenced by the coating method and the involved processes. Electroplating variables change the microhardness of Ni–Co coatings. By increasing the amount of Co by up to 49 wt%, microhardness is raised from 250 to about 480 Hv. However, a further increase in Co content leads to a drop in the microhardness down to 350 Hv. This behaviour can be explained by the reverse Hall-Petch relation [224,225]. In fact, in Ni-rich alloys, Co results in finer grains, however, Co content increment in Co-rich alloys increases the grains size. The grain size can be determined from TEM micrographs and XRD data. The data from these methods reveal differences that can be explained by residual stresses [10,225]. Coatings with a grain size above 15 nm followed the Hall-Petch relationship. Interactions of dislocation boundary and twin boundaries are effective for the strengthening of alloys in this range of grain size. However, there is a breakdown in Hall-Petch behaviour with the grain sizes lower than 15 nm. Thus, maximum
hardness occurs at a certain critical grain size.

The mechanism of an inverse Hall-Petch relationship in Ni and Ni–Co deposits is the same due to identical hardness data in both coatings. The critical size of grains for breakdown in Hall-Petch behaviour can be defined based on dislocation pile-up in the grain. At the grain sizes smaller than the critical size, the dislocation pile-up in the grain can be stopped. According to Nieh and Wadsworth analysis [226], the critical grain size \( l_c \) can be defined by Eq. (21)

\[
l_c = \frac{3Gb}{\pi(1 - \nu)H}
\]

(33)

In which \( H \) is the microhardness of the material; \( \nu \), \( G \), \( b \) and \( \nu \) are the Poisson ratio, the shear modulus of the coating and Burger's vector magnitude, respectively. According to this equation, at grain sizes greater than the \( l_c \), the Hall-Petch relation is stable, but the relationship is reversed at the grain sizes smaller than \( l_c \). However, the analysis is based on dislocation pile-up, which is inadequate to elucidate the reason for Hall-Petch breakdown. Indeed, the breakdown in this relation is associated with deformation mechanisms such as sliding in grain boundary (twins or general high- and low-angle boundaries) and intergranular diffusion. This can be related to the structure of the coating. Fcc structures such as nano-structured Ni [225], Cu [227] and Al [228], possess low twin density, so the reverse Hall-Petch effect occurs by sliding and boundary diffusion. Nanostructured coatings such as Co [229] and Ni–Co [186] have a high density of twins resulting in their hcp structure. The Hall-Petch breakdown in these coatings is probably due to predominant migration of twin boundaries at very fine grains. This issue requires detailed and extensive further studies.

In addition to the above considerations, it is necessary to consider variables influencing the grain size and hardness of Ni–Co coatings. Presence of ceramic nanoparticles such as \( \text{Al}_2\text{O}_3 \) [205], \( \text{SiC} \) [197] and \( \text{ZnO} \) [230] can improve the microhardness and other mechanical properties of Ni–Co coatings. The movement of grain boundaries and dislocations due to dispersion strengthening is limited in the presence of nanoparticles which act as an obstacle against them, resulting in hardness improvement of the coating. In general, the hardness of nanocomposite material is influenced by two important factors [231]; (1) the content of strengthening nanoparticles and (2) the hardness of the metal matrix. In a specific metal matrix, nanoparticles are the most important factor influencing microhardness.

The amount and size of nanoparticles have two different hardening mechanisms [197]: (1) the strengthening based on the dispersion hardening and (2) the strengthening based on the particle. Pulse parameters including duty cycle and frequency affect the microhardness in nanocomposite coatings. Yang et al. have reported that decreasing the duty cycle from 80 to 20% resulted in enhancement of the microhardness of Ni-Co-SiC coatings from 620 Hv to 670 Hv due to changing the nanoparticles content from 6 to 10 vol%. Increase in pulse frequency led to increases in microhardness as a result of grain refinement.

10.2. Tensile properties

Ni coatings are known as high strength and tough materials in industrial applications. Ni–Co alloys have higher mechanical properties (strength, toughness, and tribological behaviour) compared to the Ni coatings. Therefore, they are suitable candidates for replacing electrodeposited Ni [135,154]. The higher mechanical properties of Ni–Co deposits are due to the effect of cobalt in the refinement of microstructure and reduced requirement of different organic structure refiners [135]. Using organic refiners results in precipitation of C and N at grains boundary which prevents the sliding of grain boundaries, resulting in lower toughness and strength [170]. Alloying with Co prevents the toughness and tensile strength from decreasing due to grain refiners such as saccharin [135,149,154]. By changing the alloy composition from pure Ni to 45 wt% Co, the yield strength and ultimate tensile strength can be enhanced, probably due to finer grains and the strengthening mechanism of Co solid solution in the deposits. Furthermore, the increase in Co content by up to 55 wt% leads to a drop in yield strength and ultimate tensile strength down to 650 and 1100 MPa, respectively. The reason for this could be the different density of coatings [138]. However, it is reported that Ni–Co coating with 49.2 wt% Co exhibits higher tensile strength in the range of 1920–2250 MPa (depending on the strain rate) [215]. The remarkable strength of this alloy is attributed to the fine grain size and hardening by the solid solution. The tensile properties of coatings can be affected by variables such as temperature [232] and strain rate [18,215,233]. Increasing the Co content by up to 25 wt% led to an increase in ductility from 8.5% to 13.5% because of finer grains [138,234]. In alloys with higher Co content, the ductility was significantly decreased [138]. In fact, in Co-rich alloys, the porosity of the coatings is increased which leads to formation of voids and nucleation of cracks in the Ni–Co coatings [154,234]. The grain size of the deposits is an important factor in the ductility of coatings. Ductility can be affected by the strain rate [215,233]. Low strain rates may increase the elongation of Ni–Co coatings resulting from grain boundary activities that collaborate in this strain rates. In Ni-8.6 wt% Co coating, by increasing the strain rate (1.04 × 10⁻⁵–1.04 s⁻¹), a transition behaviour of ductile-brittle-ductile was observed [233].

10.3. Fracture surface and fracture toughness of Ni–Co coatings

According to the tensile strength results of Ni–Co deposits, the existence of plasticity on the fracture surfaces can be predicted. As stated in the previous section, changes in Co content lead to different tensile properties such as elongation, reduction in area, tensile strength, yield strength, and various other properties. Thus, the fracture surface of the coatings can be influenced by these differences. The morphology of all coatings included obvious dimples resulting in the necking of cross-section [18]. The presence of many grain boundaries in nanostructured materials leads to sliding resistance and the extension of local shear planes to more than one grain size. Consequently, it provides the condition for dimple morphology [235]. This type of fracture surface in Ni–Co coatings has been observed in the previous studies [18,169,215,233]. The size of dimples ranges from 400 nm to 1 µm, which is larger than several grains [18,215]. By increasing the Co content up to 25 wt%, size of the dimples is decreased. This is probably because of increasing the grain boundary, twinning, and triple junction. The large voids on Ni-55%Co fracture surface can be attributed to the porosities due to electrodeposition process at the bath containing high Co ions. These porosities result in lower ductility in Co-rich Ni–Co coatings [138].

Addition of various nanoparticles, such as SiC, leads to a greater number of dimples with a smaller size than Ni–Co deposits due to the prone sites including the interface of nanoparticles and matrix. Addition of a surfactant such as SDS improves the ductility of Ni–Co nanocomposite coatings [169]. However, tensile testing parameters such as strain rate can affect fracture mode. Gu et al. [233] have reported that the fracture surface of Ni-8.6 wt% Co deposits deformed at strain rates within the low and high ranges (1.04 × 10⁻⁵ and 1.04 s⁻¹) were ductile, including deep dimples and rough surfaces. At strain rates of 2.08 × 10⁻³ and 1.04 × 10⁻² s⁻¹, however, the morphology of fracture surfaces revealed brittle and ductile modes with a mixed structure containing shallow dimples and cup-and-cone morphologies.

The fracture toughness of Ni–Co coatings, as an indication of resistance to fracture for a material containing a crack, is rarely investigated. Anthony et al. [62] determined this property for the coating with Co content, according to ASTM E399-72. Raising the Co content results in a decrease in fracture toughness. There is a reverse relationship between strength and toughness. The difference between toughness of Ni–43Co was due to the different dimension of specimens and as-electrodeposited and heat treated specimens.
10.4. Superplasticity

Superplasticity is defined as a state in which any given material is able to bear a large degree of deformation before its breaking point, usually larger than 200% during the tensile deformation [236]. This characteristic is often determined at elevated temperatures (T > 0.5Tm), in which Tm is the melting point. Superplastic behaviour of Ni–Co coatings is similar to conventional materials resulting from increasing stress with raising rate of strain and reducing the temperature [171,232]. The relationship between elongation and strain rate at different deformation temperatures for Ni–Co and Ni-Co-Si3N4 was investigated [171,232]. It was shown that the process temperature was an important factor for elongation of coatings. There was no superplasticity of Ni–Co coatings at temperatures of 723 and 823 K. Superplastic behaviour for Ni–Co coating (279% elongation) was only observed at 773 K and 5 x 10⁻³ s⁻¹ strain rate, in comparison to 692% elongation in Ni-Co-Si₃N₄ at the 723 K temperature and the same strain rate. The difference in superplasticity of Ni–Co and Ni-Co-Si₃N₄ coatings is because of thermal stability and normal grain growth of the nanocomposite coating. In fact, Si₃N₄ nanoparticles prevent the growth of Ni–Co grains. The high percent of elongation could be related to both dislocation slip and grain boundary sliding. Change in grain size is an important factor for superplastic behaviour of materials. At the elevated temperature of 773 K, Co atoms are unable to inhibit the grain growth of Ni. Comparison of grain size in Ni [237], Ni-SiC [238], Ni–Co [171] and Ni-Co-Si₃N₄ [232] reveals that Ni-Co-Si₃N₄ coating possesses the lowest grain growth rate. The elongation of Ni is lower than that of Ni–Co and Ni-Co-Si₃N₄ coatings. Therefore, it can be concluded that the solid solution of cobalt in the Ni matrix will exhibit limited superplastic behaviour.

10.5. Internal stresses

Internal stresses in Ni–Co coatings are affected by operational conditions. These stresses can be measured by XRD according to the displacement of the peaks [205], deflection of strip equipped with an analyzer of deposit stress [146,239,240] and various other methods [241]. According to the latter method, the internal stress (σ) can be calculated by Stoney’s equation:

$$\sigma = \frac{Yz(x_d^2 + x_s^2)}{x_s x_d L^2}$$

where Y, z and L are the Young's modulus, measured displacement of the electrodedeposited strip, and the length of strip electrodeposited, respectively. x_s and x_d are the thickness of electrodeposited strip and the total thickness of the coating.

Fig. 19 shows the effect of pH, current density and saccharin on the residual stresses of Ni₅Coₓ coatings electrodeposited in a chloride electrolyte. The coatings exhibited minimum internal stress (220 MPa and 20 MPa with and without saccharin, respectively) at the pH value of 4. In the low current density range (1–10 mA cm⁻²), the internal stress was measured at 220 MPa in a saccharin-free bath, whereas it had a value of 360 MPa at 15 and 20 mA cm⁻². In general, the residual stresses are decreased with the addition of saccharin to the bath. Saccharin, as a source of sulfur, helps transform tensile stresses to compressive. Studying the deposit stress in Ni-Co-Fe coatings reveals that by increasing the temperature from 25 to 50 °C in the electrolytes containing saccharin, the internal stress is reduced from 61 to 32 MPa [240].

The effect of Co content on deposit stress indicates that by increasing the Co content in the deposit, the internal stress mode was changed from compressive for Ni-rich alloys (Co < 49 wt%) to tensile for deposits with Co > 49 wt% in Fig. 20a). These results were obtained in a sulfate bath containing saccharin in accordance with Park et al. [146]. It is shown in Fig. 20a) that, by controlling the composition and structure and deposition of the functionally graded Ni–Co coatings, the internal stress drops to 4–6 MPa. Internal stresses in Ni–Co composite coatings are essential. By increasing alumina nanoparticles content from 0 to 5 wt%, the internal stress is increased from 230 to 300 MPa in the additive-free bath and DC condition, respectively, as shown in Fig. 19b). PRC electrodeposition leads to a reduction in residual stress resulting from the uniformity of coating and suppression of hydrogen adsorption.

11. Magnetic properties

Magnetic properties of a material include magnetic anisotropy, magnetic flux density, saturation magnetisation, perpendicular magnetic anisotropy, perpendicular coercivity, permeability, magnetic remanence and squareness which may be affected by the Co content of Ni–Co deposits, thickness, surface roughness, additives, and other electrodeposition parameters [242–247]. Fig. 21a) and b) demonstrate the impact of bath composition and pH on the saturation magnetisation (Mₛ) and coercivity (Hc), respectively. According to Fig. 21a), by raising the Co²⁺/Ni²⁺ in the bath (increasing the Co content in the coating), Hc and Mₛ are increased to 125.2 kA m⁻¹ and 175.1 kA m⁻¹, respectively. This result is reported in previous studies as well [140,248]. In fact, the magnetic dipolar moment of Ni is lower than that of Co, therefore the Co/Ni ratio in the Ni–Co deposit influences on Mₛ. The higher value of Hc at pH 2.0 can be related to the higher concentration of defects in the Ni–Co coatings [137]. Magnetic properties can be altered by heat treatment at different temperatures. By increasing the annealing temperature from 25 to 450 °C, Mₛ will be in range of 144.8–342.6 kA m⁻¹, but the value of Hc will be lowered from 15.3 kA m⁻¹ reduced to 7.3 kA m⁻¹ [2] as a result of the new phase of Ni–Co, finer grain size and separation of the hydrogen adsorbed during the electrodeposition process [2,249]. However, the preferential texture of coating probably affects Hc [250]. It has been shown [176] that

![Fig. 19. The effect of (a) pH and (b) current density on deposit stress of Ni–Co coatings: (○) without saccharin and (△) containing 0.01 M saccharin [146].](image)
addition of glycine to the electrolyte leads to the emergence of morphologies such as acicula at high amounts of Co with harder magnetic deposits, yet Ni\textsubscript{e}Co deposits containing high amounts of Ni possess subtler magnetic behaviour with round shaped grains.

Magnetoresistance (MR) involves changes in electrical resistance of a material in the condition where a magnetic field is applied. MR studies have proven that Ni\textsubscript{e}Co coatings containing 0–80 wt% Co exhibited magnetoresistance (AMR) properties. Increasing the magnetic field resulted in higher longitudinal magnetoresistance (LMR) and lower transverse magnetoresistance (TMR) properties. By increasing the Co content in the Ni\textsubscript{e}Co coatings, LMR and TMR were altered by 3.5–11% and 3–8%, respectively [248].

Giant magnetoresistance (GMR) has a negligible magnetic impact on alternative ferromagnetic and non-magnetic conductive multilayers. Electrodeposition of Ni–Co (Cu)/Cu multilayers on gold substrates has demonstrated that GMR is effected by Ni and Co content in the ferromagnetic layer, thickness and number of layers. The multilayer which was electrodeposited in citrate baths with lower pH values did not exhibit GMR [251]. The role of the interface of the layer in GMR is significant. There is a linear relationship between a number of interfaces and GMR [252]. Toth et al. [253] have shown that the impact of surface roughness was important in GMR of Ni-Co/Cu electrodeposited multilayers.

12. Corrosion resistance

Corrosion resistance of alloy deposits is a function of their composition and microstructure. Corrosion study of Ni–Co deposits with different Co content in 3 wt% NaCl revealed that by increasing the amount of Co in the coatings, corrosion potential ($E_{corr}$) shifts towards less noble values, and the corrosion current density ($j_{corr}$) is increased [80,254] contrary to other results [24,255]. However, it has been reported that Ni-17% Co coating possess the highest corrosion resistance among the coating with 0, 17 and 42 wt% Co [220,256].

Corrosion behaviour of Ni–Co deposits is influenced by several important parameters: (1) Co content, (2) phase structure, (3) orientation, (4) grain size and (5) surface morphology. Ni is nobler than Co, therefore it is expected that by adding Co to Ni coatings, the activity of alloy coatings becomes greater than Ni coating. However, the microstructure is another important factor affecting the corrosion behaviour. Corrosion resistance of a single-phase structure is higher than a dual-phase structure due to the formation of galvanic cells. Yet the phase structure of Ni–Co coatings in the range of 0–49 Co is not changed and maintains a steady effect on corrosion behaviour of coatings. Another important factor affecting the corrosion resistance is the preferred orientation. As mentioned earlier (Fig. 16h), by increasing the Co content, RTC percentage of deposits is altered. Therefore, it can be concluded that the higher resistance of Ni-17%Co is because of (111) orientation. Grain size is another explanation for corrosion behaviour of Ni–Co coatings. Ni–Co coatings with higher Co content exhibit finer...
grains resulting in a high density of grain boundaries. Ni-17% Co had 48 nm grain size compared to 15 nm for Ni-42% Co. Consequently, the moderate grain size of Ni-17% Co is another reason for higher corrosion resistance of 10.08 kΩ.cm². In another study [234], it was similarly reported that Ni-Co with moderate Co content (Ni-20%Co) exhibited lowest $i_{corr}$ value in 3.5% NaCl solution. The lowest corrosion rate of this coating was related to its high, smooth and dense surface. The impact of deposition current on corrosion behaviour in 3.5% NaCl indicates that the increase in deposition current density leads to an increase in $i_{corr}$ due to variations in surface structure and alloy composition [3]. Comparison of steel and brass as a substrate for Ni-Co coatings showed that Ni-20Co had better corrosion resistance in both cases, yet the corrosion efficiency was improved in at the brass substrate [234].

Corrosion behaviour of coatings is affected by media [257,258]. Ni-Co coatings displayed different corrosion behaviour in basic solutions such as NaOH. EIS studies demonstrated that there was a flat apex in Bode diagrams at moderate frequencies, indicating the passivation of Ni-Co deposits in 10% NaOH. It has been proposed that the passivation occurs due to the bilayer structure of MO and M(OH)₂ [185]. However, cyclic voltammetry experiments have proven that the passivation has been a result of Co(OH)₂ and CoOOH. A small oxidation peak exists at $-0.20 \text{ V}$ in the first cycle which belongs to Co(OH)₂. The second peak observed at 0.12 V is corresponding to CoOOH. The difference between the second cycle and the first is due to the formation of Co oxides [72]. It has been proposed that the presence of Co in the deposit hinders the growth of oxide layer [193].

In some cases, a third element is added to the Ni-Co coatings for various purposes which can affect corrosion behaviour. It has been reported that $i_{corr}$ was lowered by reducing the Fe content and increasing the Ni content in Ni-Co-Fe coatings (for magnetic goals), resulting in denser and smoother ternary films [259]. In case of Ni-Co-W coatings, it was shown that Co and W had a different impact on $i_{corr}$ [3]. The addition of P to Ni-Co coatings leads to an amorphous structure and deterioration of corrosion resistance [9].

The corrosion resistance of Ni-Co coating can be improved in presence of micro- or nanoparticles. Various particles such as Al₂O₃, SiC, TiO₂, WC and MWCNT have been added to the coatings. Immersion corrosion studies in 3.5% NaCl and 5% HCl indicated that adding SiC nanoparticles to Ni-Co coating resulted in lower corrosion rates. According to potentiodynamic polarisation tests, in Ni-Co-SiC nanocomposite coatings, $E_{corr}$ shifts towards more positive values and $i_{corr}$ is decreased compared to Ni-Co coatings [258], which is in agreement with the previous results [22]. SiC nanoparticles fill defects such as holes, gaps, and crevices, as well as reducing the size of the defects, resulting in a more compact microstructure. In this case, the size of

![Fig. 22. Wear track of (a) pure Ni, (b) Ni-58Co, (c) Ni-75Co and (d) Ni-83Co against an AISI-52100 6 mm diameter, stainless steel ball with a hardness of 700 HV in a reciprocating wear test at a humidity of 40-50% with a load of 14 N, sliding frequency of 1 Hz, sliding stroke 2.69 mm and 5.38 mm s⁻¹ sliding speed over a time of 25 min [262].](image-url)
particles is of great importance. Ni-Co-SiC coatings with nanoparticles exhibited higher corrosion resistance compared to the coatings containing micro-size particles [260].

In addition, nanoparticles are similar to inert corrosion barriers, effectively limiting their growth. In other words, they decrease the effective surface area exposed to the electrolyte by uniform distribution in the deposit, so that the \( E_{\text{cor}} \) shifts to more positive values. However, incorporation of CeO nanoparticles reduced the corrosion resistance of coatings. Lower corrosion resistance can be attributed to CeO agglomerations in the coating. 

Adding high amounts of TiO\(_2\) to Ni–Co electrodeposition bath leads to lower corrosion resistance resulting from the agglomeration of nanoparticles [261], similar to Ni-Co-SiC coatings [262]. The nanoparticles lead to the formation of numerous micro-galvanic cells (with nanoparticles and Ni–Co matrix acting as cathode and anode, respectively). Thus, uniform distribution of nanoparticles is capable of changing the mechanism of corrosion, unlike the negative effect of agglomeration. Corrosion associated with erosion has a synergistic effect on the corrosion behaviour of materials in pipelines. It has been demonstrated that Ni-Co-SiC/Al\(_2\)O\(_3\) nanocomposite coatings have a positive effect on erosion-enhanced of API X-65 pipes in oil sand slurry consisting NaCl, NaHCO\(_3\), silica sands and other additives [153,263].

13. Tribological properties

Addition of Co to Ni has a positive impact in decreasing the wear rate and coefficient of friction (COF) of Ni–Co coatings. In Ni-rich alloys, the effect of Co on COF is negligible. Co content higher than 49 wt% leads to a decrease in COF, for instance, Ni–81 wt% Co deposit has a lower friction coefficient. Moreover, alloys with high Co content exhibit more stable friction behaviour in comparison to Ni-rich alloys [154]. This behaviour can be attributed to the different phase structure of the coatings. In alloys with high Co content, crystal transformation from fcc to hcp is the reason for the decreased coefficient of friction. COF can be influenced by deposition parameters affecting the alloy content such as current density [152,264]. By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]). By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]). By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]). By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]). By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]). By adding 5 wt% Co to pure Ni, the wear rate is increased from \( 12 \times 10^{-5} \) to \( 25 \times 10^{-5} \) mm\(^3\) N\(^{-1}\) m\(^{-1}\) (dry current density [152,264]).

Tribological studies have shown that tribofilm and wear debris act as a third body in the tribo-system. Fig. 22 demonstrates the wear track of Ni–Co coatings with different Co contents. Microhardness, COF and wear rate of the coatings are also presented in the SEM micrographs. As can be seen in Fig. 22d), the worn surface of Ni–83Co is shallower than the other coatings. The EDS analysis of the highlighted areas in the Fig. 22 and wear debris is listed in the Table 4. The Fe content in area A is high (20 at.%), having been transferred from the steel ball. This suggests that the wear mechanism of pure Ni includes severe adhesion. The presence of oxygen and iron confirms the formation of tribofilm in this coating due to the absence of these elements in the deposited coating. According to Fig. 22b), the wear track of Ni–S8Co includes three zones: (1) a smooth zone B with 7 at.% Fe, (2) a transition zone with small cracks and (3) a debris covered zone with 2 at.% Fe. The higher wear rate of Ni–S8Co can be related to the internal stresses leading to the formation of cracks in the coating. Ni–75Co contains no iron on the highlighted area C in Fig. 22c) or from the resultant debris (Table 4).

The absence of iron and oxygen in wear track confirms that no tribofilm was created on the worn surface of Ni–75Co. Ni–83Co contains the lowest amount of debris in Fig. 22d), indicating the lowest

### Table 4

<table>
<thead>
<tr>
<th>Content (at.%)</th>
<th>Debris</th>
<th>Pure Ni (Area A)</th>
<th>Ni-58Co (Area B)</th>
<th>Ni-75Co (Area C)</th>
<th>Ni-83Co (Area D)</th>
</tr>
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<tbody>
<tr>
<td>O</td>
<td></td>
<td>63</td>
<td>48</td>
<td>0</td>
<td>0</td>
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<td>Ni</td>
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<td>18</td>
<td>23</td>
<td>16</td>
</tr>
<tr>
<td>Co</td>
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<td>84</td>
</tr>
<tr>
<td>Fe</td>
<td></td>
<td>20</td>
<td>7</td>
<td>0</td>
<td>0</td>
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</table>

<table>
<thead>
<tr>
<th>Content (at.%)</th>
<th>Pure Ni</th>
<th>Ni-58Co</th>
<th>Ni-75Co</th>
<th>Ni-83Co</th>
</tr>
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<tbody>
<tr>
<td>O</td>
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<td>39</td>
<td>36</td>
<td>49</td>
</tr>
<tr>
<td>Ni</td>
<td>50</td>
<td>28</td>
<td>16</td>
<td>4</td>
</tr>
<tr>
<td>Co</td>
<td>0</td>
<td>31</td>
<td>48</td>
<td>47</td>
</tr>
<tr>
<td>Fe</td>
<td>10</td>
<td>2</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>coating</td>
<td>Test</td>
<td>Pin or ball material</td>
<td>Force (N)</td>
<td>Speed (mm.s⁻¹)</td>
</tr>
<tr>
<td>-------------------------</td>
<td>---------------</td>
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<td>----------------</td>
</tr>
<tr>
<td>Ni-Co</td>
<td>Pin-on-disk</td>
<td>Al₂O₃</td>
<td>0.12-0.24</td>
<td>0.12-0.24</td>
</tr>
<tr>
<td>Ni-Co</td>
<td>Ball-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.25-0.69</td>
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<tr>
<td>Ni-Co</td>
<td>Ball-on-disk</td>
<td>GCr15 steel</td>
<td>0.4-0.5</td>
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<td>Ni-Co</td>
<td>Ball-on-plate</td>
<td>Al₂O₃</td>
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<td>-</td>
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<td>AISI 1040 steel</td>
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<tr>
<td>Annealed Ni-Co</td>
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<td>Si₃N₄</td>
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<td>-</td>
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<td>25</td>
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<td>Ni-Co-CNTs</td>
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<td>AISI S2100 steel</td>
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<tr>
<td>Ni-Co-ZnO</td>
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<td>AISI S2100 steel</td>
<td>0.15-0.23</td>
<td>0.15-0.23</td>
</tr>
<tr>
<td>sol-enhanced Ni-Co-TiO₂</td>
<td>Pin-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.33-0.62</td>
<td>0.33-0.62</td>
</tr>
<tr>
<td>Ni-Co-Si₃N₄</td>
<td>Ball-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.33-0.72</td>
<td>0.33-0.72</td>
</tr>
<tr>
<td>Ni-Co-MoS₂</td>
<td>Ball-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.15-0.23</td>
<td>0.15-0.23</td>
</tr>
<tr>
<td>Functionally graded Ni-Co</td>
<td>Ball-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.20-0.28</td>
<td>0.20-0.28</td>
</tr>
<tr>
<td>Functionally graded Ni-Co/CaO</td>
<td>Ball-on-disk</td>
<td>AISI S2100 steel</td>
<td>0.1</td>
<td>0.1</td>
</tr>
</tbody>
</table>
wear rate compared to the other coatings. There are no traces of iron or oxygen in the wear track (area D). The iron content in the debris was also zero. These findings confirm the lack of tribofilm or oxidation in this coating. The wear tracks without tribofilm related to Ni–75Co and Ni–83Co led to significant reduction of friction and improvement of wear resistance. This can be related to the hcp structure of Co-rich coatings [12]. The amount and type of additives has a great effect on tribological properties of Ni–Co coatings. Co-rich coating resulted from a sulfate bath containing 0.5 g dm$^{-3}$ BD and 2 g dm$^{-3}$ saccharin [14] exhibited lower wear rate compared to Co-rich coating deposited from an additive-free sulfate bath [154] at same sliding wear condition. This is due to the higher hardness of former coating.

Several studies [268,269] have attributed the higher wear resistance of Co-rich coatings to the low-stacking fault energy (SFE) of these coatings. It has been demonstrated that materials with low SFE possess higher galling resistance than the materials with higher SFE and equal hardness [269]. In fact, substitution of Ni in Co-based alloys leads to a decreased SFE and lowers the rate of strain hardening, therefore improving plasticity. This makes the alloy susceptible to galling and reduces its wear resistance.

Tribological properties of Ni–Co coatings can be improved by incorporation of particles in the alloy and production of micro/nano-composite coatings. Ni–Co composite coatings are electrodeposited using different types of micro/nanoparticles. Incorporation of Al$_2$O$_3$ nanoparticles into the Ni–Co deposits resulted in an overall decrease in wear weight loss and higher microhardness due to dispersion and particle hardening [139]. An optimal value of current density led to the formation of solid solution which is ductile after oxidation heat treatment [229]. The Co$_2$O$_4$ nanoparticles had little effect on the COF of Ni–28Co coating (2% increment in COF). However, the COF of Ni–77Co was approximately two orders of magnitude compared to Ni-Co-SiC. Introduction of lateral stresses from SiC nanoparticles into the counterpart resulted in a higher COF [271]. Similar observations have been reported for Ni-Co-SiC nanocomposite coatings [273]. Investigating the size of SiC particles in the micro/nm range indicated that the COF was not affected by particle size [272], unlike the effect of ZnO micro/nanoparticles on COF of Ni–Co coatings [230]. In addition, the number of SiC particles had an impact on COF and wear loss of Ni–Co coatings [231]. Ni-Co-SiC nanocomposite coatings exhibited better wear resistance in comparison to Ni–Co alloy coatings. Anti-wear properties in Ni-rich and Co-rich coatings has been investigated [271,272]. SiC nanoparticles had little effect on the COF of Ni–28Co coating (2% increment in COF). However, the COF of Ni–77Co was approximately two orders of magnitude compared to Ni-Co-SiC. Literature [271,272] stated that the oxidation rate of alloy coatings was increased by raising Co content, and that the oxide scale on the surface of Ni-Co-ZrO$_2$ nano composite coatings and thermal barrier coatings are better than Ni–Co coatings [292,293]. XRD patterns of oxidised coatings indicate that the oxide scales of Ni-7, 15Co were the only solid solutions of Ni(Co)O, but the scale of Ni–30Co was a mixture of Ni(Co)O solid solution and (Ni, Co) Co$_2$O$_4$ spinel phase. According to Raman spectra, the top oxide layer of Ni–30Co consists of Co$_3$O$_4$ phase. Study of thermal oxidation kinetics demonstrated that the oxidation rate of alloy coatings was increased by raising Co content, and that the oxide growth followed a parabolic law [298].

Efforts have been made to improve high-temperature oxidation of Ni–Co coatings through the addition of various nanoparticles such as ZrO$_2$. The oxidation study of Ni-Co-ZrO$_2$ composite coating at 573, 873 and 1173 K revealed lower weight gain of the coating compared to Ni–Co alloy coating [290]. In fact, ZrO$_2$ nanoparticles decrease the effective area for diffusion of oxygen, thus leading to lower oxidation rate. The oxide scale on the surface of Ni-Co-ZrO$_2$ nano composite coating was uniform and free of cracks [291]. High-temperature oxidation is often used as an expletory method for fabrication of spinel coatings such as (Ni, Co) Fe$_2$O$_4$. This phase exhibits exceptional thermal stability and high-temperature conductivity. These coatings were produced by composite electrodeposition of Ni-Co-Fe$_2$O$_3$ coating followed by the high-temperature oxidation process [292,293]. XRD patterns of Ni and Ni-Co-Fe$_2$O$_3$ coatings oxidised at 1000 °C for 3600 min showed that the pre-oxidised Ni-Co-Fe$_2$O$_3$ coatings displayed higher resistance to hot corrosion at 960 °C in molten salts of Na$_3$AlF$_3$-AlF$_3$-CaF compared to pure Ni [294]. However, it has been reported that for these coatings, the corrosion rate under sodium chloride at 800 °C and air condition was high due to weak adhesion of corrosion products [31].

However, the high-temperature resistant coatings such as diffusion coatings and thermal barrier coatings are better than Ni–Co deposits. There have been numerous attempts in order to enhance the properties in Ni-Co-Al coatings by formation of Ni and Co aluminides [295]. The properties can be improved by additional treatments such as aluminizing to form aluminides, as reported in other systems [296].
15. Heat treatment of Ni–Co coatings

15.1. Physical properties

Ni–Co coatings were heat treated in the temperature range of 200–800 °C. The important factors in the heat treatment of coatings include annealing temperature, treatment duration and a coating composition which impacts physical and mechanical properties. XRD patterns of Ni-rich and Co-rich alloys annealed at different temperatures revealed that no change in the phase structure of Ni-rich coating by increasing the heat treatment temperature. This is in agreement with the previous studies [2]. In addition, by increasing the annealing temperature, FWHM is narrowed, which indicates grain growth within the coating.

The grain size of Ni–20Co was increased from 13 nm to 20, 47 and 57 nm by annealing at 523, 623 and 823 K, respectively [297]. At higher temperatures, crystallographies grow randomly and non-uniformly. By increasing the temperature, the grains become larger, however only a small change was observed in the lattice parameter of fcc structure [298]. This has also been demonstrated by SEM and TEM micrographs and bright field images [2,285]. Structural changes in Co-rich alloys are different from Ni-rich alloys, as shown in Fig. 23. According to XRD patterns, Co-5.5Ni has an hcp phase structure with 20 nm grain size. The volume percent of this phase is decreased by increasing the heat treatment temperature. Pure hcp phase was transformed to a mixed phase of fcc and hcp by annealing at 823 K. By increasing the temperature, fcc grains grow whereas hcp grains size was reduced to 7 nm. The austenitic transformation from hcp to fcc phase may be due to chemical composition variations in the fcc phase [297]. According to Ni–Co binary phase diagram, the allotropic austenitic transformation occurs almost at the same temperature of approx. 700 K [299].

15.2. Thermal stability

Thermal stability of Ni–Co coatings is greatly affected by chemical composition. Thermal stability is studied by differential scanning calorimetry (DSC). Fig. 24a) shows DSC diagrams for monocrystalline Ni–Co coatings with different Co contents. All coatings exhibit a wide range of temperature from the beginning up to the peak temperature (Tp) with low heat flow. Values of Tp for Ni–Co alloys containing 37, 52 and 74 wt% Co are 557, 591 and 596, respectively. The release of heat energy in Tp is maximum, thus it can be used as a representative of thermal stability. It can be concluded that the thermal stability of the coatings is increased by raising Co content in the alloys. Scanning of samples in different heating rates is a kinetic resolution for growing of grains in Ni–Co coatings. Ni–74Co exhibited maximum Tp at various scan rates including 0.17, 0.33 and 0.67 K.s⁻¹ [298]. The activation energy needed for the growing of grains is obtained from the relationship between Tp and heating rate, according to the Kissinger equation [300]:

\[
\ln\left(\frac{b}{T_p^2}\right) = -\frac{E}{RT_p} + C
\]

In which b is heating rate, E and R are activation energy of deposits for growing of grains and universal gas constant respectively, and C is a constant. The values of activation energy of Ni–37Co, Ni–52Co, and Ni–74Co were measured as 1.61, 2.02 and 2.08 eV, respectively [298]. Consequently, Ni–Co coatings with higher Co content are more resistant to grain growth. This can be ascribed to segregation of Co atoms in grain boundaries, resulting in slower migration of boundaries. Figs. 24b) and 2 cc) compare the average grain size (dₐₐ) before and after heat treatment. Heating has resulted in larger grain size and creation of twins.

In addition to the initial microstructure, other parameters such as impurities lead to fluctuations in thermal stability. It has been reported that increasing the concentration of impurities such as sulfur increased the thermal stability of Ni–Co coatings [298]. This is due to an effect termed solution drag effect. Sulfur is supplied from additives such as saccharin. It is suggested that sulfur impurities limit the grain growth. Thermal stability of Ni–Co coatings can be improved by adding a third alloying element. It is expected that adding alloying elements such as phosphorus and boron enhance grain growth resistance of Ni–Co coatings. However, investigations in this field are limited and the impact of the alloying element should be further studied.

15.3. Effect of heat treatment on mechanical properties

Studying grain growth via methods such as XRD and TEM is difficult since grain size cannot be accurately measured. Changes in grain size due to heat treatment lead to a variety of properties such as hardness, toughness, electrical and magnetic properties. Annealing of Ni–Co coating containing 22–50 wt% Co in the temperature range of 575–728 K for 60 min resulted in lower yield and ultimate strength, as well as higher ductility and fracture toughness resulting from the increased grain size [62,301,302].

The microhardness of Ni–50Co and Ni–85Co is increased after annealing in the range of 30–200 °C. This is due to the release of internal stresses [30]. By heat treatment in the temperature range of 200–400 °C, microhardness of Ni–Co alloy and Ni-Co-CoO₂ composite

![Fig. 23. XRD patterns of (a) Ni–20Co coating and (b) Ni-94.5Co at different temperatures [297].](image-url)
coatings is decreased as a result of recrystallization. At annealing temperatures higher than 400 °C, microhardness is rapidly reduced which is attributed to the growth of grains in Ni_{25}Co and Ni_{50}Co coatings. The unchanged microhardness of Ni_{85}Co is due to the higher thermal stability of this coating. The decrease in microhardness of the coatings containing CeO₂ is subtler than Ni–Co alloy coatings [303]. Nanoparticles have a pinning effect on grain boundaries. A similar trend has been observed in Ni–Co composite coatings with other nanoparticles [304]. In addition to mechanical properties, magnetic properties [2] and catalytic properties [28] are also impacted by heat treatment.

16. Electrocatalytic properties of Ni–Co surfaces

Ni–Co coatings are utilised as an electrocatalyst in the water electrolysis for two reactions [28]: (1) hydrogen evolution reaction (HER) and oxygen evolution reaction (OER). Investigations have shown that among active metals, Ni, Co, and their alloys are among the best catalysts for HER in alkaline medium. The effect of chemical composition on HER has been studied in previous studies [305,306]. Fig. 25 illustrates HER activities of the coatings as a function of Co content by CV. Ni–Co coatings exhibit better HER activity compared to pure Ni. Alloys containing Co within the range of 28–95 wt% showed higher current density of HER. According to Fig. 25b), the current density is decreased as a function of the cyclic number. It may be due to dealloying [307] and delamination [308] occurring after several cycles. In fact, hydrogen bubbles are generated during the test and cover the active sites. This leads to deterioration of catalyst performance. All the coatings showed similar trends, and degradation behaviour is not changed by Co content. In addition, the different decay ratios between −30 and −18% can be influenced by surface morphologies of coatings [26]. Study of discharge potentials for Ni–Co coatings with different Co content at room temperature and 40 °C have revealed that the coatings containing 41–64 wt% Co exhibited lower overvoltage, resulting in optimal catalytic properties [309,310].

Tafel slope is essential in the determination of the controlling step in hydrogen discharge. According to the Tafel curves of Fig. 26, the slope is changed from about −30 mV to −124 mV at 6 A dm⁻². This indicates that hydrogen discharge is controlled by two reactions, as following [306,309]:

---

**Fig. 24.** DSC plots showing the exothermal signal of grain growth as a function of scanning temperature (b = 0.17 K s⁻¹) of the three Ni–Co alloys [283], (b) and (c) TEM dark field of Co-rich alloy with average grain size (d_{ave}) before and after annealing, respectively [218].

**Fig. 25.** Electrochemical characterisation of Ni–Co deposited on Cu from electrolytes containing 0.50 M NiSO₄·6H₂O and 0.01–0.50 M CoSO₄·7H₂O in 0.50 M H₃BO₃. (a) Cyclic voltammograms of Ni–51Co alloy in 6.0 mol dm⁻³ KOH at 298 K as a function of cycle number at a sweep rate of 50 mV s⁻¹. (b) Recorded current densities of Ni₁00, NiCo alloys, and Co₁00 at −1.6 V vs. SCE as a function of cycle number [26].
with a smooth structure [313]. Recently, porous Ni–Co coatings with a sea cucumber-like structure have been fabricated through the evolution of hydrogen-assisted electrochemical deposition process with superior electrocatalytic activity and stability [314].

17. Ni–Co microstructured and nanocomposite coatings

Incorporation of micro/nanoparticles in the metallic matrix results in a combination of properties which cannot be achieved independently by any other metallurgical methods. Uniform distribution of the nanoparticles such as alumina, SiC, diamond, TiO$_2$, and WC can improve the microhardness, wear resistance, corrosion resistance, high-temperature inertness, and anti-oxidation properties. As was previously mentioned, nano- and micro-particles enhance microhardness, wear resistance and mechanical behaviour as a result of dispersion hardening. Furthermore, incorporation of nanoparticles increases the corrosion resistance. According to other researches, the corrosion resistance improvement of coatings containing nanoparticles is attributed to the trapped ceramic particles inside the coating [315]. Nanosized ceramic particles within the coating are electrochemically neutral and act as a physical barrier against penetration of corrosive ions, such as chloride ions, thus improving the corrosion behaviour. In other words, the neutral particles fill the grooves, cavities, and gaps, effectively preventing the start and the spreading of corrosion defects. For Ni–Co coatings, the effect of different particles is summarised in Table 6.

18. Ni–Co alloys with additional alloying elements

Various ternary alloying elements such as W, Fe, Cu, P, B, Mo and Zn can be added to Ni–Co alloy coatings. Each of these elements provides specific properties. Electrodeposition of ternary or quadruple alloys is more complicated than electrochemical deposition of binary alloys or individual pure metals. Various third elements utilised in Ni–Co coatings are summarised in Table 7. The most prominent third elements added to Ni–Co coatings are considered below.

Table 6 Various micro/nano particle inclusions in Ni–Co coatings along with their effects.

<table>
<thead>
<tr>
<th>Class</th>
<th>Particle type</th>
<th>Electrolyte</th>
<th>Particle size (nm)</th>
<th>Particle amount in bath (g dm$^{-3}$)</th>
<th>Present age in coating</th>
<th>Goal</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Oxide particles</td>
<td>Al$_2$O$_3$</td>
<td>Watts-type</td>
<td>500</td>
<td>20–60</td>
<td>–</td>
<td>Improving corrosion/erosion resistance of pipe steels</td>
<td>[316]</td>
</tr>
<tr>
<td></td>
<td>SiO$_2$</td>
<td>Watts-type</td>
<td>20–40</td>
<td>10–25</td>
<td>–</td>
<td>Improving corrosion resistance and microhardness</td>
<td>[317]</td>
</tr>
<tr>
<td></td>
<td>TiO$_2$</td>
<td>Watts-type</td>
<td>nm</td>
<td>2–8</td>
<td>0–3.3 wt%</td>
<td>The coatings with optimum amount of 2.5 wt%</td>
<td>[76]</td>
</tr>
<tr>
<td></td>
<td>YZA</td>
<td>Sulfamate</td>
<td>μm</td>
<td>25</td>
<td>2–20 wt% Zr</td>
<td>Improving thermal stability</td>
<td>[304]</td>
</tr>
<tr>
<td></td>
<td>CrO$_2$</td>
<td>Sulfamate</td>
<td>20–30</td>
<td>25–100</td>
<td>–</td>
<td>Improving thermal stability</td>
<td>[303]</td>
</tr>
<tr>
<td></td>
<td>ZrO$_2$</td>
<td>Sulfamate</td>
<td>–</td>
<td>4</td>
<td>–</td>
<td>Improving electrocatalytic activity</td>
<td>[318]</td>
</tr>
<tr>
<td>Carbid particles</td>
<td>SiC</td>
<td>Watts-type</td>
<td>40</td>
<td>0–8</td>
<td>6–12 wt%</td>
<td>Lowering corrosion rate</td>
<td>[256]</td>
</tr>
<tr>
<td></td>
<td>SiC</td>
<td>Watts-type</td>
<td>50</td>
<td>30</td>
<td>6–10 wt%</td>
<td>Investigating the effect of duty cycle and frequency on SiC content</td>
<td>[197]</td>
</tr>
<tr>
<td></td>
<td>Waters-type</td>
<td>50</td>
<td>15</td>
<td>–</td>
<td>Gradient (0.5–5.5)</td>
<td>Improving wear resistance of functionally graded Ni–Co coatings</td>
<td>[321]</td>
</tr>
<tr>
<td>Nitride particles</td>
<td>Si$_3$N$_4$</td>
<td>Sulfamate</td>
<td>1 μm</td>
<td>20</td>
<td>4.4–8.1 wt%</td>
<td>Increasing the corrosion resistance</td>
<td>[220]</td>
</tr>
<tr>
<td></td>
<td>TiN</td>
<td>Watts-type</td>
<td>&lt; 3 μm</td>
<td>20–40</td>
<td>–</td>
<td>Improving microhardness</td>
<td>[322]</td>
</tr>
<tr>
<td>Other particles</td>
<td>Mo$_2$</td>
<td>Watts-type</td>
<td>10</td>
<td>1</td>
<td>–</td>
<td>Improving microhardness</td>
<td>[323]</td>
</tr>
<tr>
<td></td>
<td>CNT</td>
<td>Watts-type</td>
<td>nm</td>
<td>1</td>
<td>–</td>
<td>Increasing corrosion resistance and microhardness</td>
<td>[324]</td>
</tr>
<tr>
<td></td>
<td>Diamond</td>
<td>Watts-type</td>
<td>6–12 μm</td>
<td>1–15</td>
<td>15.5–48.4 wt%</td>
<td>High diamond particles by sediment co-deposition led to lower wear rates</td>
<td>[326]</td>
</tr>
<tr>
<td>Mixed particles</td>
<td>Al$_2$O$_3$ + SiC</td>
<td>Watts-type</td>
<td>Al$_2$O$_3$: 45</td>
<td>0–40 (Al$_2$O$_3$:SiC:1:1)</td>
<td>SIC:2.2–2.0</td>
<td>Mixed nanoparticles led to higher corrosion resistance compared to separate nanoparticles</td>
<td>[328]</td>
</tr>
</tbody>
</table>

Fig. 26. Tafel plots for corrosion of Ni–Co coatings of various compositions on an 8 cm$^2$ aluminium mesh in (30 wt% KOH at 60 °C) [309].

I) Electrochemical desorption (Volmer-Heyrovsky route):

\[ M + H_2O + e^- \leftrightarrow MH_{ads} + OH^- \]  

(37)

II) Chemical desorption (Volmer-Tafel route):

\[ MH_{ads} + H_2O + e^- \leftrightarrow H_2 + M + OH^- \]  

(38)

\[ M + H_2O + e^- \leftrightarrow MH_{ads} + OH^- \]  

(39)

\[ MH_{ads} \leftrightarrow H_2 + 2M \]  

(40)
Recently, Ni-Co-Fe ternary alloys have attracted a lot of attention as magnetic materials since they exhibit improved magnetic and magneto-resistance properties, such as higher saturation induction and magnetisation and lower coercivity compared to binary magnetic alloys [329]. Therefore, Ni-Co-Fe films have been introduced as a candidate for MEMs [330–332]. Increasing the Fe content in the coatings led to an increase in saturation magnetisation [331]. In addition, Ni-Co-Fe coatings have attracted attention due to their notable physical and chemical properties. It has been reported that these coatings possessed suitable corrosion resistance and desirable electrocatalytic properties [259,333].

Tungsten, similar to P, Mo, and Ge is unable to be electrodeposited from the electrolyte on its own. In other words, W is a reluctant metal whereas Ni and Co are inducing metals [21]. Ni–Co coatings containing W are deposited from acidic and alkaline baths. The acidic baths are practically not worthwhile due to unsuitable deposits [21,334]. The presence of Co and W has beneficial effects on microstructure, corrosion resistance and mechanical properties [335]. Depending on the deposition conditions, the microstructure of Ni–W and Ni-Co-W is either amorphous or crystalline, with a grain size in the range of nanometer [3,336–338]. High thermal stability of this coating results in the grain size being maintained at high temperatures [339]. Increasing the W content has been reported to enhance the microhardness [3,340].

Ni–P and Ni-Co-P films have been suggested as a replacement for hard chrome coatings, owing to their high wear resistance and hardness [15,341,342]. Ni-Co-P coatings are used in fuel cell [343,344] and redox flow cell [345] applications owing to their high corrosion resistance and good mechanical properties. However, phosphorus-containing coatings exhibit high COF in the range of 0.5–0.7 under dry sliding, depending on the counterparts [346,347]. Previous reports have stated that Ni–Co deposits have low friction coefficient (COF) and excellent wear resistance [15,341,342]. Thus, it can be concluded that an alloy combination of Ni, Co, and P (Ni-Co-P) will exhibit low COF and reduced wear weight loss. The structure of the coatings, depending on P content, can be either amorphous, semi-crystalline or nanocrystalline [348]. The mechanical properties and tribological behaviour of Ni-Co-P can be improved following heat treatment. It has been reported [342,349,350] that heat treatment of Ni–P deposits at 400 °C considerably improves the hardness. Heat treatment changes the structure of the coatings from amorphous/semi-amorphous to the crystalline structure. Furthermore, dispersed intermetallic compounds (such as Ni3P, Ni12P5) are precipitated in the matrix. These compounds hinder the movement of dislocation, resulting in higher hardness. The decrease in hardness at higher temperatures (T > 400 °C) can be related to oxide formation, grain coarsening and phase transition [15].

Fig. 27a demonstrates the microhardness of Co-Ni-P coating as a function of heat treatment temperature for 1 h. Fig. 27b shows the COF of Co-Ni-P coating heat treated at various temperatures. COF of as-deposited and annealed coatings were measured to be about 0.3 compared to 0.6 for hard Cr coating. The subtle COF of this coating can be related to the presence of Co in the coating. Microhardness and COF affect the wear rate of Co-Ni-P coatings (Fig. 27c). The lower wear rate of coating annealed at 400 °C is a result of the highest hardness resulting from precipitation hardening by Ni12P5 intermetallic particles. Lower hardness and grain coarsening lead to higher wear rate of Co-Ni-P coating annealed at 500 °C. However, it has been reported [351] that Ni-P-SiC composite coating heat treated at temperatures ≥ 400 °C demonstrated lower COF and wear rate. This is related to the formation of H3PO4 during wear test, creating a solid lubricant between the coating and counterpart. According to literature [351–354], Ni3P reacts with oxygen and forms H3PO4, which has a great influence on sliding behaviour. The annealing of the coating at higher temperatures leads to higher amount of Ni3P, and thus formation of more H3PO4 [351].

Ni-Co-P coatings have been widely used as magnetic recording devices and hard magnetic coatings [355,356], corrosion resistance materials [9,357], anti-wear coatings [15], microwave absorbers [358],
electrocatalytic films for hydrogen generation and water electrolysis.

19. Fabrication of novel Ni–Co deposits

The Ni–Co coatings studied so far have been simple monolayer coatings with a uniform chemical composition throughout the thickness profile. Recently, coatings with specific structural patterns, such as multilayer and functionally-graded patterns, have been developed which exhibit excellent properties such as high corrosion resistance, low wear rate, and exceptional mechanical properties.

19.1. Functionally graded Ni–Co alloys and nanocomposite coatings

In these coatings, the Co or nanoparticles content is gradually varied from the substrate/coating interface to the surface. This is carried out by changing the parameters including current density, stirring rate, injection of nanoparticles or Co source in the bath, and changing of pulse parameters such as pulse frequency and duty cycle [361]. Graded Ni–Co coatings were successfully fabricated by controlling cobalt sulfate during the coating process and showed a gradual change in the amount of Co and a phase transformation of fcc to hcp towards the surface of the deposit. This coating demonstrated lower internal stresses and coefficient of friction, as well as higher wear resistance at high temperatures [239].

Nanocomposite coatings with gradual structures have various advantages which prevent degradation of various mechanical properties, including decreased ductility due to the difference in mechanical properties between the hard particles and the soft substrate. Functionally graded Ni-Co-SiC nanocomposite coatings were electrodeposited by gradual variation at peak current density [321]. Fig. 28 shows the chemical composition, SiC nanoparticles content and grain size throughout the thickness profile. It can be observed that by increasing the current density from 2 to 15 A dm⁻² during the coating process, grain size and Co content are reduced along the thickness profile. However, the SiC nanoparticles content is increased towards the surface.

The peeling test on these coatings indicated that they exhibited enhanced adhesion to the substrate compared to uniform coatings [321]. In fact, the value of mismatching at the coating/substrate interface is reduced and less stress is created at the interface due to the gradual change in the number of nanoparticles. Due to higher micro-hardness and better adhesion of these coatings, the wear resistance and corrosion resistance are enhanced [239,286,321,362–365]. Thus, low internal stresses and high adhesion of the coating to the substrate are two important factors in corrosion and tribological behaviour of coatings for prolonged working conditions.

19.2. Ni–Co multilayer coatings

Electrodeposition has various advantages over electroless technique including low cost, higher deposition rate, more stable baths, high efficiency and flexibility (single layer or multilayer deposition as intermittent or gradient). Ni–Co multilayer coatings are able to be electrodeposited from one bath containing both Co and Ni ions by the alternative change of current density or pulse parameters such as duty cycle. The properties of the coatings are a function of layer thickness and composition [366]. Fig. 29 shows the cross-sectional micrograph of
According to the Maltz model \cite{97}, inhibition of the more noble metal is due to surface blocking by the adsorbed species.

Sasaki et al. \cite{94} presented a diffusion model by using the competitive adsorption impact and blockade act of hydrogen atoms. According to this model, the included metal mono-hydroxide adsorption from the elemental bath is based on a Langmuir isotherm, whereas from a binary point of view, Ni-Co baths obey competitive Langmuir adsorption \cite{94}:

$$\theta_i = \frac{K_{iC_i}}{1 + \sum_{j=1}^{n} K_{jC_j}}$$

(44)

By defining \(\theta_i\) and \(k\theta_o\) as the number of adsorption sites and a factor of pre-exponential kinetics, respectively, the rate constant is corrected as the following equation owing to the changing number of the surface sites \cite{94}:

$$(k\theta_o)_{\text{alloy}} = (k\theta_o)_{\text{elemental}} \frac{K_{\text{alloy}}}{K_{\text{elemental}}}$$

(45)

In this relationship, \(K_{\text{H}}\) is the overall rate constant for a reaction involving two molecules. Surface coverage of the metals in elemental electrodeposition is lower than that of metals in alloy electrodeposition due to the adsorption deference between competitive Langmuir and single metal.

As recognised by the investigators, theoretical predictions of these models are a function of the numerical values chosen for the parameters. There is no quantitative fitting to the experimental result and only numerical comparisons are presented. Vazquez-Arenas \cite{106} have suggested a model based on statistical data that fits the model to experimental results for Ni-Co codeposition. In this model, the 1-D flux of species Ni(II), Co(II), H\(^+\) and OH\(^-\), as follows:

$$N_j = -D_j \frac{\partial C_j}{\partial y} + \nu_j C_j$$

The solution velocity \((\nu_j)\) can be expressed by:

$$\nu_j = -0.51023 \Omega^{1/3} \nu^{-1/3} \nu^2$$

(47)

Under steady-state conditions, the balance of materials within this layer are determined as below \cite{106}:

\(- \nabla \cdot N_{\text{Ni(II)}} = 0\)

(48)

\(- \nabla \cdot N_{\text{Co(II)}} = 0\)

(49)

\(- \nabla \cdot N_{\text{H}^+} + \nabla \cdot N_{\text{OH}^-} = \nabla \cdot N_{\text{B(OH)\(_3\)}} + \nabla \cdot N_{\text{B(OH)\(_3\)}} = 0\)

(50)

\(- \nabla \cdot N_{\text{B(OH)\(_3\)}} = 3 \nabla \cdot N_{\text{B(OH)\(_3\)}} = 0\)

(51)

The calculations indicate that the B(OH)\(_3\) flux controls the pH at the surface during Ni-Co alloy deposition.
21. Conclusions and future outlook

This review has considered Ni–Co electrodeposited coatings and their scope, the mechanism of deposition, deposition techniques, parameters affecting microstructure and alloy composition, deposit properties (physical, mechanical, magnetic, corrosion, high temperature oxidation features and thermal stability of Ni–Co deposits) as well as possible structural patterns in Ni–Co coatings. The unique and suitable properties of Ni–Co alloys and nanocomposite coatings render these coatings a desirable choice in corrosion, wear, mechanical and electrocatalytic applications. Modification of Ni–Co coatings by structural patterning, such as functionally graded and multilayer Ni–Co coatings, improves the corrosion and tribological properties. This review has endeavored to provide a summary of collated information on important parameters, electroplating baths, the mechanism of Ni–Co deposition, methods of electrodeposition and the resultant properties of Ni–Co alloys and composite coatings. Aspects requiring further R & D can be listed:

1. As discussed in Sections 8.2 and 8.3, pulse and pulse current reversal electrodeposition can produce coatings with uniform microstructure and chemical composition. Applying anodic current in pulse reverse plating lowers hydrogen reduction and internal stresses. However, there is scarce and contradictory information regarding the deposition mechanism in PRC methods and its effect on anomalous deposition of Co in these coatings.

2. Incorporation of nanoparticles in the coatings leads to enhanced characteristics such as better corrosion resistance, higher hardness and wear resistance, suitable mechanical properties, better thermal stability and oxidation resistance. Development of strategies such as the deployment of horizontal electrodes to increase the nanoparticle content in the coatings may improve the properties of Ni–Co coatings. Usage of a mixture of nanoparticles with various purposes (such as hard particles with self-lubricating particles) in the electrolyte facilitates the deposition of multi-purpose coatings.

3. Electrocatalytic properties. As seen in Section 14, Ni–Co coatings exhibit better electrocatalytic properties than pure Ni. Hydrogen production using Ni–Co coatings can be improved by the implementation of additional steps, and adding various additives in the Ni–Co electrolytes such as (1) producing special morphologies, such as nanocones, via additional crystal modifiers such as polyethylene glycol, and adding sulfur and phosphorus sources to the electrolyte for electroplating Ni-Co-sulfide and Ni-Co-phosphide coatings. Metallic sulfides and phosphides are excellent electrocatalysts [375,376]. These characteristic can be improved further with the addition of nanoparticles to the coatings and employing PRC electrodeposition.

4. Modifying structural patterns. As seen in Sections 19.1 and 19.2, functionally graded and multilayer structures have been successfully fabricated. Electrodeposition of Ni–Co multilayer coatings with thin layers in the range of nanometer will improve corrosion resistance and mechanical properties such as toughness, hardness and wear resistance.

5. Thermal stability and high-temperature applications. Thermal stability of Ni–Co coatings can be improved with the addition of a third alloying element such as phosphorus and boron. However, the high-temperature resistant coatings such as diffusion coatings and thermal barrier coatings are much better than Ni–Co electrodeposited coatings. The properties can be improved further by additional treatments such as aluminising, resulting in nickel and
cobalt aluminides.

6. Additive manufacturing. The electrodeposition of iron-group metals including Fe, Ni, and Co is probably the easiest alloy system. Therefore, Ni–Co coatings are a suitable candidate for the production of special members via additive manufacturing. Electrodeposition additive manufacturing is now routinely used for the development of certain printed circuit boards, integrated circuits, and hard drive components. Fig. 31 indicates probable future applications of Ni–Co deposited alloys across diverse industrial sectors.

References

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