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Tribological and Corrosion Performance of Electrodeposited Nickel Composite Coatings

Nicholus Malatji and Patricia A.I. Popoola

Additional information is available at the end of the chapter

Abstract

The inclusion of second-phase particles in nickel-based matrix to fabricate composite coatings presents a promising solution to combating corrosion and wear deterioration of materials during service. Composite coatings possess better surface properties such as wear resistance, high microhardness, thermal stability, and corrosion resistance than the traditional nickel coatings. Their excellent properties enable them to be used in advanced industrial applications where they will be constantly exposed to severe and degrading environments. There are various surface modification techniques that are employed to produce these coatings and electrodeposition has received wide range of use in fabrication of nickel matrix composites. This technique is associated with low cost, simplicity of operation, versatility, high production rates, and few size and shape limitations. To produce advanced electrodeposits with better performance during application, the optimization and further developments of the process remain vital. Therefore, this chapter aims to review the electrofabrication and properties of nickel composite/nanocomposite coatings for corrosion and wear applications.

Keywords: Electrodeposition, nickel composite coatings, corrosion resistance, wear resistance, hardness

1. Introduction

Nickel matrix composite/nanocomposite coatings have gained a variety of use in many industrial applications where high wear and corrosion performance are required. The applications where these coatings are employed include automotive, aerospace, electronics, petrochemical, nuclear, marine, and many more [1,2]. The incorporation of nanostructured particles into the matrix imparts special characteristics that are not exhibited by the traditional micro-sized composite coatings. The nanocomposite coatings possess improved properties

such as high hardness, excellent corrosion resistance, thermal stability, wear resistance, and self-lubrication properties [3]. The nanoparticles incorporated into the matrix include those of metal oxides, carbides, nitrides, borides, polymers, and carbon-based materials [4–6].

Electrodeposition is one of the surface modification techniques that are used to fabricate nickel nanocomposite coatings. This technique has several advantages over the other processing methods which include low cost, simplicity of operation, versatility, high production rates, industrial applicability, and few size and shape limitations [7]. However, co-deposition of nanostructured inert particles using electrodeposition has its own challenges. Agglomeration of particles in the electroplating bath, inhomogeneity in the distribution of particles in the matrix, and low content of particles in the coatings are some of the drawbacks associated with this process [8]. These problems compromise the quality of the coatings and result in poor performance during application. Therefore, proper process development and optimization are required to counteract the limitations.

Many researches have been conducted in an attempt to address these limitations. Additions of chemical agents into electrolytic solutions to aid co-deposition of the particles have been found by many researchers to reduce agglomeration of particles and increase their incorporation in the matrix. These additives disturb the electrostatic stabilization of the particles and hence promote their suspension in the solution [9]. Pulse current electrodeposition is another method that has been employed to enhance co-deposition and improve uniform distribution of particles. This type of plating has three independent variables for controlling co-deposition as compared to direct current plating which only has one variable [10]. Ultrasonic energy has also been used to improve the inclusion of particles into the metal matrix. It enhances mass transport of particles to the cathode for co-deposition, reduces the thickness of the diffusion layer, and disperses the particles in the electrolyte [11,12].

2. Electrodeposition of nickel composite/nanocomposite coatings

Electrodeposition of composite coatings has been studied and researched by several scholars over the past few decades. The focus of the research is centred around the development and fabrication of advanced and novel surface coatings that can withstand both physical, chemical, and mechanical deterioration under service conditions. In order to produce these high-quality coatings, the mechanism of co-deposition of reinforcement particles with the matrix, optimization of the process operating parameters, and the properties of the resultant deposits need to be fully understood.

3. Basics of Electroplating of Nickel

Electroplating of nickel involves the passage of current between two electrodes (anode and cathode) immersed in an electrolyte containing nickel salts to cause dissolution of Ni^{2+} ions in the anode to be deposited at the cathode. Equation 1 and 2 show the anodic and cathodic

reactions that take place during nickel deposition. The anode is mainly a nickel plate while the cathode is any metal or material that needs to be protected or decorated. The nickel ions deposited at the cathode are replenished by those formed as the result of the dissolution of the anode. According to Faraday's law of electrolysis, the amount of nickel dissolved at the cathode is equal to the amount of nickel deposited at the cathode, which is directly proportional to the product of current and time [13].

Anodic:

$$Ni \rightarrow Ni^{2+} + 2e^-$$ (1)

Cathodic:

$$Ni^{2+} + 2e^- \rightarrow Ni$$ (2)

There are many bath solutions that have been developed for producing different types of nickel deposits. The ones that have gained more usage include the Watts and sulphamate baths. These plating baths are reinforced with surfactants and other additives to improve the quality of the deposits such as brightness, surface morphology, and other functional properties.

4. Mechanism of Co-deposition

Many models have been developed to understand the mechanism of co-deposition of particles into metallic matrix. These models predict the processes that are involved during particle co-deposition and their adsorption rate into the coatings. The processes include electrophoresis, mechanical inclusion, adsorption, and convective-diffusion. One of the most used and accepted model by scholars is Guglielmi's two-step adsorption model. In the first step of particle incorporation, the particles are loosely adsorbed on the cathode covered by a cloud of metal ions. Strong adsorption of particles follows in the second step with current density playing a key role in the particles to be strongly adsorbed on the cathode. The strongly adsorbed particles are embedded into the growing metallic layer [14]. The author related the volume fraction of co-deposited particles (α) to the volume percent of particles suspended in the plating bath (C) with the Langmuir adsorption isotherm as shown in equation 3

$$\frac{C}{\alpha} = \frac{Mi_o}{nF\rho_m v_o} \exp(A - B)\eta \left(\frac{1}{k} + C\right)$$ (3)

where is the atomic weight of the electrodeposited metal i_o the exchanging current density, the valence of the electrodeposited metal, F the Faraday constant, ϱ_m the density of electrodeposited metal, the overpotential of electrode reaction, $i = i_o \exp(A \rightarrow)$ and k the Langmuir isotherm

constant, mainly determined by the intensity of interaction between particles and cathode. The parameters v_o and B are related to particle deposition, and both play a symmetrical role with the parameters i_o and A related to metal deposition [15]. Ref. [16] improved Guglielmi's model by using three modes of current density to differentiate the reduction of adsorbed ion on the particles. This new model involved three steps, where in the first step particles are convectively forced to the surface followed by loose adsorption and then irreversible incorporation of particles into the matrix by reduction of adsorbed ions. Ref. [17] incorporated a third-order polynomial equation to further improve Guglielmi's model. This corrective factor will help account for the effects of adsorption and hydrodynamic conditions. Many other models have been developed which involved statistical approach to predict the chances of particles being included into the deposit. However, all these models cannot predict the effect of particles on electrocrystallization and are limited to specific conditions.

The manner of incorporation of particles into metal matrix depends mainly on the electrodeposition process parameters. Some of the most important parameters include the speed at which the bath is stirred, the applied current density, and electrolyte composition. Bath agitation serves as a medium that assists particles to be transported to the cathode, while applied current density and electrolyte composition are responsible for the formation of ionic cloud around the introduced particles. There are three possibilities for particles to be incorporated in to a metal matrix [18]:

- Coatings that are just covered by adsorbed particles on the surface.

- Coatings containing entrapped particles and

- Coatings containing particles truly embedded uniformly into the metal matrix.

A schematic diagram of particle incorporation into a metal deposit is shown in Figure 1. The manner in which particles are incorporated into the coating determines the quality of the resulting deposits. Coatings containing uniformly distributed and truly embedded particles exhibit superior properties than the other manners of incorporation.
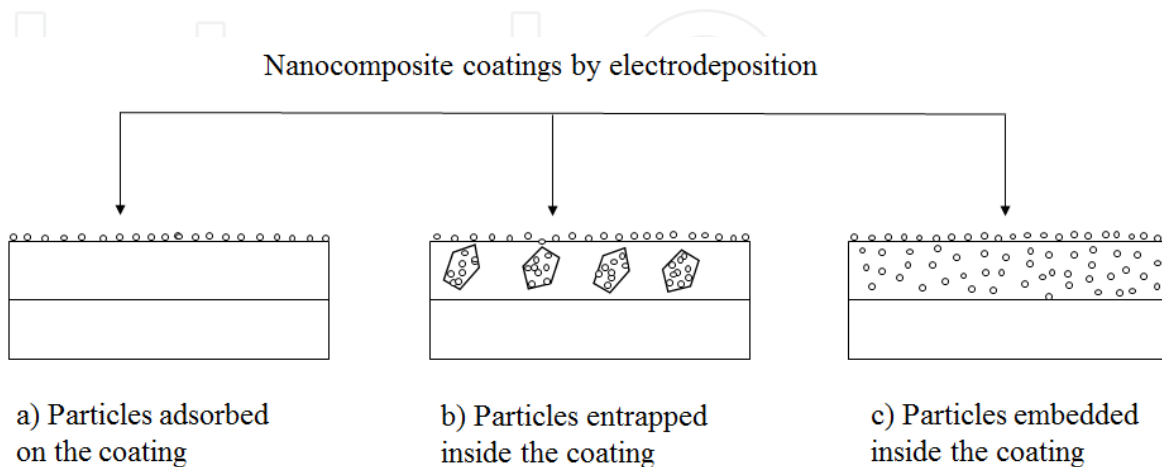

Nanocomposite coatings by electrodeposition

a) Particles adsorbed on the coating

b) Particles entrapped inside the coating

c) Particles embedded inside the coating

Figure 1. Schematic representation of different co-deposition possibilities

5. Effect of process operating parameters

Electrodeposition of metal matrix nanocomposite coatings is very complex and requires the process operating parameters to be optimized to produce high-quality deposits with improved functional properties. There are several parameters that are very important in fabrication of the composites but only the following will be covered in this review. These include current density, type of current, particle size, particle loading, stirring speed, bath composition, time, and temperature. The typical bath composition and parameters are shown in Table 1.

Bath Composition	g/l	Parameters	
$NiSO_4.H_2O$	145	Time	2–16 min
NaCl	16.67	Current density	3.75 mAcm^{-2}
H_3BO_3	11.11	Temperature	40–80°C
Fe_2O_3	2.37–76	pH	4.6
		Anode	Nickel rod
		Cathode	Mild steel

Table 1. Bath composition and plating parameters [35]

5.1. Current

Current is one of the most important parameters that are used to control the plating process. It is used to reduce dissolved metal cations in solution to form a protective layer on the cathode. The rate in which metal cations are transferred to the cathode for plating determines the amount of second-phase particles that will be incorporated into the metal matrix [14]. Higher current densities enhance deposition rate and thus increasing the chances for the reinforcement of particles to be adsorbed on the cathode. The current density was found to influence the content of alumina particles present in the Ni–P matrix [19]. The increment of current density from 5 to 20 A/dm^2 increased the content of Al_2O_3 particles from 7.75 to 13.65 vol.%. The hardness and phosphorus content of the deposits were also found to be affected by varying the current density. The hardness property of the coatings had direct relationship with the increase in current density while the phosphorus showed an inverse correlation. Ref. [20] obtained similar results when they studied the incorporation of CNT particles into Ni matrix. The CNT content in the coating increased with rising current densities. However, it is not in all cases where increasing current density during plating yields coatings with high micro-hardness values and particle content. Ref. [21] established an optimum current density of 0.8 A/dm^2 for fabrication of Ni–Cr_2O_3 nanocomposite coatings with excellent mechanical proper-ties. Increasing the current density beyond the optimal conditions had no positive influence on the microhardness values of the resultant deposits. Plating in lower current densities requires time to achieve the desirable thickness and hence gives more time for the particles to be available at the cathode. This increases the chance of the particles to be homogenously incorporated into the matrix, leading to formation of harder surfaces due to dispersion

hardening. Higher current densities increase deposition rate but reduce controllability of the co-deposition process. Ref. [22] obtained similar results when nano-titania particles were added into a nickel electrolyte. At constant pH, increasing current density yielded deposits with low TiO_2 content and increased mean grain size. Table 2 shows the effect of current density on compositional, structural, and mechanical properties of N–W and Ni–W–Al_2O_3. Lower current densities favour good incorporation of tungsten in the matrix, high macro-residual stresses, and small crystallite sizes. However, incorporation of alumina also depends on the type of ceramic phase. Sigma Aldrich alumina particles follow the trend of tungsten, and inclusion of Taimicron alumina shows a deviation. Therefore, it can be concluded that optimization of operating current is required for electrodeposition of nickel composite/nanocomposites to produce coatings with enhanced surface properties.

j (A/dm^2)	W (wt.%)	Al_2O_3 (%)	(MPa)	k (nm)
Ni-W				
4	44±0.9	-	447±67	8
5	42.4±0.8	-	217±76	10
7	40.5±1.0	-	114±33	10
8	37.6±0.7	-	-209±58	13
Ni-W-Al_2O_3 (SA)				
4	37.0±0.6	1.7±0.2	-	8
5	35.3±0.7	1.8±0.2	1150±46	9
7	31.0±0.6	1.1±0.1	1044±114	11
8	26.6±0.5	0.5±0.3	710±85	12
Ni-W-Al_2O_3 (TA)				
4	35.6±0.7	6.4±0.3	-	6
5	34.4±0.7	5.4±0.2	1360±102	7
7	28.5±0.6	5.6±0.2	1460±80	6
8	23.3±0.5	7.0±0.3	781±186	5

Table 2. The effect of current density on the content of tungsten and alumina in the Ni matrix, macro-residual stresses and crystallite size [23]

Direct current plating had been and is still commonly used for fabrication of thin films. However, this plating technique is associated with slow deposition rates and many defects in
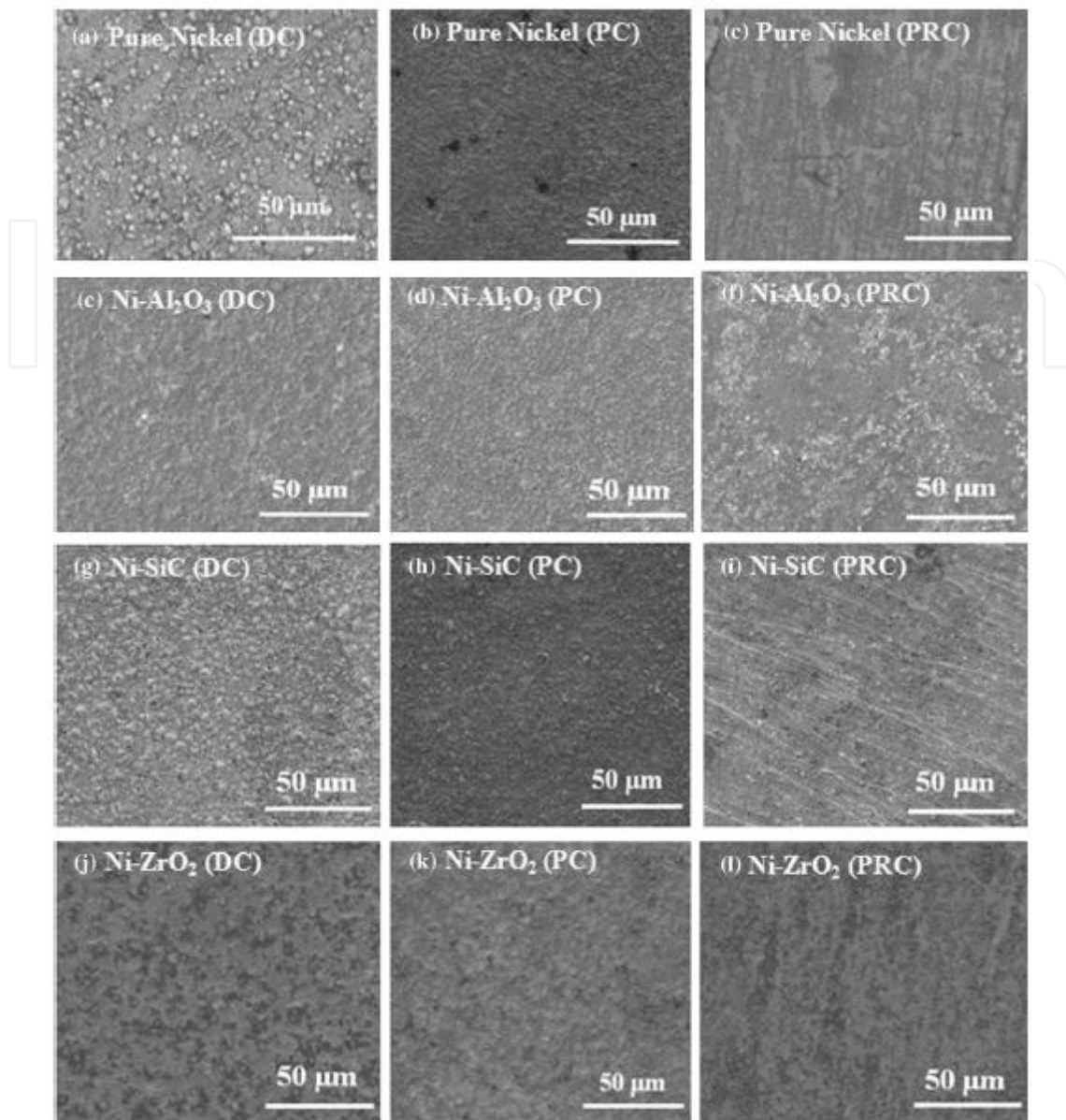
Figure 2. SEM micrographs of the plated samples [24]

the resultant deposits. Pulse current (PC) and pulsed reverse current (PRC) electrodeposition techniques have been developed to address the drawbacks associated with this deposition method. These methods allow better control of the structure and properties of the coatings [25]. The methods have several operating parameters (such as time period in which the pulses are imposed, relaxation time, pulse frequency, and pulse current density) that can be varied and optimized to achieve better deposit with enhanced surface properties as compared to the conventional method. Fine microstructures can be obtained from these plating methods by allowing high overpotential and low surface diffusion which favour the formation of new nuclei and thus perturbing grain growth [9]. Ref. [24] compared the morphologies and mechanical properties of nickel composite coatings produced by different electrodeposition techniques (DC, PC, and PRC). PC and PRC deposits exhibited fine and homogenous micro-

structures more than DC ones (shown in Figure 1). The surface roughness was also reduced and the content of the reinforcement particles in the coatings increased. The high content and uniform Al$_2$O$_3$, SiC, and ZrO$_2$ particles incorporated into the nickel matrix improved the microhardness and tribological properties of the deposits. Ref. [9] obtained similar results when Ni–Al$_2$O$_3$ composite coatings fabricated from both DC and PC plating at the same current density were compared. The particle content in the coating increased linearly with increasing current density for PC deposits, while the increase of particle content in DC coatings became negligible in current densities higher than 3 A/dm^2.

5.2. Particle loading

The concentration of the reinforcement particles in the solution to be co-deposited with the matrix has a significant influence on their adsorption rate at the cathode. According to Guglielmi's two-step adsorption model, high particle content in the plating bath increases the adsorption rate of the particles on the cathode [14]. However, when the particle concentration in the bath reaches saturation, agglomeration occurs leading to reduced incorporation or formation of deposits with surface defects [26]. Inclusion of TiO$_2$ nanoparticles into nickel matrix was found to be dependent on the bath particle loading. The least bath particle loading of 5 g/l of TiO$_2$ yielded the lowest weight of particles of about 1.8 wt.%, while introducing 15 g/l of the particles increased the particle content in the deposit to be about 3.8 wt.% at the constant current density of 40 mA/cm^2 [7]. Similar behaviour was obtained throughout the experiments when other current densities were used (see Figure 2).

The optimum particle loading for SiC particles into nickel matrix was found to be 20 g/l by ref. [4]. Addition of more particles beyond the optimal levels led to decrease in incorporation of the particles into the coating. The decrease was ascribed to the agglomeration of the SiC particles due to their poor wettability. As much as high content of particles in the bath increases their availability at the cathode, the capturing capacity of the growing metal remains unchanged [27]. Therefore, particle entrapment into the matrix requires conducible conditions to produce high-quality coatings with enhanced surface properties.

5.3. Particle size

Nanoparticles have gained wide use in fabrication of nanocomposite coatings due to their excellent and attractive properties. Their incorporation into metal matrixes is associated with better surface morphologies, improved corrosion resistance, thermal stability, and excellent mechanical properties as compared to their micron and submicron counterparts. However, co-deposition of these particles is associated with many challenges. According to the study conducted by ref. [27], zeta potential of the particles is one of the major driving forces responsible for how micron-, submicron-, or nano-sized particles behave differently in the plating bath. The results showed that micron-sized SiC particles exhibited more negative than the nanoparticles. This indicates that the micron-sized SiC particles are easily adsorbed by the nickel cations. The higher the positive or negative zeta potential the particles possess, the more stable they are in solution since they repel each other and thus limiting the formation of aggregates. Due to the high repulsion forces that exist between the micron-sized particles,
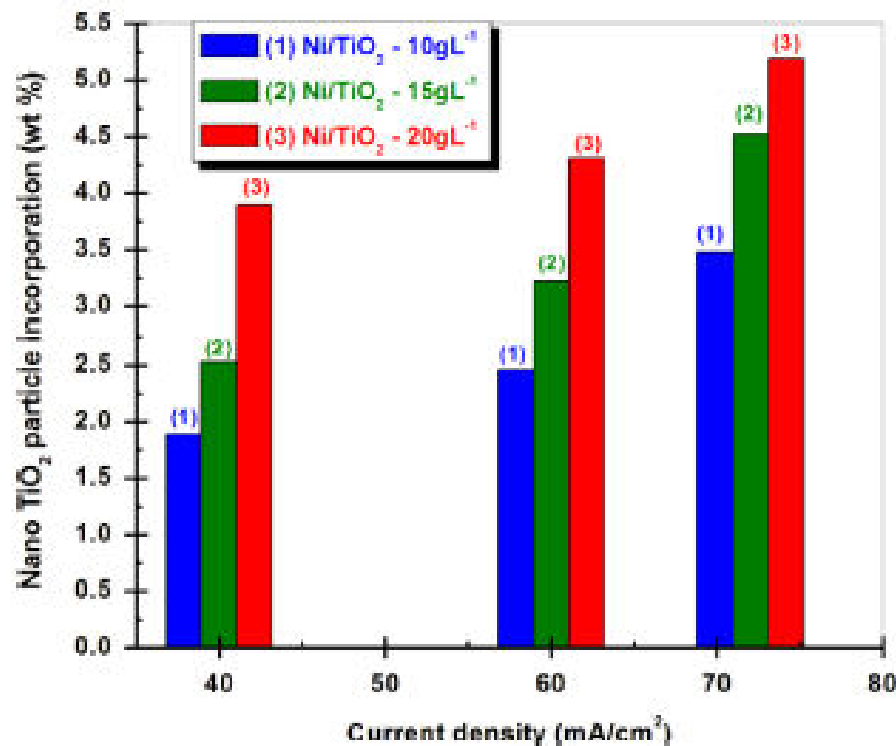
Figure 3. Correlation between TiO$_2$ content in the deposit with current densities [7]

electrodeposition under high particle loading is possible and thus increasing the chance of more particles to be embedded in the matrix. The authors found that the micron-sized particles were uniformly distributed in the coating as compared to agglomerated nanoparticles. However, these particles were not uniformly distributed along the surface in normal direction which can severely affect the fabricated film properties. Ref. [28] found that particles with average size of 5 μm had lower hardness values than their 10 and 50 nm counterparts. This result can easily be explained by the Hall-Pecth equation (4):

$$\sigma = \sigma_o + A / d^{1/2} \tag{4}$$

where *d* is the grain size and σ$_o$ and *A* are constants. According to the equation, it can be seen that smaller grain size has a positive influence on the yield strength since the relationship is inversely proportional. Nanoparticles also has the ability to fill the microholes, gaps, and other surface defects present on the surface of the matrix than micron- or submicron-sized particles [29]. This results in fine microstructures with minimal surface defects and better functional properties. The size of the particles also affects the amount of particles that will be incorporated as shown in Table 3. Finer particles are difficult to incorporate in the matrix than coarser ones. Therefore, the operating parameters such as stirring speed, pH, and current density are very crucial to be optimized to facilitate better uniform distribution and high incorporation rate of fine particles in the deposit.

Particle size	SiC in coating (vol%)	Number density (particles cm²)	Distant between Particles (nm)
10 nm	15.2	2.89×10^{17}	1.51×10^{1}
50 nm	22.02	3.37×10^{15}	6.67×10^{1}
5 nm	55.24	8.44×10^{9}	4.91×10^{3}

Table 3. Volume percent and number density of SiC particles in composite coatings with the distance between particles [28]

5.4. Bath composition

Electrolyte ionic strength, bath additives, and pH are some of the operating parameters that affect the zeta potential of second-phase particles as explained before. The pH of the bath is a function of bath composition which includes the electrolyte and chemical additives. Strong acid or bases can be added to adjust the pH to be acidic or alkaline. Particles have different zeta potential at different pH depending on their nature. Therefore, various ceramic particles will have more positive or negative charge on either acidic or alkaline conditions. Titania particles were found to exhibit negative zeta potential in acidic solution of pH= 4.3 and positive zeta potential at alkaline conditions with pH of 9.5 [30]. A maximum particle content of 4.3 wt. % was achieved from alkaline baths while 3.3 wt.% resulted from acidic solutions. This shows that the conducible co-deposition of TiO_2 particles with nickel is achievable under high pH values at particle loading of 10 g/l and current density of 1 A/dm². A decreasing trend (from 2 to 5) in particle incorporation with increasing pH values was noticed by ref. [22]. At plating conditions of pH=2, particle loading of 100 g/l and current density of 5 A/dm², a maximum of 8 vol.% of TiO_2 incorporation was achieved. However, the authors did not study further the behaviour of the particle incorporation in alkaline solutions. The results obtained by the different authors show that particle incorporation depends on several factors than pH of the solution. The electrolyte is the carrier of electroactive species which are responsible for the formation of ionic cloud around the particles to enable their transportation to the cathode for entrapment in the matrix [31]. Variation of nickel sulphate in the bath from 200, 250, and 300 g/l showed significant effect on the incorporation rate of reinforcement particles as reported by ref. [28]. The volume of incorporated SiC particles increased with increasing nickel sulphate content upto 250 g/l and decreased when the concentration was further raised. The effect of electroactive species on SiC particles content present in the coating is shown in Figure 3. Electroactive species to adsorb on the strengthening particles is not sufficient at low nickel sulphate concentration, reducing their entrapment in the coating. Rapid reduction of nickel ions occurs at higher nickel sulphate concentration before the particles can be properly co-deposited, leading to low adsorption rate. High ionic strength of plating solution has also been reported to promote particle agglomeration causing the formation of deposits with defects and low particle content [26].

Chemical additives are added in the bath to serve different functions. These functions include controlling the final appearance of the deposit, altering crystal growth kinetics, and influencing the zeta potential of the second-phase particles. The addition of SDS (sodium dodecyl sulph-
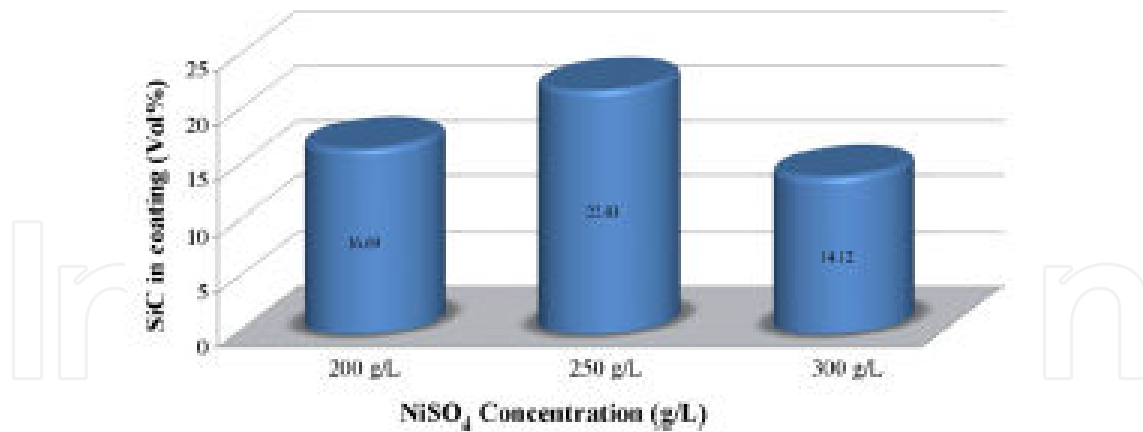
Figure 4. SiC volume percent for various nickel sulphate concentrations in the bath [26]

onate) and saccharine promote smoothening of the Ni coating surfaces [8]. The coatings fabricated from solutions containing the additives exhibited smaller grain sizes. The addition of ethanol (25 and 50 vol.%) into nickel bath solution induced grain refinement resulting in finer microstructure [32]. The effect of ethanol on the crystal size of nickel and nanocomposite coatings is shown in Table 4. The truncated pyramidal crystals were modified to globular grains as a result of the presence of ethanol in the electrolyte. The crystal size of 85 nm of the Ni–Al$_2$O$_3$ nanocomposite coating produced from additive free bath was reduced to 25 nm when ethanol was added.

Vol% Ethanol	Pure Nickel	Ni–Al$_2$O$_3$
0	131	85
25	70	54
50	39	25

Table 4. Effect of ethanol on the crystal size of pure nickel and Ni–Al$_2$O$_3$ nanocomposite coatings

5.5. Stirring speed

Stirring speed is one of the important parameters that control the mechanism of particle incorporation. Mechanical inclusion of particles into the coating forms part of the three processes that are involved in entrapment of particles into a metal matrix [31]. Mechanical agitation aids in the transportation of particles to the cathode to be readily available for adsorption [33]. However, very high or low agitation can have adverse effect on the incorpo‐ ration rate of the particles. Low stirring speeds offer low energy to break the agglomerate to fine particles and hence reduce their availability for incorporation. High stirring speeds are associated with high impinging velocity of the particles to the cathode and not giving enough retention time for the particles to be adsorbed on the cathode [27]. Particle size has an effect on the required stirring speed since it is easier to keep coarse particles in suspension in solution

than the finer ones. Nanoparticles easily agglomerate when they are added in the plating bath. Therefore, fabrication of nanocomposite coatings requires higher stirring speeds than their composite counterparts. Other forms of agitation have been used in literature and these include the use of ultrasonic energy to keep particles in suspension, enhance mass transport, and reduce diffusion layer thickness [34]. A schematic diagram of electrodeposition cell assisted with ultrasonic energy is shown in Figure 4. The use of ultrasound also helps to modify the surface morphologies of coatings fabricated with conventional DC plating technique [10].
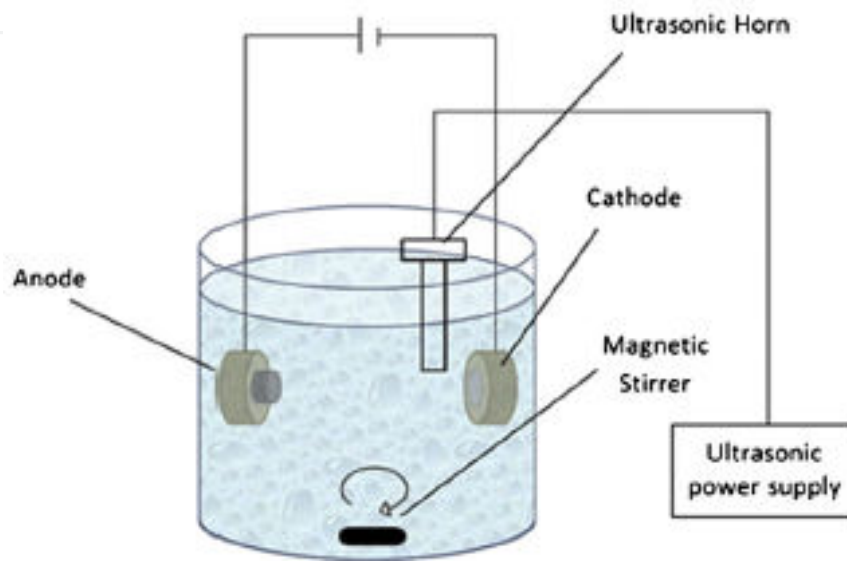

Figure 5. Typical electrodeposition cell assisted with ultrasound energy [34]

5.6. Time and temperature

Particles require time to remain around the cathode to increase the chances of their incorporation. Ref. [35] reported that longer deposition time allows for the formation of thicker and compact coatings with improved microhardness. The highest microhardness values were achieved at a deposition time of 14 min, and beyond this time no adherent spherical globules were formed. Temperature also plays a significant role in co-deposition process. Increase in temperature enhances reaction kinetics, leading to more nickel ions to be transferred to the cathode. The content of SiC particles has been found to be a function of temperature by ref. [36]. Increasing temperature up to 50°C increased the content of the particles in the coating. Above optimal conditions, a decrease in incorporation rate was observed. Thermodynamic movement of ions improves with temperature and the particulates' kinetic energy also increases. This causes rapid deposition, which poses a risk on the control of crystal growth and uniformity in distribution of particles within the matrix. According to ref. [37], increase in temperature reduces adsorpability of the particles and hence decrease in overpotential cathode and electric field. Ref. [35] obtained similar results when Fe_2O_3 nanoparticles were co-deposited with nickel.

6. Nickel composite/nanocomposite coatings and their properties

Nickel composite coatings have been developed to withstand challenging and aggressive conditions during service. These coatings exhibit excellent corrosion resistance, tribological properties, and thermal stability. There are several types of nickel base matrix composite coatings that have been developed over the past few years. These include Ni, Ni–P, Ni–B, Ni–W, and Ni–Co matrix composites. In this topic, the structural and functional properties of these coatings will be discussed.

6.1. Ni composite coatings

The inclusion of second-phase particles into nickel matrix influences the evolution of the coatings surface morphologies. The nickel matrix characterized by pyramidal crystal structure was changed to spherical structure through the addition of inert titanium nanoparticles [38]. The composite coatings also exhibited smaller crystallite sizes than those of the metallic matrix. Particle loading plays a major part in refinement of grains and the smallest grains can be obtained in optimum conditions. Embedment of GNS–TiO_2 nanocomposite into nickel coatings yielded similar results [39]. The reduction in grain size was attributed to the growth-inhibiting ability of reinforcement nanoparticles which are adsorbed on the grain boundaries and thus restricting further growth. The presence of uniformly distributed nanoparticulates in the matrix reduces surface defects (pores, microholes, gaps, crevices, etc.) in the deposits [40]. Coatings with minimal surface defects possess few active sites for chemical attack and thus improve their corrosion resistance. Addition of 50 g/l of nano-SiC particles in a nickel plating bath reduced the current density of nickel coatings from 7.09 to 0.03 $\mu A/cm^2$ [41]. The Tafel plots of pure nickel and Ni–SiC nanocomposite coatings are shown in Figure 5. Improvement in corrosion resistance is depended on the amount of second-phase particles incorporated, and coatings with higher particle content are associated with increased positive potential shift and lower corrosion currents [42]. These nanoparticles also act as inert physical barrier to the initiation and development of defect corrosion.

Ref. [43] incorporated TiCN (titanium carbon nitride) particles into a nickel matrix and the results obtained were similar to those of SiC. The highest volume of 23.9% TiCN yielded coatings which exhibited the highest potential and lowest current density. Addition of ceria particles into electrolytic nickel solution yielded composite coatings which possessed lower potentials, current densities, and corrosion rates [44]. The results obtained by the authors show that these particles cause cathodic protection when incorporated in a nickel matrix. The particles reduce active surface area and cause blockage on the cathode for HER (hydrogen evolution reaction) to occur. Incorporation of ceramic particles into a metallic matrix does not always guarantee improvement in corrosion resistance of the coatings. The inclusion of carbon nanotubes was found to cause negative potential shift and thus increasing the corrosion rate of the matrix on copper substrate [20]. The poor corrosion resistance shown was due to the porous nature of coatings which was dependent on CNT content. However, ref. [45] obtained different results when Ni–CNT coating was electrodeposited on Ti–6Al–4V alloy. The corrosion resistance was notably enhanced by the presence of CNT. These results show that
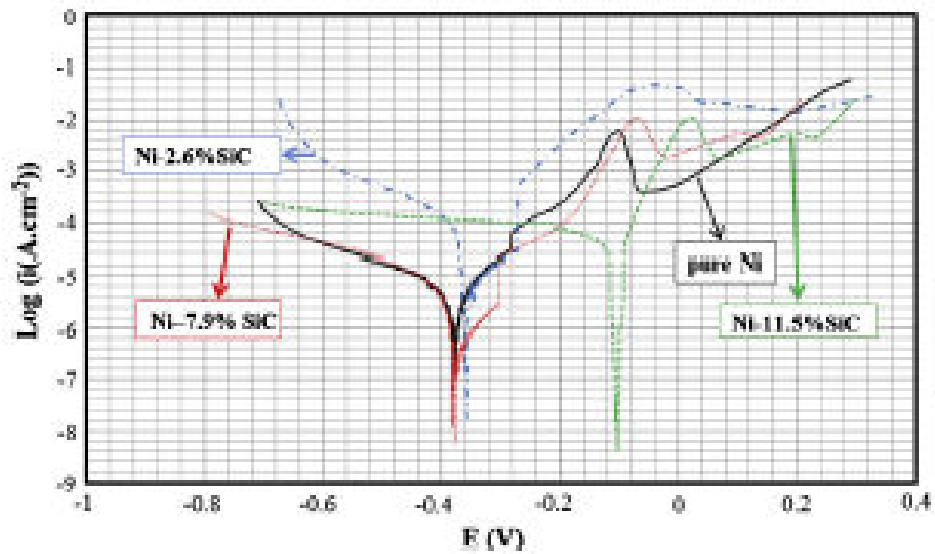
Figure 6. Polarization curves of Ni and Ni–SiC nanocomposite coatings

improvement of functional properties depends not only on incorporated particles but also on different factors such as type of substrate and operating parameters.

Composite	Wear loss mm³	Wear coefficient	Average coefficient of friction
Ni–SiC	10.838×10^{-3}	2.276×10^{-6}	0.798
Ni–Si$_3$N$_4$	4.817×10^{-3}	1.282×10^{-6}	0.890
Ni–Al$_2$O$_3$	8.304×10^{-3}	1.648×10^{-6}	0.845

Table 5. Tribological properties of Ni–SiC, Ni–Si$_3$N$_4$, and Ni–Al$_2$O$_3$ composite coatings [46]

Refined microstructures exhibiting small and uniform grains are also characterized by high hardness and excellent wear resistance. The particles have pinning effect allowing little or no movement of dislocations. Co-deposition of nickel with SnO$_2$ nanoparticles yielded coatings with high hardness, low friction, and better wear resistance [47]. The improvement of mechanical properties was a function of the content of incorporated particles. Samples with the highest ceramic particle content exhibited the highest hardness values, lowest wear volume and friction coefficient. It can be seen from Table 5 that various incorporations yield different results. This is due to the fact that different ceramic materials exhibit their unique properties. Si$_3$N$_4$ particles have been reported to exhibit high hardness and self-lubricating properties; hence, their incorporation into a metallic matrix enhances its tribological characteristics [48]. Other particles that have been reported to possess self-lubricating properties include carbon nanotubes and molybdenum sulphide [45, 49]. The deposits that contain these particles exhibit reduced coefficient of friction and high wear resistance as compared to the matrix.

6.2. Ni–P composite coatings

Ni–P alloy coatings exhibit refined microstructure, high hardness, and good corrosion resistance and high wear resistance under moderate conditions [50]. The good properties displayed by these coatings owe to the formation of stable phases such as Ni_3P that leads to precipitation strengthening. However, their exposure to heat treatment conditions makes them brittle and thus rendering the coatings unfit for wear applications. The hardness of the alloy has also been reported to rise with increasing phosphorus content of up to 8 wt.% and decreases beyond that [51]. The incorporation of nano-carbon was reported to induce a positive potential shift of 60 mV to the Ni–P matrix by ref. [50]. The authors also found that the composite coatings possessed higher potentials and low current density after heat treatment than the non-heat-treated Ni–P and Ni–P–C coatings. The formation of thermodynamic stable phases through the recrystallization of rich phosphorus Ni–P alloy is responsible for the super corrosion resistance exhibited by the heat-treated composites. The hardness property of Ni–P–Al_2O_3 was found to be improved when both P and Al_2O_3 content in the deposit were higher [51]. This result obtained by the authors show that phosphorus and second-phase particles content in the deposit have significant influence on the mechanical properties of Ni–P composite coatings. The addition of SiC particles in Ni–P matrix reduced the roughness of the coatings [52].

6.3. Ni–Co composite coatings

The evolution of surface morphology of Ni–Co alloy mainly depends on cobalt content in the coating. This inclusion of the metal induces the formation of fine and compact microstructure with globular crystallites [53]. The presence of cobalt in the nickel coatings enhances their corrosion and mechanical properties which are maintained even when the coatings are exposed to elevated temperatures [54]. The incorporation of nano-Si_3N_4 particles improved the microhardness and lowered the friction coefficient of Ni–Co matrix [48]. The increase in microhardness and reduction in friction coefficient were found to be dependent on the quantity of the reinforcement particles present in the coating. Higher Si_3N_4 content in the deposits gave yield to high microhardness and lower wear loss. Si_3N_4 particles possess self-lubricating properties and reduce the load bearing for the matrix. Variation of normal load and sliding speed has been reported to affect the tribological behaviour of Ni–Co–CNT composite coatings [55]. The friction coefficient decreased with increasing normal load and sliding speed. Carbon nanotubes form lubricious transfer layer on the wearing medium during sliding and thus reducing friction. This lubricious transfer layer forms as the result of wear debris that are generated during sliding and accumulate on the counterpart surface. The rate of transfer and accumulation of the lubricious layer is a function of temperature and rises due to the increasing normal load and sliding speed. The friction coefficients of Ni–Co alloy and Ni–CNT composite coatings are shown in Figure 7. Similar results have been obtained by [56]. Ni–Co–MWCNT films fabricated by DC, PC, and PRC electrodeposition techniques exhibited lower friction coefficient and wear rate at high sliding speed.

The inclusion of micro- and nano-sized SiC particles revealed that the presence of these particles in the deposits has a positive influence on the grain growth of Ni–Co matrix [57]. The micro- and nano-composite coatings exhibited small grain sizes and improved functional
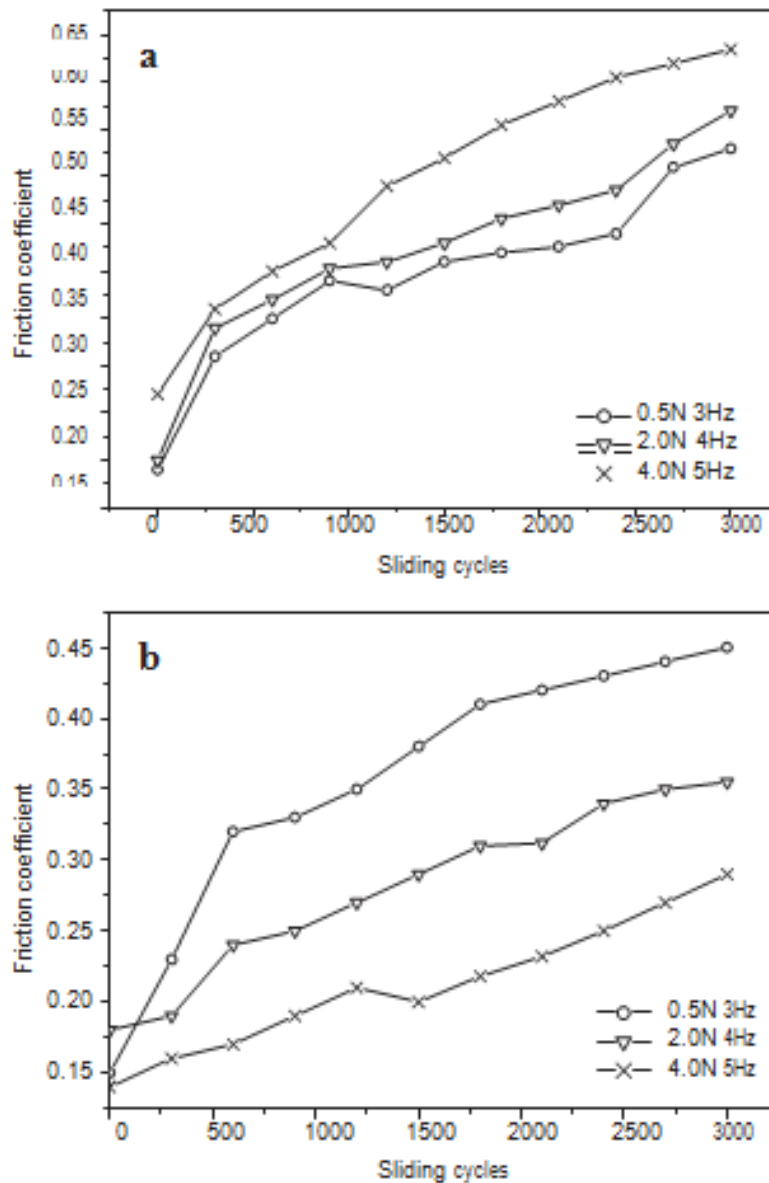
Figure 7. Friction coefficient of (a) Ni–Co alloy and (b) Ni–Co–CNT composite coating under different loads and sliding speeds [55]

properties such as hardness and corrosion resistance. However, the improvement of properties depended also on the size of the particles with nanoparticles strengthened matrixes exhibiting the best enhancement. Incorporation of SiC nanoparticles into Ni–Co matrix also prevents erosion-enhanced corrosion in oils and slurry hydrotransport system [58]. The combined effect of the wear and corrosion resistance of the particles makes it difficult for the turbulence of the flowing slurry to erode the coating and thus minimizing the exposure of the active surface of the substrate to chemical attack. Ref. [59] studied the effect of fly ash on the corrosion resistance of Ni–Co matrix. The inclusion of the fly ash particles yielded deposits with high potentials and low corrosion current. The deposits also exhibited high hardness values as compared to

the Ni–Co matrix, thus proving fly ash to possess better mechanical and electrochemical properties. While reinforcing of Ni–Co matrix with second-phase particles has a positive influence on the resultant deposits, the improvement of functional properties depends on the nature of reinforcement particles and process parameters.

6.4. Ni–B composite coatings

Co-deposition of nickel with boron leads to the formation of stable Ni_3B or Ni_2B phases which improve the hardness, thermal, and tribological properties of nickel coatings. Their exposure to heat treatment further enhances their hardness, resistance to wear degradation, and reduces friction coefficient. During heat treatment, grain coarsening is induced which weakens the hardness of the coatings. The mechanical weakening induced by grain growth is counteracted by the formation of hard and thermodynamically stable Ni_3B particles, hardening the coatings [60, 61]. Increasing boron content favours the improvement of mechanical properties of the coatings, especially hardness and wear resistance [62]. However, Ni–B alloy coatings with high boron content possess corrosion resistance lower than that of the matrix (see Figure 6). Therefore, this effect of boron on the functional properties of the coatings renders alloys to be more suitable for applications where excellent mechanical properties are required.
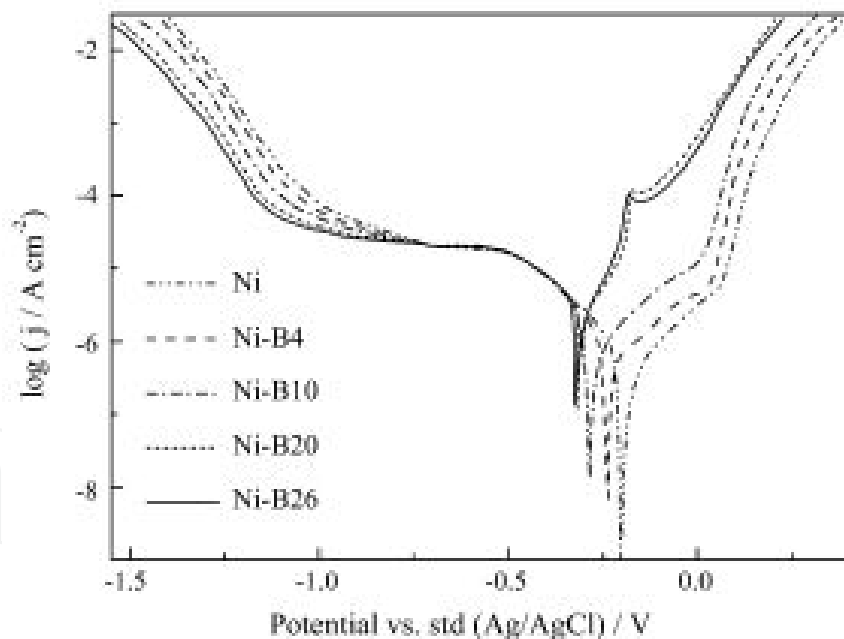

Figure 8. Polarization curves of Ni and Ni–B alloy coatings [62]

The addition of diamond particles modifies the microstructural and hardness properties of Ni–B alloy but has no positive influence on the improvement of its corrosion resistance. However, the combined effects of TMAB (trimethylamine borane) and diamond nanoparticles have significant effect on Ni–B electrochemical behaviour even though it cannot improve the

corrosion resistance of Ni matrix [8]. Sol-enhanced TiO_2 nanoparticles yielded similar behaviour with 12.5 ml/l of the particles increasing microhardness of Ni–B from 677 to 1061 HV. The improvement of hardness was also accompanied by reduction in friction coefficient and low volume wear loss [63]. The TiO_2 sol leads to dispersion strengthening and fining of grains, hence the improvement in hardness and tribological behaviour. Therefore, the incorporation of second-phase particles in Ni–B alloy matrix has not proved to increase nickel coating corrosion resistance, but its mechanical and tribological properties.

6.5. Ni–W composite coatings

The behaviour of Ni–W alloy is similar to that of Ni–B. The presence of tungsten in the nickel matrix improves mainly the mechanical properties of the coatings but not their corrosion resistance [64]. Therefore, research to make Ni–W alloy coatings to possess excellent wear and corrosion resistance has intensified to extend the applications of the coatings. The addition of reinforcement particulates and subjecting the coatings to post-plating heat treatment have been used in an effort to enhance their surface properties. Incorporation of SiO_2 into Ni–W matrix influences the morphology of the coatings and the resultant microstructure is subject to the content of SiO_2 in the coating as shown in Figure 7. The composite coatings are uniform and crack-free. The particles also improved the microhardness and corrosion resistance of the matrix [65]. The lowest particle loading of 2 g/l of SiO_2 yielded coatings with best anti-corrosive properties (see Table 6). The optimum particle concentration of 10 g/l in the bath gave the highest microhardness.

Samples	SiO_2 addition (g/l)	E_{corr}/V	i_{corr}/μA cm^{-2}
A	0	−0.588	13.95
B	2	−0.562	8.76
C	5	−0.580	16.75
D	10	−0.603	24.64
E	15	−0.630	37.43
F	20	−0.672	44.14

Table 6. Corrosion parameters of Ni–W alloy and Ni–W–SiO_2 nanocomposite coatings

Ref. [25] deposited Ni–W–TiO_2 nanocomposite coating using both DC and PC methods. The corrosion resistance for all the deposits increased with the content of TiO_2 in the coating. PC-plated coatings also had superior corrosion resistance than their DC counterparts. However, ref. [66] obtained different results when they plated the nanocomposites using both methods. DC-electrodeposited Ni–W–TiO_2 nanocomposite coatings exhibit inferior corrosion resistance as compared to Ni–W alloy and pulse-plated Ni–W–TiO_2 coatings. Therefore, the current regime and other plating process parameters have significant influence on the improvement
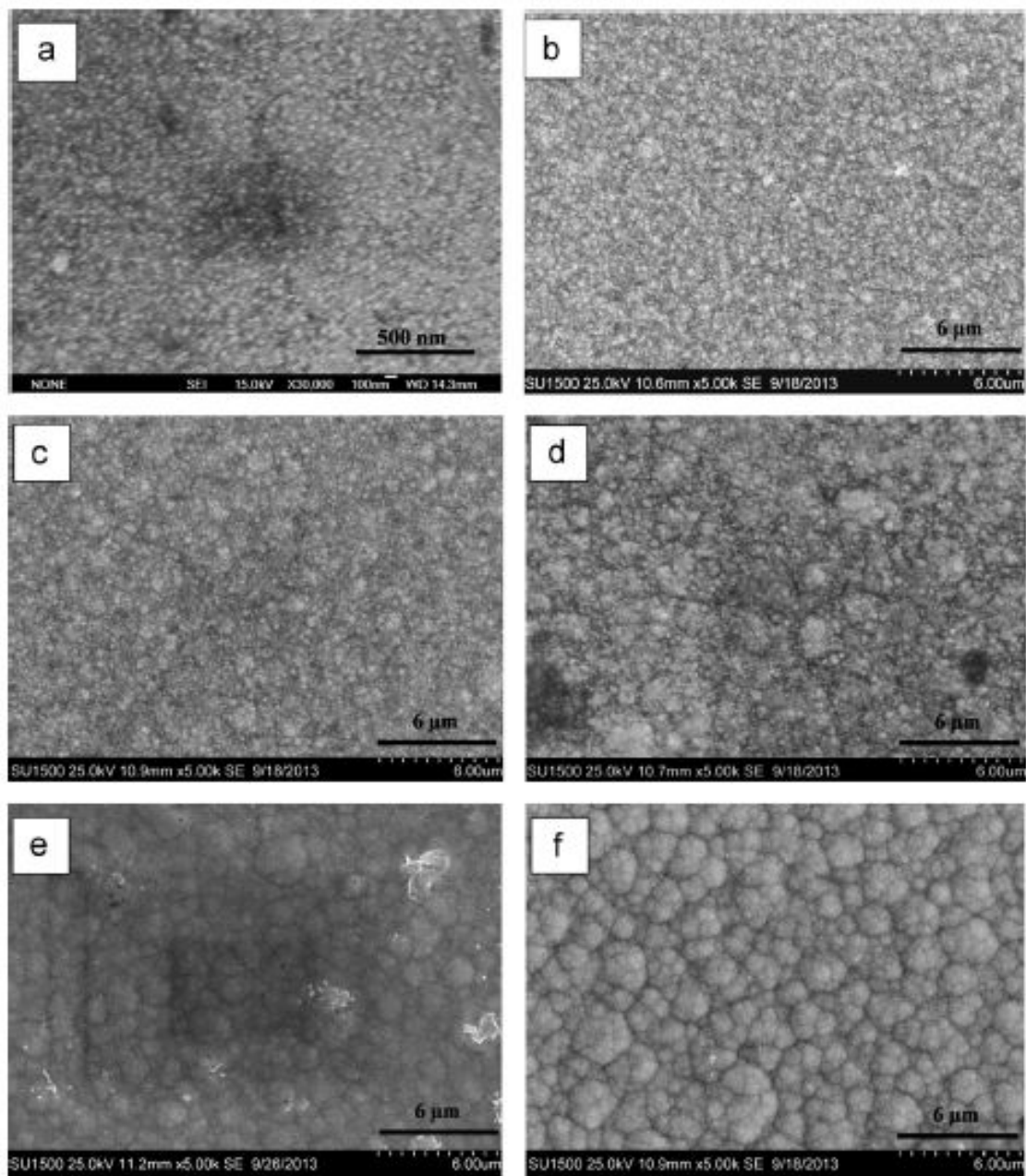
Figure 9. Surface morphologies of Ni–W alloy and nanocomposite coatings [65]

of functional properties. PTFE (polytetrafluoroethylene) particles co-deposited with Ni–W alloy using pulse current electrodeposition showed improvement in morphology, hardness, corrosion resistance, and tribological properties of the deposits [67]. The increase in particle content in the coatings from 0 to 20 g/l had positive influence on the mentioned properties. PTFE particles are chemically inert and possess low coefficient of friction when compared to other polymers. SiC nanoparticles showed similar behaviour when they were incorporated into Ni–W alloy [68]. Boron nitride particles possess excellent self-lubrication properties and reduce the surface roughness of Ni–W alloy, thus decreasing friction of the coatings and improving their wear resistance [69]. The inclusion of the particles also significantly affects the

corrosion resistance of the coatings (30 mV potential shift). Ref. [70] reported MoS_2 particles to lower friction the coefficient of Ni–W matrix and enhance its tribological properties.

7. Applications

Electroplated nickel composite/nanocomposite coatings find applications in machining and finishing of tools requiring excellent corrosion and wear resistance, low friction, and high thermal stability. Wear, friction, and corrosion pose a serious threat to machine lifespan, energy consumption, and performance. These phenomena also compromise the safety of the personnel where the machine is used. Therefore, engineers prefer machines that have long lifespan, save energy, and have better performance throughout its service life. These machines or tools are made of lighter and cost-effective materials such as aluminium and steel, to enhance their quality; materials harder and chemically stable than them are used as coatings to protect them from surface degradation. Nickel, nickel alloy, and composite/nanocomposite coatings are perfect candidates for improving the quality of these materials.

Ni–SiC nanocomposite coatings are used to offer wear protection of aluminium-made engine pistons in automotive industry [70]. These parts operate under high temperatures and wear conditions. Other candidates that perform similar function of lining of cylinders in aluminium engines are Ni–Al_2O_3, TiO_2, WC, Cr_2O_3, etc. [71].

Electrodeposited Ni/diamond coatings have found applications in grinding and cutting tools, such as precision cutting wheels for dicing semiconducting silicon plates [71]. These also include nickel alloy composite coatings such as Ni–W reinforced with diamond nanoparticles. These coatings exhibit high hardness, excellent wear resistance, and elevated thermal stability.

Ni–PTFE composite coatings find use in precise mechanical parts [17]. These possess self-lubricating properties and are convenient for applications that require low friction. Other suitable coatings to perform similar functions are Ni–CNT, MoS_2, graphite, Si_3N_4, Ni–B, and BN composite coatings. They also exhibit high oxidation resistance.

8. Conclusion

This chapter outlines the fabrication of nickel composite/nanocomposite coatings, their properties, and applications. Due to the excellent properties exhibited by these coatings such as high hardness, excellent corrosion resistance and wear resistance, self-lubricating properties, and high thermal stability, the coatings have a good potential to replace chromium-based coatings. Their mechanism of co-deposition and optimization of process parameters need to be understand well to produce better coatings with improved surface properties. This understanding will also enable extension of their applications in the future to serve as alternatives for other coatings fabricated by cost and energy-intensive processes.

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