Chapter 3

Parametric Variables in Electro-deposition of Composite Coatings

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Additional information is available at the end of the chapter

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Abstract

Nowadays, synergy of the attractive properties of materials while avoiding limitations of their use in isolation is a major driver for flexibility in design and manufacture. This allows tailoring of materials' properties to meet specifications. Composite technology utilizes an excellent combination of properties: strength, stiffness, light weight, wear, chemical, corrosion, and temperature resistance, which transcend those of the constituent materials. Engineering structures, equipment, and vessels in key industries that are material-dependent are susceptible to deterioration process and damage over time in their service conditions. Composite coatings through electro-deposition offer a reliable cost-effective means of impacting special surface properties for corrosion protection, better appearance, and mechanical properties' enhancement. The properties of the composite coatings can be optimized by varying the type, size, amount and distribution of the particles content incorporated among others.

Keywords: Co-deposition, Nano-particles, Current density, Micro-hardness, Agglomeration, Metal deposit and Microstructure

1. Introduction

1.1. Composite coating

A composite coating is a multi-phase coating with well-controlled phase distribution and geometry to optimize the properties of the matrix phase and reinforcement co-deposited phase or phases. Composite coatings have been used to achieve combination of specific properties of corrosion and wear resistance, corrosion inhibition and electrical conductivity, tribological control and self-lubrication. At times, two apparently opposed properties are specified such as high tensile strength and at the same time high ductility. The most common applications include controlling corrosion of various structures like steel, bridges, offshore platforms, underground pipelines, and mechanical driving equipment.

1.2. Nanotechnology applications in composite coating

Based on the principles that govern material behavior, it has been established that a material or device with particles size less than 100 nm length is in the nanotechnology domain. These particles primarily promote the mechanical and metallurgical properties of composite coatings in the areas of micro-hardness, corrosion resistance and tribological control and frictional and wear properties. Therefore, nanotechnology helps in characterizing the co-deposit of composite coatings to enhance specific features in the coating formulation.

Nanotechnology applications in coatings have gained tremendous ground in research and developments in recent years. This is a result of two factors:

- Increased availability of different types of nanoparticles of metal oxides, metal carbides and clays
- Advancements in technologies that can handle inert particles of a different material in the metal matrix coating structure at the nano-scale

1.3. Electro-deposition

Electro-deposition is a deposition technique that applies metallic coatings to metallic or other conductive surfaces through electrochemical processes. It is an excellent means of producing a composite coating successfully on metal surfaces. In this method, the distribution of particles is uniform, the rate of deposition is high, and the temperature of operation is low (i.e., < 100^0C). Compared to high-temperature methods such as pyrometallurgy and powder metallurgy, control of the microstructure and composition is easier.

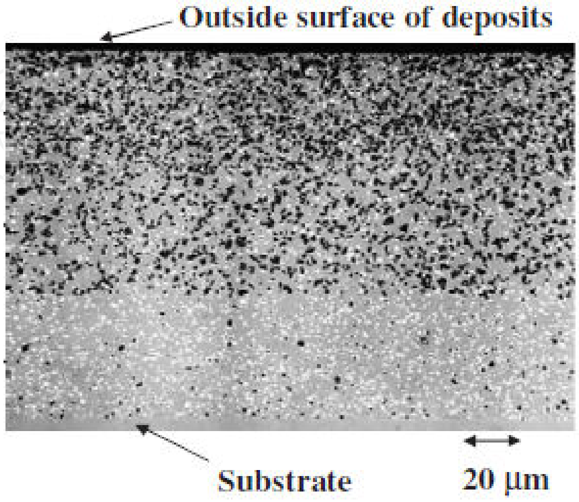


Figure 1. Co-deposition of nanoparticles on metal substrate (Low et., al) [1]

1.4. Purpose of electroplating

- **Functional applications:** It is used principally to apply metal coatings that impart specific surface properties such as wear and abrasion resistance, tribology control and self-lubricating property, reflectivity, and conductivity.
- **Decorative and protective applications:** Metals such as tin, zinc, and steel, which are not really attractive in appearance, are plated to give them an aesthetic look and protective outer layer. Chromium, nickel, brass, copper, and precious metals such as gold, platinum and titanium are common metals applied to variety of items.
- **Corrosion control applications:** Electroplating is applied on metal to enhance materials' surface properties and also impart corrosion resistance. For instance, tin-plated food containers are highly resistant to corrosion and so can preserve their content well.

1.5. Electro-deposition parameters

The structure and properties of composite coatings depend on many parameters, including:

- Particle characteristics (type, shape, size, particle concentration, surface charge)
- Electrolyte composition (electrolyte concentration, additives, temperature, pH, surfactant type and concentration)
- Current density (direct current, pulsed current, pulse time, duty cycle, potentiostatic control)
- Hydrodynamics (laminar, mixed, turbulent regimes)
- Electrode geometry (rotating disk electrode, rotating cylinder electrode, plate-in-tanks, parallel plate electrodes, and many variations).

Owing to their high surface energy, reinforcement particles can be easily agglomerated. Subsequently, obtaining uniform distribution of these particles is an important aim that can be achieved in optimum parameters.

1.5.1. Particle type and concentration

Particle size influences the rate of incorporation into the metal deposit. The rate of incorporation of metal deposit per unit volume is inversely proportional to the nanoparticles size. The volume fraction of nanoparticles in the metal deposit increases substantially when the amount of nanoparticles concentration in the solution increases. A saturation state of particles in the deposit is reached at high nanoparticle concentration in the solution.

1.5.2. Pulse frequency

Micro-hardness as well as co-deposition of particles increases on variation of frequency from 0.1Hz to 10Hz and is followed by sharp decrease from 10Hz to 100Hz frequency. For frequencies below 10Hz, reduction rate of metal ions is higher as compared to ions adsorbed on nanoparticles, which reduce the nanoparticles content in the composite coating. At very high frequency, the content of nanoparticles in composite reduced because the shorter OFF time is not enough to remove concentration gradient of nanoparticles adjacent to the cathode. Wear loss and micro-hardness of composites significantly decreases when pulse frequency increases from 10Hz to 1000Hz. Significant adhesive wear is observed at higher frequencies.

1.5.3. Current density

By definition, current density is the current per unit surface area of the cathode. It is expressed in mA/cm^2 of surface of the electrode.

Current density actively governs metal deposition and co-deposition process. An increase in current density results in more rapid deposition of the metal matrix and fewer particles are embedded in the coating. To obtain uniform deposition, the current density must be minimal, so that the rate of particles’ incorporation into the growing metal will exceed the adsorption on the cathode. Reinforcement of nanoparticles into metal matrix not only restrains the grain growth but also reduces the plastic deformation of metal matrix by combined effect of grain refining and dispersion strengthening, resulting in significant increase in hardness of composite coatings.

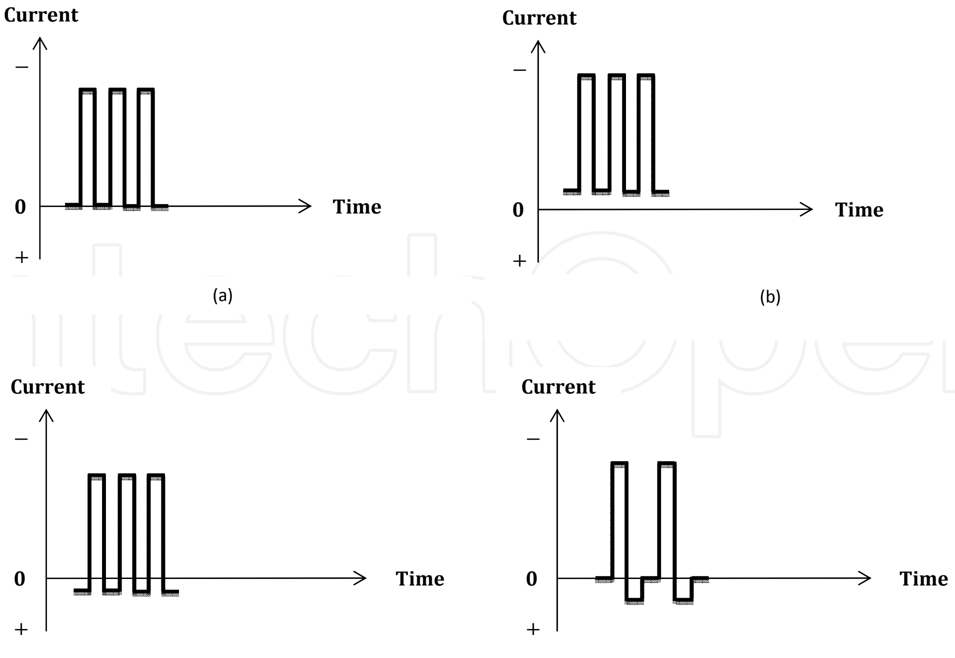
The current density can be measured in the following terms:

- Direct current
- Pulsed direct current
- Pulsed reverse current.

Direct current technique is based on the concept that the incorporation of nanoparticles occurs simultaneously with the reduction reaction of an ionic species to form the metal surface. **Pulsed direct current** works on the concept of alternating two or more direct cathodic currents for various deposition times. This allows the incorporation of higher concentrations of nanoparticles as well as producing a wider range of deposit compositions and properties. **Pulsed reverse current** technique, as the name connotes, has similar characteristics but imposes a cathodic current during the ON time and an anodic current during the OFF time. This method has been the most successful for incorporating higher concentrations of nanoparticles because it helps to eliminate a fraction of the electrodeposited metal during the OFF time. Pulse reverse current technique ensures refine surface microstructure, increased incorporation rate of nanoparticles into the metal deposit and uniform size selective entrapment of particles. During the anodic period, larger sizes of nanoparticles dissolve, whereas smaller nano-particles continue to be entrapped.

1.5.4. Duty cycle

As duty cycle increases from 10 to 100%, micro-hardness as well as incorporated particles decrease significantly. Lower duty cycle gives longer OFF time for arrival of nanoparticles at the double layer. Therefore, more nanoparticles are reinforced in composite coatings at lower duty cycle and coatings become harder. The improvement in hardness at lower duty cycle is mainly due to grain refinement at pulse OFF-time longer than ON-time.



(a) (b) (c) (d)

Figure 2. Showing different phases of current density during deposition (a) Pulse direct current with zero current during off time; (b) Superimposed pulse direct current with cathodic current during off-time; (c) Pulse reverse current with anodic current during off time; (d) Pulsed reverse current with combination of zero and anodic current during off time.

1.5.5. Bath agitation

Electrolyte agitation increases convection of bath contents and therefore enhances the flux of the particles reaching the cathode surface. Intensive agitation may cause adverse effect by disconnection and removal of the particles by turbulent streams of the electrolyte.

Bath agitation serves the purposes of keeping the particles evenly distributed, well suspended in the electrolyte and effectively transported to the cathode surface. Excessive agitation has tendency of removing particles from cathode surface before they can be embedded in the metal deposit. This is due to turbulence initiated by the electrolyte in the bath.

For industrial applications, the popular methods used in open tanks include the overhead blade stirrer, the reciprocating plate plunger or a pumped recycle loop of the electrolyte. For laboratory investigations, magnetic stirrers, rotating disk or cylinder electrodes and parallel plate channel flow can be employed. In contrast, the commonly used plate-in-tank geometry provides poorly defined fluid flow conditions.

1.6. Nano-composite Coatings

The backbone of composite coating is multi-phase union of matrix and second-phase particles in correct ratio. Matrix plays the role of continuous phase and the solvent to disperse the second phase.

Types	Chemical Compositions	Concentrations
Watts Bath	Nickel sulphate: $NiSO_4 \cdot 7H_2O$ Nickel chloride: $NiCl_2 \cdot 6H_2O$ Boric acid: H_3BO_3	$240g/l$ $20g/l$ $30g/l$
Sulphate Bath	Nickel sulphamate: $Ni(SO_3 \cdot NH_2)_2$ Nickel chloride: $NiCl_2 \cdot 6H_2O$ Boric acid: H_3BO_3	$300-450g/l$ $0-30g/l$ $30-45g/l$
Chloride Bath	Nickel sulphate: $NiSO_4 \cdot 7H_2O$ Nickel chloride: $NiCl_2 \cdot 6H_2O$ Boric acid: H_3BO_3	$50-75g/l$ $100-130g/l$ $50-55g/l$

Table 1. Different types of electrolytic baths

Composite coating can be classified on the basis of the matrix and the reinforcing co-deposited particles. The matrix phase on a broader scale can be grouped into:

- Metal matrix
- Ceramic matrix
- Polymer matrix

The common metals used as matrices for electrolytic co-deposition are: Silver (Ag), Chromium (Cr), Cobalt (Co), Iron (Fe), Zinc (Zn), Nickel (Ni), Copper (Cu) and Gold (Au).

A variety of composite coatings can be deposited by reinforcing different nanoparticles. Reinforcement particles can be carbides (TiC, SiC, WC,Cr_2C_3)[2,3,4,5,6,7], borides [8], oxides (ZnO, In_2O_3, ZrO_2, CeO_2, Al_2O_3,Cr_2O_3,SiO_2,TiO_2) [9,10,11.12], graphite, diamond, or solid lubricants, such as polyethylene and polytetrafluoroethylene [13,14]. Variable amounts of these particles in the coatings become precipitated to impart special properties to the deposited layers. These properties mainly depend on the microstructure of the matrix phase of a composite coating and the amount and distribution of co-deposited particles (non-metallic inclusions) which are influenced by many process parameters.

2. Literature review

2.1. Categories of Co-deposition of particles

2.1.1. Co-deposition of wear-resistant particles

Nano-diamond particles dispersed in Ni-Co matrix form good composite coating on AISI 1045 steel substrate [15]. This composite coating formed in a Watts-type bath using electro-deposition showed enhanced hardness coupled with excellent anti-wear performance and lower frictional coefficient. This was due to well-dispersed diamond particles in the Ni-Co matrix and better wetting and bonding ability between the nano-diamond particles and Ni-Co matrix.

Zn-ZrO_2-SiC composite coating has been fabricated to improve the mechanical and thermal resilient properties of mild steel [16]. The surface properties imparted by this ternary- phase composite layer showed enhanced micro- hardness above 60% of the control sample. There was also minimal wear response ad abrasive deformation under the examined conditions.

Nano-particles of alumina (Al_2O_3) in nickel matrix have been found out to agglomerate [17, 18]. Agglomeration affects the amount and uniform distribution of co-deposited particles in the metal matrix. Hexadecylpridinium bromide (HPB) added as cation surfactant in the electro-deposition bath improved the quantity of Al_2O_3 particles co-deposited and also reduced particle agglomeration to achieve uniform distribution of Al_2O_3 particles in the nickel matrix. It was also found out that the wear resistance of the composite coatings increases as the concentration of the surfactant increases to a peak of 150 ml^{-1} after which a decreasing trend of wear resistance set in under -sliding and oil-lubricated conditions. This happened as a result of increased brittleness of metal matrix at peak of the surfactant concentration.

Composite coating of Ni-P Al_2O_3 was formed on material of AISI 1045 steel disks by electroless deposition technique [19]. The second phase particles of Al_2O_3 in the Ni-P –based matrix evidenced well the output of hardness and wear resistance of the deposits. Heat treatment was carried out at intervals of 1 h across three consecutive temperature ranges of 200, 400 and 600^0C. The result showed that composite coating heattreated at 400^0C has maximum hardness and wear resistance.

With the aid of cetyltrimethylammonium bromide (CTAB) in a modified Watts bath, co-deposit of Fe_2O_3 has been successfully dispersed in Ni-Co matrix [20] to form composite coatings of Ni-Co- Fe_2O_3. The results showed that co-deposition of Fe_2O_3 particles with Ni-Co matrix is favored at higher concentration and there is refinement of the crystallite of the composite deposit. The deposition of Co is favored at high concentration of CTAB.

The mechanical parts of machine under constant motion are subject to continuous friction, wear and tear. Nano- particles of Al_2O_3, TiO_2, Si_3N_4 and diamond were consecutively dispersed onto nickel matrix to form composite coatings to study their tribological behaviors and wear mechanisms [21]. The SEM results of the composite samples revealed refine microstructures and enhanced micro-hardness compared with pure nickel coating. Only the Ni- Al_2O_3 and Ni-diamond composite coatings showed improved tribological properties.

Nickel-based composite coating is the most popular wear-resistant composite coating used in abrasive tools, gear systems, chains assembly, measuring tools and gauges. Nickel matrix composites with various dispersed phases (Al_2O_3, SiO_2, SiC, WC and diamond) are fabricated by electrolytic co-deposition from Nickel sulphamate and Watts electrolytes.

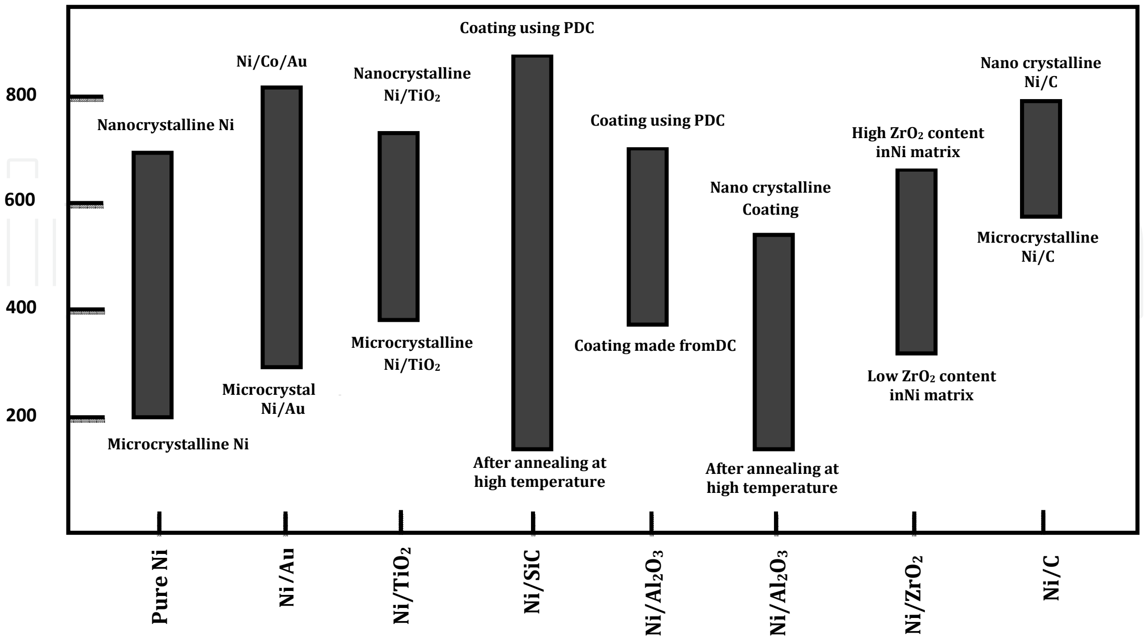


Figure 3. Vickers micro-hardness values for different ranges of particle size in a nickel deposit.

2.1.2. Co-deposition of corrosion -resistant particles

Apart from using the conventional electroplating technique (CEP), sediment co-deposition technique (SCD) has gained acceptance for higher level of co-depositing particles in the metal matrix with better dispersion and uniformity. Feng et al. [22] investigated the corrosion resistance and high-temperature oxidation resistance of Ni- Al_2O_3 nano- composite coatings using SCD technique. The incorporation of the nano-alumina particles in the Ni matrix refined the Ni crystallite and changed the preferential orientation of composite coating. Ni- Al_2O_3 composite coating produced compared with the one fabricated using CEP technique proved that the former had improved corrosion and oxidation resistance.

Fayomi et al. [23] carried out a research on mild steel protection in chloride medium to develop ceramic composite coating that will reduce its susceptibility to corrosion attack. Zn-TiC/TiB composite coating was produced via electro-deposition method. The coatings showed better adhesion strength, improved hardness and enhanced corrosion resistance compared to the TiC/TiB -coated mild steel.

Three different nano- oxides of Al_2O_3, Cr_2O_3 and SiO_2 have been reinforced in Zn matrix using electro-deposition process to produce composite coating on mild steel [24]. The incorporation of Al_2O_3, Cr_2O_3 and SiO_2 nanoparticles in the ternary composite showed grain refinement, modified orientation of Zn matrix and good synergetic effect on the corrosion resistance of Zn-based coatings. Zn-Cr_2O_3 nano- composite had the highest micro-hardness while Zn-Al_2O_3 nano-composite was found to exhibit the highest corrosion resistance coupled with lowest wear loss.

In the research work carried out by Yong et al [25], ultrasonic technique was used as a direct replacement of conventional mechanical agitation to foster effective stirring, dispersion and suspension of the second phase particles in the electrolytic bath. The XRD analysis of the developed nickel-based composite coatings containing TiN nano-particles shows that application of ultrasonic agitation and use of nano-particles of TiN refined the Ni grains, resulting in good corrosion resistance.

A comparative study of the properties of EN, EN-SiC, EN-PTFE and EN-SiC-PTFE composite coatings was conducted on the coating properties using electroless plating [26]. The results showed that electroless nickel (EN) composite coatings incorporated with PTFE and/or SiC particles demonstrated significantly improved mechanical and tribological properties as well as low surface energy, which are desired for anti-sticking and wear-resistant applications. It is evident that the Ni matrix substantially enhanced corrosion resistance by improving the autocatalytic properties and homogeneity.

Electro-deposition mechanism of Ni-Al composite coating was studied from a modified Watts solution by means of zeta potential analysis, voltammetry and electrochemical impedance spectroscopy (EIS) [27]. The findings showed that addition of Al particles shifts the reduction potential of Ni to more negative values, which is attributed to a decrease in the active surface area. Also the loop size of EIS curves increases with addition of Al particles to Ni electrolyte because of an increase in charge transfer resistance. It was also demonstrated that the co-deposition behavior of Ni−Al composite coatings obeys the Guglielmi’s model.

Shi et al. [28] studied effects of current density, stirring rate, nanoparticle concentration and temperature of plating bath on the composition of Ni–Co/SiC nano- composite coatings with various contents of SiC nano-particulates by electro-deposition technique. The result showed that Ni–Co/SiC nano- composite coatings have higher micro-hardness and better wear resistance than the Ni–Co alloy coating, which is attributed to the grain-fining and dispersive strengthening effects of the co-deposited hard SiC nano-particulates. The better corrosion resistance of the Ni-Co/SiC nano -composite coatings may be ascribed to the favorable chemical stability of the SiC nano-particulates, which help to reduce the whole size in the nano composite coatings and prevent the corrosive pits from growing up.

To improve the resistance of the hydro-transport pipe steel to corrosion and erosion in oil sand slurry, a Ni–Co–Al_2O_3 composite coating was fabricated by [29] using electrolytic deposition on X-65 pipe steel substrate. Electrolytic deposition of Ni–Co/Al_2O_3 composite coating showed significant improvement in the resistance of hydro-transport pipe steel to corrosion and erosion in oil sand slurry. The micro-hardness and wear resistance of the composite coating are much higher than the steel substrate and increase with the increasing Al_2O_3 particle amount in the coating.

2.1.3. Co-deposition of solid lubricant particles

Cardinal et., al. investigated characterization and frictional behavior of nano-structured Ni-W-MoS_2 composite coatings by pulse plating from an Ni-W electrolyte containing suspended MoS_2 particle [30]. MoS_2 concentration was varied with the coating composition, morphology, crystalline structure, micro-hardness and frictional behavior. The result obtained indicated that co-deposited lubricant particles strongly influenced the composite Ni-W coating properties. As the MoS_2 concentration in the coating increases, both the tungsten content and the coating micro-hardness decrease while the average grain size increases. With low MoS_2 content, result showed lesser friction coefficients and similar micro-hardness. Therefore, there is a solid lubricant concentration regime where co-deposition of MoS_2 particles into Ni-W nanostructure alloys improves the frictional characteristics of the coating with a consistently lower friction coefficient.

Sangeetha used direct current and pulse current methods to incorporate polytetrafluoroethylene (PTFE) polymer to an optimized Ni-W-BN nano -composite coating deposited on a mild steel substrate [14]. It was observed that the co-deposition of PTFE solid lubricant particles on the Ni-W-BN nano-composite coating resulted in a moderately smooth surface, greater micro-hardness, a lower friction coefficient, excellent water repellency and enhanced corrosion resistance. The pulse current technique showed enhanced performance over the direct current coating due to uniform and smaller grain deposits.

2.2. Applications of composite coatings

Composite coatings have been successfully used to overcome high temperature corrosion, oxidation and wear in many ground breaking applications. Nickel coatings with 8-10 volume % of silicon carbide are used to increase the life of internal combustion engine cylinder bores and in portable chain saws. Composite coatings based on chromium carbide in a cobalt matrix are used as wear-resistant coatings in gas turbines, where they are required to perform for extended periods at temperatures of up to 800^0C. Chromium deposits with alumina inclusions are used in piston rings for diesel engines. Single crystal diamonds locked into a nickel matrix form the cutting-edge in tools such as chainsaws, grinding disks or dental drills [31].

3. Mechanisms of co-deposition process

3.1. Definition of Co-deposition process

Co-deposition is a process of incorporating fine particles of metallic, non-metallic compounds, or polymers from an electrolytic or an electroless bath in the electroplated layer to improve material properties such as: hardness, wear-resistance, corrosion-resistance, tribological control, lubrication, tensile, and fracture strength [32].

Co-deposition of particles into metal deposit is governed by physical dispersion of particles in the electrolyte and electrophoretic migration of particles [33]. Among different models presented for co-deposition mechanism of solid particles into a metal matrix, Guglielmi's model is the most adopted one. It has also been examined with different co-deposition systems such as: Ni–SiC, Ni–TiO_2, Ni- Al_2O_3, Cu- Al_2O_3, Cr-C, Zn-Ni particles, Co-SiC, and Ni-MoS_2 [33, 34]

3.2. Co-deposition of particles on metal surface

One of the common mechanisms of co-deposition process consists of five consecutive steps:

- Formation of ionic clouds around the particles (bulk electrolyte, typical length in cm)
- Convective movement toward the cathode (convection layer, typical length < 1 mm)
- Diffusion through a hydrodynamic boundary layer
- Diffusion through a concentration boundary layer (diffusion layer, typical dimension of μm)
- Adsorption at the cathode where particles are entrapped within the metal deposit.

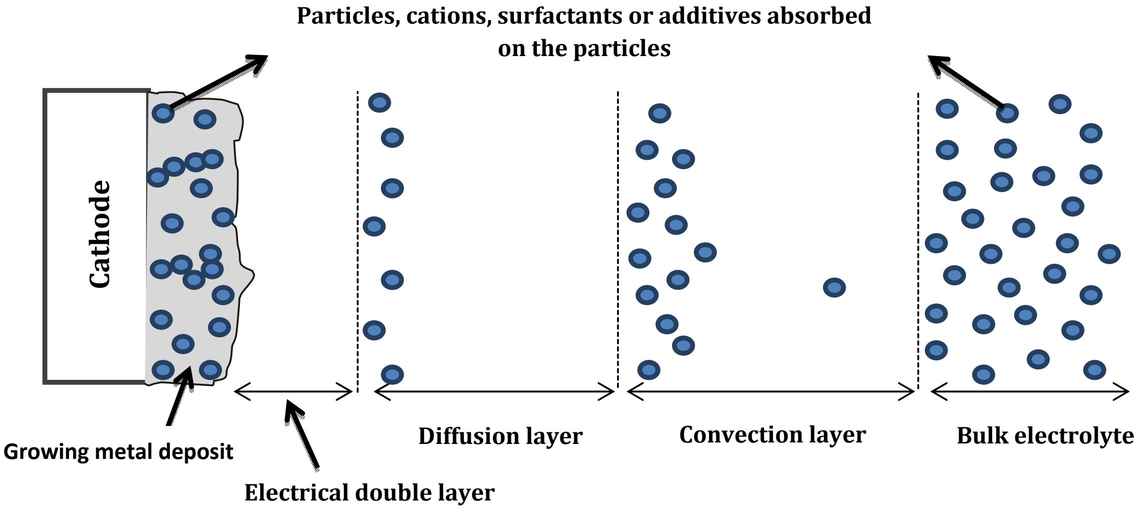


Figure 4. The processes involved in co-electro-deposition of insoluble particles into a growing metal matrix to form a composite metal coating

3.3. Description of Guglielmi's model

Guglielmi established in his findings that concentration of bath particles affects the rate at which an electro-deposit gets incorporated on metal. He therefore quantified the rate of particle incorporation as a function of current density. Guglielmi based his model on the similarity between the experimental co-deposition and Langmuir isotherm curves. Assumptions of Langmuir are as follows:

- The surface of the adsorbant (cathode) is in contact with a solution (electrolytic bath) containing adsorbate (second phase nanoparticles) which is strongly attracted to the surface.
- The surface has a specific number of sites (growing metal surface area) where the solute molecules can be adsorbed.
- The adsorption involves the attachment of only one layer of molecules to the surface, i.e. monolayer adsorption.

Using co-deposition of Ni-Al system as a case study [27], the mathematical equations deduced by Guglielmi's model are governed by the following parameters and equations:

α - Volume fraction of particles in the deposit; C - concentration of particles in the plating bath;

W- Relative atomic mass of metal; n- Valence of deposited metal; F- Faraday's constant; d - Density of deposited metal; v_0 - Constant for particle deposition; A and B are constant for metal deposition and particle deposition; k– Adsorption coefficient; J_o - Exchange current density of deposited metal; η - over-potential; θ- Surface coverage of embedded particles.

$$\frac{\alpha}{1-\alpha} = \frac{nFdv_0}{WJ_0}\exp\left[\left(A-B\right)\eta\right]\cdot\frac{kC}{1+kC} \tag{1}$$

Divide through by C: $\frac{\alpha}{C(1-\alpha)} = \frac{nFdv_0}{WJ_0}\exp[(A-B)\eta]\cdot\frac{k}{1+kC}$

Multiply through by $(1-\alpha)^{\left(\frac{B}{A}-1\right)}$:

$$\frac{\alpha}{C\left(1-\alpha\right)^{\left(2-\frac{B}{A}\right)}} = \frac{nFdv_0}{WJ_0}\exp\left[\left(A-B\right)\eta\right]\cdot\frac{k}{1+kC}\left(1-\alpha\right)^{\left(\frac{B}{A}-1\right)}$$

Take the reciprocal of each term:

$$\frac{C(1-\alpha)^{\left(2-\frac{B}{A}\right)}}{\alpha} = \frac{WJ_0}{nFdv_0}\exp\left[\left(B-A\right)\eta\right]\cdot\left(\frac{1+kC}{k}\right)\left(1-\alpha\right)^{\left(1-\frac{B}{A}\right)}$$

Rearrange the terms on the right:

$$\frac{C\left(1-\alpha\right)^{\left(2-\frac{B}{A}\right)}}{\alpha} = \frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}\cdot\left(\frac{1}{k}+C\right)\cdot\left\{\exp\left[\left(B-A\right)\eta\right]\cdot\left(1-\alpha\right)^{\left(1-\frac{B}{A}\right)}\right\} \tag{2}$$

Assuming:

$$\exp\left[\left(B-A\right)\eta\right]\cdot\left(1-\alpha\right)^{\left(1-\frac{B}{A}\right)} = 1 \quad or \quad \exp\left[\left(A-B\right)\eta\right] = \left(1-\alpha\right)^{\left(1-\frac{B}{A}\right)}$$

Then

$$\frac{C\left(1-\alpha\right)^{\left(2-\frac{B}{A}\right)}}{\alpha}=\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}\cdot\left(\frac{1}{k}+C\right) \tag{3}$$

Expand the bracket on the right to get

$$\frac{C\left(1-\alpha\right)^{\left(2-\frac{B}{A}\right)}}{\alpha}=\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}\left(\frac{1}{k}\right)+\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}C$$

Compare with $y=mx+d$, the equation of a straight line. Where m is the slope (also written as *tanφ*), and d the intercept:

$$\underbrace{\frac{C\left(1-\alpha\right)^{\left(2-\frac{B}{A}\right)}}{\alpha}}_{y}=\underbrace{\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}\left(\frac{1}{k}\right)}_{d}+\underbrace{\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)}}_{m}\underbrace{C}_{x}$$

Thus the slope is simply the coefficient of C. ie

$$slope=m=\tan\varphi=\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}J_0^{\left(1-\frac{B}{A}\right)} \tag{4}$$

Equation (5) follows quickly from the logarithm law $\lg(PQ^R)=\lg P+R\lg Q$.

$$\lg\left(\tan\varphi\right)=\log\frac{WJ_0^{\frac{B}{A}}}{nFdv_0}+\left(1-\frac{B}{A}\right)\lg J_0 \tag{5}$$

where the slope is giving as $\left(1-\frac{B}{A}\right)$. The ratio $\frac{B}{A}$ of the slope can be pre-determined for fitting the experimental data. This ratio is obtained in the following way:

For coatings produced with different current densities, the plot of $C(1-\alpha)^{2-{}^{B}\!/_{A}}$ against C presents a series of straight lines. The selected $\frac{B}{A}$ ratio must converge these lines towards the same point on the C –axis i.e., $\left(C={}^{-1}\!/_{K}\right)$

The logarithm of slopes of lines lg(tanφ) obtained from the graph of $C(1-\alpha)^{2-{}^{B}\!/_{A}}$ versus C plotted against $\log J$, i.e., lg(tanφ) versus $\log J$ lies on a straight line. According to Equation (5), the slope of this line is equal to $\left(1-\frac{B}{A}\right)$. The obtained $\frac{B}{A}$ ratio should be equal to the selected one.

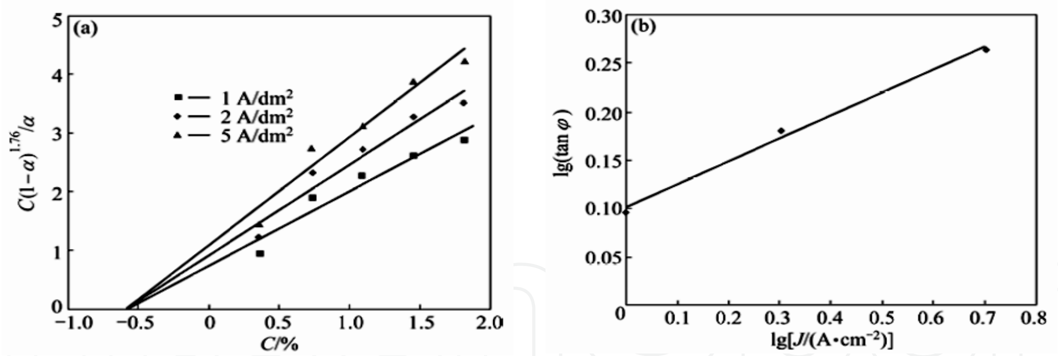


Figure 5. Graphical representation of experimental deductions of Ni-Al co-deposition system

In Fig. 5(a), the experimental results considering the $\frac{B}{A}$ ratio equal to 0.24, have been presented. It is clear that experimental data can be well-fitted on a series of straight lines, which converge toward the same point on the C-axis. From extrapolation of these lines, the $^{-1}/_{K}$ point of intersection with C-axis is equal to −0.62. This makes it possible to obtain the adsorption coefficient value of K.

In Fig. 5(b), the logarithm of the slopes of the straight lines $\lg(\tan\varphi)$ is plotted against $\lg J$. The slope of this line is 0.76 and so the $\frac{B}{A}$ ratio is 0.24. This value is exactly equal to the $\frac{B}{A}$ value considered previously for initial curve fitting. Hence, the co-deposition behavior of Ni −Al system is in good agreement with the Guglielmi's model.

Composite electroplating is a two-step process according to Guglielmi's model. At first, solid particles during electro-deposition are surrounded with cloud of adsorbed ions, which are weakly adsorbed at cathode surface by van der waals forces. In the second step, the loosely adsorbed particles become strongly adsorbed onto cathode surface by Coulomb force and consequently entrapped within metal matrix. The main drawback of this model is absence of mass transfer effect during electro-deposition process such as the adsorption of ionic species on the particle surface, the nature of particle, the ions to be reduced, the bath components, and the hydrodynamic conditions.

Bonino et., al. in their model uses statistical approach that Gugliemi neglected [35]. The model describes the amount of particles that are likely to be incorporated at a given current density. Mass transport of particles is proportional to the mass transport of ions on the working electrode. Volume ratio of particles in the metal deposit will increase under charge transfer control and decrease under mass transport control.

A widely accepted model is developed by Kurozaki, which includes the transport of solid particles from the solution to the cathode surface by agitation. This model is developed in the following steps:

- Uniform dispersed particles are transported to the electric double layer via mechanical agitation.
- Charged particles are transported to the cathode surface by electrophoresis.

- Solid particles are adsorbed at the cathode surface due to Coulomb force between particles and adsorbed anions.
- Finally, the particles are incorporated into the growing metal.

Particles dispersed in the electrolyte bath are in constant Brownian motion. Whether the particles approach one another, their separation or agglomeration mainly depends on the existing energies between those particles. When attraction energy is larger than repulsion energy, particle agglomeration occurs and when repulsion energy is higher than attraction energy, particle separation occurs. The condition and nature of the system mainly determines the magnitude of net force for the production of agglomerated structures. Therefore, knowledge of interfacial region attraction is very important in understanding dispersion stability of solid particles with electrolyte.

4. Conclusions

The rate of embedding nanoparticles in matrix solution onto metal deposit depends on the applied current density, hydrodynamics and characteristics of the particles. High incorporation rates have been confirmed by using:

- High concentration of nanoparticles in the electrolytic bath.
- Particles at nano scale compared to micron scale.
- A lower concentration of the electro-active species.
- Ultrasonic agitation compared to mechanical agitation.
- Pulse reverse current technique compared to direct current technique.

Various electro-deposition techniques (direct current, pulsed direct current, and pulsed reverse current) have been employed to incorporate nano-sized particles into metal deposits. These techniques have enabled the fabrication of composite coatings with diverse properties not available with pure metal or alloy coatings. It has been established that pulse current deposition technique compared to direct current deposition for the production of nano-composite showed more refined surface microstructure and increased incorporation rate into the metal deposit.

Inorganic (inert) nanoparticles are used as second phase in composite coating. They possess good chemical stability, high micro-hardness and good wear resistance and enhance corrosion resistance in the composite coating. They modify crystal growth to form a nano-crystalline metal deposit and also cause a shift in the reduction potential of a metal ion.

Agglomeration of nanoparticles occurs under condition of greater attraction energy. The adverse effect can be reduced or eliminated by controlled application of ultrasonic agitation, surfactants, and pulse reverse direct current.

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