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Electrochemical Synthesis of Nanocomposites

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<http://dx.doi.org/10.5772/62189>

Abstract

This chapter presents an overview of research efforts focused on both fabrication and properties of nanocomposites prepared by electrodeposition. The nanoparticles can improve the base material in terms of wear resistance, damping properties, and mechanical strength as well as electrical properties. Different kinds of matrix, such as metals, polymers, and ceramic matrix, have been employed for the production of composites reinforced by nano-ceramic particles such as carbides, nitrides, and oxides as well as carbon nanotubes. Theoretical aspects and mechanisms related to the electrodeposition process of nanocomposite films, from aqueous solutions, are discussed.

Keywords: Nano-structured coatings, Electrocodeposition, Theoretical models, Characterization techniques, Applications

1. Introduction

Materials are considered nanosized when one of the components dimensions are in the nanometer scale, with typical dimensions smaller than 100 nm. Nanocomposites are composites in which one or more of the phases has dimensions in the nanoscale [1].

Nanocomposites are commonly known as materials consisting of two or more dissimilar materials with well-defined interfaces. Generally, one material forms a continuous matrix while the other provides the reinforcement [2].

They are reported to be the materials of 21st century in the view of possessing design uniqueness and property combinations that are not found in conventional composites. The general understanding of these properties is yet to be reached, even though the first inference on them was reported as early as 1992 [3]. Various techniques have been considered to prepare nanocomposite materials including thermal, plasma spraying and physical and chemical vapour deposition. Among these methods that is widely used, electrodeposition (ECD)), which offers several advantages when compared with other techniques [4]. Electrodeposition offers a lot of advantages over other surface modification techniques:

- Capability of manufacturing nanostructured multi-component films.
- High purity of deposited materials.
- Applicable to substrates of complex shape.
- Can be used for deposition of ceramics, glasses, polymers, composites.
- Rigid control of the composition and microstructure of deposit.
- Low cost of equipment and materials.
- Easy to be scaled up to industry level.
- This process avoids the problems associated with high temperature and high pressure processing.
- Reduction of waste often encountered in dipping or spraying techniques [5, 6].

Research into the preparation of nanocomposite coatings, by electrochemically co-deposition of fine particles with metal from electrolytic solutions, has been investigated by numerous authors [7-12].

As in the case of micro-composites, nanocomposite materials can be classified, according to their matrix materials, in three different categories;

- Metal Matrix Nanocomposites (MMNC) such as Cr/ Al_2O_3 [13], Ni/ Al_2O_3 [14], Co- TiO_2 [15], Zn-Ni/ TiO_2 [16], Al/CNT [17], Mg/CNT [18].
- Ceramic Matrix Nanocomposites (CMNC); such as $\text{Al}_2\text{O}_3/\text{ZrO}_2$ [19], ceramic/CNT [20],
- Polymer Matrix Nanocomposites (PMNC), such as Thermoplastic/thermoset polymer/layered silicates [21], polyester/ Fe_2O_3 [22], polyester/ TiO_2 [23].

Nanocomposite materials have been extensively investigated in bulk and thin film forms because of their wide range of applications, starting from traditional industries, such as general mechanics and automobiles, paper mills, textiles, and food industries, to high-technology industries, such as microelectronics and magnetoelectronics [24]. In addition, the applications of nanocomposite coatings include wear and abrasion-resistant surfaces, lubrication, high hardness tools, dispersion-strengthened alloys, and protection against oxidation and hot corrosion. It has been also used to produce high surface area cathodes that have been used as electro catalysts for hydrogen electrodes in industrial water electrolysis [25, 26].

2. Theoretical models of composites electrodeposition

2.1. Models neglecting the hydrodynamics of fluids

In 1972 Guglielmi [27] proposed the first mechanism on electrocodeposition of inert particles in the metal matrix, and later this mechanism has been adopted by various authors. The model proposed by Guglielmi does not consider mass transfer.

According to this mechanism the process involves a two-step mechanism, as follows;

- In the first step, when the particles approach the cathode they become weakly adsorbed at the cathode surface by Van der Waals forces.
- In the second step, particles are adsorbed strongly on the cathode surface by Coulomb forces and consequently are incorporated into the growing metal matrix.

The loose adsorption coverage, a ratio of the area covered by loosely adsorbed particles to the total electrode area, was expressed in terms of the concentration of suspended particles using the classical Langmuir adsorption isotherm. For the strong adsorption rate, the volume of particles strongly adsorbed was given by a Tafel-type exponential relationship at high over potentials that depended on kinetic constants. The volume of metal electrodeposited was obtained by Faraday's law. Thus, the volume fraction of incorporated particles was then formulated as a function of the bulk concentration and the electrode over potential. From this model the volume fraction of incorporated particles, α' , can be mathematically expressed by:

$$\frac{\alpha'}{1-\alpha'} = \frac{zF\rho_m V_0}{M_m i_0} e^{(B-\eta)} \frac{KC_{p,b}}{1+KC_{p,b}} \quad (1)$$

where M_m is the atomic weight, ρ_m is the density of electrodeposited metal respectively, i_0 the exchanging current density, z the valence of the electrodeposited metal, F the Faraday constant, η the electrode reaction over potential, $C_{p,b}$ the particle concentration in the bulk electrolyte. k is the Langmuir isotherm constant, which is mainly determined by the intensity of interaction between particles and cathode. The parameters V_0 and B are related to particle deposition, and they play a symmetrical role with the parameters. In addition, i_0 and A are related to metal deposition.

In 1987, in order to overcome the shortcoming in the Guglielmi's model Celis et al. [28] proposed another model. The model consists of five consecutive steps:

- The particles are surrounded by ionic clouds;
- Convection towards the cathode surface;
- Diffusion through the hydrodynamic boundary layer;
- Diffusion through the concentration boundary layer;
- Adsorption of particles at the cathode and particles are entrapped within the metal deposit by the reduction of the ionic cloud.

In Celis model, an equation relating weight of particle (W_p), with the weight increase per unit time and surface area (ΔW_p) due to particle incorporation. The weight fraction of particles embedded in percentage is;

$$\frac{\Delta W_p}{\Delta W_m + \Delta W_p} \times 100 \quad (2)$$

One of the limitations of this model is that the data needed for probability coefficient are not available [29].

In 1995, a theoretical model was proposed by Fransaer et al. [30] to describe the variations in the flow of current to disk electrodes caused by a finite number of spherical and probate particles. They developed a boundary collocation method to calculate the resistance variations and the influence on current in the presence of particles and in their absence. The increase in resistance to the flow of particles was measured as a function of the diameter of the particle. The resistance is increased by larger particles to a greater degree than smaller particles. The primary current distribution around a particle was plotted as a function of the aspect ratio of the particle. The position of the particle was also determined, from its influence on the current as it flows past the electrode.

2.2. Models including the hydrodynamics of fluids

In 1974 Foster and Kariapper et al. [31] performed adsorption studies on composite coatings. They proposed that if the particles in suspension acquire a positive surface charge, they could be incorporated into the metal film by electrostatic attraction. Their model is based on the following expression;

$$\frac{dV_p}{dt} = \frac{N^* h C_v}{1 + h C_v} \quad (3)$$

where V_p is the volume fraction of the particles in the deposit, N^* is the number of collisions of particles suitable for the co-deposition per second and C_v is volume percent of particles in the plating bath (%).

The parameter h was related to several parameters given by the following expression;

$$h = h^* (q \Delta E + L i^2 - ab) \quad (4)$$

where h^* is a constant, q is the charge density on a particle, ΔE is the potential field at the cathode, i is the current density, L is the bond strength of the metal/particle per surface area, a is related to the shape and b depends on agitation.

In 1987, Valdes et al [32] reported a model for co-deposition on a rotating ring disk electrode (RRDE). The equation of continuity based on differential mass balance was chosen as a starting point where different mass transport processes (Brownian diffusion and convection) for particles have been considered. According to this model, the electrochemical rate of particle deposition can be written as;

$$r_p = K^0 (C_s^p) n \left[\exp\left(\frac{\alpha Z F}{RT}\right) \eta_a - \exp\left(\frac{1 - \alpha Z F}{RT}\right) \eta_a \right] \quad (5)$$

Where K^0 is an electrochemical rate constant which depends on C_s^P , the concentration of electroactive species (metal cations) adsorbed on the surface of the particles, n is valance and η_a is the activation overpotential.

In 1992, Fransaer et al. [33] proposed a trajectory model suggested for particle co-deposition on a rotating disk electrode (RDE). This particle is based on particles larger than 1 micrometer in size. In this model, Navier-Stocks equation for RDE was resolved by using Taylor expansion. The velocity of the particle that can reach towards the cathode is;

$$\frac{dz_p}{dt} = a_p^2 v_{stag} \frac{F'_{stag}}{F'} - \frac{F_{ext}}{6\pi a_p F'} \quad (6)$$

Where F_{ext} is the external force at any instant along the particle, F'_{stag} is the force propelling the particle towards the electrode, F' is the resistance force felt by the particle while it is moving perpendicular towards electrode, a_p is the particle radius.

In 2000, according to the model of Vereecken et al. [34], the particles kinetics and residence time at the electrode surface have been considered. Convective-diffusion controls the transport of particles to the surface. The influence of particle gravitational force and hydrodynamics is accounted for various current densities. It is valid only when the particle size is smaller than the diffusion layer thickness. In their model they used Fick's first law and diffusion layer thickness. By combining both they got;

$$J_p = -1.554 v^{-\frac{1}{6}} D_p^{2/3} (C_{p,b} - C_{p,s}) \omega^{\frac{1}{2}} \quad (7)$$

where $C_{p,s}$ is the particle concentration at the surface, $C_{p,b}$ is particle concentration in the bulk, D_p is the diffusion coefficient, v is the kinematic viscosity of the solution and ω is the rotation speed of the electrode.

The ratio of the number of moles of particles to the number of moles of metal atoms equals the ratio of their fluxes J_p / J_m .

J_p can be written as;

$$J_p = \frac{3V_{m,M}}{4\pi r^3 z F N_A} \frac{x_y}{1 - x_y} i \quad (8)$$

Where $V_{m,M}$ is the molar volume of metal film, N_A is the Avagadros number, x_y is the volume fraction of the particles in the film, r is the radius of the particles, F is Faradays constant, z is the charge of metal ions, i is the current density.

$$Jm = \frac{i}{zF} \quad (9)$$

Combining equations 7, 8, 9;

$$\frac{x_y}{1-x_y} = \frac{4\pi r^3 z F N_A}{3V_{m,M}} \left(1.554 v_p^{\frac{1}{6}} D_p^{2/3} \right) (C_{p,b} - C_{p,s}) \frac{\omega^{\frac{1}{2}}}{i} \quad (10)$$

Where v_p is the volume fraction of particles, ω is the rotation rate.

As indicated in Figure 1, the model of nanoparticles co-deposition suggested by Timoshkov et al. [35], is based on the following stages:

- Coagulation of ultra-fine particles in electrolytic bath,
- Formation of quasi-stable aggregates,
- Transport of the aggregates to the cathode surface by convection, migration and diffusion,
- Disintegration of the aggregates in the near-cathode surface,
- Weak adsorption of ultra-fine particles and aggregate fragments onto the cathode surface,
- Strong adsorption of dispersion fraction and embedment.

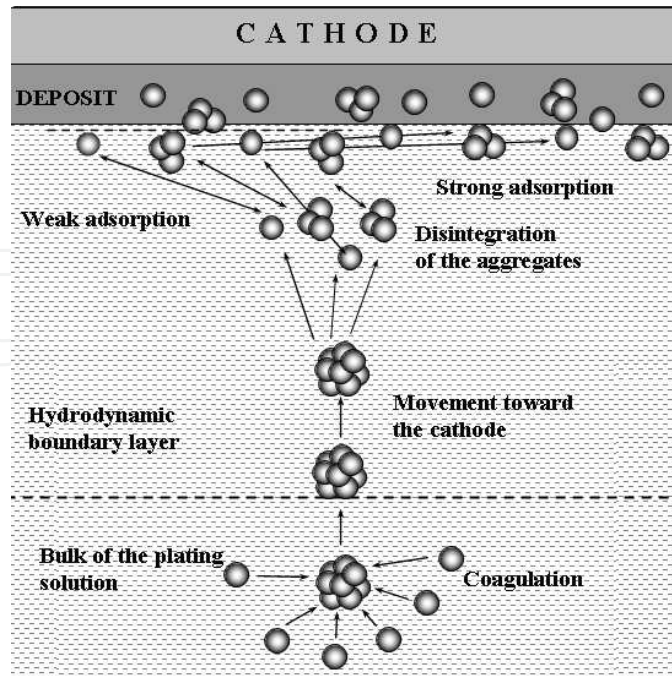


Figure 1. Model of nanoparticles co-deposition process [6, 35]

3. Particle interactions and suspension stability

3.1. The DLVO theory

The state of dispersion of particles in suspension can be controlled by careful manipulation of the inter-particle forces and their interactions. A quantitative description of the relationship between stability of suspension and energies of interactions between colloidal particles and other surfaces in a liquid has been given by the classical DLVO (Derjaguin-Landau-Verwey-Overbeek) theory. According to this theory, the stability of a colloidal system is determined by the total pair interaction between colloidal particles, which consists of coulombic double-layer repulsion and van der Waals' attraction. The total energy V_T of interaction of two

$$V_T = V_A + V_R \quad (11)$$

The attractive energy V_A of the London-van der Waals' interaction between two spherical particles can be expressed by:

$$V_A = -\frac{A}{6} \left(\frac{2}{S^2 - 4} + \frac{2}{S^2} \right) \quad (12)$$

where A is the Hamaker constant and $S = 2 + H/a$, with H the shortest distance between the two spheres and a the particle radius. If $H \ll a$, Equation (2) can be simplified to:

$$V_A = -A \frac{a}{12H} \quad (13)$$

The repulsive energy V_R is:

$$V_R = 2\pi\epsilon\epsilon_0 a \Psi \ln[1 + e^{-kH}] \quad (14)$$

where ϵ is the dielectric constant of the solvent, ϵ^0 is the vacuum dielectric permittivity, Ψ is the surface potential, $1/k$ is the Debye length:

$$k = \left(\frac{e^2 \sum n_i z_i}{\epsilon\epsilon_0 kT} \right)^{\frac{1}{2}} \quad (15)$$

where e is the electron charge, k is the Boltzmann constant, T is the absolute temperature, n_i is the concentration of ions with valence z_i [6].

3.2. Particle charging

The charge on the particles can be developed according to the following mechanisms:

- a. Ions are selectively adsorbed onto the solid particle from the electrolyte.
- b. Ions are dissociated from the solid phase into the electrolyte.
- c. Dipolar molecules are adsorbed or orientated at the particles surface.
- d. Electrons are transferred between the solid and liquid phase due to differences in work function.

Charged particle in a suspension is surrounded by oppositely charged ions. In the so-called boundary layer, the concentration of these ions is higher than their concentration in the bulk electrolyte. These ions and the particle should move in opposite directions when an electric field is applied. At the same time, the ions are also attracted by the particle, and as a result, a fraction of the ions surrounding the particle will not move in the opposite direction but move along with the particle. Accordingly, the speed of a particle is not determined by the surface charge but by the net charge enclosed in the liquid sphere, which moves along with the particle [6, 29].

3.3. Particle transport

The particle transfer toward the cathode surface occurs by four mechanisms, namely convection, migration, diffusion, and Brownian movement.

Convection: It includes thermal and stirring effects, which can be increased extensively by applying vibration, shock, and other stirring types and temperature gradients.

Migration: It is the movement of positive ions and negative ions, or charged particles, through the electrolyte under the effect of applied potential between the electrodes immersed in that electrolyte. The migration process occurs only for charged particles.

Diffusion: Electrode reaction decreases the concentration of oxidant or reductant at the electrode surface, producing a concentration gradient. Thus, the species movement from the higher to the lower concentration is enhanced. The diffusion process occurs for both charged and uncharged particles.

Brownian's movement: It is dependent on the particle size and may be ignored for particle size larger than 1 μm [24].

3.4. Other interparticle forces

During the electrodeposition process of nanocomposites, the following forces are taken into consideration:

- Mechanical forces, resulting from interaction with the fluid flow and other particles, gravity and buoyancy.
- Electrical forces, due to the electric field presented in the electrolyte.
- Molecular forces working on the particle in the vicinity of the cathode electrodes surface [24].

4. Effect of deposition parameters on ECD

The electrodeposition process and thus the resulted microstructure of composite coating can be affected by many parameters, such as:

- The electrolyte condition: chemical composition of the electrolyte bath, presence of additives, pH, temperature, and electrolyte stirring.
- Current conditions: current density and type of applied current (pulse or DC).
- The properties of the reinforcing particles: particle size, surface properties, concentration, and type of dispersion in the electrolyte [23, 36].

a. Current Density

Current density plays an important role in controlling the deposition rate which will in turn affect the concentration, composition and morphology of incorporated particles in the coatings. It also influences the thickness of the composite films, such that as the current density increases the thickness of the coatings increases. Low current density produces films with large surface irregularities. When the current density is increased, the amount of particle incorporation obtained has been found to increase for the Ni-TiO₂ system with a relatively slow agitation, decrease for natural or synthetic diamond in Ni and for Cr particles co-deposited in Ni and to be unaffected when co-depositing alumina in Ni [24].

Particles reinforcement in the composite coatings varies with current density. At first, incorporation increases sharply at the beginning with increase in current density till it reaches maximum value followed by sharp decrease. Therefore, hardness of composite coatings mainly increases due to the combined effect of both grain refining as well as of dispersive strengthening. When electroplating at lower current densities, metal ions dissolved from anode are transported at low rate and hence there is insufficient time for these ions to adsorb on particles resulting in weak Coulomb force between anions adsorbed on particles leading to lower concentration of electrodeposited particles in the composite coatings. On the other hand, at higher current densities, metal ions dissolved from anode are transported faster than particles by the mechanical agitation which causes a decrease in co-deposition of particles as well as hardness of composite coatings. Therefore, selection of optimum current density is important to enhance the concentration of particles in the composite coatings [37]. The maximum current density for preparing nanocomposite coatings is limited by the limiting current density.

The DC electrodeposition methods are often associated with slower deposition rates and coating defects such as surface roughness, porosity, poor adhesion, undesirable microstructure, etc. Recently, pulse current (PC) and pulse reverse current (PRC). ECD methods have attracted significant attention to improve deposition rates and microstructure of the coatings for improved mechanical and corrosion properties [24, 25].

b. Bath Temperature

According to Akarapu [25], two contrary behaviors were observed regarding the effect of temperature on the obtained crystallization size. This discrepancy was due to the two contra-

dictory effects of temperature increase on the thermodynamic and kinetic driving force of nucleation process. As the electrolyte's temperature increases, the thermodynamic driving force of crystallization decreases and the critical size of the nucleus will increase. This will lead to lower nucleus densities and formation of coarse grain. On the other hand, the increase in temperature leads to enhancement of the kinetic driving force. This results in an increase in the rate of nucleation and thus fine grains formation [25].

c. Bath Agitation

Agitation of the plating solution is important in determining particle incorporation. There are various methods of agitation employed include circulation by pumping, purging, of air, ultrasonic agitation, and the plate pumper technique. In general, if the agitation is too slow (laminar flow), the particles in the bath may not disperse completely, except when their density is low. If the agitation is too high (turbulent), particles will not have sufficient time to get attached to the surface, and this results in poor particles incorporation [25].

Increase in the bath agitation in the parallel plate electrode setup has been found to increase the amount of particles co-deposited within the electroplated film for the Ni- Al_2O_3 and Ni- TiO_2 systems. When the agitation is increases, a greater number of particles arrive at the electrode surface and the amount of particle incorporation in the metal film increases. However, if the agitation is too intense, the residence time for the particles at the electrode surface is insufficient and the particles are swept away before they can be incorporated into the growing metal film [25]. The amount of co-deposition has also been observed to decrease in the Cu-SiC and Cu-CrB₂ systems with increasing agitation [24].

d. Particle Characteristics

Particles can be characterized by their composition and crystallographic phase, as well as by their size, density, and shape. The particle composition can have a dramatic impact on the amount of incorporation obtained for a particular bath composition. For instance three times more TiO_2 than Al_2O_3 has reportedly been incorporated into a Ni matrix, under the same deposition conditions. The particle size also effects on the amount of co-deposited particles in the composite coatings. For example when the particle size in the electrolyte increases then amount of adsorbed ions on the surface increases, which leads to the increase in the migration velocity of the particles and also results in a higher columbic force of attraction, leads to increase in the amount of the particles. But the density of particles in the coating decreases as the particle size in the electrolyte increases [25].

The electrode/particle interaction will be affected by the particle properties, such as material type, shape, size, surface charge, concentration, and dispersion in the bath. The co-deposition of nano-sized particles produces a composite coating with a much higher hardness than that achieved with micron-sized particles. The smaller the particle, the more difficult the co-deposition into the metal matrix due to the high tendency of agglomeration. In addition, the smaller the particle size, the greater the effect of colloidal properties (van der Waals, electrostatic, and solvent interaction forces) [24].

e. Bath composition

The composition of the co-deposition bath is not only defined by the concentration and type of electrolyte used for depositing the matrix metal, but also by the particle loading in suspension, the pH, and the additives used. A variety of electrolytes have been used for the electro co-deposition process to form metal matrix of copper include acid copper sulphate bath, alkaline pyrophosphate bath. Electrolyte concentrations typically range between 100-600 g/l and the particle loading in suspension has ranged from 2-200 g/l [25].

According to Narasimman et al. [38], various additives can be used for preventing the agglomeration of particles, increasing the volume fraction of reinforcing particles in the deposit, and providing good dispersion and thus high hardness. The addition of surfactants plays a role in modifying the surface charge and reducing the particle agglomeration, thus improving their electrostatic adsorption on the cathode surface. As a result of decreasing the agglomeration of particles, the amount of effective particles would be significantly increased, resulting in higher amounts of the reinforcing particles. The addition of surfactants changes the zeta potential of the particles.

The effect of additives in the plating bath on the microstructure and physical properties of deposits was reported by many researchers. For example, the addition of saccharin to plating electrolyte was found to improve the ductility and brightness. The role of additives on a grain refining can be summarized as follows:

- As refiner, blocking the surface by complexation, decreasing the adsorbed ions diffusion on cathode, and thus inhibiting the growth of crystals.
- Controlling the evolution rate of hydrogen on cathode.
- Changing the cathodic overpotential [38].

5. Types of Nanocomposites

5.1. Metal matrix nanocomposites

Various processes are used to manufacture MMCs which are described here. These processes are classified on the basis of temperature of the metallic matrix during processing. Accordingly, the processes can be classified into five categories: (1) liquid-phase processes, (2) solid-liquid processes, (3) two- phase (solid-liquid) processes and (4) in situ processes. (5) deposition techniques [39-40].

5.1.1. Electrodeposition of nickel nanocomposites

Nickel nanocomposite coatings are used in a wide variety of industrial and engineering applications, such as consumer electronics, chemical, computer and telecommunications industries in order to improve corrosion and wear resistance, modify magnetic and other properties. For nickel matrix electrodeposits, a great variety of particles have been used such

as oxides i.e. TiO_2 [41, 42], Al_2O_3 [43], CeO_2 [44, 45], ZrO_2 [46], graphene oxide GO [47], carbon nanotubes CNT; $\text{Al}_2\text{O}_3/\text{Y}_2\text{O}_3/\text{CNT}$ [48], carbides like SiC [49–51], WC [52] and nitrides such as TiN [53] and Si_3N_4 [54].

The Ni- TiO_2 system was selected because nickel is an industrially important coating for corrosion protection [42]. Generally the volume fraction of co-deposited particles is limited for nanoparticles and usually it is inversely proportional to their size. For example, Shao et al. [43] studied the rate of incorporation of two different sizes of Al_2O_3 nanoparticles (50 nm and 300 nm) into a nickel deposit. Using similar operating parameters (1000 rpm, 20 mA cm^{-2}), it was found that the percentage volume fraction of the 300 nm Al_2O_3 in the nickel deposit was much higher compared to the 50 nm Al_2O_3 . The presence of nanosized particles in a metal deposit may induce changes in the crystalline structure of the metallic coating.

Ni- CeO_2 nanocomposite coatings were prepared by co-deposition of Ni and CeO_2 nanoparticles with an average particle size of 7 nm onto pure Ni surfaces from a nickel sulphate. The as-codeposited Ni- CeO_2 nanocomposite coatings showed a superior oxidation resistance compared with the electrodeposited pure Ni coating at 800°C . The co-deposited CeO_2 nanoparticles blocked the outward diffusion of nickel along the grain boundaries. However, the effects of CeO_2 particles on the oxidation resistance significantly decrease at 1050°C and 1150°C due to the outward-volume diffusion of nickel controlling the oxidation growth mechanism [45].

According to Zeng et al [46], increasing concentration of the CeO_2 nanoparticles in the bath increased the weight percent of CeO_2 particles in the nanocomposite coatings, and improved the micro-hardness, and the friction, corrosion, and wear behaviour of the coatings. However, excessive CeO_2 nano-particle loadings were detrimental to the coating properties.

Ni- Al_2O_3 -SiC hybrid composite films with an acceptable homogeneity and granular structure having 9.2 and 7.7 % vol. Al_2O_3 and SiC nanoparticles, respectively were developed successfully by M. Masoudi et al [50]. Both micro hardness and wear resistance increased owing to dispersion and grain-refinement strengthening of nanoparticles. The oxidation resistance of the Ni- Al_2O_3 -SiC hybrid composite coatings was measured to be approximately 41 % greater than the unreinforced Ni deposit and almost 30 % better than the Ni- Al_2O_3 composite coatings.

Ni-SiC nanocomposite coatings were applied on AZ91 magnesium alloy from Watts bath with different SiC content. Micro-hardness of specimens was measured and the results revealed a significant enhancement: from 74 Vickers for bare AZ91 magnesium alloy to 523 Vickers for coated specimen. The obtained data showed the superior corrosion resistance for the coated AZ91 magnesium alloy [51].

The effect of incorporation of Si_3N_4 particles in the Ni nanocomposite coating on the micro hardness, corrosion behaviour has been evaluated by Kasturibai et al. [54]. The micro hardness of the composite coatings (720 HV) was higher than that of pure nickel (310 HV) due to dispersion-strengthening and matrix grain refining and increased with the increase of incorporated Si_3N_4 particle content. The corrosion potential (E_{corr}) in the case of Ni- Si_3N_4 nano-composite had shown a negative shift, confirming the cathodic protective nature of the coating [54].

According to R. Abdel-Karim et al. [55], Ni–Mo nanocomposite coatings were prepared using a nickel salt bath containing suspended Mo nanoparticles using direct current. The crystallite size (18–32 nm) and the surface roughness increased by raising the current density. A remarkable deterioration in the corrosion resistance of Ni–Mo composites was observed with the increase of Mo content. This could be due to crystallite size-refining and surface roughness effect and correspondingly a large surface area. Resulted high surface roughness lead to improved electrocatalytic effect for hydrogen evolution.

5.1.2. Electrodeposition of copper nanocomposites

The conventionally used reinforcements in the Cu matrix such as oxides, carbide nanoparticles etc., have resulted in considerable improvement in the mechanical properties. Copper- TiO₂ nano composites were deposited from an acidic copper sulphate bath. Due to relation of optical properties and photo responsively of TiO₂ nanoparticles to nanoparticle size, surface area and morphology, optimization of these parameters in order to having efficient response have crucial importance. Good quality deposits (finer grain size and more homogeneous) were obtained at rather low pH [56].

According to Quayum et al. [57], Cu-NPs /ZnO / ITO composite film electrode has been prepared by electrodeposition of Cu nanoparticles (NPs), ZnO nanorods on indium tin oxide (ITO). Cu-NPs/ZnO composite electrode had high sensitivity and stability and showed higher catalytic current for glucose oxidation in the field of biosensors.

According to Li et al. [58], Cu/C composites were successfully fabricated by three step electrodeposition. The effects of hot pressure temperature and alloy element Fe on the interface characteristic of Cu/C composite were investigated. The addition of alloy element Fe not only improves the tensile strength and the lateral shear strength of the Cu/C composite, but also changes the interface bond type from the physical bond type to the chemical bond type.

The Cu/ZnO nanocomposite films have been synthesized by cathodic electrodeposition [59]. The SEM and TEM images reveal the formation of hexagonal two-dimensional ZnO sheets and Cu nanoparticles. The Cu/ZnO nanocomposite film showed good emission current stability.

Chrobak et al. [60], studied both elastic and magnetic properties of the Cu+ Ni nanocomposite coatings with dispersed Ni nanopowder particles obtained by applying the electrolytic deposition method. The magnetization curves $M(T)$ showed a superparamagnetic effect at $T < 50$ K which depends on dispersion of magnetic particles in a nonmagnetic matrix. It was also shown that the observed decrease of the apparent Young's modulus due to an increase of coating roughness.

Pavithra et al. [61], demonstrated the synthesis of very hard Cu-Graphene composite foils by a simple, scalable and economical pulse reverse electrodeposition method with a well-designed pulse profile. Carbon as a reinforcement material, in the form of fibres, nanotubes etc., will result in superior mechanical, electrical properties and an extremely high thermal conductivity. The improved strength of metal matrix composites is due to its excellent mechanical properties of Graphene. In addition, graphene is also shown to block dislocation motion in a nanolayered metal-graphene composites resulting in ultrahigh strength [62].

5.1.3. Electrodeposition of cobalt nanocomposites

Nanocrystalline cobalt and cobalt-based alloys are good candidates for the replacement of the highly toxic electroplated hexavalent chromium. They have excellent mechanical and wear-resistant properties, high saturation magnetization, and good thermal stability. Nanocrystalline cobalt and its alloys have higher hardness over the polycrystalline counterparts. Electrochemically prepared Co nanodeposits have three to five times higher coercivity (H_c) than conventional polycrystalline Co [63].

Cobalt composites containing incorporated TiO_2 particles are interesting materials, due to the semiconducting properties of TiO_2 , with applications as photocatalysts, particularly in the treatment of polluted water, but, in the same time, due to magnetic properties of Co matrix. More attention has been focused on ferromagnetism in Co-doped TiO_2 anatase films, nanocrystals, nanorods and nanotubes, with potential applications in spintronics. The inclusion of TiO_2 in a nanocomposite layer with increasing current density causes the decrease of saturation magnetization from 279.5 (a.u.) to 76.0 (a.u). Magnetic anisotropy of nanocomposite films depends on the concentration on morphology and magnetic properties of Co- TiO_2 electrodeposited nanocomposite films [63]. According to Sivaraman et al. [64], the electrodeposited the composites exhibited a partially amorphous/nanocrystalline character, with the crystalline fractions originating from the hexagonal-close packed structure of Co. A refinement of the Co crystallite size was observed in deposits containing higher weight percentage of yttrium compounds. The hardness increased with the yttrium content.

5.1.4. Electrodeposition of chromium nanocomposites

Deposition of thick Cr from Cr (III) bath is cumbersome and thin Cr does not have enough wear resistance. The electrodeposition of Cr- Al_2O_3 nanocomposite from Cr (III) bath appears a feasible way for improvement of wear resistance, hardness, lubricity and high temperature resistance of the deposited layer [65].

Cr- TiO_2 nano-composites were prepared by electrodeposition. The addition of TiO_2 in the coating led to improvement corrosion resistance of the composite coating as compared to the pure chromium coating. This improvement is due to the physical barriers produced by TiO_2 to the corrosion process by filling crevices, gaps and micron holes on the surface of the chromium coating. This excellent corrosion resistance of the composite coatings provides wide applications in modern industry [66].

Juneghani et al. [67] examined Cr-SiC nanocomposite coatings with various contents of SiC nanoparticles prepared by electrodeposition in optimized Cr plating bath containing different concentrations of SiC nanoparticles. The co-deposited SiC nanoparticles are uniformly distributed into the Cr matrix which improves the corrosion and wear performance of coating.

5.1.5. Electrodeposition of zinc nanocomposites

Zinc deposits provide good protection to iron and steel components due to its sacrificial nature, low cost and ease of application. Nanocrystalline zinc shows improved properties such as

hardness, ductility, corrosion and wear resistance. The graphene based metal materials have been widely reported that the graphene as a support material for metal nanoparticles to obtain catalytic, optoelectronic and magnetic properties. The GO sheets were reduced to be rGO sheets after electrodeposition process while Zn^{2+} also reduced on the surface of rGO sheets. Due to the greatly increasing in the specific surface area, the Zn/rGO film may be used as efficient catalyst for the reaction of methanol generated by carbon dioxide and hydrogen (Figure 2) [68].

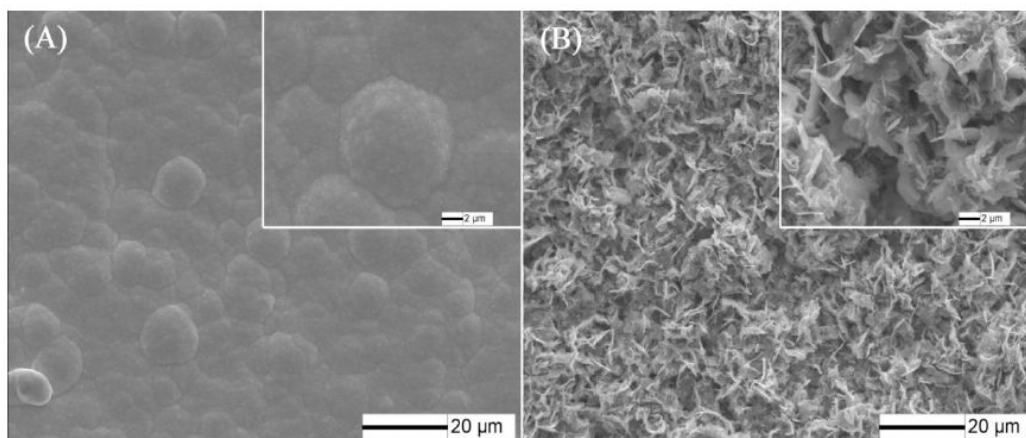


Figure 2. Representative SEM images of (A) Zn film and (B) Zn/rGO film. The insets are the corresponding high-resolution images [68].

Indeed, pure zinc coatings suffer from poor mechanical properties and the incorporation of a second hard phase during the electrodeposition process (e.g. ceramic nanoparticles such as ceria (Figure 3) [69], SiO_2 [70] or Al_2O_3 [71], is of great importance.

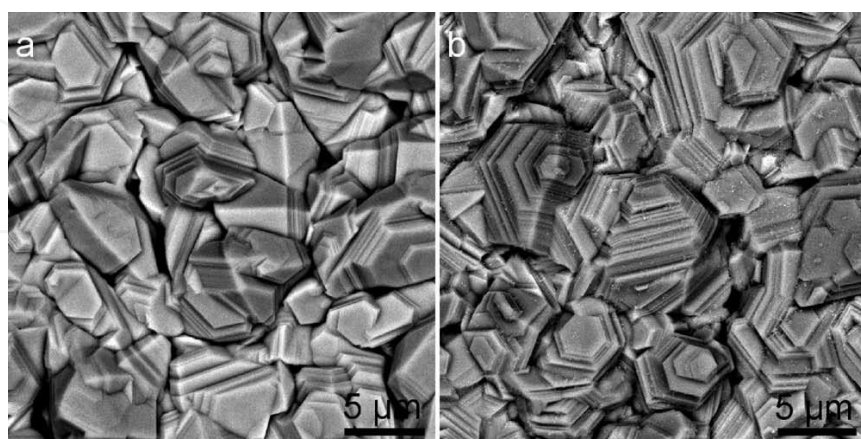


Figure 3. Surface SEM image of (a) pure zinc and (b) zinc-ceria nanocomposite coatings [69].

According to Gomes et al. [72], Zn- TiO_2 coatings were successfully prepared by co-deposition method. The film's surface is rough and the TiO_2 agglomerates are randomly distributed on

the metallic matrix formed by stacked hexagonal plates oriented in different direction. These unique characteristics are essential for the thermal conversion of Zn to ZnO. The photo-electrochemical degradation of organic molecules was achieved with this type of Ti/ZnO-TiO₂ photoanodes (Figure 4).

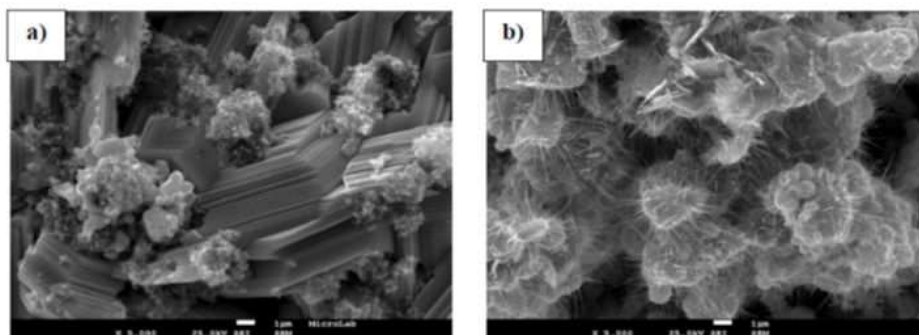


Figure 4. FEG-SEM images for (a) as-deposited and (b) annealed Zn-TiO₂ nanocomposite films [72].

5.2. Ceramic Matrix Nanocomposites

Ceramic matrix composites (CMCs) can extensively overcome the intrinsic brittleness and lack of mechanical reliability of monolithic ceramics, which are otherwise attractive for their high stiffness and strength. In addition to mechanical effects, the reinforcing phase can improve electrical conductivity, thermal expansion coefficient, hardness and thermal shock resistance. The combination of these characteristics with intrinsic advantages of ceramic materials such as high-temperature stability, high corrosion resistance, light weight and electrical insulation, makes CMCs very attractive functional and structural materials for a variety of applications. A wide range of reinforcing fibers have been investigated, including those based on SiC, carbon, alumina, and mullite. However, carbon fibers are among the highest performance toughening elements investigated [73, 74].

Electrodeposition of ceramic films employing electrochemical methods is a fast evolving field. The methods for electrodeposition may be divided into two: electrophoretic and electrolytic deposition. Electrolytic deposition can be driven using cathodic currents by either reducing the metal ions, which causes their deposition, e.g., Cu₂O, or by driving a proton dependent reducing process, leading to an increase of the pH on the electrode surface and the subsequent metal hydroxide deposition. The deposition of ceramic nanocomposite materials is of utmost importance in different fields spanning from supercapacitors to anticorrosion films and from coatings of medical implants to advanced lubricant materials [75].

5.3. Polymeric matrix nanocomposites PNCs

Cathodic electrodeposition of polymer-metal and polymer-ceramic materials is an area of intense interest. Such materials exhibit interesting mechanical, thermal, electrical, optical and magnetic properties whose applications have motivated the development of electrochemical

techniques [76, 77]. PNCs are among the most promising class of new materials because they are light weight, flexible, low cost, anti-corrosive, and have good process ability and mechanical properties. Most polymers are electrical insulators and are used for a variety of insulating applications in industry. However, the inherent electrical insulation means polymers tend to hold the electrostatic charges, and allow the electromagnetic frequency interference (EMI) to travel through without loss [78].

Some polymer/nanoparticle (NP) composites have already been reported in the literatures, such as polyaniline/metal oxide NP composites, PPy/TiO₂, PPy/Ti, PPy/Au, PPy/Ag, PPy/Pt, and PPy/Pd, prepared by electrodeposition [79]. The incorporation of metal nanoparticles into the conducting polymer offers improved performance for both the host and the guest. They can be applied in application in electronics because incorporation of metal clusters is known to increase the conductivity of the polymer. The applications of these composites have also been extended to various fields such as, sensors, photovoltaic cells, memory devices, protective coatings against corrosion, and supercapacitors. The application of these composites in catalysis is of particular interest. The polymer allows the control of the environment around the metal center, thus influencing selectivity of the chemical reactions [80].

Conducting polymer/inorganic oxide nanocomposites have recently attracted great attention due to their unique microstructure, physiochemical and electro-optical properties, and a wide range of their potential usage in battery cathodes and in the construction of nanoscopic assemblies in sensors and microelectronics. Conductive polymer/ZnO nanocomposites coating were prepared on type-304 austenitic stainless steel (SS) using H₂SO₄ acid as electrolyte by potentiostatic methods. It was found that ZnO nanoparticles improve the barrier and electrochemical anticorrosive properties of polymer [81].

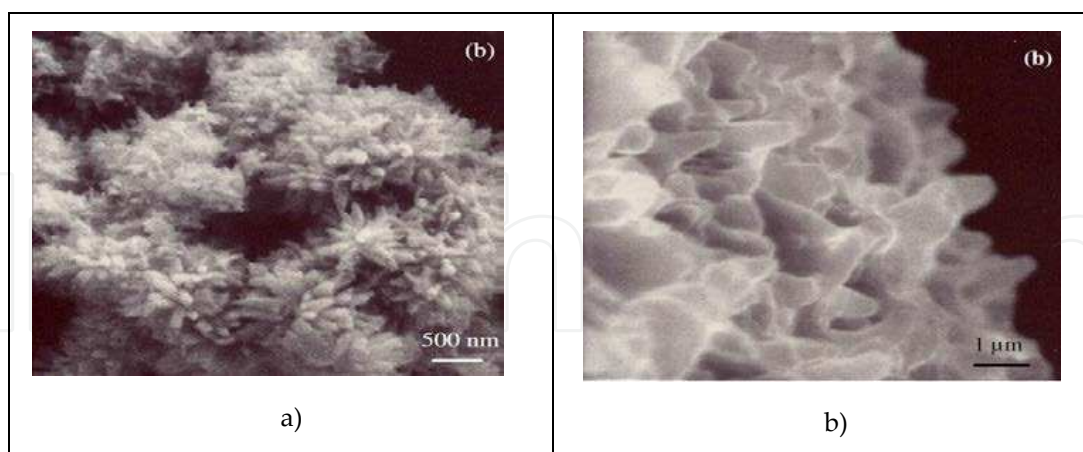


Figure 5. SEM micrographs of the deposits; (a) ZnO NPs, (b) ZnO NPs [81].

Electrically conducting polypyrrole (PPy)–iron group (Ni, Co, Fe and their alloys) composite films have been electrodeposited at cathodic process to give “tailored” soft and hard magnetism. The composites of the PPy doped with dodecylsulfate (DS) (PPy–DS) with NiFe alloy showed soft magnetism with coercivity H_C , $k < 9$ Oe, while the PPy–DS with CoMnP alloy

showed hard magnetism with HC, $k > 1085$ Oe. These results indicated the possibility conducting polymer–magnetic metals composites fabrication by electrodeposition [82].

The incorporation of metal nanoparticles into the conducting polymer offers enhanced performance for both the host and the guest. They have diverse application potentials in electronics because incorporation of metal clusters is known to increase the conductivity of the polymer. The applications of these composites have also been extended to various fields such as, sensors, photovoltaic cells, memory devices, protective coatings against corrosion, and supercapacitors. Of particular interest is the application of these composites in catalysis. The polymer allows the control of the environment around the metal center, thus influencing selectivity of the chemical reactions [83].

Y. Lattach et al. [84] stated that nanocomposite anode materials for water oxidation have been readily synthesized by electrodeposition of iridium oxide nanoparticles into poly (pyrrole-alkylammonium) films. Electroanalytical investigations have shown that the electrocatalytic activity of iridium oxide nanoparticles is fully maintained when they are incorporated in the polymer matrix.

Electrodeposition process was carried out by dispersing UHMWPE powders in an electrolytic solution of cobalt sulphate/cobalt chloride solution to obtain Co/UHMWPE composite coating on stainless steel substrate (304L). UHMWPE was selected as surface modifier element, due to its high biocompatibility and low coefficient of friction. This material can be used in many biomedical applications [85].

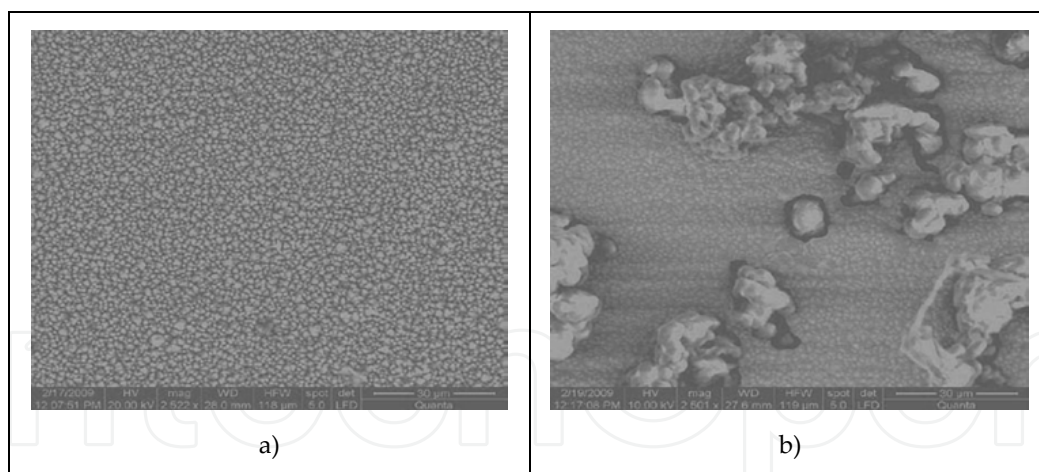


Figure 6. SEM surface morphology of coatings obtained at current density of 48 mA/cm^2 and deposition time of 30 min: (a) Pure Co; (b) Co/UHMWPE Composite Coatings with 30 g/L [85].

6. Conclusions

In conclusion, materials science and engineering has experienced a tremendous growth in the field of nanocomposite development with enhanced chemical, mechanical, and physical

properties. The progress in nanocomposites is varied and covers many industries. Nanocomposites with a variety of enhanced physical, thermal and other unique properties can be manufactured. They have properties that are superior to conventional microscale composites and can be synthesized using simple and inexpensive techniques. Theoretical aspects and mechanisms related to the electrodeposition process of nanocomposite films, from aqueous solutions, were discussed. The three types of matrix (metal, ceramic, polymers) nanocomposites were presented, underlining the needs for these materials and some recent results on structure, properties and potential applications.

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