THE ANNALS OF “DUNAREA DE JOS” UNIVERSITY OF GALATI.
FASCICLE IX. METALLURGY AND MATERIALS SCIENCE
N^0. 3 – 2012, ISSN 1453 – 083X

NANOCOMPOSITE COATINGS OBTAINED BY ELECTRO-CO-DEPOSITION OF INERT PARTICLES WITH COBALT-A REVIEW

Florentina Simona ŞORCARU, Lidia BENEA[*]
Dunarea de Jos University of Galati, Faculty of Metallurgy and Materials Science,
Competences Centre: Interfaces-Tribocorrosion-Electrochemical Systems (CC-ITES)
email: Florentina.Sorcaru@ugal.ro,
*Corresponding author: Lidia.Benea@ugal.ro

ABSTRACT

The paper focuses on review investigations of electrodeposition processes of metallic coatings containing dispersed nanosized particles. The nanosized particles, suspended in the electrolyte by agitation and/or use of surfactants, can be electro-co-deposited with the metal. The inclusion of nanosized particles can give (i) increased microhardness and corrosion resistance, (ii) modified growth to form a nanocrystalline metal deposit and (iii) a shift in the reduction potential of a metal ion. Many operating parameters influence the quantity of incorporated particles, including current density, bath agitation (or movement of work piece) and electrolyte composition. High incorporation rates of the dispersed particles have been achieved using (i) a high nanoparticle concentration in the electrolyte solution, (ii) smaller sized nanoparticles; (iii) a low concentration of electroactive species, (iv) ultrasonication during deposition and (v) pulsed current techniques. Compositional gradient coatings are possible having a controlled distribution of particles in the metal deposit and the theoretical models used to describe the phenomenon of particle co-deposition within a metal deposit are critically considered.

KEYWORDS: metal–matrix composites (MMCs), nano composites, coating, functional composite, nano particles

1. Introduction

The number of publications dealing with obtaining functional matertials has considerably increased lately. In addition, to the increased number of publications in this area, a comprehensive review of the mechanism and process of electrodeposition of nano composite layers is necessary.

In this case the purpose of this pape is to addres the need for reviewing the publications in the literature. Composite layers in cobalt matrix may provide properties comparable or even better (hardness, corrosion resistance and abrasion resistance) than other composite layers especially for high temperature applications. The objective of this paper is to investigate the parammeters for obtaining nanocomposite layers in cobalt matrix. There are few reports in the literature on the preparation of composite layers in cobalt matrix by using inert particles incorporation namely carbides - SiC [1, 2, 3] oxides (Cr_2O_3, [4], ZrO_2 [5, 6], CeO_2 [7] lantanides [7]).

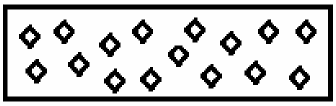
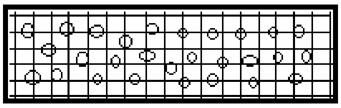
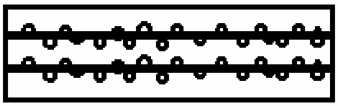
2. Electrochemical method

Nanocomposite layers with unique properties may be produced by different methods [8].

The most widely used method of obtaining composite materials is electrochemical co-deposition as it features clear advantages in comparison with other similar methods (chemical deposition by evaporation, electrochemical deposition by evaporation, plasma spraying vaccumm spraying) (Table 1) [9].

The electrochemical co-deposition is easier to apply because it requires simple facilities and low cost reactants as compared with the other methods; therefore the basic advantage of this method is efficiency. Table 1 lists a number of nanostructures materials obtainable by electrodeposition [9].

***Table 1**. Various types of nanostructured materials which may be produced by electrodeposition methods [9].*

Methods of electrodeposition	Nanoparticles in a metal deposit
Direct current (DC) Pulsed direct current (PDC)	Single metal deposit and nanoparticles 
Pulsed reverse current (PRC) Potentiostatic (P)	Alloy deposit 
Pulsed potentiostatic (PP)	Multilayer deposit 

Nanocomposite structures have long been known for their properties due to extremely fine microstructures [8]. Functional surfaces of improved and extremwely complex optical, magnetic, mechanic, chemical and tribological properties are attractive for industrial and biomedical applications [8, 10]. Electrodeposition is a method involving co-electrodeposition of metal, nonmetal or polymer particles into the metal layer under the effect of an electric field. Thus, the co-electrodeposition of various metal matrices such as Ni and Zn, with a large variety of powders from hard carbides like SiC, oxides ZnO, has been intensively studied by Abdel Aal & al. [8]. During this process, particles are suspended in a solution of conventional electrolyte, captured in the metallic matrix producing composite layers. Moreover, the degree of particles inclusion depends on the nature of used particles (size, shape), and the working conditions (current density, temperature, pH of solution, deposition time, concentration of the particles used in the electrolyte solution) [8].

Functional surfaces are considered nanocomposite layers when one of the sizes of the components is of nanometric order, of typical dimensionsa below 100 nm. There is a variety of nanometric particles, ranging from 1nm to 100nm, that have successfully been incorporated into metallic matrrix by electrodeposition [9].

Particles such as oxides of Al_2O_3 [12, 13, 14, 15], ZrO_2 [16, 17], TiO_2 [18, 19], CeO_2 [20, 21] or carbides like SiC [1, 2, 3].

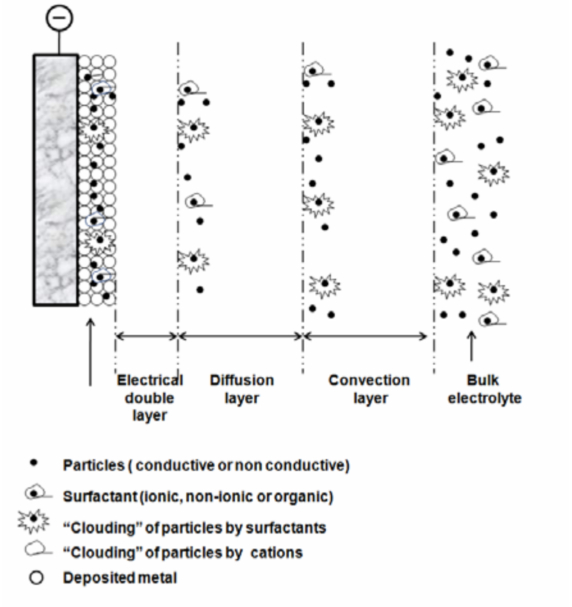


***Fig. 1.** Mechanism of particle co-deposition in a metallic metallic matrix adapted acc to (Low 2006) [9]*

The inclusion of dispersed particles into a metal matrix has been a scientific novelty and composite layers feature quite interesting properties. The inclusion of the disperse phase into composite layers implies a complex interaction (Fig. 1) of the particles with the hydrodynamic electric field with the metal crystal growth surface and depends on the electrolyte concentration [11]. The metallic matrices most widely used are Ni [23, 24, 28, 29, 30, 31, 56], Cu [15], Zn [10], Co [1, 2, 3]. In spite of all these also attractive are metallic alloys such as Ni-Zn, Ni-Co [25], [26]. Obtaining functional surfacs by electro-co-deposition requires stable suspensions, ceramic particles positively charged. It is extremely important to prevent particles clustering in suspension so as to ensure a controlled deposition and an even distribution of particles in the composite layers. The most investigated composite systems have been Ni-SiC due to their potential technological applications [23-31]. Taking into account the wide variety of metals that can be used; the process of co-electro-deposition makes it possible to produce a wide range of composite layers which, unlike pure metallic layers, feature improved physical, chemical and electro-chemical properties [11, 27, 31]. The use of composite layers starts back in 1950 on automotive engines [4] which progressively develop [11]. In 1970 and 1980, researches have focused on the need to produce layers of improved mechanical properties, to increase steadiness to corrosion and wear. In the 90s’ new areas emerged, such as electrocatalysis associated with an increased interest in particle sizes. In his work, Musiani comments upon the new applications reached by the process of electrodeposition [32]. The concentration of the particles incorporated into the electrolyte solution is the essential parameter to successfully obtain composite layers, as they determine to a great extent the properties of the composite layers such as corrosion and wear resistance, corrosion protection to high temperatures as compared with the corresponding values of the pure metals or alloys [32]. Another essential factor is the even distribution of particles in metallic matrix [33]. It should, however, be underlined that the morphological and structural characteristics of the metallic matrix are strongly affected by the presence of nanoparticles [11]. The future of these materials strongly depends on the capacity of producing them by low cost reliable procedures. The co-electro-deposition method meets part of these requirements since it is an economical and less costly technique than other preparation procedures. These are some of the reasons why this method has become so popular [4, 11, 32]. The processing temperature (room temperature) reduces to a minimum the chemical reactions and the interdiffusion between substrate and composite layers. The layer thickness can be accurately controlled by monitoring the time, the current density and the bath composition (pH) which can be adapted as shown by Bicelli & Co in 2008 [34]. Therefore the structure, morphology and properties of the composite layers are fundamentally affected by the electrodeposition parameters such as electrolysis conditions (composition and the electrolytical bath stirring speed, presence of additives, temperature, pH) [11] and the particle properties (type, size, shape, concentration and dispersion into the electrolytical bath) [9, 27, 32].

3. Mechanism of co-electro-deposition of inert particles in a metallic matrix

Much information on the electrodeposition mechanism is obtained from the literature. Co-deposition mechanisms for inert particles co-deposition into the metallic matrix have been developed by means of micrometric – sized particles [9, 27, 35].

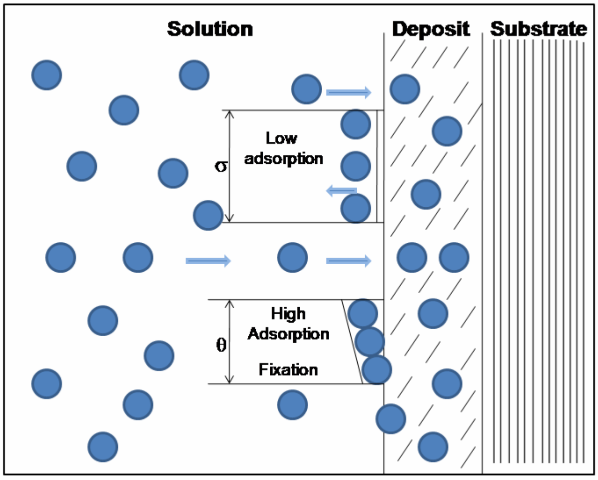


Fig. 2. *Electrodeposition process proposed by Guglielmi, adapted after [36]*

The first proposed model was reported in 1962 by Whithers followed by the model advanced by Martin & Williams in 1964 [35]. But the first model applied even today is the model of Guglielmi [36] who regards the deposition process as a succession of two phases: a slight electrochemical adsorbtion phase and a strongly chemical phase. The physical sense of both phases has not been assigned a clear mathematical expression yet and the model fails to consider the issues related to the electrolyte stirring (Fig. 2), a model verified for particles of SiC and TiO_2 in Ni matrix and for alumina particles in Cu matrix.

The model proposed by Celis & co (1987) [37] makes use of the concept of probability to describe the amount of particles to be incorporated at a given current density and implies the existence of some stages of incorporation of particles into the metallic matrix: (i) reduction of ions at cathode, (ii) adsorbtion of particles onto the cathode This model has been validated by examining the (Al_2O_3) particles in Cu matrix [37].

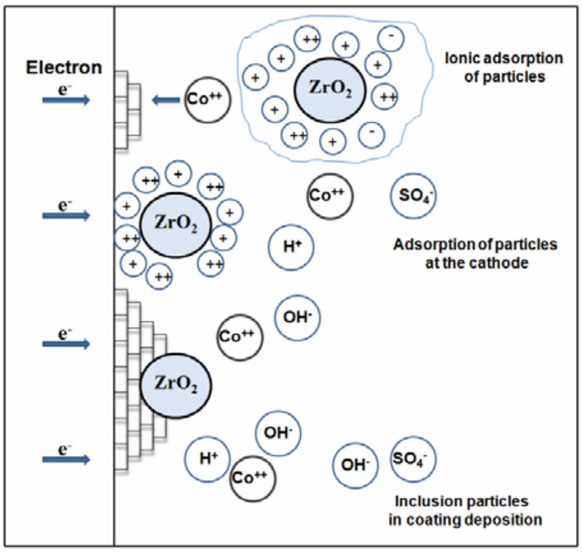


Fig. 3. *Electrodeposition process proposed by Celis, Buelens et al. adapted for the system Co/ZrO_2 after [37]*

Out of the experimental results reached accounting to this model, we mention: Ni-AZY [38], Ni-SiC [22, 29, 30, 31], Ni-TiO_2 [19], CeO_2-SiO_2/Ni-W-P [40], Ni-Al_2O_3 [41, 42, 43, 44, 48], Ni-SiO_2 [45, 46], Ni-Co/SiC [38] and Ni-MoS_2/Al_2O_3 [47], Cu-CeO_2 [49], Co-ZrO_2/CeO_2 [50], Ni-CeO_2 [51].

However, the interaction particle-electrode, their relative importance and attraction force is still an issue for further discussions. On these principles focused Vereecken and collaborators [52] who stated that the transport of particles up to the surface of a substrate is controlled by difussion and the influence of the particle gravity force is represented by the different current densities used to obtain composite layers.

More recently, in 2007, Lee and Talbot [11] proposed a model by which it can be found the amount of nanoparticles incorporated into a kinetic process and the mass transfer in the electro-chemical deposition region which is consistent with the experimental data provided on the system Cu-Al_2O_3.

Nowadays, the models used to describe particle inclusion are limited to certain conditions and empirical studies in laboratory are still very important in this respect. Future models describing the process of particle co-electro-deposition in a metallic or non metallic matrix shall need special attention to be focused on: characteristics and properties of nanoparticles (composition, dimension, density, crystallographic structure), along with the operating parameters during the co-electrodeposition process [11].

The validity of the theoretical models of incorporation underlying the inclusion of particles into a metallic matrix requires special attention because the electrochemical process of co-electro-deposition is not fully understood yet [11, 27, 32].

4. Process parameters

The amount of particles incorporated into the metallic matrix (metal or alloy) is the most important parameter taken into account when such functional surfaces are being obtained. As shown in previous sections, composite properties are determined to a large extent. In order to obtain a composite of exceptional properties, the effect of the process parameters on the content of the particles should therefore be known. Besides the practical meaning of these effects, also a necessary condition is to understand the mechanism of particle co-deposition.

In the long run it has been found that there are many, direct or indirect process parameters which affect the content of particles in the composite layers [9, 37, 53, 54].

A large variety of particles (micro and nanometrice dimensions) has successfully been incorporated by co-electro-deposition. Table 2 shows a number of types of particles included into a metallic matrix by co-electro-deposition.

Table 2. *Inclusion of other types of particles into metal deposits by electrodeposition*

Nanoparticles	Metallic matrix	Substrate	Ref.
SiC	Ni	steel	[55, 56, 57]
SiC	Ni-Co	Cu	[22, 58]
CeO_2	Cu	steel	[21]
Al_2O_3	Ni, Co	steel	[59, 60]
CeO_2, L_2O_3	Co	steel	[7, 61]
ZrO_2	Cu	steel	[62]
TiO_2	Zn	steel	[63]
CeO_2	Ni	steel	[64]
Al_2O_3	Ni	steel	[41, 66]
SiC	Co	steel	[3]
ZrO_2	Co	steel	[67]

The inclusion of nanometric particles into metal layers depends on process parameters including the particle characteristics, concentration [11, 68, 69], type, shape dimension, electrolyte composition (concentration of electrolytes, additives, temperature, pH) [11], curent density [9, 11, 27, 32] and electrodes geometry (disc, plate or other variants), stirring speed [11].

Composition of the electrolyte is known as an important factor which influences the process of co-electro-deposition [7, 9, 11]. However, an accurate image of the effect of the experimental parameters is often hard to get. In most recent papers reported it is suggested the existence of three global factors to be identified as affecting the co-deposition, namely (1) density of the applied current, (2) type and concentration of particles and (3) electrolyte stirring speed [9, 11, 27, 32].

5. Current density

There is a variety of techniques to be used, such as direct current, pulse current and reverse pulse current. In electrodeposition, the method most widely used to obtain nanocomposites, the most important parameter is the current density. This technique is based on the concept that inclusion of nanoparticles occurs simultaneously with the reduction reaction on the metal layer surface. Hong-Kee Lee [70] researches the effect of SiC particles of micro and nanometric sizes in a Ni matrix.

Taking into account the effects of the deposition parameters, pH of the depostion bath, the current density and the stirring speed, the particle concentration, some authors notice two different effects of the current density:

1) a small or zero influence of the current density on the number of particles incorporated;

2) others say that a significant effect takes place along with the presence of one or more particles stirring speed depending on the current density resorted to (Ni-SiC) [71].

It has been found that the degree of inclusion of the disperse phase decreases with increased current density for the systems Cu-ZrO_2 [62], Ni-Al_2O_3 [41, 66], and also that an increased current density leads to a higher inclusion of the dispersed phase in the metallic matrix [1] for the systems Ni-TiO_2 [7], Co-SiC [72]. The current density also was found to affect the amount of alumina nanoparticles in the Ni matrix electrodeposited [73].

6. Electrolyte stirring

Particles to be included into a metallic matrix should be carried away from the solution to further reach the cathode surface [1, 9, 27, 32] According to the literature [74] it becomes obvious that the electrolyte stirring speed enables particle transport and an increased stirring speed results in a larger amount of particles being incorporated [9, 11]. In spite of this, Hovestad &Co (1995) [27] reported that a too high electrolyte stirring speed decreases the particle co-deposition, because a too high speed makes the particles collide and thus remove the particles from the cathode surface before inclusion.

Therefore, all researchers have made use of a certain type of electrolyte bath stirring and sometimes [9, 11, 27, 32, 75] have mixed the electrolyte particles before experiments so as to reach a stable suspension. The electrolyte mixture help the clustered particles separate and homogenous deposits be obtained, containing finely dispersed and well distributed particles [11].

The effects of such a parameter on co-electro-deposition should be accounted for by the fact that particles affect suspension stability. Beside particles conveyance, stirring is also used to keep particles in the suspension.

Suspension stability increases with reduced degree of inclusion of particles (θ), which in the case of spherical particles is given by Stokes law [27].

$$\vartheta = 2gr_p^2(\rho_p-\rho_e)/9\eta \qquad (1)$$

with: **v** - rate of incorporation of the particles, **g** - acceleration due to gravity (g = 9,81 m/s^2), $\mathbf{r_p}$ - particle radius (m), ρ_p - particle density (kg/m^3), $\boldsymbol{\rho_e}$ - density of the solution (kg/m), $\boldsymbol{\eta}$ - viscosity (expressed in kg/m s).

Suspension stability directly depends on the particles size and density which is different for each particular type of particles. Moreover, density and viscosity of the electrolyte are determined by the elements of the bath and temperature [11, 27].

The basic purpose of the electrolyte stirring speed is to keep the particles in suspension and prevent their settlement or foating in the electrolytic solution. Stirring may be reached through air bubbling, by electrolyte recirculation or by means of a laboratory magnetic stirrer [9, 11, 27].

7. Bath composition

Although these parameters are less investigated than particle properties, current density or stirring speed, the electrolyte composition is also an important parameter in the co-electro-deposition process [9, 11, 27, 32]. From the researches it is found that the composite layers the easiest to obtain are those in matrix of Ni, Fe, Zn, the more difficult to obtain are those based on Ag, while the most difficult are those related to chrome (due to the higher hydrogen current output and the presence of a cathodic film on these metals) [4]. A certain electrolyte compsition and certain electrolysis conditions facilitate inclusion of the dispersed phase into the matrix or its removing (ex: Cu-Al_2O_3: easier to obtain from base electrolytes) [4].

8. pH of plating baths

Investigations [27, 32, 74, and 75] on the effect of the bath pH provide comparable results. Particle inclusion drastically decreases in acid electrolyte solutions (pH from 2 to 3) and stays almost constant or slightly decreases over this level [11, 27].

- *electrolyte pH* plays an essential role in making composite coatings especially in case of particles interaction with the matrix being formed due to the variation of the dispersed phase as a result of the excess ions of OH^- or H_3O^+, and interaction of the hydrogen which gets separated [11, 27, 74, 75].

9. Additives

In order to incorporate particles into the metallic matrix, an important role is played by additives [11, 27, 76, 77]. By adding small amounts of monovalent cathions such as tetra-etilen pentamina (TEPA), alanina, etilendiamino tetraacetic acid (EDTA), gelatin, dodecil sodium sulphate [64] favourise particle co-deposition. Inclusion of nanoparticles of TiO_2 in a Zn matrix [75] is improved by adding cetyl-trimethyl-ammonium bromide which is an anionic tension active agent.

Kanagalasara Vathsala [27] adds a surfactant (SDS) in the electrodeposition bath to stabilize the suspension of ZrO_2 particles. Tension activators improve the suspension stability by increasing the moistening of the particles in suspension thus providing a better adhesion to the cathode surface [27]. The moistening capacity of the particles is not a major problem in co-deposition but there are additional advantages when using cationic tension activators [27, 76]. These cationic tension activators provide a positive degree of inclusion of the particles, prevents clustering and electrostatic attraction at the cathode. Similarly, by using a tension activator agent, H. Gül & Co [65] have made Ni coatigns containing about five times more particles of alumina (Al_2O_3), as compared with other exeperiments. The disadvantage of using tension activators is that these are incorporated in the deposit [65].

10. Conclusions

Co-electrodeposition of inert particles in a metallic matrix is a suitable technique of making functional layers. Especially in this field it provides a good alternative to other techniques and makes it possible to produce functional surfaces of unique properties. Many independent parameters influence the process of co-deposition.

An accurate classification of the effect for each parameter is hard to obtain as these are often different and in some cases even contradictory. Particle concentration, current density and stirring speed seem to be the most meaningful parameters. Most researchers suggest that the mechanism of growing the codeposited layers plays an important role and this calls for further investigations.

The mechanism of co-electrodeposition implies transportation of particles to the cathode surface by means of the stirring speed and inclusion into the metal takes place by reducing the ions adsorbed. The attempts to develop models capable of predicting the mass of particles inclusion under experimental conditions have failed so far. Nowadays, models involving detailed descriptions of particles transportation and particles interactions with the cathode provide a promising perspective of obtaining functional surfaces.

A number of co-electro-deposition techniques (DC, PVD, etc) have been used to include particles of nanometric dimensions in metallic matrix. Such techniques made it possible to obtain functional surfaces featuring a wide range of properties which are clearly better than those of pure metals or alloys.

In some cases (DC), it has been shown that this method is inferior to PVD for making nanocomposites. Benefits of these procedures include surface nanostructures, increased degree of inclusion into the metallic matrix and selectively, the particles size.

Inclusion of nanometric particles may provide a growth of the metallic crystalls forming a deposit of nanocrystalline metal. Inclusion of nanometric particles may increase microhardness and corrosion resistance.

The different theoretical methods that describe the dispersed phase behavior in a metallic matrix require special attention; the experimental studies are carried out on current densities, mass transport, and degree of inclusion of nanoparticles.

Co-electro-deposition of particles is significantly better by decreasing the pH and adding additives into the electrolytes. Inclusion of particles in a metal matrix results in functional surfaces with physical, chemical or mechanical properties depending on thickness.

Now the process of co-electro-deposition of the nanoparticles is still in progress but has already shown certain advantages for various applications. This technology of functional surfaces has a great potential for further developments in industry and biomedicine.

Acknowledgement

The authors gratefully acknowledge project C2-02/01-03-2012 (CEA-IFA) for funding.

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