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Electrodeposition of Metal Matrix Nanocomposites: Improvement of the Chemical Characterization Techniques

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1. Introduction

In this chapter, critical aspects related to the electrodeposition conditions of metal matrix nanocomposite films, from aqueous solutions, are discussed. The efficiency of the use of these films in different technological applications strongly depends on their compositional, morphological and structural characteristics, which are directly related to the preparation method and deposition conditions (e.g. current density, substrate, pH, ions concentration, size and quantity of nanoparticles, electrolyte agitation etc.). Therefore, the correct chemical and physical characterization of nanocomposite coatings is crucial to optimize their synthesis and, thus, their performances. A fast and reliable in-depth chemical characterization of the nanostructured layers is of critical importance to assist the degree of nanoparticles dispersion into the metallic matrix as well as to evaluate their routine manufacturing quality. The use of direct solid elemental analysis techniques, such as glow discharge (GD), coupled to both optical emission and mass spectrometry provides some unique analytical advantages for the fast analysis of nanocomposite coatings namely to determine nanoparticles concentration, homogeneity and coating thickness.

2. General aspects

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. Due to the large number of published works over the last decades, only some review works are cited regarding the state of the art on this subject (Hovestad & Janssen, 1995; Low et al., 2006; Stojak et al., 2001).

Materials are considered nanosized when one of the components dimensions are in the nanometer scale, with typical dimensions smaller than 100 nm. A variety of nanosized particles, ranging from 4 nm to 800 nm diameters, have been successfully incorporated into metallic electrodeposits (Low et al., 2006). These include oxides such as Al_2O_3, ZrO_2, TiO_2 and Cr_2O_3 or carbides like SiC, WC, TiC or nitrides like Si_3N_4 (Bahrololoom & Sani 2005; Jung et al., 2009; Srivastava et al., 2010; Krishnaveni et al., 2008; Stroumbouli et al., 2005; Gay et al., 2001).The metals mostly used are copper and nickel (Low el al., 2006) however other

metals like zinc, silver and, alloys have been used (Gomes et al., 2005; Gay et al., 2001; Tulio & Carlos 2009; Muller et al., 2002; Tian & Cheng, 2007). The most studied system has been the Ni-SiC due to its potential technological applications (Low et al., 2006; Hovestad & Janssen 1995; Benea et al., 2002; Zimmermann et al., 2002; Hou et al., 2002; Garcia et al. 2001; Gyftou et al., 2005; Lekka et al., 2005). Therefore, considering the variety of metals, which can be electrodeposited, electrochemical composite deposition enables the production of a wide range of composite materials that compared to the pure metal coatings have improved physical and (electro)chemical properties (Hovestad & Janssen, 2005). For example, Cu-alumina and Ni-alumina composite coatings exhibit ultimate tensile strengths, and lower ductility than pure copper or nickel deposits (Lozano-Morales & Podlaha, 2004).

The first application of electrochemically deposited composites dates back to the beginning of the twenty century. Sand particles held by a nickel matrix were utilized as anti-slip coatings on ship stairs (Hovestad & Janssen, 2005). During the 1970s and 1980s, investigations were focused on the need to produce coatings with enhanced mechanical, corrosion and tribological properties. During the 1990s, new areas such as electrocatalysts and photoelectrocatalysts production were emerging, associated with an increasing interest on the particles size. This is due to the higher activity of the semiconducting nanoparticles in comparison with the macro sized particles related to changes on the optical bad gap and surface area (Low et al., 2006). In 2000, Musiani had done a review paper focused on the new applications for the metallic composite materials (Musiani, 2000). Concerning photoelectrochemical activity, the principal application of these materials is strongly linked to the degradation of organic molecules and depends on the high surface-to-volume distribution of the nanoparticles (Tacconi et al. 2000). Although the use of metallic matrix composite electrodes, on the organic pollutant degradation, is still rare, some studies indicate that the metallic matrix has a positive influence on the semiconductor photocatalytic activity (Deguchi et al., 2001). The authors of this chapter are developing, with success, the preparation of photoelectroactive thin films consisting of nanoparticles (TiO_2) dispersed on a metallic matrix (Zn or Zn alloys) suitable to be used as electrode materials for degradation of pharmaceuticals from simulated sewage water (Gomes et al., 2010).

The amount of incorporated particles is the key parameter for the success of metal matrix composite applications, since it largely determines the composite properties such as wear resistance, high-temperature corrosion protection, oxidation resistance and self-lubrication when compared with the corresponding values for pure metal or alloys deposits (Lozano-Morales & Podlaha, 2004; Vaezi et al., 2008). In addition, uniform distribution of co-deposited particles within the metal matrix was found to be another crucial parameter (Stankovic & Gojo, 1996; Vidrine & Podhala, 2001). Nevertheless it must be highlighted that the metal matrix morphological and structural characteristics are strongly affected by the particles presence. Furthermore the co-deposition of a sufficient amount of non-agglomerated particles should lead to production of harder and more resistant coatings (Zanella et al., 2009). Particle-reinforced composite coatings based on nickel and alumina are being applied in different technological fields with high demands on friction and corrosion resistance (Jung et al., 2009). Lekka et al. show that the co-deposition of SiC nanoparticles leads to a more noticeable grain refinement and, as a consequence, the nanocomposite deposits present a very high microhardness, 61% higher than pure copper deposits, and an increase of 58% of the abrasion resistance (Lekka et al., 2009).

Future applications of these materials depends on the ability to produce them with controlled composition and properties, using inexpensive and reliable techniques.

Electrodeposition method meets some of these requirements, since it is an economical and versatile technique compared to other preparation techniques. Moreover, it is quickly scaled up to industrial production, offering an inexpensive method to produce large area samples. These are some of the reasons that make this method so popular. In addition, the low processing temperature (around room temperature) minimizes interdiffusion or chemical reaction between the substrate and coating species. The film thickness can be accurately controlled by monitoring the consumed charge and the composition can be tailored by the electrical applied profile and bath composition (Bicelli et al., 2008). The occlusion electrodeposition, or electrochemically co-deposition method, where the particles incorporation occurs simultaneously with the metal ions reduction, uses a precursor bath loaded with the particles to be occluded. This technique is widely used to obtain metal matrix composites due to its ease of preparation, low cost and versatility (Rajeshwar, 2002). The concentration of particles suspended in solution varies from 2 up to 200 g/L producing composites with typically 1-10 vol.% of embedded particles (Stojak et al., 2001).

With the increasing availability of nanoparticles, the interest of the low-cost and low-temperature composite electroplating is continuously growing, with the major challenge being the achievement of high co-deposition rates and homogenous distribution of the particles in the metallic matrix (Gyftou et al., 2008).

Fundamentally, the electrocodeposition process and hence the structure, the morphology and the properties of the composite coatings is affected by the electrodeposition parameters like the electrolysis conditions (composition and agitation of the electrolytic bath, presence of additives, temperature, pH), the electrical profile (Gomes et al., 2005; Fustes et al., 2008) and the particle properties (type, size, shape, surface charge, concentration and dispersion in the bath) (Maurin & Lavanant, 1995; Hovestad & Janssen 1995; Kantepozidou et al., 1996).

3. Theoretical models of metal matrix composite electrodeposition

In a simple way, the particle incorporation in a metal matrix could be described as a four-step process: (1) formation of surface charge on particles in suspension, (2) particle mass transfer from the bulk of the suspension to the electrode surface, (3) particle-electrode interaction (4) particle incorporation and irreversible entrapment simultaneously with the growing metal layer (Figure 1).
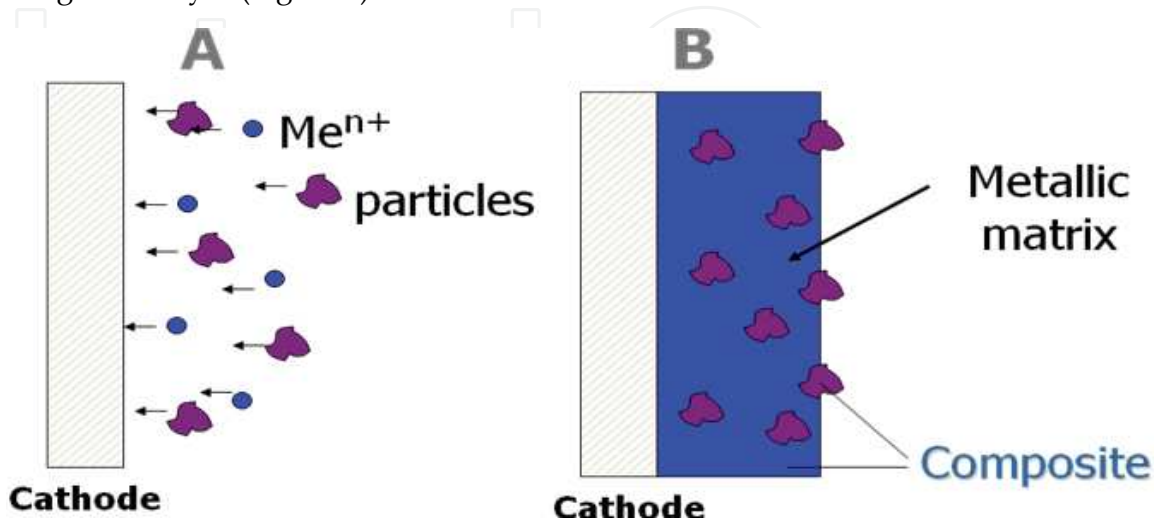

Fig. 1. Some of the steps involved in the metallic matrix composite electrodeposition.

Most of the electrochemical co-deposition mechanisms for the dispersion of inert particles into metallic coatings have been developed for micron-sized particles (Low, 2006). The first model developed was the Guglielmi's model which is based on two steps process involving a loose adsorption and strong adsorption of the particles (Guglielmi, 1972). The first step is a loose physical adsorption of the particles on the cathode, with a high degree of coverage, and without discharge of the electro-active ions adsorbed on the particles. The fractional coverage follows a Langmuir adsorption isotherm. The second step is the strong electrochemical adsorption of the particles, caused by the applied electrochemical field, accompanied by the discharge of the electro-active ions. Both steps take place at the same time all over the cathode surface. If a particle is strongly adsorbed on the cathode, it will be embedded in the growing metal layer by the electrodeposition of free solvated electro-active ions from the plating bath (Jung et al., 2009; Tian & Cheng, 2007).

From this model the volume fraction of incorporated particles, α, can be mathematically expressed by:

$$\frac{\alpha}{1-\alpha} = \frac{zF\rho_m V_o}{M_m i_o} \cdot e^{(B-A)\eta} \cdot \frac{kc_{p,b}}{1+kc_{p,b}} \qquad (1)$$

where M_m and ρ_m are the atomic weight and 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 overpotential, $c_{p,b}$ the particle concentration in the bulk electrolyte and k the Langmuir isotherm constant, mainly determined by the intensity of interaction between particles and cathode. The parameters V_0 and B are related to particle deposition, and both play a symmetrical role with the parameters i_0 and A related to metal deposition (Wang & Wei, 2003). The validity of Guglielmi's model has been verified with different deposition systems, such as SiC and TiO_2 particles with nickel from sulfamate bath (Guglielmi, 1972), or α-Al_2O_3 particles with copper from a copper sulfate plating bath (Celis & Roos, 1977; Lee & Wan, 1988).

However the model neglects hydrodynamics, particle size and ageing effects what is its main drawback (Jung et al., 2009).

The model developed by Celis (Celis et al, 1987) uses probability concept to describe the amount of particles that can be incorporated at a given current density and assumes that five steps are involved into the incorporation of the particles: (1) formation of an ionic cloud around the particles; (2) transport of the particles by convection to the hydrodynamic boundary layer; (3) transport of the particles by diffusion to the cathode; (4) free ions and electro-active ions adsorbed on the particles are adsorbed at the cathode, and (5) electrochemical reduction of the absorbed ions at the cathode with the embedding of the particles into the growing metallic matrix.

This model was satisfactory used for the Cu-Al_2O_3 and Au-Al_2O_3 systems. Later on Fransaer proposed another model (Fransaer et al., 1992) that was developed to non-Brownian particles, particles with a diameter bellow 1 μm, involving two steps: (1) reduction of metal ions (described by Butler-Volmer expression) and (2) co-deposition of particle (described by trajectory expression). This model has been used successfully on the qualitatively explanation of experimental data for Zn-polystyrene composite depositions. From a mechanistic point of view, this trajectory model offers a very good description for getting a better insight into composite deposition. Nevertheless the particle-electrode interaction forces and their relative importance remain a point of discussion. Another contribution in

this area is the model of Vereecken (Vereecken et al, 2000) that takes into account the particles kinetics and residence time at the electrode surface. The transport of particles to the surface is controlled by convective-diffusion. 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. The authors show that incorporation of 300 nm Al_2O_3 particles into nickel films can be well described by this model. More recently Lee and Talbot (Lee & Talbot, 2007), proposed a model to predict the amount of nanoparticle incorporation in a kinetically as well as in the mass transfer limited region of the electrochemical deposition which agrees well with the experimental data of the Cu-Al_2O_3 system.

Currently, the models used to describe the inclusion of particles are restricted to specific conditions, so empirical laboratory trials remain very important. Future models, describing the co-deposition process, will require special attention to interactive variables such as the nanoparticle characteristics (composition and crystallographic phase, size, density, and shape) and the operating electrolysis parameters. The validity of the various theoretical models, underlying particle incorporation in a metal matrix, still requires attention, since the electrochemical co-deposition is still not fully understood (Low, 2006; Vidrine & Podlaha, 2001).

4. Particle characteristics

Nanocomposite coatings have been studied increasingly in the last 10 years. However the results are often contradictory and inconsistent and they are, therefore, difficult to compare with micro-composites (Medeliene, 2002; Malfatti et al., 2005; Zanella et al., 2009). The mass transport of the inert particles towards the cathode surface is a crucial factor in determining the extent of their occlusion within the growing metallic matrix (Zhou et al., 1997). The particle electrode interaction depends on the particle surface properties, which are determined by the particle type, bath composition, pH and metal surface composition.

For some systems like Ni-SiC, the two-step co-deposition mechanism proposed by Guglielmi is valid. In addition the results show that the ultra-fine SiC is more difficult to co-deposit than the coarse SiC, and the rate determined step is controlled by the transferring process of loose adsorption to strong adsorption (Wang & Wei, 2003). With the same quantity of powder in the bath, the embedded micro-powder content is about 25–30 wt % while the nano-powder content is always less than 1 wt % (Zanella et al., 2009; Shao et al., 2002).

The smaller the particle the most important are colloidal forces (van der Waals, electrostatic attraction/repulsion and hydrophobic/hydrophilic interaction forces). The most difficult to quantify are the hydrophobic/hydrophilic interaction forces, as no general theory describing such forces may be found in the literature (Socha et al., 2004).
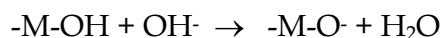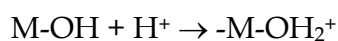
Particles dispersed in a continuous electrolyte solution are in constant Brownian motion. When two particles approach one another, the energy existing between the particles determines whether the particles will separate or agglomerate. Generally, particle agglomeration occurs when larger attraction than repulsion energy exists between them. The magnitude of the net forces involved, in producing an agglomerated structure, clearly depends on the conditions and the nature of the system. The knowledge of the interfacial region structure is an important factor in order to understand the dispersion stability of solid particles within the electrolyte (Kuo et al., 2004).

At higher ionic strength of the electrolyte or lower particle charge, the particles may agglomerate irreversibly. If the ionic strength increases, the agglomeration of the particles

increases too. However if the state of agglomeration is reversible it can be easily turned into the dispersed state by mechanical stirring. Repulsive forces can be tuned via experimental conditions as pH, ionic strength, etc. The zeta potential, which is a quantitative measure for the particle surface charge, gives an indication of the stability of the colloidal system. As consequence, a higher zeta potential induces a lower degree of particle agglomeration producing a higher concentration of non-agglomerated particles in the electrolyte (Simunkova et al., 2009). In electrocodeposition the stability of the colloid dispersion is mandatory, since the particles shall be preferentially incorporated in the form of individual particles in order to improve the particle incorporation and as consequence the composite properties. Simunkova et al. show, for the nickel composites, that as electrostatic repulsion within the dispersion increases, particle agglomeration slows down and the concentration of non-agglomerated particles rises resulting in an enhanced amount of particles incorporated in the electroplated Ni layers (Simunkova et al., 2009). Effective particle dispersion in the electrolyte solution creates more opportunities for loose particle adsorption onto the electrode. Smaller agglomerated particle groups have a higher attraction force from the electric field that produced effective adsorption (Kuo et al., 2004).

The zeta potential of nano- and micro-scaled particles is influenced by many factors, such as the source of particles (variable preparation and stabilization), the treatment with different surfactants, the electrolyte concentration (ionic strength), the particle morphology and size, the pH of the solution, and the state of hydration (Moreno et al., 1988; Wernet & Feke, 1994; Morterra et al., 1994; Leong et al., 1995; Kim et al., 1998; Kagawa et al., 1987).

The particles always interact with the electrolyte and therefore chemical and physical adsorption of electrolyte ions onto the particle occurs. This adsorption and the initial particle surface composition determine the particle surface charge, which induces a double layer of electrolyte ions around the particle. In electrolytes double layers play a major role in the interactions between particles and also between particles and the electrode (Hovestad & Janssen, 2005). In aqueous media, the oxide particles, due to protonation– deprotonation of the superficial groups can change their surface charge depending on the solution pH (Simunkova et al. 2009) according to:

$$M\text{-}OH + H^+ \rightarrow \text{-}M\text{-}OH_2^+$$

$$\text{-}M\text{-}OH + OH^- \rightarrow \text{-}M\text{-}O^- + H_2O$$

For example the TiO_2 point of zero charge (pzc) is ca 6.0, thus for pH values lower than 6.0, the positively charged TiO_2 particles would be expected to be electrostatically attracted to the cathode surface, thus assisting in their solution transport via migration. On the contrary, at solution pH values higher than the pzc, the TiO_2 particles would be negatively charged and thus repelled from the cathode surface (Zhou et al., 1997). For the $Ni\text{-}TiO_2$ system, the experimental data revealed that co-deposition of TiO_2 nanoparticles is favoured at low pH values and current densities, implying that there is a plentiful adsorption of H^+ on the titania surface. As the particle surfaces become positively charged they will be strongly adsorbed on the cathode leading to an enhanced electrolytic co-deposition (Spanou et al., 2009).

Nevertheless, in some published works, it is pointed out the electrodeposition of negatively charged particles into Ni matrix with success. These findings are in contradiction with the traditional theory of particles transport towards the cathode by means of electrophoresis (Low et al., 2006). This might be correlated to the absolute value of the zeta potential. This factor is very important for the degree of incorporation and not only the polarity of the zeta potential as mentioned previously.

According to the model developed by Bund and Thiemig, negatively charged particles are preferentially attracted by the positive excess charge in the electrolytic part of the electrode electrical double layer. When the particle comes closer to the electrode, the shell of adsorbed ions on the particle is stripped off, within the electric double layer and the particle becomes incorporated into the growing metal layer (Bund & Thiemig, 2007).

As general accepted the transport of the particles to the cathode surface occurs by electrophoresis, mechanical entrapment, adsorption and convective-diffusion mechanisms (Low et al., 2006). Electrolyte agitation is usually necessary to maintain the particles in suspension and to transport the particles to the electrode surface. Vaezi et al. have verified that increasing the stirring rate up to 120 rpm causes the increase of the percentage of incorporated SiC nanoparticles but when the stirring rate is too high, a decreasing trend of the weight percent is observed, principally caused by the collision factor. At a high-stirring rate, because of the turbulent flow in the bath, the SiC nanoparticles on the cathode surface are washed away and thus the SiC nanoparticles percentage in the composite coating decreases. It was assumed that increasing the stirring rate, increases the forces acting on the nanoparticles, resting on the cathode surface, decreasing the weight percentage of the SiC nanoparticles in the composite coating (Vaezi et al., 2008).

The co-deposition of nanoparticles during electrochemical deposition of a metallic film depends on the rate of the metal deposition and on the flux of particles to the film surface which is strictly related with the applied electric profile. The growth rate of the metal film is determined by the deposition current density.

Generally, the strong adsorption is the rate-determining step of the electrodeposition process because it is more difficult to occur than the loose adsorption. The strong adsorption can be promoted by high overpotential corresponding to increasing current density. As a result, the particle content in the coatings increases with increasing current density. Nevertheless, at higher current density, the improvement of metal deposition rate caused by the increase in current density exceeds the promotion effect of particle incorporation, which leads to the decrease in the particle content (Guo et al., 2006).

The relationship between cathodic current density and incorporation rate, for different particle concentrations in the bath, has been studied by Gay et al.. It was concluded that for low current densities (0.5 A dm^{-2}), the incorporation rate is very weak <2% and for higher current densities (1.5 to 2 A dm^{-2}), the coatings appear rough. In these latter cases, the incorporation rate is still very weak (approx. 1%) whatever the plating bath concentration is (Gay et al., 2001).

Studies on the Ni-TiO$_2$ system done by Aal et al. show that the wt. % of co-deposited TiO$_2$ increases with current density. According to the Stokes model, assuming that the colloidal particle is sphere-shaped, the electrophoretic velocity (V_E) under an electric field (E) can be expressed by:

$$V_E = \mu_E E = \frac{q}{6\pi\eta r} E \tag{2}$$

where μ_E is the electrophoretic mobility, q the particle charge, r the particle radius , and η the viscosity of the suspension. Considering this, the increase of the current density accelerates the electrophoretic velocity of the TiO$_2$ particles and increases the Coulombic force between the Ni^{2+} adsorbed on the particles and the cathode which consequently increases the TiO$_2$ content in the Ni deposit (Aal & Hassan, 2009). Similar behavior was revealed for the Ni-SiC composites (Wang & Wei, 2003).

Otherwise, it has been observed that the amount of embedded SiC particles increases with both increasing concentration of suspended SiC particles and additives' presence in the electrolyte (Gyftou et al., 2008). Indeed the particle loading in suspension is a very important parameter. At low loadings, co-deposition is limited by the supply of particles to the electrode. As the particle loading increases, so does the incorporation level. But at the highest loadings (beyond which particle settling becomes significant), the increase in incorporation is not proportional to the increase in loading and a constant value is attained (Stojak et al., 2001).

In many cases the enhanced performance of the composite film is mainly caused by a change in the metal matrix growth mode or crystallite size and not so much by the presence of the particles themselves. In general the crystallite size of the metal matrix decreases due to the presence of the nanoparticles in the electrolyte. For instance the crystallite size of the nickel matrix was reduced from 115 to 30 nm due to the presence of 120 g/L alumina nanoparticles. Some studies have focused on the particle effect on the metal reduction rate and the conclusions are in somehow contradictory (Lozano-Morales & Podlaha, 2004). Few works have shown that there is no change in the metal deposition rate with particle addition to the electrolyte. Lozano-Morales et al. show, for Cu-Al$_2$O$_3$ nanocomposites, that, at a particle loading of 12.5 g/L, there is no change in the kinetic behaviour whatever the rotation rate is. However, the Cu reduction is inhibited, in kinetically limited region, when 39 g/L particles are added. Under mass-transfer control, the limiting current density remained the same at low particle loadings and was enhanced for higher particle concentrations (Lozano-Morales & Podlaha, 2004).

The cathodic polarization curves for the deposition of the Ni–SiC composites containing different concentrations of SiC nanoparticles are shown in Figure 2.
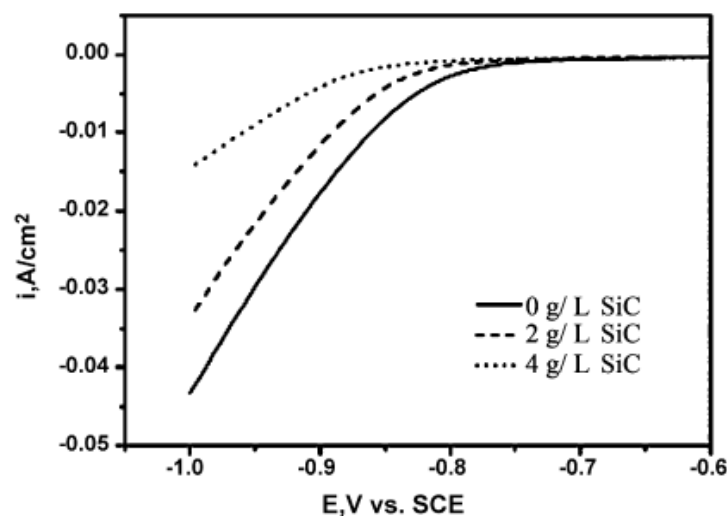

Fig. 2. Cathodic polarization curves for the deposition of Ni–SiC at different concentrations of SiC nanoparticles in the bath (Vaezi et al., 2008). (Reprint with the permission from Elsevier Limited)

It is clear that the addition of SiC nanoparticles to the electrolyte, shifts the reduction potential of nickel towards larger negatives values, but the slope of the curve keeps unchanged. This shift is attributed to a decrease in the copper cathode active surface area, owing to the adsorption of the SiC nanoparticles, and may also be related to the decrease in the ionic transport by the SiC nanoparticles, which does not significantly affect the electrochemical reaction mechanism (Vaezi et al., 2008). By contrast Benea et al., found for

the same system that the addition of SiC nanoparticles displaces the nickel reduction curve (Figure 3) to more positive potentials. The shift in the reduction potential was attributed to an increase in the active surface area due to the adsorbed particles on the nickel cathode and to a possible increase in ionic transport by the nanoparticles (Benea et al., 2002).
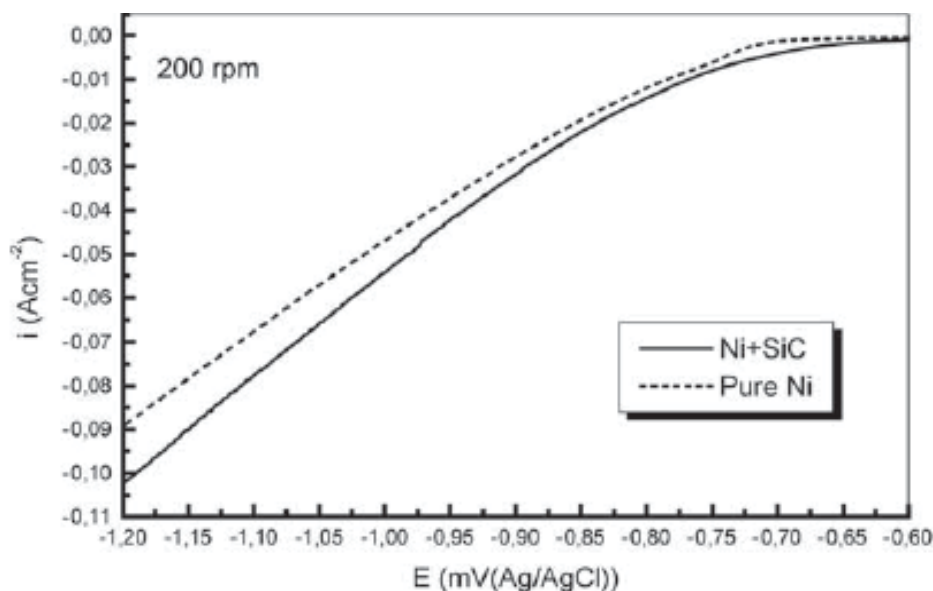

Fig. 3. Cathodic potentiodynamic diagrams for electrodeposition of nickel in presence and absence of SiC nanoparticles. Sweep rate is 0.5 mV/s (Benea et al., 2002, a). (Reprint with the permission from Elsevier Limited)

The lack of reproducibility shown by these two results could be correlated to the different deposition conditions used namely, cathode nature, particle size, solution pH and temperature.

In addition, the metal deposition rate, determined by average current density, have a huge influence on the particle content of the coatings as mentioned before (Guo et al., 2006).

5. Pulse plating methodology

Various electrodeposition techniques namely pulsed current, pulsed reverse current and pulsed potentiostatic can be employed to improve the incorporation of nanoparticles into metal matrix (Jung et al., 2009).

Several published studies have proved that the application of pulsed current (PC) technique in nickel electroplating results in the production of composite deposits with enhanced mechanical properties, higher percentages of incorporation and more uniform distribution of the particles in the metallic matrix than those attained by direct current (DC) technique (Stroumbouli et al., 2005).

Electrochemical deposition by pulsed current, is a very versatile method, since apart from the type, shape and amount of dispersed particles in the electrolyte, the composite properties can be optimized by the variation of the electrodeposition parameters such as current density, duty cycle and pulse frequency. The formation of deposits with desired composition, structure and porosity can be promoted by an adequate choice of these parameters (Chandrasekar & Pushpavanam, 2008).

The pulsed current parameters are the pulse length t_{on}, the time between two pulses t_{off}, the pulse height i_p and the average current density i_A, (Figure 4) defined as:

$$i_A = (i_p \cdot t_{on}) / (t_{on} + t_{off})$$ (3)

The duty cycle is the ratio of pulse length (on-time) and the sum of on- and off-time and frequency is the inverse of the sum of t_{on} and t_{off}. The imposed pulse height causes the depletion of ions near the cathode. During t_{off}, ions migrate to the interfacial region and when t_{on} comes after the end of the first cycle, the repeating of the cycles occurs.
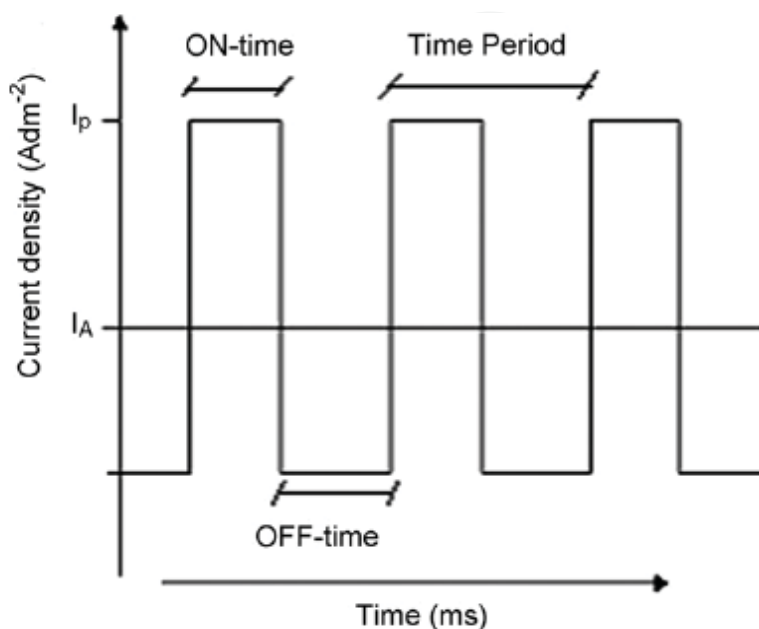

Fig. 4. Typical pulse-current waveform (Chandrasekar & Pushpavanam, 2008). (Reprint with the permission from Elsevier Limited)

By modifying these parameters changes on the cathodic overvoltage may occur, which affects the rate and activation energy of nucleation. At a given average current density, a decrease on the metal crystallite dimensions, with the decreasing of t_{on}, when followed by a short t_{off}, have been reported. These results have been assigned to an increase of the number of crystal nucleus formed (Bicelli et al., 2008). In addition longer t_{off} promotes the arriving of more particles near the cathode and consequently a higher number of particles are incorporated. Therefore pulse plating techniques are very important for the tailoring of nanocomposites.

In the case of Ni- SiC co-deposition, the application of pulsed current techniques results in the production of composite coatings with higher percentages of incorporation, reduced crystallite sizes and a more uniform distribution of SiC particles in the Ni matrix than those achieved under direct current regime (Gyftou et al., 2008).

In the pulsed-reverse current technique (PRC) a stripping time is introduced into the plating cycle, during which the metal surface protrusions selectively dissolves, what ensures a more uniform deposit (Chandrasekar & Pushpavanam, 2008). Comparing the PRC with the direct current method: (1) the amount of nanoparticles in a metal deposit can be enhanced, (2) a lower concentration of nanoparticles in the electrolyte solution can be used and (3) selective entrapment of nanoparticles with similar sizes can be achieved (Low, 2006). These features make this technique most adequate for the preparation of composites, enabling an increase of the particle incorporation in the metal matrix. Studies on the preparation of Zn-TiO$_2$ nanocomposite using the PRC technique have shown an improvement on the TiO$_2$ content in the nanocomposite (Fustes et al., 2008).

In general, for pulse plating and pulse reverse plating, high amounts of incorporated particles were found at low values of the average current density (Thiemig et al., 2007). On the other hand, various authors assumed that the duty cycle and pulse frequency affect the volume percentage of incorporated particles in the coatings. It is interesting to note that the influence of the duty cycle on the amount of incorporated particles is much bigger than the effect of the pulse frequency. These results indicate that when the pulse off-time is longer, i.e. at low duty cycles, more particles are incorporated into the coating, due to continuous agitation, with renovation of the bath composition near the cathode. It seems that the duty cycle, has a greater influence on the amount of incorporated particles than simply the length of the off-time, indicated by pulse frequency (Bahrololoom & Sani, 2005). This effect is illustrated in figure 5 for the Ni-ZrB$_2$ system. Moreover, in a study of pulse plating nickel-alumina composite coatings, Bahrololoom and Sani investigated both the effect of the duty cycle and frequency on the composites hardness. They concluded that decreasing duty cycle and frequency together, increased the composites' wear resistance in the same way that pulse parameters influence their hardness (Bahrololoom & Sani, 2005).
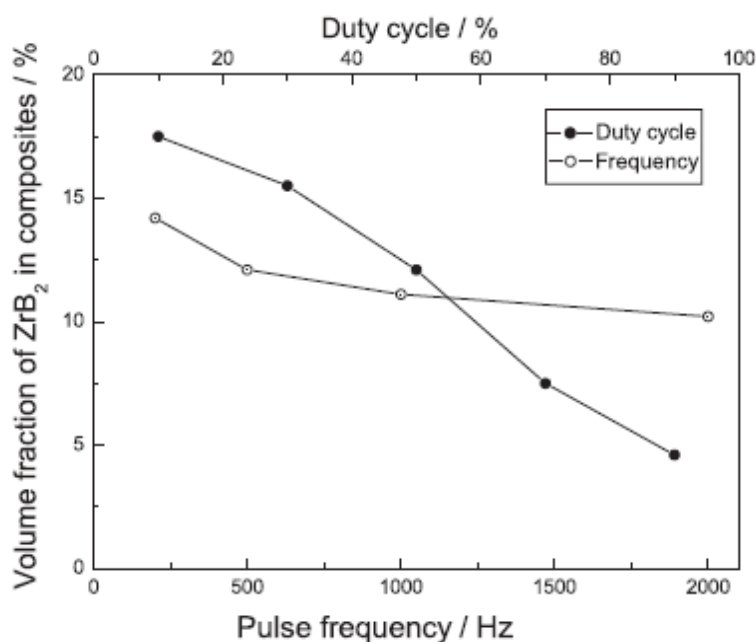

Fig. 5. Effect of the pulse frequency with 50% duty cycle and the duty cycle with 500 Hz frequency on the volume fraction of embedded ZrB$_2$ particles at an average current density of 5 A dm^{-2} (Guo et al., 2006). (Reprint with the permission from Institute of Metal Research)

At constant average current density, a lower duty cycle means a higher peak current density. Consequently, as showed previously, the strong adsorption of particles is improved by high overpotentials (Yeh & Wan, 1994). At high current densities, metallic ions are transported faster than the particles, which are transported by the mechanical agitation. Hence, the co-deposition of particles becomes particle-transfer controlled. Besides, at higher current densities the particles do not have enough time to be loosely adsorbed on the electrode surface and, as a consequence, a lower level of incorporation of the particles is obtained. In addition, at higher current densities, the hydrogen bubbles generated at the cathode surface, tend to attract the particles and prevent them from co-deposition in the metal matrix (Krishnaveni et al., 2008).

6. Characterization techniques

The relationship between the nanocomposite characteristics, synthesis conditions and properties must be well established since it affects future applications of these materials. Modifications on the composition, namely, the amount and distribution of the incoporated nanoparticles, structure and morphology of the nanocomposite films induced by changes on the deposition conditions must be properly evaluated by the analysis of the bulk and surface characteristics of the deposit.

To reach this objective X-ray diffraction (XRD), scanning electron microscopy coupled with energy dispersive X-ray spectroscopy (SEM/EDS), atomic force microscopy (AFM), X-ray photoelectron spectroscopy (XPS) and electrogravimetric analysis are ex-situ characterization techniques usually used.

From the XRD characterization technique it is expected to obtain information mainly about metallic matrix, namely, the crystal structure, texture and matrix crystallite size. Although the presence of particles can also be detected. The metal crystallites size is usually determined from the broadening of the strongest XRD reflection according to Scherrer equation (Cullity, 1978).

The preferred orientation of the zinc electrodeposits has been estimated from the X-ray data according to the methodology developed by Bérubé (Bérubé & L´Espérance, 1989), where the texture coefficient (T_c) is calculated by using the equation (4):

$$T_c = (I_{(hkl)} / \sum I_{(hkl)}) \times (\sum I_{p(hkl)} / I_{p(hkl)}) \qquad (4)$$

where $I_{(hkl)}$ is the diffraction line intensity of the (hkl) reflection of metal electrodeposits and $\Sigma\, I_{(hkl)}$ the sum of the intensities of all the diffraction lines monitored. The index p refers to the reference metallic powder sample. A value of T_c greater than 1 indicates a preferred orientation of the (hkl) reflection compared with the random distribution of the grains in the reference metallic powder. This methodology gave good results for nanocomposites with Ni or Zn matrixes (Thiemig & Bund, 2008; Fustes et al., 2008).

The most important conclusion from the published data is that the solid particles, present in the solution exert strong influence on the texture of the growing metal layer, even if they are not embedded in the metal. Considering the electrodeposition of Ni-SiC, Gyftou et al. have concluded, from the study of the textural perfection of the deposits, that the presence of nanoparticles led to the worsening of the quality of the [1 0 0] preferred orientation, observing a mixed crystal orientation through [1 0 0] and [2 1 1] axes when high concentration of embedded particles were used (Gyftou et al., 2008).

Some authors (Spanou et al., 2009) assume that the modification of metallic orientation in addition to the decrease of crystallite size point to an effective incorporation or embedding of the particles. In accordance with this, the embedding SiC nano-particles in a Ni metallic matrix resulted in the deposition of composite with smaller crystallite sizes and more structural defects than those of pure Ni deposits (Gyftou et al., 2008; Angerer et al., 2009). In a qualitative approach Fustes et al. used the XRD to correlate the amount of TiO_2 in the Zn-TiO_2 coatings with the particles concentration in solution (Fustes et al., 2008).

Concerning the morphology and elemental composition of the surface and cross-over sections the composites are, in general, analysed by SEM/EDS. This analysis of the co-deposited layers are performed in order to characterise the coating morphology, to confirm particle incorporation and estimate the particle distribution in the layer (Simunkova et al., 2009). The deposits surface roughness is usually affected by the presence of particles in suspension. In general, composite coatings are considered to be rougher than the particle-free coatings due to the entrapment of particles (Krishnaveni et al., 2008).

Investigations of nickel dispersion coatings cross sections were carried out by Bahrololoom and Sani in order to clarify the composition and qualitative particle distribution induced by modifications of the duty cycle and frequency values (Figure 6). The authors had concluded that the amount of particles could increase due to the variation of these parameters without any modification in the other electrodeposition conditions.
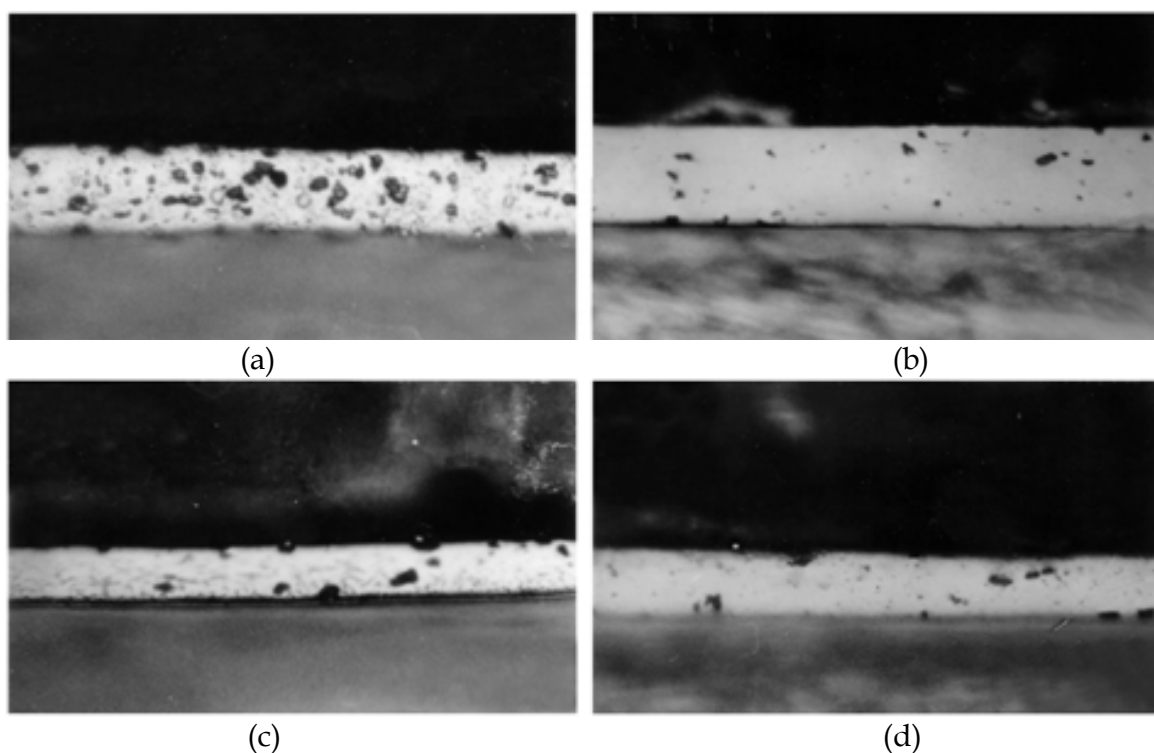

(a)   (b)

(c)   (d)

Fig. 6. Photomicrographs of the cross sections of nickel–alumina composite coatings electrodeposited with an average pulse current density of 5 A dm2 and at various pulse duty cycles and frequencies. (a)- 20% duty cycle and 50 Hz frequency, (b)- 80% duty cycle and 50 Hz frequency, (c)- 60% duty cycle and 20 Hz frequency, (d)- 60% duty cycle and 80 Hz frequency (Bahrololoom & Sani, 2005). (Reprint with the permission from Elsevier Limited)

Other authors like Erler et al. used the cross-section technique to gain information of the particles distribution through the Ni-TiO$_2$ coating. They showed that the particles are not uniformly distributed, in view of the fact that there is an "initial layer with no or very few particles", whatever the particle type is. At the initial stage, super-saturation of nickel atoms adsorption and three-dimensional nucleation can occur only on the substrate particle-free areas. Therefore, a particle free metallic layer has to be deposited by the growth of the initial crystals. Next the particles can stick to the "rough" nickel surface and will be overgrown. The proportion of incorporated particles increases and reaches a stationary value (Erler et al., 2003). The particles distribution gradient in the metallic deposit can be intentionally achieved in a single electrolyte bath by the simple alteration of the applied current density or potential and/or by modulation of the particles hydrodynamics and concentration in the solution (Low et al., 2006). AFM analysis provides available surface morphology characterization at the nanometric scale and due to high resolution imaging, surface roughness values can be estimated (Gomes et al., 2005; McCormack et al., 2003). Tu et al. have investigated by XPS the interaction between Al$_2$O$_3$ or SiO$_2$ nanoparticles and a nickel metal matrix. They have concluded that there is not only a mechanical connection, but also a

chemical combination between the nanoparticles and the nickel matrix, at the interface, in the composite coating (Tu et al., 2008).

Besides the qualitative characterization, the quantification of the amount of co-deposited nanoparticles is also a very important issue and could be accomplished by several techniques such as SEM, EDS, induced coupled plasma spectroscopy (ICP), glow discharge (GD) spectrometries and other chemical analysis methods.

In order to determine the amount of incorporated alumina in Ni composites, Jung et al. have measured the density of composite samples using Helium pycnometry. This is a nondestructive method that does not require special sample geometries, an advantage in relation to gravimetric methods. Due to the large difference in density between the nickel matrix and the incorporated alumina particles, the particles volume fraction in the composites could be evaluated after a mathematical treatment of the experimental data (Jung et al., 2009).

In 1977, Celis et al., used atomic-absorption spectrometry to determine the amount of alumina in a copper matrix and have shown that this technique can be applicable "with reasonable accuracy" down to 0.02 wt% for 1 g samples (Celis et al., 1977). More recently ICP technique was used to estimate the amount of TiO_2 in $Zn-TiO_2$ composites (Deguchi et al., 2001; Frade et al., 2010). However, it is a rather tedious and time consumption approach, since in most cases the sample has to be dissolved. Moreover, no information about particles distribution is obtained (just averaged composition).

Considering the EDS analysis, the measurements can be performed both on the surface as well as in the cross section of the composite films. The EDS analysis domains should have well defined size and, at least, three points chosen randomly should be used for the estimation of an average value (Bund & Thiemig, 2007). The wt% average value, as obtained, is variable and depends on the considered system and the deposition conditions, as referred previously. It must be noticed that currently this is one of the most used methodology for the quantitative analysis though it is only appropriate for semiquantitative analysis due to technical limitations.

In the literature, there is little discussion of the accuracy or reproducibility of the analytical techniques used for determining the corresponding matrix and particle composition. Hence, an accurate and reproducible analytical method is needed for verifying the particle incorporation and distribution. Although the effects of the process variables, of which many are interrelated, can also vary for different particle-electrolyte systems and electrodeposition conditions used (Stojak et al., 2001).

Nowadays GDs are used for depth profile analysis in many different fields. In fact, GDs are implemented as routine technique for quality control in many industries (steel, aluminium, car-manufacturing, etc) and as a valuable tool in materials science. GDs are being used to reveal processes at the surface (e.g. passivation on highly corrosion-resistant stainless steel), as well as to understand the behavior (tribological properties, corrosion, diffusion processes, etc) of surface treatments such as physical or chemical vapour deposition or ion implantation (Bayón et al., 2010). Moreover, GDs have demonstrated their capabilities to assist the improved synthesis of specialized materials, including glass coatings (Muñiz et al., 2008), biomedical implants (Kern et al., 2006), photocatalyzers (Yuksel et al., 2009), thin films for the photovoltaic (Sánchez et al., 2010) and microelectronic industries (Schwaller et al., 2006). The emerging impact of glow discharges (GDs) either coupled to optical emission spectrometry (OES) or mass spectrometry (MS) for practical surface and thin film analysis is based on many proved remarkable features, including high depth resolution, multielement capability, low detection limits, minimal matrix effects, accurate quantification,

comparatively low price, easiness of use and high sample throughput. Though GDs had been mostly known as powerful analytical tools for depth profiling analysis of relatively thick films (microns range) such as galvanized steels, in recent years they have demonstrated a good performance also for depth profile analysis of thin films. It had been traditionally considered that analytical information from the outermost surface regions of the solid sample was inaccessible by GD-OES and GD-MS due to the rather unstable discharge often observed at the beginning of each analysis. However, instrumental improvements and development of proper operation methodologies have completely changed this picture and examples demonstrating the analytical potential of GD devices for ultra-thin film analysis (less than 10 nm thick) have emerged during the last few years (Fernandez et al., 2010).

Provided that the sample is compatible with vacuum, GD-OES can analyse practically any solid material (Marcus & Broekaert, 2003). The formation of a GD takes place in a low pressure chamber through which a gas (usually high purity argon) is continuously flowing. The device consists of a grounded anode and a cathode (the sample). A potential breaks down the discharge gas, yielding Ar ions which are attracted towards the sample. By the process of sputtering, atoms, electrons and ions are liberated from the sample and through collisions in the plasma the atoms from the analyte are excited and ionized (see Figure 7). Therefore, GDs allow the generation of analytical information from a sequential two-step process: first, the analytes are sputtered from the solid material producing a crater with a diameter of a few mm (so, it is a destructive technique). Next, the sputtered atoms are excited and ionized in the discharge (thus allowing for OES or MS detection) giving rise to an extremely rapid technique for bulk and depth profiling analysis. The most common mode of operation in GD spectroscopy is the application of a direct current (dc) voltage. The dc-GD has demonstrated to be a rapid and easy-to-handle technique for the elemental analysis of electrically conducting samples; unfortunately, the dc mode is restricted to the direct analysis of conducting materials. The use of radiofrequency (rf) powered GDs has tremendously increased the application field due to their ability to sputter both conducting and insulating materials. The analytical similarities between rf- and dc-GDs indicate that any quantitative schemes developed for dc-GDs could be extended to the other one, and the main differences is the choice of the experimental control parameters in each discharge.

Using dc-GDs three key parameters should be considered: pressure in the discharge chamber, voltage and electrical current. These parameters are interdependent and when fixing two of them no choice for the selection of the third one is left. Working with rf-GDs, there are also three operating parameters which can be controlled: discharge pressure, dc-voltages developed at the sample and rf-generator output power. For conductive samples, the dc bias potential and the applied potential are closely related, so, in this case to measure the applied rf potential is accurate enough. However, at present this is not so easy for non conducting samples in commercially available instruments. Therefore, the experimental operating conditions of analysis for insulators by rf-GD must usually be defined by fixing the applied rf-power and pressure.

Further, GD devices have been traditionally operated in a continuous mode providing a steady-state population of sputtered atoms. However, the GD can be also operated in a pulsed mode (dc and rf) wherein each pulse generates a packet of sample atoms (Belenguer et al., 2009). A pulsed GD is created by periodically applying a pulse of high power during milliseconds or even microseconds. During each pulse, an atom/ion packet from the surface material is generated and will expand along the discharge chamber. Pulsed GDs allow an
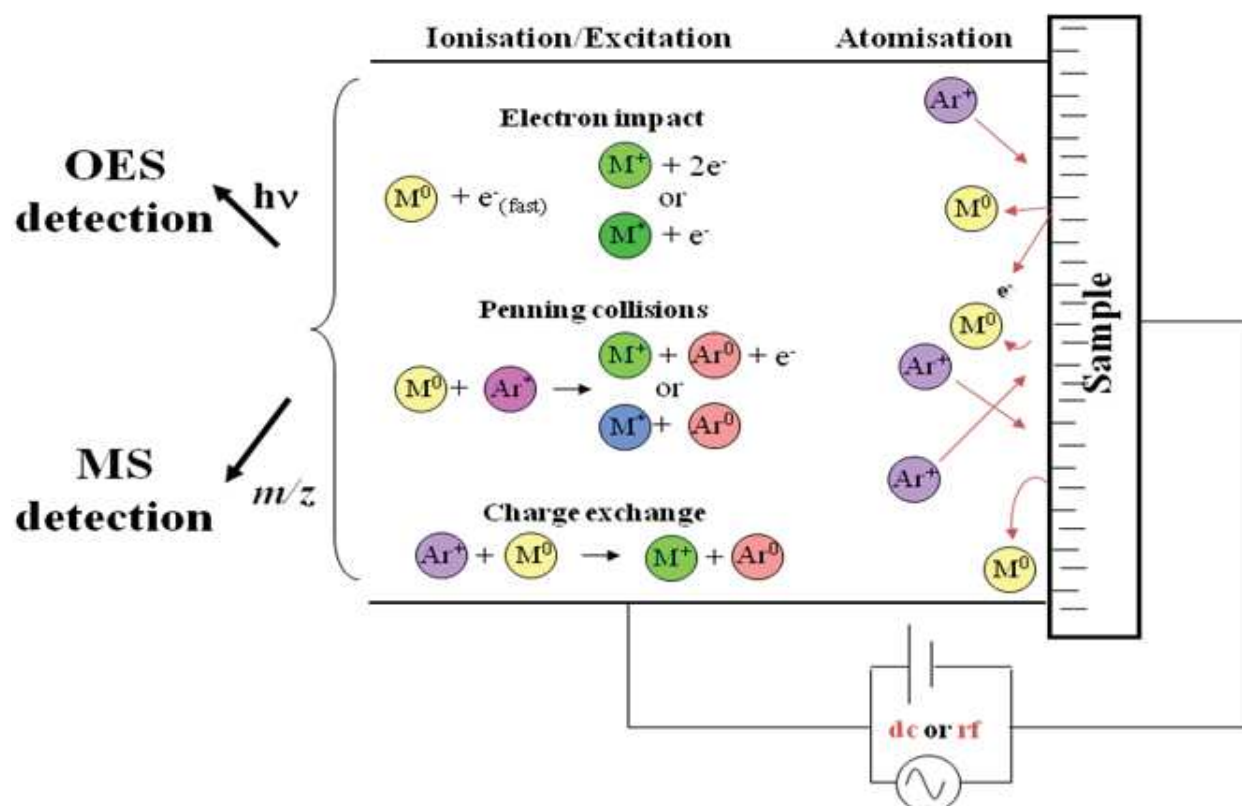
Fig. 7. Basic processes and instrumentation in glow discharge - optical emission and mass spectrometry

additional way of controlling the plasma by selecting the pulse parameters (e.g. pulse and period lengths). For example, high instantaneous powers can be applied without sample thermal degradation by just varying the duty cycle of the pulses, giving rise to higher instantaneous signals of analyte ions/photons than the steady state discharge. However, in average the sputtering rate is much lower and so pulsed GDs offer a great potential for ultra-thin layers. Moreover, different discharge processes take place at different times within a single pulse and this allows, when coupled to a mass analyser with a time resolved signal acquisition spectrometer such as the TOF (time of flight), to obtaining quasi-simultaneous structural, molecular and elemental information from the sample (Fliegel et al., 2006).

It is known that emission and ionization yields are also affected by small amounts of hydrogen (Weyler & Bengtson, 2010) and, in general, by light elements (C, N and O) in the plasma, coming either from contamination of the plasma gas (Ar) or from the specimen sputtering (i.e. sample constituents). Thus, correction algorithms should be used in such cases. Moreover, the presence of various species of gaseous elements originated from adsorbed gases and contaminants (such as H_2O, C-H compounds) should be most carefully taken into account for thin film analysis. As a result of the pre-vacuum technology required in GD instruments, serious contamination by water and hydrocarbons can be found in GD sources. Such contaminants disturb a fast achievement of the needed balance in the plasma and, moreover, the experimental results could be misinterpreted. Such disturbing influence of contamination on the GD analyses is generally reduced by adopting different strategies (which can be combined), including: (i) reduction of gas adsorption and increase of gas desorption before every measurement (e.g. by very quick sample change and venting with a

clean noble gas at pressures slightly higher than the ambient atmospheric pressure and by evacuation with high pumping speed and an increase of the source temperature, respectively); (ii) pre-sputtering with a piece of monocrystalline silicon (the sputtering of sacrificial material is undertaken under conditions similar to those used for the analysis of the sample, being in this manner the inner surfaces of the anode covered with this low-out gassing coating) (Inayoshi et al., 1999); and (iii) use of a low energy plasma to allow for a soft cleaning of the specimen surface prior to the analysis (Molchan et al., 2009), mainly removing contaminants from the surface of the target material.

For depth profile analysis, "analyte concentrations *versus* sample depth profile" (quantitative profiles) are frequently required. Thus, the "measured elemental signal intensities *versus* time profile" (qualitative profiles) experimental curves have to be transformed by means of adequate algorithms and such transformation requires proper calibrations. In principle, this conversion could be difficult mainly due the unavoidable variations of the main sample constituents along the analysis time, which give rise to changes in the electrical discharge conditions. Fortunately, a most interesting feature of GDs is the low matrix effects observed which allow for rather simple quantification schemes.

Concerning the characterization of nanocomposite films by GD sources, few attempts have been performed during the last decade, mainly using GD-OES. For Zn-TiO$_2$ nanocomposite films on steel with thicknesses of 10-15 μm, prepared from a ZnCl$_2$-based bath, GD-OES was successfully used to optimize the preparation conditions (Deguchi et al., 2001). Figure 8 shows the qualitative depth profile obtained by GD-OES for two TiO$_2$-Zn nanocomposite films prepared at different conditions. Depth profile observed in Figure 8b shows that a small amount of TiO$_2$ particles is present only near the surface of the film, whereas in Figure 8a Ti is distributed throughout the film and its signal intensity remarkably increases as it approaches the surface. Thus, it should be highlighted that GD-OES allow us to clarify that the synthesis TiO$_2$ particles are incorporated throughout the film and the loaded amount increases near the surface.

GD sources can be employed for the characterization of different types of nanocomposite films like Ni-SiC nanocomposite (Lekka et al., 2010) giving GD-OES information about the metallic matrix thickness and the amount and distribution of the particles through the film.

Additionally, GDs sources can be employed as a complementary technique to scanning electron microscopy (SEM) for the characterization and optimization of synthesis procedures of Ni-Zn-TiO$_2$ nanocomposites (Fernández et al., 2010). Figures 9a and 9b show SEM images obtained for Ni-Zn-TiO$_2$ nanocomposite films deposited onto steel substrates by electrodeposition in sulphate and chloride solutions. As can be seen, depending on the bath conditions the surface morphology is different: metallic grains with different shapes and sizes were observed using sulphate and chlorine baths. Qualitative profiles obtained by GD-OES for the two synthesis conditions are collected in Figures 9c and 9d, showing valuable information. In both cases, it is possible to discriminate the Ni-Zn-TiO$_2$ film from the steel substrate and a homogeneous distribution for Ni, Zn and TiO$_2$ along the coating were observed. However, Zn and Ti were more homogeneously distributed for the sulphate medium as well as better defined interface and a higher thickness of the film were also obtained.

Therefore, this analytical tool offers a tremendous interest to assist the synthesis optimization process as well as for the quality control of nanocomposite films in a wide variety of applications.
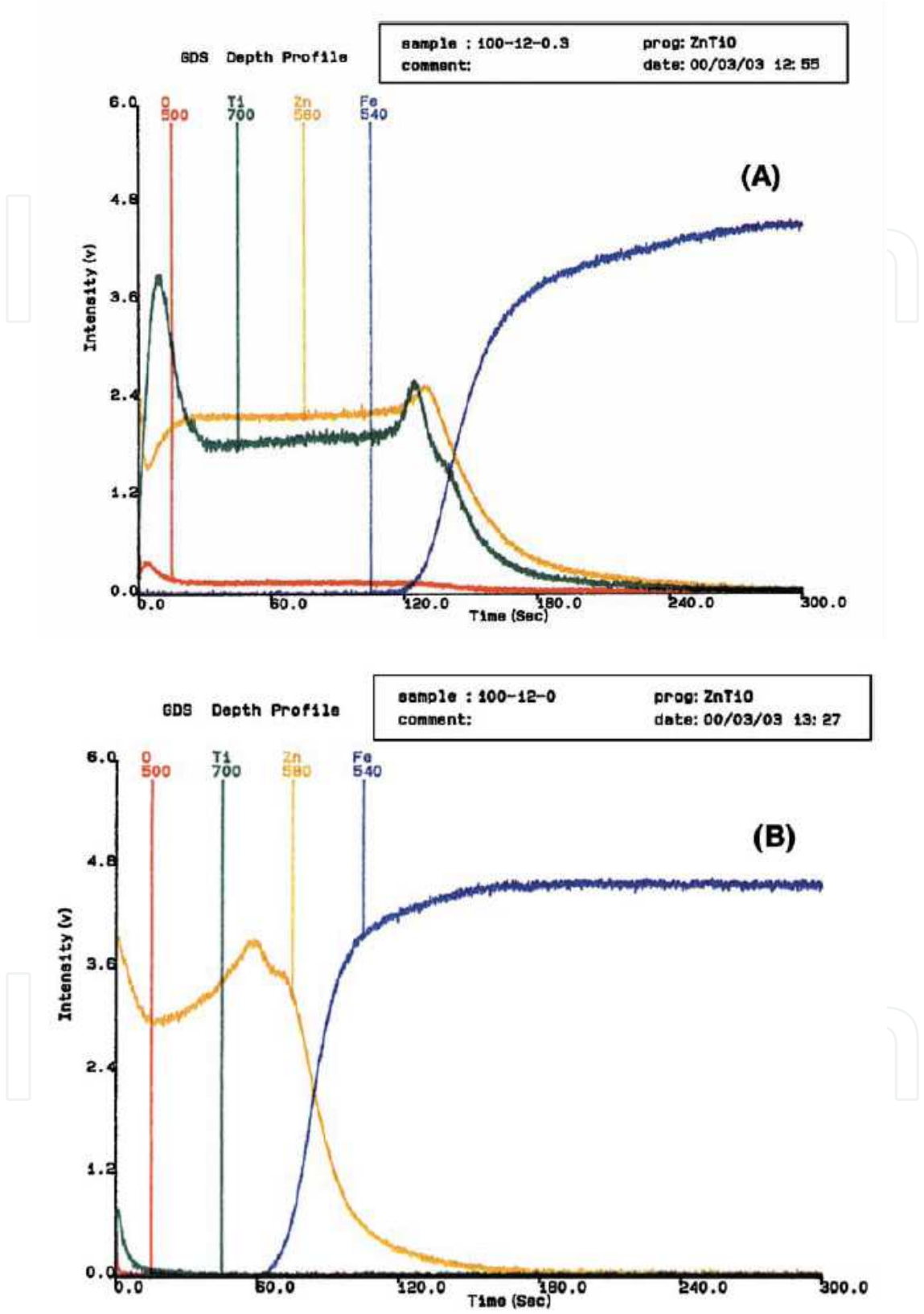
Fig. 8. GD-OES depth profiles for the TiO_2-Zn nanocomposite films prepared at I_d = 12 A dm^{-2}. A) TiO_2-Zn(0.3,100)/Steel; B) TiO_2-Zn(0,100)/Steel (Deguchi et al., 2001). (Reprint with the permission from Springer)
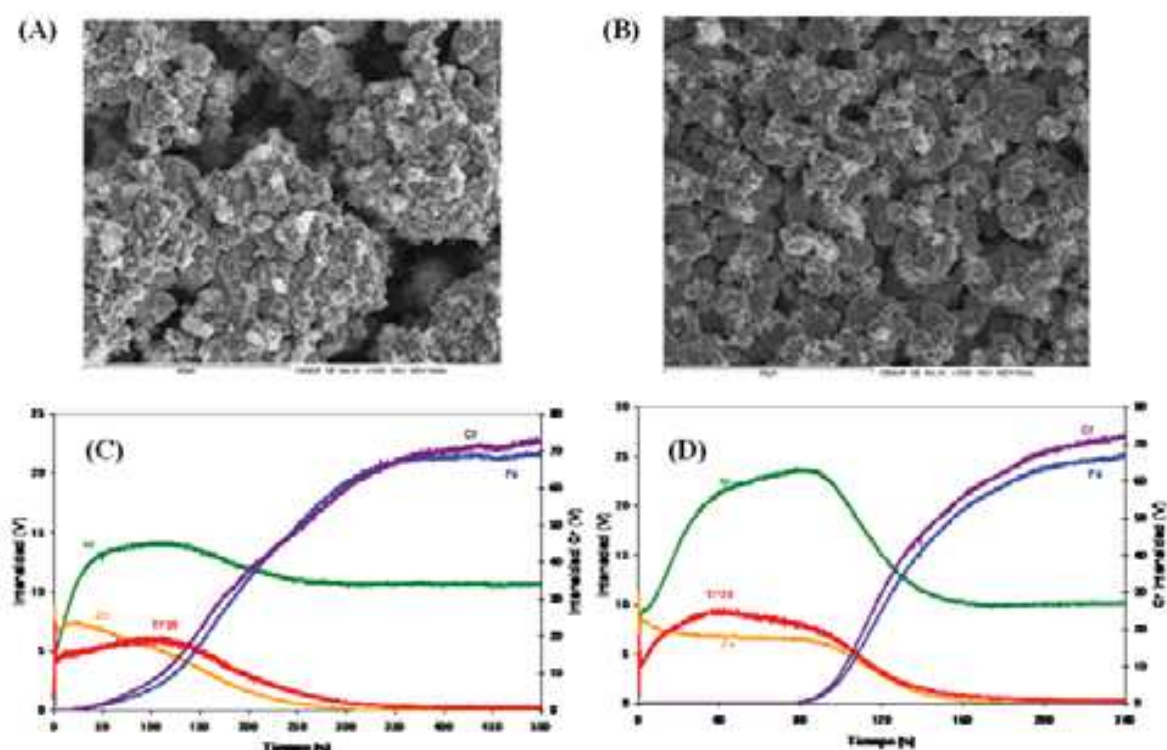
Fig. 9. Characterization of Ni-Zn-TiO$_2$ nanocomposite films deposited onto steel A & B) SEM images in sulphate and chloride baths, respectively C & D). Qualitative depth profiles obtained by GD-OES (600 Pa, 30 W) in sulphate and chloride baths, respectively (Fernández et al., 2010).

7. Conclusions

Nowadays, a wide variety of complementary analytical tools are available for the compositional, morphological and structural characterization of nanocomposite films. Concerning compositional analysis, the achievement of accurate, precise and sensitive information usually requires of liquid-based samples (e.g. ICP), so the specimen has to be previously dissolved. The need for dissolution steps gives rise to rather lengthy and tedious procedures; moreover, spatial distribution (lateral and depth) is lost. Fortunately, the use of direct solid analysis techniques allows to overcoming the above problem. In particular, the minimal matrix effects typical of GD based techniques allow reliable quantitative depth information with good detection limits and fast analysis times. GDs allow the study of possible processes of diffusion between layers as well as the determination of the nanoparticles concentration and thickness in the coating. Therefore, GD sources have proved to be an excellent analytical tool for the quality control and optimization of the nanocomposite films during which fast chemical in-depth profile information is necessary to ensure their performance.
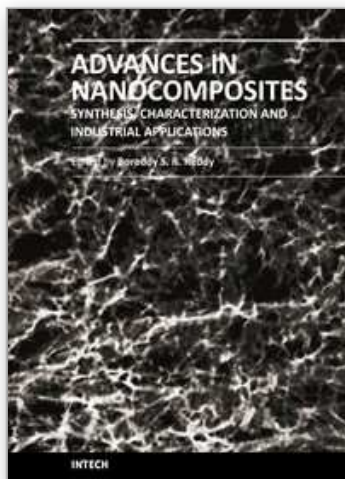
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Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications

Edited by Dr. Boreddy Reddy

Advances in Nanocomposites - Synthesis, Characterization and Industrial Applications was conceived as a comprehensive reference volume on various aspects of functional nanocomposites for engineering technologies. The term functional nanocomposites signifies a wide area of polymer/material science and engineering, involving the design, synthesis and study of nanocomposites of increasing structural sophistication and complexity useful for a wide range of chemical, physicochemical and biological/biomedical processes. "Emerging technologies" are also broadly understood to include new technological developments, beginning at the forefront of conventional industrial practices and extending into anticipated and speculative industries of the future. The scope of the present book on nanocomposites and applications extends far beyond emerging technologies. This book presents 40 chapters organized in four parts systematically providing a wealth of new ideas in design, synthesis and study of sophisticated nanocomposite structures.

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