

Sònia Albert Calbetó

Nickel matrix micro/nano SiC composite electrodeposition

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ABSTRACT - RESUMEN DE LAS PARTES DEL CONTENIDO DEL PROYECTO:

Electrochemical codeposition is widely used in the last decade to produce composite metal matrix coatings. Hard particles such oxides or carbides embedded in a metal matrix coating aim to increase its mechanical and wear properties. The use of nanometric particles could also change the microstructure of the electrodeposits leading to a more compact structure and thus to an increased corrosion resistance. The aim of this work is the production of pure nickel, nickel containing SiC micro-particles and nickel containing nano-particles electrodeposits. The electrodeposition was carried out using a nickel sulphamate plating bath containing or not suspension of micro/nano sized SiC particles. The deposition was done using both direct and pulse current at different frequencies. The produced deposits have been characterized regarding their microstructure, SiC content, microhardness and corrosion resistance in a CO₂ containing media. The microstructure has been observed by SEM (Scanning Electron Microscope) on top surface and cross section after metallographic etching. The SiC content was evaluated by GDOES (Glow Discharge Optical Emission Spectroscopy). The microhardness was measured in cross section to avoid the influence of the substrate. The corrosion resistance in CO₂ containing media was evaluated by potentiodynamic polarization curves.

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Abstract

Electrochemical codeposition is widely used in the last decade to produce composite metal matrix coatings. Hard particles such as oxides or carbides embedded in a metal matrix coating aim to increase its mechanical and wear properties. The use of nanometric particles could also change the microstructure of the electrodeposits leading to a more compact structure and thus to an increased corrosion resistance.

The aim of this work is the production of pure nickel, nickel containing SiC micro-particles and nickel containing SiC nano-particles electrodeposits.

The electrodeposition was carried out using a nickel sulphamate plating bath containing or not suspension of micro/nano sized SiC particles. The deposition was done using both direct and pulse current at different frequencies.

The produced deposits have been characterized regarding their microstructure, SiC content, microhardness and corrosion resistance in a CO₂ containing media.

The microstructure has been observed by SEM (Scanning Electron Microscope) on top surface and cross section after metallographic etching. The SiC content was evaluated by GDOES (Glow Discharge Optical Emission Spectroscopy). The microhardness was measured in cross section to avoid the influence of the substrate. The corrosion resistance in a CO₂ containing media was evaluated by potentiodynamic polarization curves.

1. Chapter 1: Theoretical part

1.1. Corrosion process ^[1-6]

1.1.1. Definition of corrosion

Corrosion could be defined as a chemical or electrochemical reaction between a material, usually a metal, and its environment that produces a deterioration of the material and its properties. Metals have a natural tendency to react with other chemical compounds such as oxygen or water, both of which are present in most natural environments, to form hydrated metals oxides (rust).

1.1.2. Forms of corrosion

Corrosion classification is usually based on one of three factors:

- *Nature of the oxidant*: Corrosion can be classified as “wet” or “dry”. A liquid is necessary to have wet corrosion, while dry corrosion usually involves high-temperature gases. Nucleation and growth phenomena of oxide layers and other compounds are the same for both kinds of corrosion.
- *Mechanism of corrosion*: This involves either electrochemical or direct chemical reactions.
- *Appearance of the corroded metal*: Corrosion can be uniform or localized. In the first case the corrosion rate is the same over the entire metal surface; in the second case, only small areas are affected.

Classification by appearance is based on identifying forms of corrosion by visual observation (with naked eye or magnification).

Fig.1.1-1 shows many forms of wet or aqueous corrosion:

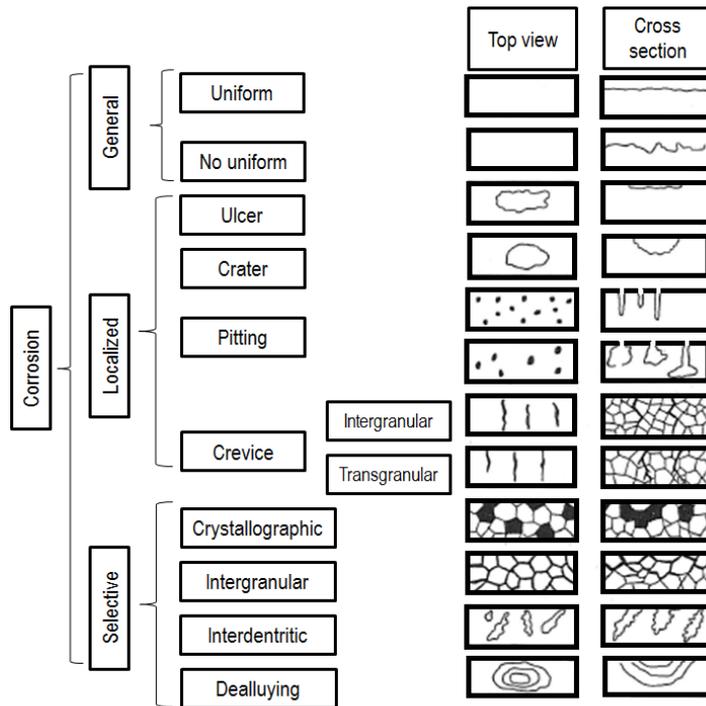


Figure 1.1- 1: Different forms of aqueous corrosion

In this work uniform, pitting and CO₂ corrosion will be studied.

- *General corrosion*

General corrosion results in a uniform penetration over the entire exposed metal surface. The general attack results from local corrosion action, the surface may be viewed as lot of small anodes and cathodes changing place all the time. The total area of anodes and cathodes is equal.

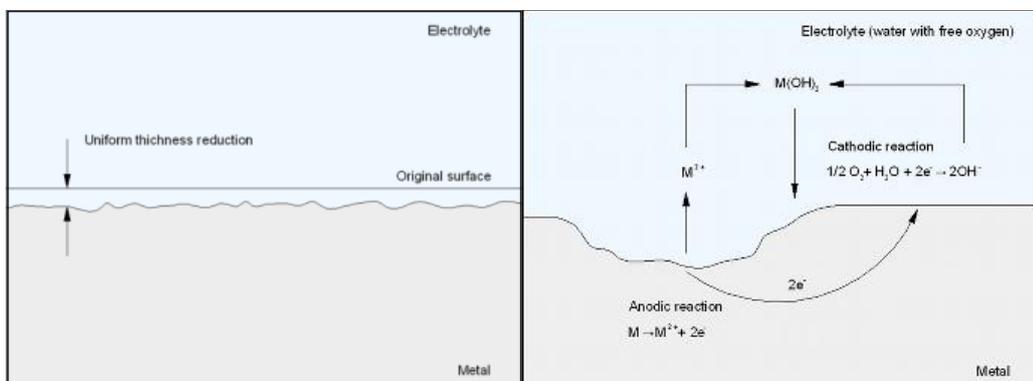


Figure 1.1- 2: (a) General corrosion is a homogeneous attack; (b) The general corrosion mechanism

The anodic reaction takes place at the metal anode, when metal atoms become into positive metal ions and negative electrons.

Metal ions are transferred to the electrolyte and electrons are transferred to the metal cathode.



The cathodic reaction takes place on the metal cathode. A typical cathodic reaction is reduction of oxygen. Electrons from the metal cathode are reacting with oxygen and water and produce negative OH⁻.



Finally, negative ions from the cathodic reaction and positive ions from the anodic reaction react and produce a neutral corrosion product. No electric charge is accumulated.

Usually, uniform corrosion results from atmospheric exposure, in salt waters or in chemical and industrial environments. All metals are affected by uniform corrosion, although passive materials, such as stainless steels or nickel-chromium alloys are often attacked by localized corrosion forms.

General corrosion is not considered to be a dangerous form of corrosion. Even if the weight loss is high, rate of penetration is small and easily measured and predicted. The rate of corrosion is influenced considerably by the electrical conductivity of the electrolyte. For example, pure water has poor electrical conductivity and the corrosion rate will be much lower than an acid solution of high conductivity.

As corrosion occurs uniformly over the entire surface of the metal substrate, it can be practically controlled by cathodic protection, use of coatings or paints, or simply by specifying a corrosion allowance.

- *Pitting corrosion*

Pitting appears on passive metals like stainless steels in electrolytes containing halogen ions (F⁻, Cl⁻, Br⁻, I⁻). The passivation film is attacked by high concentrations of halide ions, causing small pits.

Several processes make the pits to grow. The metal becomes active in the pits. The small pits will act as "anodes", while the remainder of the oxide film acts as a "cathode". The unfavourable area ratio increases the rate of corrosion. Reduction of hydrogen may be an additional corrosion process since the pH inside the pit may be very low. Over time, pitting corrosion will cause the cavities to combine and create larger cavities.

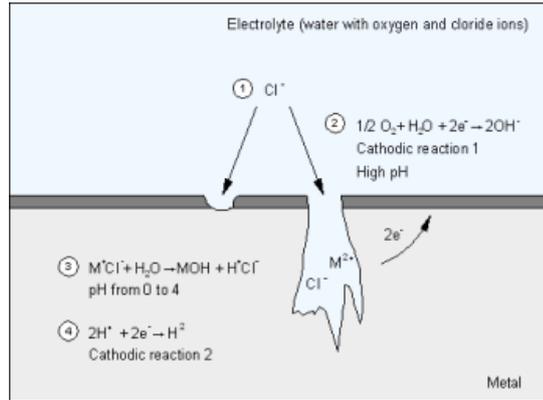


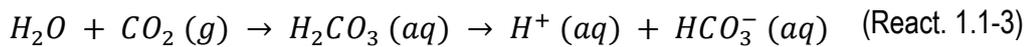
Figure 1.1- 3: Pitting corrosion

Pitting is a dangerous form of corrosion. Rate of penetration can be 10 to 100 times higher than general corrosion. A small number of pits on a non-corroded surface are easily overlooked.

The passivation film may also be broken due to erosion. That includes high velocity fluid flow or turbulence, especially with abrasive solids. For some materials pitting corrosion will occur even at very low concentrations of dissolved oxygen and the corrosion will increase as the concentration of oxygen increases.

- *CO₂ corrosion*

Carbon dioxide (CO₂) is a normal substance in oil and gas reservoirs. CO₂ and water make carbonic acid H₂CO₃. The carbonic acid will further dissociate to H⁺ and HCO₃⁻ ions. Dry CO₂ is non-corrosive to metals and alloys.



The H⁺ ions will reduce the pH in the solution. Carbonic acid is a weak acid, since only a small part of the acid will dissociate to ions. But, large concentration of CO₂ and thus H₂CO₃ combined with a small resistance to dissociate to ions, make the reduction of hydrogen to an effective reduction process.

The electrons come from oxidation of the metal (React. 1.1-1).

Susceptibility increases when pressure, CO₂ concentration and temperature increase; and decreases with high H₂S concentration.

Some carbon dioxide stays as CO₂ molecules, not all of the carbon dioxide is converted into carbonic acid. Increased pressure and carbon dioxide concentration makes more carbonic acid and thus more H⁺ and HCO₃⁻ ions. The process of making more carbonic

acid when increasing the pressure is quite slow. The reverse reaction of making CO₂ and water when reducing the pressure is much faster.

Corrosion increases with increased temperature as for most corrosion processes. The pH will also be increased at increasing temperature, since the amount of CO₂ dissolved in the water will be reduced at increased temperature and thus reduce the amount of carbonic acid.

High concentration of H₂S reduces the corrosion significantly due to sulphide films formation.

1.1.3. Thermodynamics

Thermodynamics predicts the direction in which the changes of the systems can occur. The only reactions that can take place spontaneously are those that have the lower energy in a system. However, thermodynamics does not provide any information about the reaction rate, that is area of kinetics.

It is used the Gibbs' free energy equation to predict if a reaction will be spontaneously or not without external influence.

$$\Delta G_T^\circ = -n F \Delta E \quad (\text{Eq. 1.1-1})$$

$$\Delta E = E_{red} - E_{oxi} \quad (\text{Eq. 1.1-2})$$

Any chemical process may occur if $\Delta G_T^\circ < 0$. The "°" and "T" means that the chemical potential of all participants were taken for calculations under standard conditions; pressure 101,325Pa and any constant temperature (usually 298K).

Corrosion in aqueous media is an electrochemical process where the corroding metal is an electrode in contact with an electrolyte.

There is also needed to define electrode potentials and the way they can be measured with reference electrode.

- *Standard equilibrium potential*

When a metal is immersed into an electrolyte, it delivers positive metal ions to the electrolyte. The metal is more positive than the electrolyte and has to give some cations to the electrolyte to be in equilibrium. Dissolving property of metal has to be measured as a potential difference between the metal and a reference cell.

Commonly is used a standard hydrogen electrode (SHE) as a reference cell and the potential difference is called standard equilibrium potential.

Potentials at other temperatures, pressures, concentration, pH etc. can be calculated by using the Nernst equation (Eq. 1.1-3). This potential is called equilibrium potential (E_e). The metal will be immune to corrosion if the potential of the metal is higher than the potential of possible reductions in the environment. If the equilibrium potential of the metal is below the equilibrium potential of possible reductions in the environment, there are two possibilities: Corrosion and passivation.

$$(E_e)_{M/M^{n+}} = (E^\circ)_{M/M^{n+}} + 2.303 \frac{RT}{nF} \log \left\{ \frac{a_{M^{n+}}}{a_M} \right\} \quad (\text{Eq. 1.1-3})$$

$$(E_e)_{Ox/Red} = (E^\circ)_{Ox/Red} - 2.303 \frac{RT}{nF} \log \left\{ \frac{a_{Red}}{a_{Ox}} \right\} \quad (\text{Eq. 1.1-4})$$

$$(E_e) = \Delta E^\circ - 2.303 \frac{RT}{nF} \log \left\{ \frac{a_{M^{n+}} \cdot a_{Red}}{a_{Ox} \cdot a_M} \right\} \quad (\text{Eq. 1.1-5})$$

Where ΔE° is the difference in standard potentials for the anodic and cathodic reactions, R is the gas constant, T is the absolute temperature, n is the number of exchanged electrons and a is the activity of each involved specie.

Usually this expression is written in terms of concentration instead of activity, because the activity of a metal is $a_M = 1$:

$$(E_e) = \Delta E^\circ - 2.303 \frac{RT}{nF} \log \left\{ \frac{c_{M^{n+}} \cdot c_{Red}}{c_{Ox}} \right\} \quad (\text{Eq. 1.1-6})$$

With these basic concepts defined it is possible to explain the Potential-pH (Pourbaix) diagram. These diagrams allow us to visualize in an easy way the areas of stability of chemical species and know what corrosion reactions can occur in a given metal-solution system.

A potential-pH diagram is a graphical representation of the relations, derived from Nernst equation, between the pH and the equilibrium potentials (E_c) of the electrochemical reactions occurring in the solution containing a specific element.

The standard equilibrium potentials are calculated from thermodynamics data (standard chemical potentials or Gibbs free energies of formation). The equilibrium relations drawn for a given ratio of activities of two dissolved species of the element give E-pH lines. The representation of the equilibrium pH for acid-basic reactions (independent of the potential) gives vertical lines. All those lines delimit E-pH domains of stability for the various species of the element (metal, oxides, hydroxides and ions).

The diagrams of all water-metal systems have the same common functions, the lower E-pH lines delimit the stability area of the metal. In the region below these lines, the metal is stable and corrosion cannot occur for this E-pH conditions. It is called the immunity region.

For E-pH condition above the line for the equilibrium between the metal and the first metallic ion, the metal is not stable, and tends to be oxidized and dissolved into ions. Hence, the system is in the activity or corrosion region.

When the reaction of a metal produces an oxide or hydroxide that forms a layer on the surface of this metal, then is said to be passivated. The area enclosed by the metal-oxide or ion-oxide equilibrium lines is the passivation region.

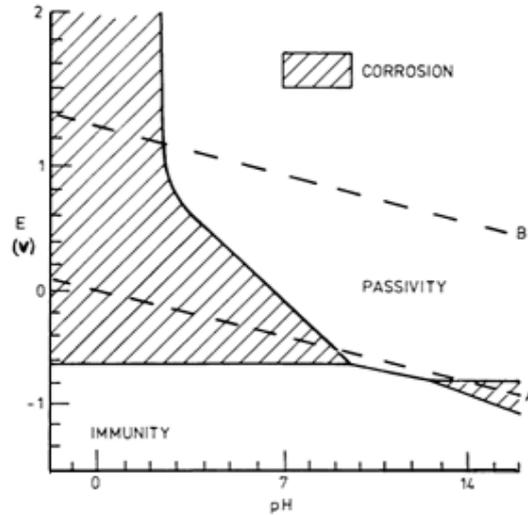


Figure 1.1- 4: Pourbaix diagram

1.1.4. Passivation

The ability of a metal to create a protective film on its surface is called passivation. The corrosion rate of corrosion in the passive state depends on the material and generally is very low. Most of the technologies that depend on the use of a metal could not exist if these metals did not present passivity.

There are two types of passivity:

- A metal active in the electromotive force (“emf”) series is passive when its electrochemical behaviour in a given environment becomes that of a metal noble in the “emf” series
- A metal is passive while, still from the standpoint of thermodynamics at an active potential in a given environment, it exhibits a low corrosion rate.

The passivation film could be broken mechanically, chemically or electrochemically. Mechanical destruction may be the result of mechanisms like erosion, adhesive wear and abrasive wear. Electrochemically destruction may be the result of halide ions like the chloride ions.

Some oxygen is required for re-healing of passivated metals after a scratch or damage. Very low values are normally required for healing.

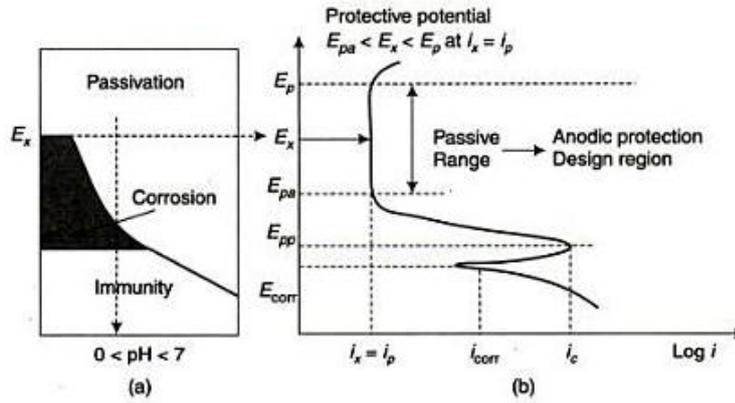
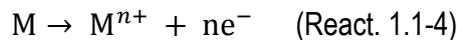


Figure 1.1- 5: (a) Schematic Pourbaix diagram and (b) active-passive curve indicating the passive region for anodic protection

1.1.5. Kinetics of aqueous corrosion

Thermodynamics shows what reactions can occur but it is necessary to know the kinetics to predict at what rate these reactions will occur.

For corrosion to occur, an oxidation and a reduction reaction must occur simultaneously. The oxidation electrochemical reactions are:

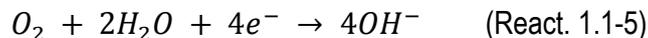


Where “M” represents a metal and “Mⁿ⁺” a dissolved metal cation.

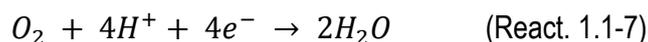
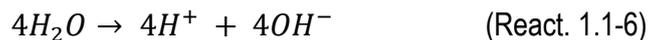
The cathodic or reduction reactions are:

- For Oxygen

The oxygen reduction is the most normal cathodic reaction in common environments like condensation in air, fresh water and seawater. The corrosion rate depends on the oxygen concentration, partial pressure and temperature. Typical reduction process in neutral electrolytes is:



The above process is in fact the total reaction of two basic processes:

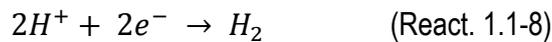


Reduction of oxygen is thus also dependent from the H⁺ ions. Reduction of oxygen in low pH fluids is normally described by using the 1.1-7 equation, while reduction of oxygen in neutral or high pH fluids is normally described by using the 1.1-5 equation.

The cathodic reaction of oxygen is stronger than reduction of hydrogen when the electrolyte is water saturated with oxygen and the pH is higher than 3. Reduction of oxygen can cause hard corrosion of carbon steel at very low concentrations of dissolved oxygen. Corrosion rate with oxygen as oxidant is often limited by the diffusion of oxygen to the metal surface. Diffusion of oxygen to the surface is easier at higher temperature. Hence, high temperature will increase the corrosion rate due to the access of more oxygen to the surface.

- *For Hydrogen*

Reduction of hydrogen is a normal cathodic reaction when acids are present. Acids like hydrochloric acid (HCl) will dissociate to H^+ and Cl^- when dissolved in water. Rate of corrosion depends on the hydrogen concentration, partial pressure and temperature.



- *For Halogens*

Fluorine (F), chlorine (Cl), bromine (Br) and iodine (I) are all forming diatomic molecules (F_2 , Cl_2 , Br_2 , and I_2) and they all form negatively charged ions (F^- , Cl^- , Br^- and I^-). None of the halogens can be found in nature in their elemental form, they are found as halide ions or molecules. The halide ions will attack the oxide layer on e.g. stainless steels and cause pitting.

The reason for finding halide ions in the nature is because all halogens are effective oxidizing agents. That means they have a tendency to acquire electrons (form a single charge ion by filling their outer electron shell with one more electron) and become ions (cathodic reaction). The substance which gives up those electrons is said to be oxidized (like metals). The halogens can be graded as oxidants based on their oxidizing strength: $F_2 > Cl_2 > Br_2 > I_2$.

Example of a halogen as oxidant is reduction of chlorine.



The corrosion rate depends on the halide concentration and the temperature. Halide ions combined with single hydrogen atoms form the hydrohalic acids like HF, HCl, HBr, HI, which is a series of particularly strong acids. Note that all halides will attack the passivation film of stainless steels and other corrosion resistant alloys.

1.1.6. Corrosion prevention

The most effective method to prevent a metal from corrosion is the application of a layer on the metal surface. The coating acts as a barrier between the metal and the environment. The most important feature when using these classes of coatings is the surface pre-treatment. It has to be clean and free of contaminants.

- *Metallic coatings*

This kind of coatings can be made by different techniques as hot-dip galvanizing, electroplating, electroless plating, high velocity spray, plasma (PVD) and ion implantation, chemical vapor deposition (CVD), cladding and weld overlays.

The major use of these metallic coatings is to prevent corrosion on carbon and low alloy steels.

- *Organic coatings*

There are several techniques for organic coatings as epoxy paints, acrylic paints, polyurethane paints, organic zinc paints, phenolic and epoxy-phenolic coatings, fluorocarbon based coatings and silicone paints and coatings. This type is preferred because of its chemical inertness to the environment, and also has a good surface adhesion property.

- *Inorganic coatings*

Inorganic coatings include surface conversions, inorganic zinc silicate, HVOF ceramic coatings, flame and arc spray ceramic coating. The common surface conversions are anodizing used on aluminium, phosphating and oxidizing processes used on steels and chromate surface conversions on steel.

1.1.7. Metallic coatings

Coatings are either anodic or cathodic to the substrate. The metal coatings which are less noble, in the electromotive force (emf) series, in comparison to the base metal are known as *anodic metal coatings*. Coatings that are anodic to a substrate in one environment may be cathodic to the same metal in a different environment. The environment may change from the surface of the coating to one that exists within any defects, such as scratches, cracks or corrosion pits. These defects are quite important if the coating is cathodic to the substrate. In this case, if the substrate is exposed to a corrosive environment, it will corrode rapidly. In the other hand, if the coating is anodic to the substrate, defects are less important. In this case, if the substrate becomes exposed, it will be protected by the corrosion of the coating.

Table 1.1- 1: The Electromotive Force Series

Element	*E, volts	Element	*E, volts
Lithium	-3.05	Cobalt	-0.277
Magnesium	-2.34	Nickel	-0.25
Beryllium	-1.7	Tin	-0.136
Aluminium	-1.67	Lead	-0.126
Manganese	-1.05	Copper	+0.345
Zinc	-0,762	Silver	+0.8
Chromium	-0,71	Palladium	+0.83
Iron	-0.44	Mercury	+0.854
Cadmium	-0,402	Platinum	+1.2
Titanium	-0.336	Gold	+1.68

*E is standard electrode potential at 25°C. The value of E for hydrogen is taken as 0.00.

It is prudent to select a coating as close as possible in potential to the substrate in moist environments, because few coating are completely free of pores, cracks and other defects. Before designing or applying a protective coating to a metal, it must be known the nature and essential properties of the substrate. The susceptibility to corrosion of a plated substrate depends on physical properties and mechanical conditions.

Nickel coatings are most widely used for their high hardness, wear and corrosion resistance, coupled with an attractive visual appearance. Thus, taps and sanitary ware, automotive components and light fitting are few examples of this widely used coatings. The metallizing of plastics using, nickel gives such components a metallic appearance, a higher reflectivity and low weight.

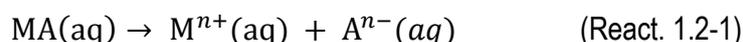
1.2. Theory of Electrodeposition [7-9, 14, 15, 20]

The electrodeposition consists of immersing the object to be coated in a solution of the metal to be plated and passing a current between the object and another electrode. Done to achieve the desired electrical and corrosion resistance, reduce wear and friction or improve heat tolerance.

In general, a metallic solution of the metal to be deposited is electrolyzed to have a uniform coating of the metal on the cathode.

The anode is normally the pure metal with some exceptions, e.g., in the chromium plating, chromium is not used as anode. During the electrolysis, the anode dissolves into the electrolytic bath and metal ions from the bath solution gets deposited over the cathode as pure metal. The following reactions show the electrodeposition process:

The electrolyte MA ionizes in the bath as:

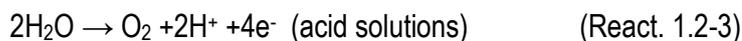


At the anode, the reactions can be carried out in two ways depending in the anode. Soluble anodes dissolve anodically into the electrolyte, whereas the reaction on insoluble anodes is generally the oxidation of water. Soluble anodes are usually used in chloride baths, and insoluble anodes are used in sulphate baths. Insoluble anodes are used to complete the electrical circuit to the solution; hence it is necessary for it to be a good conductor and to be unattacked by the bath with or without current flowing.

For soluble anodes the reaction is:



And for insoluble anodes there are two reactions depending on the pH of the solutions:



At the cathode, metal ions get reduced and deposited as metal atoms:



1.2.1. Mechanism of electrodeposition

The mechanism of the electrodeposition is similar to the crystal growth and develops in two steps: (1) Formation of nuclei covering electrode with few atomic layers of metal (2) Growth of deposits and the thickness of the layer.

Formation of nuclei requires high voltage although once formed, nuclei will grow pretty fast at low voltage. The atoms (ad atoms), which are formed during the plating on the crystal plane quickly, occupy suitable sites, that is, kink site where atoms interact with three neighbours. Atoms also occupy edge site (two neighbours) and sometimes occupy terrace site (one neighbour).

The growth takes place as follows:

- a. Mass transport in solution by diffusion of ions to the surface of electrode.
- b. Electron transfer to form an ad atom (a mobile or absorbed atom).
- c. Diffusion of ad atoms across the surface to kink sites.

1.2.2. Electrocrystallization

The deposit formation is determined by the following steps:

- Ions of the solvent move through the cathode by diffusion, migration and convection.
- There is an electron transfer between the cathode and the ions.
- Partial or total loss of the solvation spheres and ad atoms formation

- The ad atoms are absorbed by the surface and spread till find a suitable place (T,L,K)
- Cluster formation
- Crystallographic development of the crystal grain

Kossel-Stranski model assumed that the strength of binding of an atom to the surface depends on its number of nearest neighbours. They applied this to a simple cubic crystal, which is also known as a Kossel crystal. This is, of course, a simple approximation to how the binding depends on the number of neighbours, but this model does contain the essence of an explanation of why there is a strong anisotropy in the growth rate of some crystals. This model, also called TLK model, is still the basis for modern statistical mechanical models of crystal growth.

The *Terrace-Ledge-Kink (TLK) model* is commonly used to describe equilibrium solid surfaces. Metal atoms are preferentially deposited at those sites on the cathode surface where their incorporation in the matrix releases the most energy. Hence, it is possible to anticipate preferential growth of nuclei at those locations where overall the free energy requirement is at minimum. Such locations include edges, corners, steps and kinks; as it possible to observe in the figure 1.2-1 (b).

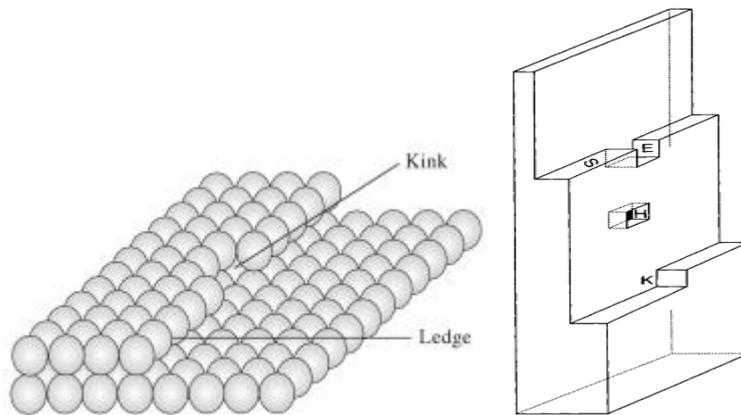


Figure 1.2- 1: (a) Atomic-scale illustration of the terrace-ledge-kink model. (b) The most commonly surface defects, growth sites at the cathode surface. E=corner; H=recess; K=edge; S=step

Incoming ad-atoms build up, either directly or after lateral diffusion, at the defect sites on the cathode surface. The stability of growing nuclei formed at these locations is determined by the local lattice energy, and can be defined as that energy that is required to incorporate more atoms into the metal matrix at the cathode.

Commonly, the electrodeposited layers are polycrystalline that is they consist of a high amount of small grains. Polycrystalline deposits can be characterised by size, shape, distribution and orientation of the crystallites. In many cases are used the following metallographic descriptions:

- *Field-oriented isolated crystals type (FI)*
At overvoltage of 0-10mV, a one-dimensional nucleation takes place. The nuclei grow to form individual crystallites, is usually oriented in the axis of the current field. Growth occurs slowly at the side faces of these crystallites and the deposits can be described as dendritic. These deposits have not useful technical properties.

- *Base-oriented reproduction type (BR)*
At overvoltage of 10-100mV, a two-dimensional nucleation takes place, and flat faced crystallites grow. The axis of growth is normal to the growth plane and is determined by the rate of the slowest step in the sequence, the two-dimensional nucleation. The technical properties of these deposits are interesting because they are similar to those of the underlying substrate.
- *Field-oriented texture type (FT)*
In the region 100-150mV of overvoltage, single crystallite initially form. If the overvoltage increases the crystallites become three-dimensional, which grow parallel to the electric field lines and whose bounds are crystallites.
- *Un-oriented dispersion type (UD)*
At overvoltage of >200mV, are form small crystals as a result of high rates of electrocrystallization. The result is a microstructure of very fine randomly oriented crystallites with two visible grain structure. Thanks to their excellent properties, deposits of this type are ideal for technical applications.
- *Twinning transition type (Z)*
This type of growth designates the transition between FT and BR type. This structure is formed when the crystallization overvoltage is large enough to allow formation of two-dimensional nuclei. Twinning may cause a reduction of the ductility of the deposited metal.

The different types described are shown in the following figure (Fig.1.2-2), on the Winand diagram.

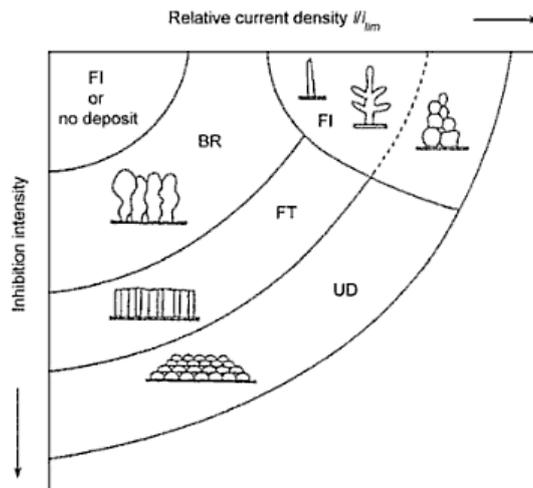


Figure 1.2- 2: Winand diagram. Depending on current density and inhibition activity

1.2.3. Electroplating bath composition

The composition of the plating bath ensures that the deposit of an even thickness over the whole of the surface to be electroplated. This depends on the *throwing power* of the electroplating bath. *Throwing power* of a plating bath is defined as the ability of the bath to produce a uniform and even deposit on the entire surface of the substrate. This is important in the electroplating bath of irregular objects. Plating will be non-uniform if the object carries cavities or holes.

Factors which determine the throwing power of the bath include (1) conductivity of the electrolyte, (2) composition of the bath and the presence of complexing agents and additives as “levellers” and “brighteners” and (3) competing electrode reactions.

In general, higher the conductivity of the electrolyte the rate of deposition will be more uniform over a complex cathode surface as voltage is minimised.

The plating bath is normally a complex mixture of soluble species of the metal being plated, electrolytes and various additives to ensure quality electroplating. The metal to be plated should be in high concentration either as simple hydrated ion or as a complex to maintain the required current density. Various electrolytes are added in high concentrations to the plating bath to give maximum conductivity, control of pH and buffering action. Complexing agents are used to make the deposition potential more negative so as to prevent spontaneous chemical reaction between the cathode and plating ion.

Certain organic additives have a remarkable influence over the nature of electrodeposits. They are classified as brighteners, levellers, structural modifiers and wetting agents according to the purpose for which they are added.

- *Brighteners* are substances that help in the formation of bright and light reflecting deposits. Only when the grain size of the deposit is smaller than the wavelength of light employed, the deposit becomes light reflecting. Hence, brighteners are used to produce microscopically fine deposits parallel to the substrate surface. Aromatic sulphones, sulphomates and compounds containing groups like $-\text{CN}$, $-\text{NCS}$ or $-\text{CO}$ act as brighteners.
- *Levellers*. Substrate surface may contain areas like dislocations where plating may take place faster than other areas. This leads to irregular deposits. When levellers are used they get adsorbed at such regions and prevent electron transfer. This ensures smoothness of the deposit in which sodium alkyl sulphomates act as levellers.
- *Structural modifiers*. All electrodeposits possess internal stress. If the stress level is high the deposit may give way to impact and undergo cracking. Structural modifiers help in modifying the structure of the deposit and make it stress-free. Saccharin is a common stress reliever.
- *Wetting agents*. During electrolysis sometimes evolution of hydrogen at the cathode may take place. The gas may get entrapped inside the metal deposits and may try to escape

when the plating is over and makes the deposit porous and breakable. This phenomenon is called hydrogen embrittlement.

Wetting agents release the hydrogen gas from the surface of the substrate and improve the adhesion of the deposit.

1.2.4. Effect of plating variables on the electrodeposit

There are several variables that may effect to the electrodeposition. Below are exposed the most important ones.

- *Current density*

It is defined as current per unit surface area of cathode expressed in terms of mA/cm² of surface of the electrode. If the applied voltage increases, the current density also increases until a limiting value is reached.

In order to obtain a uniform deposit, the current density should be low, so that the surface diffusion process is faster than the electron transfer (limiting step). As a result, the ad atoms can find kink sites, the most suitable positions.

If the current density is increased, electron transfer is retarded because of surface diffusion though ad atoms cannot reach the most favourable places.

If the current density gets over the limiting value, hydrogen gas is liberated and exhaustion of H⁺ ions at cathode is higher, resulting in dispersed deposits containing metal oxides and hydroxides.

- *Plating metal ion concentration*

Moderate concentration is used to get a thin layer of deposit. If it increases mass transfer process decreases which affects plating bath badly. To get thick deposit of metal, slightly higher metal concentration is used. To increase the conductivity of the bath electrolytes which do not participate on the electrode reactions can be used. This also controls the pH. For example, in copper plating, diluted sulphuric acid can be used.

- *pH*

At low pH, evolution of hydrogen creates a burnt deposit. On the other hand, at high pH, electrode surface gets coated with insoluble hydroxides. Hence, optimum pH value must be maintained using buffers.

- *Conductivity*

Using a higher conductive solution is certainly advantageous from the economic point of view because it represents lower energy consumption and reduces the tendency to form rough deposit.

- *Temperature*
A good deposit takes place at slightly elevated temperature to increase diffusion of ions on the surface. Many metals are plated between 35 and 60°C.
- *Agitation*
It is a way to keep the bath agitated and enriched of metal ions on the cathode surface and allowing the use of higher current density. Mechanical or magnetic stirrers, flowing air or cathode movement could be used. Working at very high speed agitation could produce turbulent flows and consequently rough deposits.

1.2.5.Pre-treatments

The strength of adhesion to the substrate is not determined by the coating material alone, but also by the properties of the coated substrate. As prerequisites for optimum adhesion, firstly the object to be coated must be given an appropriate pretreatment and secondly the coating material must be matched to the substrate in terms of specific films properties. In addition to this, the substrate governs the method of application and the possible curing methods, which are determined most importantly by the heat resistance and by its dimensions.

The pretreatment would be different depending on the type of substrate. For example, there are substrates that are easily to coat such as carbon steel, copper or brass; materials that need an special pretreatment such as stainless steel, aluminium or plastics; and substrates that are hardly to coat such as titanium or glass.

The surface of the substrate to be coated usually contains impurities like rust, scale, oil or grease and dust particles. The substances, if are present at the time of coating, will give porous and discontinuous coating. In order to get a uniform and smooth protective coating, these substances are removed by the following methods.

- *Degreasing*
Oil and grease may be removed by cleaning with organic solvents such as chloroform, toluene and acetone. Immersion in hot alkaline solutions is the most commonly used cleaning technique. For example, sodium carbonate and sodium hydroxide are used in this method. To remove organic impurities aqueous solutions or organic solvents are used. Chlorinated hydrocarbons are commonly used. They can effectively eliminate the greases and oils. Cleaning action can be improved by using ultrasounds in immersion baths.
- *Chemical methods*
To remove oxide scales and corrosion products (rust) from the surface chemical methods, including pickling, are used. Usually, for treating steel and zinc are used sulfuric or hydrochloric acids, but for aluminum are used nitric or hydrofluoric acids. Because of its low vapor pressure, sulfuric acid was preferred. The losses and pollution are reduced. Nowadays, hydrochloric acid is mostly used because it cleans better the metal surface and its evaporation is limited because usually closed containers are used on this process.

Sometimes organic inhibitors are added in the pickling with acids to limit the action to the impurities or oxides and prevent dissolution of the base metal. Addition of surfactants has a limiting degreasing effect.

Pickling with aqueous caustic soda solution is widely used to clean aluminum, taking into account their amphoteric properties. Even though, after alkaline treatment, the surface should be treated with acid to remove adherent layers and polishing the surface.

- *Mechanical cleaning*

This method is mainly used to remove scale, rolling skin, burr, and paint residues. Rust and corrosion products are also removed by abrasion such as grinding, wire brushing and polishing. Blasting methods (sandblasting, compressed air, or water jet) remove impurities.

- *Electrochemical method*

The electrochemical method is used to remove oxides which are not removed by other methods. The base metal is made either anode or cathode with an electrolyte (acid or alkaline). At the anode the oxides are dissolved in the electrolyte and leave the base metal, whereas at the cathode the metal oxides are reduced to metal.

1.2.6. Pulse current

Pulsating the current (or voltage) permits the plating process to be operated at higher average current density than the plating without the formation of dendrites. Furthermore, the composition of alloy deposits can be varied by changing the pulse parameters while keeping the average current density constant.

Pulsed current could be classified in two main groups: (1) unipolar pulse; all the impulses have the same polarity and (2) bipolar pulse; alternating anodic and cathodic pulses.

Pulsed current techniques involve application of a forward current for a certain time interval with a short, high-energy reverse pulse periodically interposed. The main difference between direct current and pulsed current is that with dc plating only voltage (or current) can be controlled, while with pulse plating three parameters- on-time, off-time and peak current density- can be varied independently.

To describe a direct current electrodeposition it is necessary to know the current density but to characterize a pulsed current wave it is necessary to describe three parameters:

- Cathodic peak current density (j_c)
- Cathodic impulse duration (t_c)
- Interval between impulses (t_p)

These variables create a mass transport situation, an electrocrystallization condition and adsorption and desorption phenomena which are not otherwise possible.

In practice, is used the term *average current density*:

$$j_{AV} = \frac{j_c \cdot t_c}{t_c + t_p} \quad (\text{Eq. 1.2-1})$$

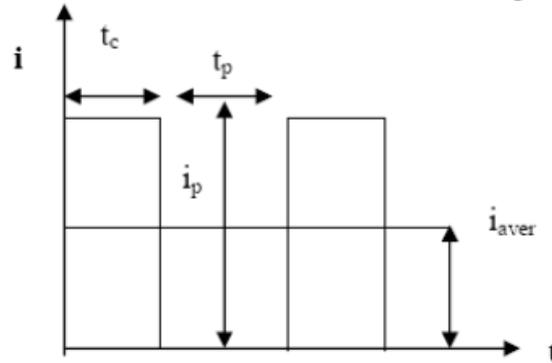


Figure 1.2- 3: Pulsed current wave

Another parameters to be described are (1) *duty cycle*; it represents the real time during the deposition is effective and (2) *frequency*; the reverse of the cycle time. These parameters could be calculated as:

$$T = \frac{t_c}{t_c + t_p} \quad (\text{Eq. 1.2-2})$$

$$f = \frac{1}{t_c + t_p} = \frac{1}{t} \quad (\text{Eq. 1.2-3})$$

The pulse current is used basically because of its capacity of modifying the electrocrystallization process, consequently the chemical and physical properties of the coatings.

The nucleation velocity is directly proportional to the current density thus, using high densities as in the pulsed current techniques; less porosity and decrease of the grain size are obtained.

1.3. Nickel electroplating ^[10-12]

The electrodeposition of nickel was first described in 1837. G. Bird electrolysed solutions of nickel chloride or sulphate for some hours and obtained a crust of metallic nickel on a platinum electrode. In 1840, the first patent for commercial nickel plating was granted to J. Shore of England who specified a solution of nickel nitrate.

Nickel plating is similar to other electroplating processes that employ soluble metal anodes. It requires the passage of current between two electrodes that are immersed in a conductive, aqueous solution of nickel salts. The flow of current causes one of the electrodes (the anode) to dissolve and the other electrode (the cathode) to become covered with nickel. The nickel in solution is present in the form of divalent positively charged ions (Ni^{2+}). When the current flows, the positive ions react with two electrons and are converted to metallic nickel at the cathode surface. The reverse occurs in the anode, where metallic nickel is dissolved to form divalent

positively charged ions, which enter the solution. The nickel ions discharged at the cathode are replenished by those formed at the anode.

1.3.1. Industrial nickel electroplating baths

The most used industrial nickel plating baths are described below.

- *Watt bath*

Most commercial nickel plating solutions are based on the one named after Watts who first introduced a bath having the formulation:

Table 1.3- 1: Composition of the Watt bath

Nickel sulphate	NiSO ₄ ·7H ₂ O	240g/l
Nickel chloride	NiCl ₂ ·6H ₂ O	20g/l
Boric acid	H ₃ BO ₃	30g/l

Nickel sulphate is used as the main source of nickel ions because it is readily soluble (570g/l at 50°C), relatively cheap, commercially available and is a source of uncomplexed nickel ions. In nickel plating solutions the activity of nickel ions is governed by the concentration of nickel salts in solution, their degree of dissociation and concentration of other components of the solution.

The presence of chloride has two main effects: it assists anode corrosion and increases the diffusion coefficient of nickel ions thus permitting a higher limiting current density.

Boric acid is used as a buffering agent in Watts nickel solution to maintain the pH of the cathode at a predetermined value. Boric acid solutions of the strength used in Watts nickel solutions have a pH of about 4.0 due to the nickel ions.

- *Sulphamate bath*

The standard sulphamate solution is widely used because of the low internal stress of the deposits, high rates of deposition and superior throwing power. Throwing power is the relationship between current distribution and uniformity of coating thickness. This is influenced by geometric factors (the shape and the position of anode and cathode) and by the electrochemical characteristics of the solution (conductivity, cathode polarization and cathode efficiency).

Because of the very high solubility of nickel sulphamate, a higher nickel metal concentration is possible than in other nickel electrolytes, permitting lower operating temperatures and higher deposition rates.

A small amount of nickel chloride is usually added to nickel sulphamate solutions to minimize anode passivity, especially at high current densities.

Table 1.3- 2: Composition of the Sulphamate bath

Nickel sulphamate	Ni(SO ₃ ·NH ₂) ₂	300-450g/l
Nickel chloride	NiCl ₂ ·6H ₂ O	0-30g/l
Boric acid	H ₃ BO ₃	30-45g/l

- Chloride bath

For heavy nickel plating the bath solution only contains chloride. The deposits obtained from them have a higher tensile stress and lower ductility than those obtained from Watts baths. The higher conductivity of chloride is employed in those electroplating baths which are kept more dilute than usual, in order to reduce physical losses, particularly from drag-out.

Table 1.3- 3: Composition Chloride bath

Nickel sulphate	NiSO ₄ ·7H ₂ O	50-75g/l
Nickel chloride	NiCl ₂ ·6H ₂ O	100-130g/l
Boric acid	H ₃ BO ₃	50-55g/l

- *Nickel sulphate bath*

A simple solution of nickel sulphate in water has a little commercial application, and the efficiency increases when is used boric acid as a buffer. However, the sulphate plus chloride solution of the Watts type is superior in performance, except with inert anodes.

- *Nickel fluoborate bath*

Nickel fluoborate is the basis of the only other bath of significant commercial importance. In addition to nickel fluoborate this solution contains boric acid and chloride ions. The solution is intrinsically highly buffered and so pH changes on plating are very small, usually the chosen value is pH=3.

The solution is easy to operate; it has high conductivity, good anode corrosion characteristics and tolerates relatively high metallic contamination, but is much more expensive than a Watts solution.

1.3.2. Electrochemical reactions during Nickel plating

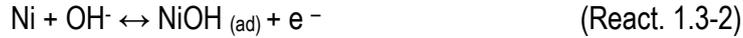
The non-uniform dissolution of electrolytic nickel observed in most commercial nickel electroplating solutions is due to the oxide film on its surface, and a correlation between the electrochemical and the physical dissolution characteristics exists.

That is, nickel dissolves non-uniformly when its solutions potential exceeds the peak potential, E_{pp}, and uniformly below that potential.

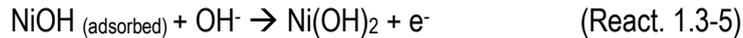
It is unlikely that the reaction taking place in the active regions is simply:



Active dissolution of nickel in a chloride-free nickel sulphate solution involves adsorbed hydroxyl ions and may proceed in three consecutive steps as follows:



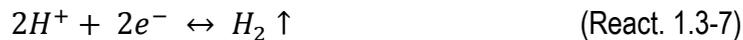
The reactions responsible for the transition from active-to-passive behavior may be written as:



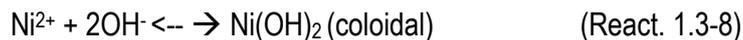
The anodic polarization characteristics of nickel are the result of the competition among these reactions. At potentials where reactions 1.3-3 and 1.3-4 are possible, the percentage of the surface area covered with an oxide film increases, According to the current density decrease during the transition range.

In the presence of chlorides, species like $\text{NiCl}_{adsorbed}$ and NiCl^+ interfere with the formation of nickel hydroxide and the oxide film. This kind of solutions increase anode efficiency to 100%, but dissolution is localized and occurs below or through the oxide film.

These reactions are competing with the hydrogen reduction reaction:



If the current density increases, the hydrogen gas developed increases thus the pH increases notably. Hence, this causes nickel hydroxide precipitation:



This effect could affect badly to the deposition; the colloidal particles disturb the crystallization and produces dark and rough coatings.

Acid boric is used to avoid this non-wished chemical process, the acid is used as a buffer and it will dissociate as:



1.4. Electrodeposition of composite coatings ^[15-20]

Codeposition is a coating protective technique which consists on introducing homogeneously inert particles of a different material in the metal matrix; this two-phase coating improves corrosion and mechanical resistance. The improvement of these properties depends on the combination of both particles and metal matrix.

Nowadays, the ability to produce new composite materials with good properties by using micro and nano particles is leading technological interests. This improvement depends mainly on the

size and the percentage of the particles codeposition, as well as on the distribution of these particles in the metallic matrix.

Concerning the type of current used during electrochemical deposition, it has been established that the application of pulse current plating techniques influences the control of metal electrocrystallization. It can perturb the adsorption–desorption mechanism occurring at the metal-cathode interface. The specific selection of the pulse current parameters results in the production of composite Ni/SiC electrodeposits with better properties, higher percentages of SiC and more uniform distribution of the particles in the metallic matrix, than by using direct current techniques.

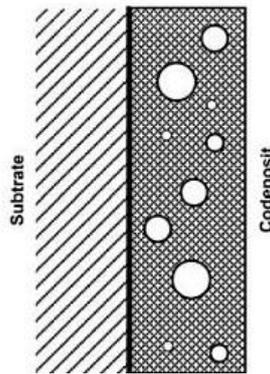


Figure 1.4- 1: Scheme of composite coatings

The principles have been known since the 1960s but the mechanics of codeposition and the conditions for optimized particle incorporation are still unclear. In the table 1.4- 1 some examples of metal/particles systems are given.

Table 1.4- 1: Particle metal matrix combinations.

Metal	Particles	Application
Ni	SiC	Wear resistant
Ni	PTFE	Friction control
Ni	Al ₂ O ₃	Dull nickel
Ni	Micro capsules	Different applications
Ni	NiFeS ₂	Catalytic properties
Co	Cr ₂ C ₃	Temperature resistance
Co-Ni	Cr ₂ C ₃	Temperature resistance
Ag	Al ₂ O ₃ , nanodiamond	Wear resistant
Au	Al ₂ O ₃ , nanodiamond	Wear resistant
Zn	SiO ₂	Corrosion resistance

1.4.1. Codeposition theory

For codeposition the particles must be dispersed in the plating bath. It is important to avoid the agglomerations of particles in the formation of stable dispersions.

For a stable dispersion the particles must have a large charge and a high activation barrier. An experimental parameter proportional to this charge is zeta potential.

The charge of the particle will be influenced by several experimental parameters. As mentioned before, typical inorganic particles used for codeposition are oxides and carbides; and those surfaces charge depends mainly on the chemical composition and the pH of the electrolyte. The characteristic pH for when the zeta potential is zero is called the isoelectric point. The zeta potential also depends on the pretreatment of the particles.

The surface potential can be change by the following electrolyte components:

- The protonation or deprotonation of the surface produces more positive or negative charges if the pH changes.
- Electrolyte ions can be adsorbed on the particle surface. Mechanical models of codeposition that have been developed, suggest the formation of a first layer on the particles by reduction of the adsorbed ions when the particle comes in contact with the metal surface.
- The size and form of the particles are important. For example, the non-spherical particles stick better to irregular surfaces.

The codeposition of particles requires a high particles adhesion on the metal surface. Therefore, not only the properties of the particles are important. The substrate surface properties should be also considered.

i. Surface charge

The particles must have a surface charge to avoid agglomeration in the electrolyte and to form a stable colloidal solution. The particle surface charge in combination with the surface charge of the electrode can influence the adhesion process.

ii. Electrolyte and particles adsorption

Adsorption of electrolyte components and the particle surface are equally important. A specific adsorption of ions can change the position of the pzc (Esin-Markov effect). Adsorption of surface-active organics will influence the hydrophobic or hydrophilic character of the surface and also change the surface tension.

iii. Surface morphology

This property is significant for the adhesion process of particles on the surface. A rough surface will provide better possibilities for the surface adhesion of particles than a very smooth surface. The surface topography will also influence the surface energy.

There are two common processes to describe the mechanism of codeposition of particles into a metal matrix, namely *physical dispersion of particles in the electrolyte* and *electrophoretic migration of particles*. Many theories have been suggested including the transport of particles due to electrophoresis, mechanical entrapment, adsorption and convective-diffusion. Table 1.4-2 provides an overview of the existing codeposition models.

Table 1.4- 2: Examples of theoretical models for codeposition

Model	Characteristics and assumptions	Deposits and process conditions			
		Reaction	Particles size, μm	Current density, mA/cm^2	Rotation speed, rpm
Guglielmi, 1972	Describes both adsorption and electrophoresis. The particles are covered by adsorbed metal ions. Particle characteristics and electrolyte conditions are accounted semi-empirically. The effect of flow is not considered.	Ni/TiO ₂ Ni/SiC	1–2	20–100	NG
Celis et al., 1987	Uses probability concept to describe the amount of particles that can be incorporated at a given current density. Mass transport of particles is proportional to the mass transport of ions to the working electrode. Volume ratio of particles in the metal deposit will: increase under charge transfer control and decrease under mass transport control.	Cu/Al ₂ O ₃ Au/Al ₂ O ₃	0.05	0–90	400–600
Fransaer et al., 1992	Uses trajectory to describe the codeposition of non-Brownian particles. Involves two steps: (1) reduction of metal ions (described by Butler-Volmer expression); (2) codeposition of particle (described by trajectory expression).	Cu/PS Ni/SiC	11 0.01–10	0–80 0–200	0–700 0–2000
Hwang et al., 1993	An improvement of Guglielmi's model. Uses three modes of current density (low, intermediate, high) to distinguish the reduction of adsorbed ion on particles. Involves three steps: (1) forced convective of particles to surface; (2) loose adsorption on the surface; (3) irreversible incorporation of particles by reduction of adsorbed ions.	Co/SiC	3	1–60	400
Vereecken et al., 2000	The transport of particles to the surface is controlled by convective-diffusion. The influence of particle gravitational force and hydrodynamics is accounted for at various current densities. Valid only when the particle size is smaller than the diffusion layer thickness.	Ni/Al ₂ O ₃	0.3	5–40	500–2000

Bercot et al., 2002	An improvement of Guglielmi's model, which incorporates a corrective factor (a 3rd order polynomial equation) to account for the effects of adsorption and hydrodynamic conditions.	Ni/PTFE	0.5	10–70	400–1000
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In Guglielmi's model the main factor which effects on the whole mechanism is the adsorption charge expressed by the zeta potential.

A three-step mechanism was proposed by Guglielmi:

- *Loose absorption*: The particles come closer to the cathode and are loosely absorbed on its surface. Those particles are surrounded by a cloud of adsorbed ions and electrolyte molecules.
- *Strong absorption*: When the electrical field is applied, the clouds of absorbed ions and molecules are separated from the particles and are strongly absorbed on the cathode.
- *Incorporation of the particles into the metal matrix*: In this step, the particles are embedded into the growing metal deposit.

The validity of Guglielmi's model has been verified for different codeposition systems, including copper with alumina from acidic sulphate solutions. However, Guglielmi's model does not allow prediction of the manner in which process parameters such as size, type and pretreatment of the particles, composition, temperature and pH of the plating solution affect the electrolytic codeposition.

In 1987 Celis et al. proposed a model that contains measurable parameters so that the prediction of the amount of codeposited particles for a given system becomes viable.

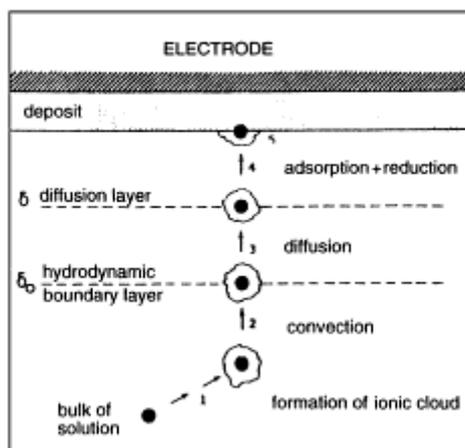


Figure 1.4- 2: The five stages in the codeposition of a particle by Celis' model

Figure 1.4-2 outlines the five-steps mechanism for a particle: (1) the adsorption of ionic species upon the particle, (2) the movement of the particle by convection toward the hydrodynamic boundary layer at the cathode, (3) the diffusion of the particle through the diffusion layer, (4) the adsorption of the particle with its adsorbed ionic cloud at the cathode surface and (5) the reduction of some adsorbed ionic species by which the particle becomes irreversibly incorporated in the metal matrix.

This model supposed that all the particles are surrounded by a cloud of adsorbed species, mainly metal ions, and can be incorporated into the metal matrix only if an efficient part of these chemical species are reduced at the same time with the metal ions on the cathode.

Also considers that the current efficiency is 100% and the particles are spherical, and is based on the influence of the electrolyte stirring.

Many theories have been proposed, but validation is still required to explain the mechanism of each type of coating and kinds of used particles.

Often, the existing models involve mathematical relationships and in all the models available so far, the effects of particle inclusion on deposit electrocrystallization have not been considered.

This aspect is important because the inclusion of particles into a metal deposit may cause reduction of the cathode surface area if the particles are non-conductive, and vice versa if the particles are conductive or modification of the deposit morphology.

Nowadays, the models used to describe the inclusion of micro sized particles are restricted to specific conditions.

From now on, future models to describe the processes of codeposition would require attention to interactive variables such as the particle characteristics (type, dimensions and concentration), the operating parameters (temperature, current density, pH and hydrodynamics) and the electrolyte composition (concentrations, presence of surfactants and additives).

1.4.2. Nickel matrix composite coatings review

Since some time ago, the codeposition of particles, such as oxides, carbides or nitrides, with metals has been introduced in various industrial applications. In particular, the electrochemical deposition of finely dispersed particles in a metallic matrix has carried out a new generation of composites, having the advantages of easy maintainability, low working temperatures, low cost and, mainly, gives the possibility to produce composite coatings with different combination of properties, by changing the electroplating parameters.

The first reference where a metal matrix composite electrodeposition is mentioned was in 1928, using copper and graphite coatings.

During the 60's, different types of micro sized particles, as carbides, oxides, PFTE or diamond powder, were used to improve the tribological properties of metal coatings, as nickel or copper.

After few years, the industries began to show interest in these new techniques that scientists were developing.

The first electroplating baths containing particles were used in the industry for systems of Ni/SiC and Co/Cr₂O₃. Those baths produced coatings for parts of car engines and aircrafts.

During the last decade, the necessity of new improved materials has revived the interest and the investigation on the metal matrix composite coatings. The restrictions for hard chromium coatings and new production nanotechnology have been the two main factors that have caused these news developments.

Usually the most studied system is nickel matrix composite coatings due to the high wear and corrosion resistance.

The idea of decreasing the size of the particles introduced in the metal matrix composite deposits and study the improved properties for new composite coatings was developed at the end of the 90's.

Kim et al. studied and produced bilayers coatings made by nickel matrix and SiC particles, using different contents of SiC in the deposit. They were able to study the effect of the particle size, the pH and the temperature of the electrolyte, the current density and the stirring rate.

Another group, Garcia et al., studied the wear resistance of Ni/SiC coatings, using smaller particles. Performing new composites with micron and submicron SiC particles they found out that the content of particles increases by reducing the particle size.

Zimmerman et al. also studied the influence of reducing the particle size in Ni/SiC systems. Moreover, they studied the influence of pulse current to reduce the grain size of nickel matrix and to increase the particles content in the composite.

Another group, Benea et al., used even smaller particles and studied the influence between the codeposition of particles and the coating microstructure and mechanical properties. The codeposition of nano particles, permits pore-free and more compact coatings and gives better mechanical properties and corrosion resistance.

Mechanical properties with systems Ni/SiC have been studied by various groups and have been proved to be a good candidate to replace hard chromium coatings.

Using micro particles and various electrochemical baths with different current conditions have shown that as higher is the amount of particles greater is the hardness of the coating.

Otherwise, the particle size affects directly the corrosion resistance and may deteriorate it. Using nanoparticles provides mechanical properties almost equivalent to those achieved using microparticles, without reducing the corrosion resistance of the coating.

There is no consistent information among those groups in relation to the protective properties of the system Ni/SiC. Most agree that using submicron particles helps corrosion resistance improvement due to microstructural modification.

According to Malfatti et al., the codeposition of SiC particles cause a decrease to current density only due to the fact that the surface of the coating is covered by ceramic particles and that almost the entire surface is covered not only by nickel but also by particles in contact with the electrolyte, not as in the case of pure nickel coatings.

Therefore, the resistance to pitting corrosion becomes lower because of the gaps between the metal and the matrix particles.

As is well known that the corrosion properties can improve if the grain size decreases; many attempts have been done to avoid the agglomerations of particles and to break columnar structure of Nickel deposits; using different types of surfactants and different pulsed currents, respectively, thus creating more homogeneous and smoother coatings.

Even though, attempts have made improvements in those kinds of coatings, their properties have not been studied.

2. Experimental part

2.1. Production of nickel matrix composite coatings

2.1.1. Substrate preparation

Panels of ASTM 387 F22 steel have been used as substrate for the production of pure, micro and nano SiC composite coatings. The metal area measures 46cm².

These steel panels have been treated before the electrodeposition process. The pretreatment was based in a three step process, which are described below.

- Degreasing with ultrasounds
In the first bath, the metal is introduced into a surfactant solution and ultrasounds are also applied to improve the strength of the solution. This bath cleans greases or oil residues of the metal surface. A 10% Galvadet solution is used and it is heated to a temperature of 80°C.
- Electrochemical degreasing
A solution of 12% Lectordet, an alkaline solution based on KOH, is used as electrolyte for the electrochemical degreasing. The steel was connected as anode, a platinum sheet was used as cathode and the applied voltage 6V.
- Pickling
The steel is immersed during 10min into an acidic solution before the electrodeposition to eliminate the possible corrosion products and to clean perfectly the surface. Each liter of acidic solution contains 300ml of hydrochloric acid, 100ml of sulphuric acid and 600ml of distillate water. The bath works at room temperature.

2.1.2. Electroplating bath

For this work a nickel sulphamate bath has been used, whose composition is as follows:

Table 2.1- 1: Nickel sulphamate bath composition

Nickel sulphamate	Ni(SO ₃ ·NH ₂) ₂ ·4H ₂ O	500g/l
Nickel chloride	NiCl ₂ ·6H ₂ O	10g/l
Boric acid	H ₃ BO ₃	25g/l

The necessary nickel ions for the deposition are given by the nickel sulphamate. As mentioned before, the nickel chloride is used to prevent of passivation film formation onto the anode surface and the boric acid is a buffer used to maintain stable the pH value around 4.

A squared titanium mesh basket plated of platinum and filled by pure nickel balls is used as anode.

For the production of the composite deposits 20 g/l of micro or nano particles of SiC are added. When the particles are added to the bath, ultrasounds are applied for 1 hour. After that, the bath has to be stirring at least 24 hours before the first electrodeposition; to be sure that the dispersion is stable and there are no agglomerations.

During the process of codeposition the solution has to be at around 50°C and continued stirring, to preserve the colloidal solution. In order to achieve the maximum possible stability is used a mechanical stirrer in a relative velocity of 1000rpm and a thermostat integrated into the bath to maintain the temperature.

2.1.3. Current conditions

For the sample production has been used both direct current and pulse current at different frequencies. The characteristic parameters of both currents are exposed below.

Table 2.1- 2: Current parameters

Parameters	Direct Current	Pulse Current
Current density (A/dm ²)	4	4
Time of electroplating (h)	2,5	5
Frequency (Hz)	---	1; 10; 0,1; 0,01
Duty cycle (%)	---	50

The duration of the electrodeposition depends on the coating thickness required. The maximum current density for pulse and direct current is the same in order to compare easily the results. The pulsed current is a square wave as is shown in the following figure.

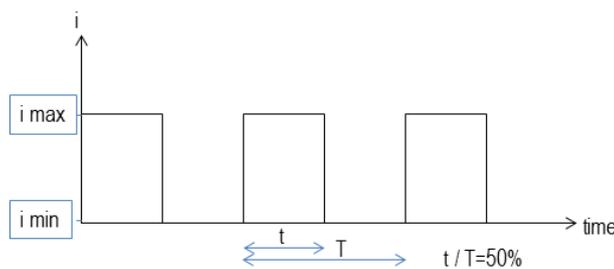


Figure 2.1- 1: Pulse current

2.2. Microstructure, composition and mechanical properties

2.2.1. Microstructural characterization

The microstructure has been observed by SEM (Scanning Electron Microscope) on top surface and cross section after metallographic etching.

For the observation in cross section the coated specimens have been embedded in resin and polished to obtain a mirror like surface. After polishing the nickel deposits have been etched using a 50% nitric acid and 50% acetic acid pickling solution.

To describe the topography of the different samples and the interaction between direct current or pulsed, and particle size; some micrographs of the top surface and cross section at different magnification are exposed below.

As can be observed on the micrographs 2.2-1 - 2.2-10 of pure nickel samples, the surface presents an irregular morphology called “cauliflower” structure.

The cauliflower structure consists of nickel grain aggregates. The size of these aggregates seems not to be influenced by the use of the pulse current.

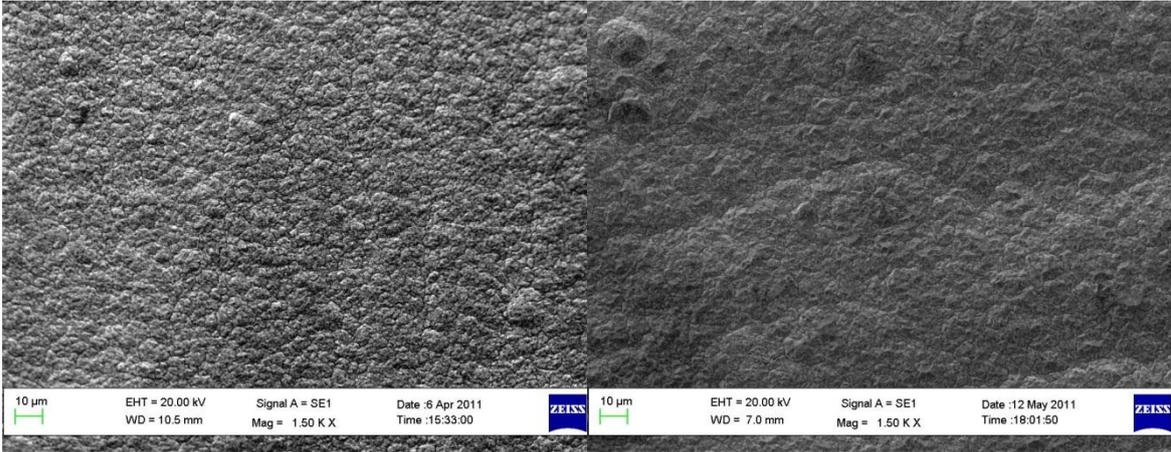


Figure 2.2- 1: Pure Nickel -under D.C.

Figure 2.2- 2: Pure Nickel -under P.C. – 0,01Hz

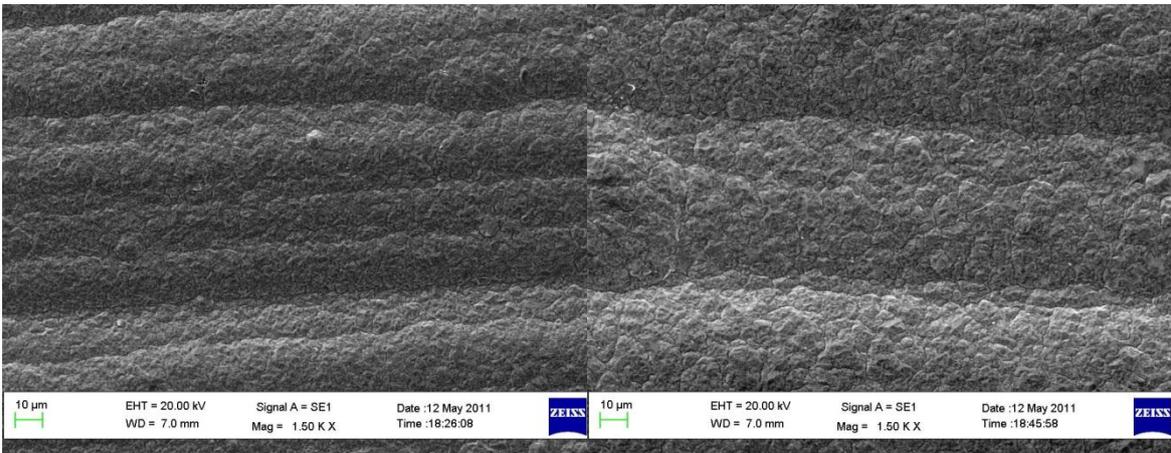


Figure 2.2- 3: Pure Nickel -under P.C. – 0,1Hz

Figure 2.2- 4: Pure Nickel -under P.C. – 1Hz

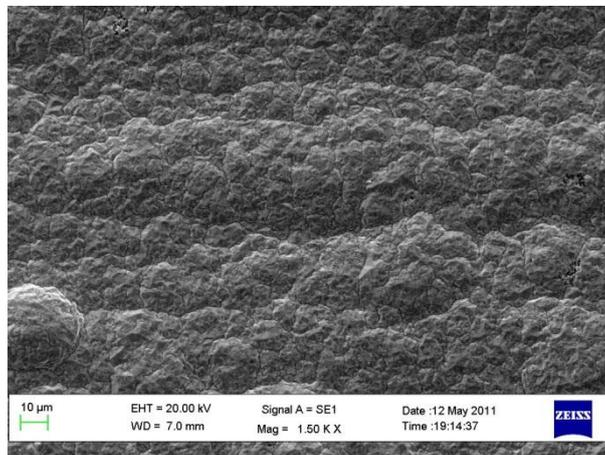


Figure 2.2- 5: Pure Nickel -under P.C. – 10Hz

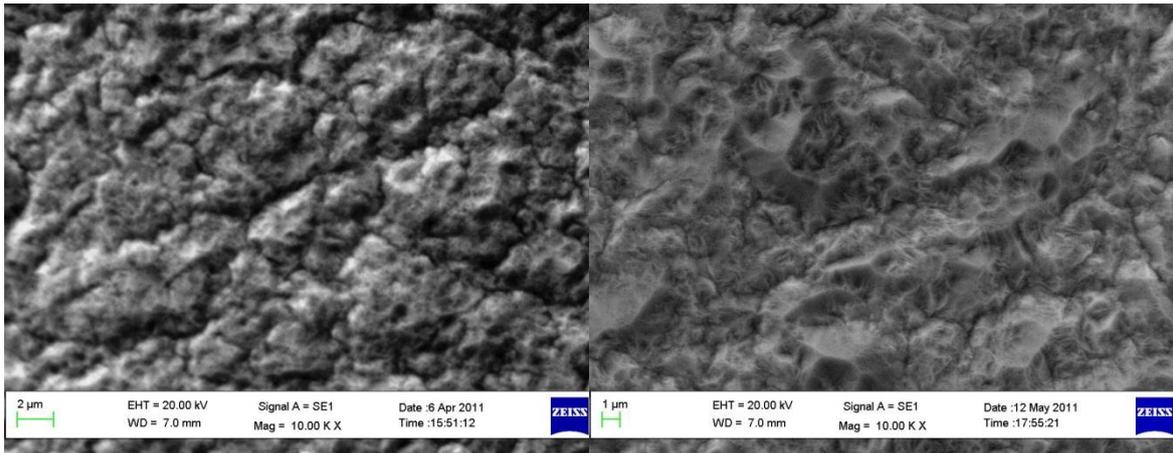


Figure 2.2- 6: Pure Nickel -under D.C.

Figure 2.2- 7: Pure Nickel -under P.C. – 0,01Hz

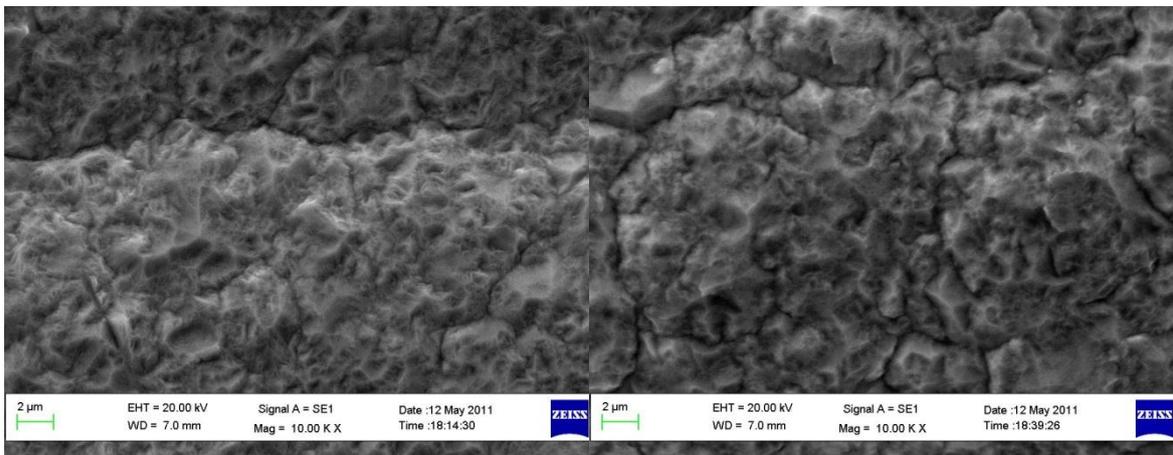


Figure 2.2- 8: Pure Nickel -under P.C. – 0,1Hz

Figure 2.2- 9: Pure Nickel -under P.C. – 1Hz

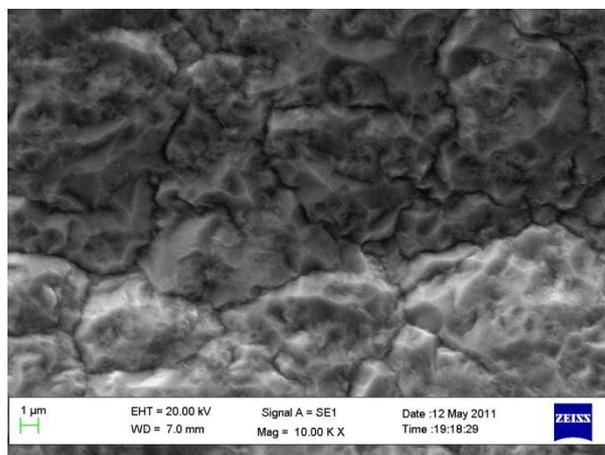


Figure 2.2- 10: Pure Nickel -under P.C. – 10Hz

On figures 2.2-11 – 2.2-20 it can be observed that the surface presents some irregularities due to the particles embedded. The nickel grains tend to embed the relatively large SiC particles forming larger nickel aggregates and thus increasing the surface roughness.

Some partially embedded particles on the surface can be observed clearly using higher magnifications. Also in this case, there are no observable differences between the deposits produced using pulse current at different frequencies.

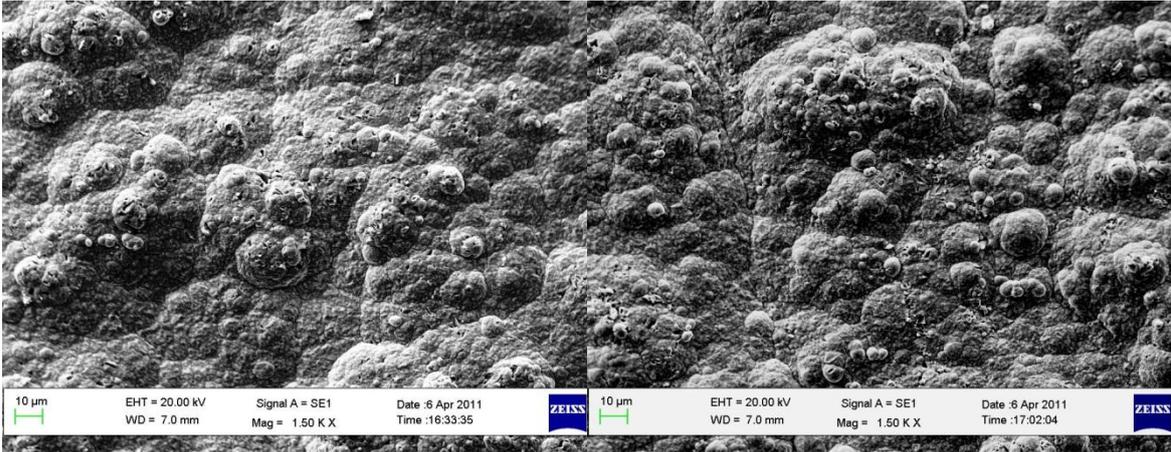


Figure 2.2- 11: Nickel - μ SiC deposit under D.C.

Figure 2.2- 12: Nickel - μ SiC deposit under P.C. – 0,01Hz

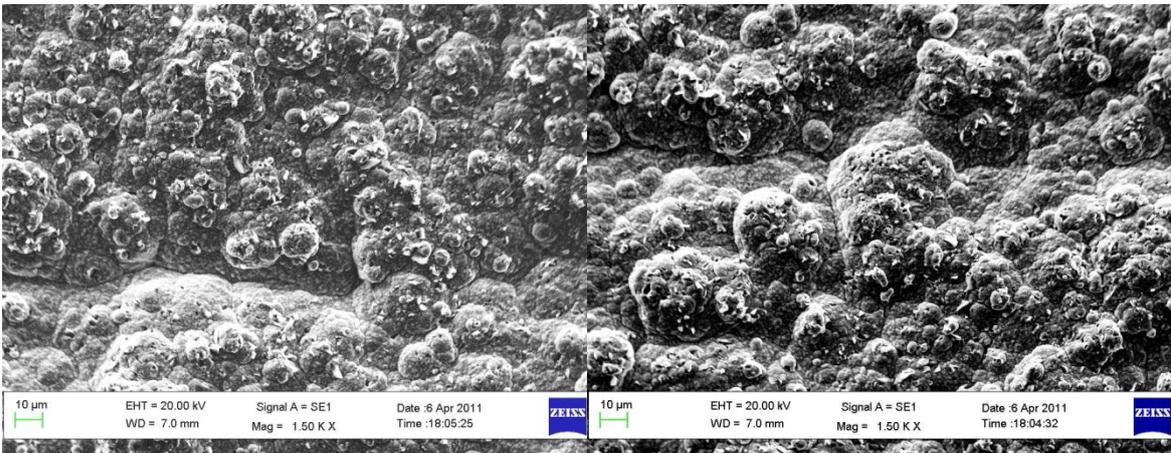


Figure 2.2- 13: Nickel - μ SiC deposit under P.C. – 0,1Hz

Figure 2.2- 14: Nickel - μ SiC deposit under P.C. – 1Hz

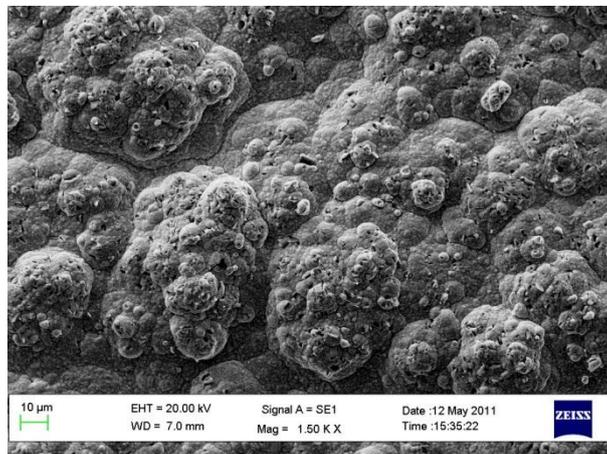


Figure 2.2- 15: Nickel - μ SiC deposit under P.C. – 10Hz

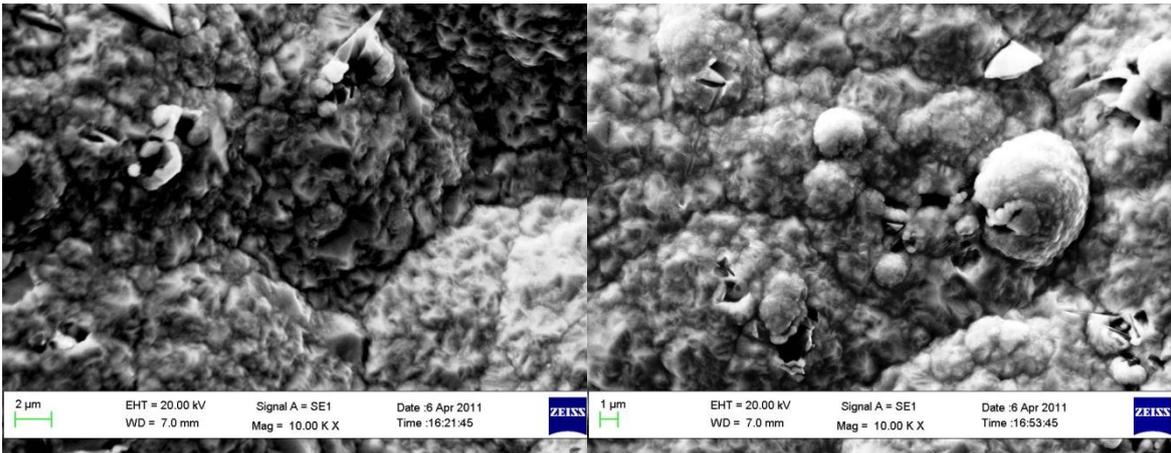


Figure 2.2- 16: Nickel - μ SiC deposit under D.C.

Figure 2.2- 17: Nickel - μ SiC deposit under P.C. – 0,01Hz

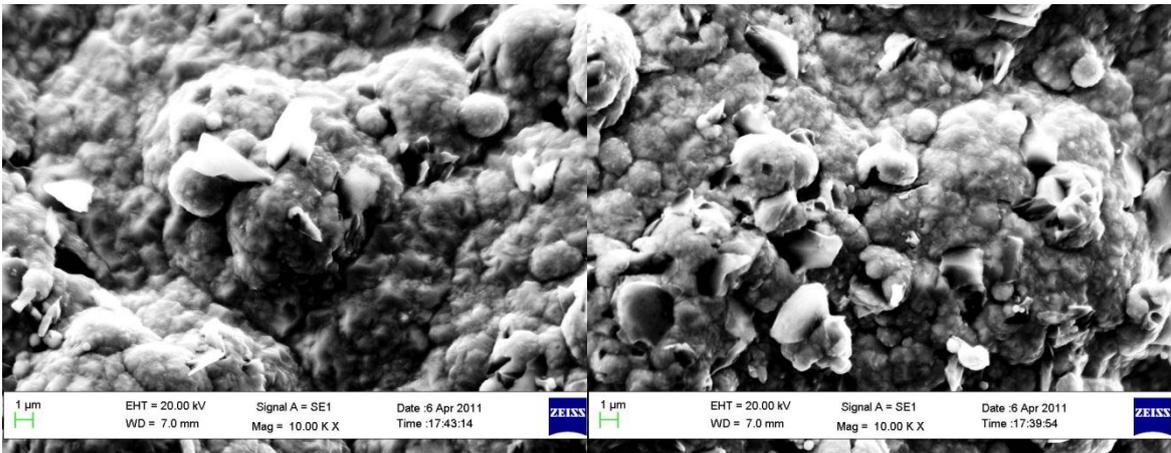


Figure 2.2- 18: Nickel - μ SiC deposit under P.C. – 0,1Hz

Figure 2.2- 19: Nickel - μ SiC deposit under P.C. – 1Hz

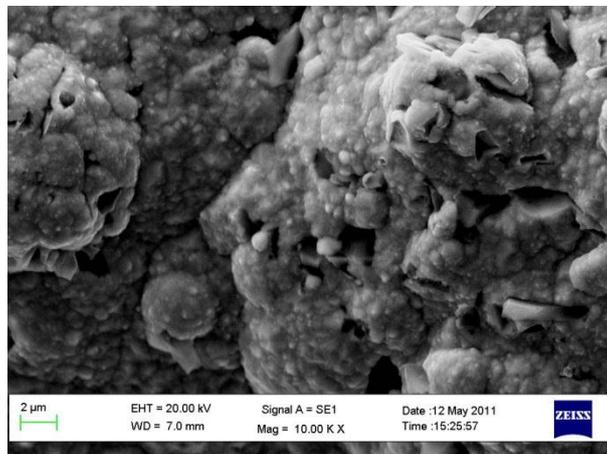


Figure 2.2- 20: Nickel - μ SiC deposit under P.C. – 10Hz

On the figures 2.2-21 – 2.2-30 of nano composites can be observed that the top surface presents cauliflower morphology which does not change using pulse current.

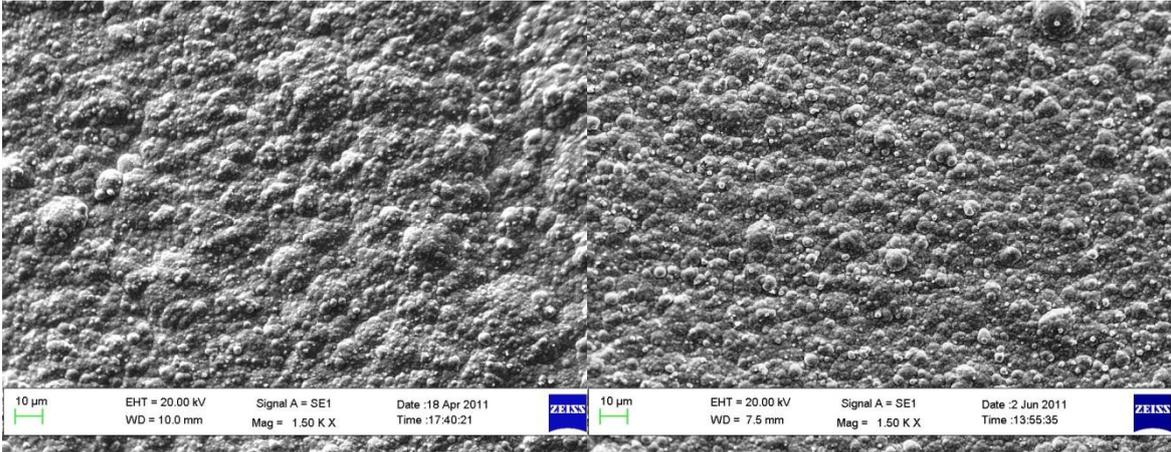


Figure 2.2- 21: Nickel - nSiC deposit under D.C.

Figure 2.2- 22: Nickel - nSiC deposit under P.C.-0,01Hz

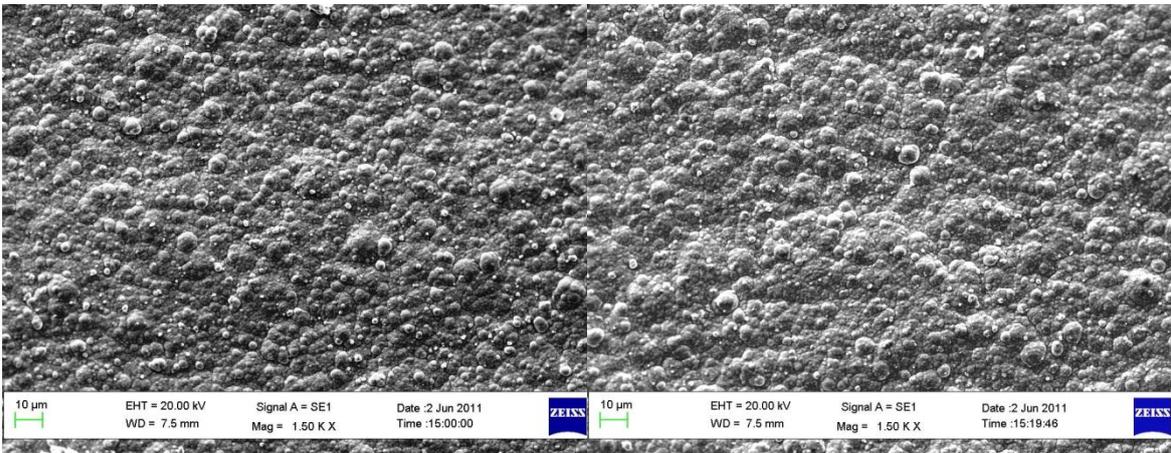


Figure 2.2- 23: Nickel - nSiC deposit under P.C. – 0,1Hz

Figure 2.2- 24: Nickel - nSiC deposit under P.C. – 1Hz

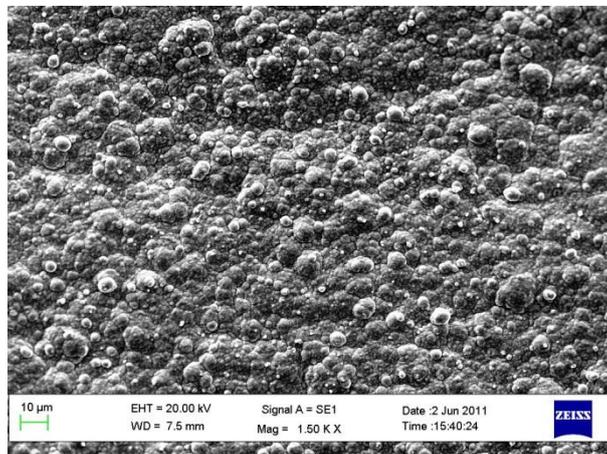


Figure 2.2- 25: Nickel - nSiC deposit under P.C. – 10Hz

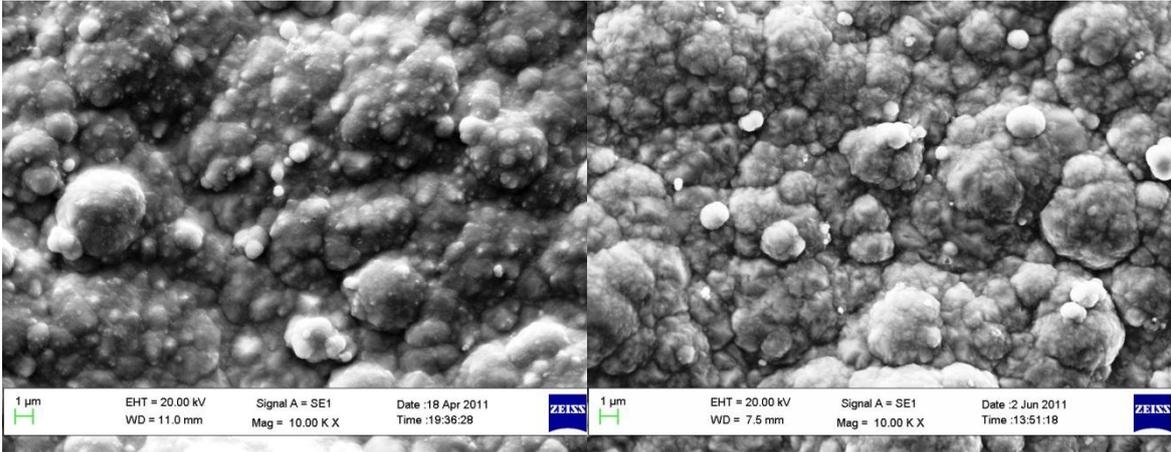


Figure 2.2- 26: Nickel - nSiC deposit under D.C.

Figure 2.2- 27: Nickel - nSiC deposit under P.C. -0,01Hz

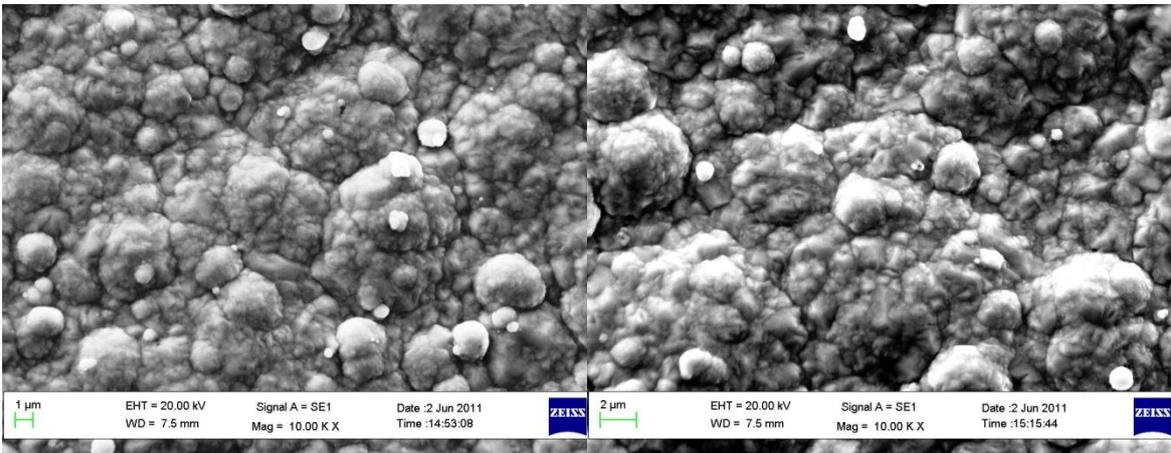


Figure 2.2- 28: Nickel - nSiC deposit under P.C. - 0,1Hz

Figure 2.2- 29: Nickel - nSiC deposit under P.C. - 1Hz

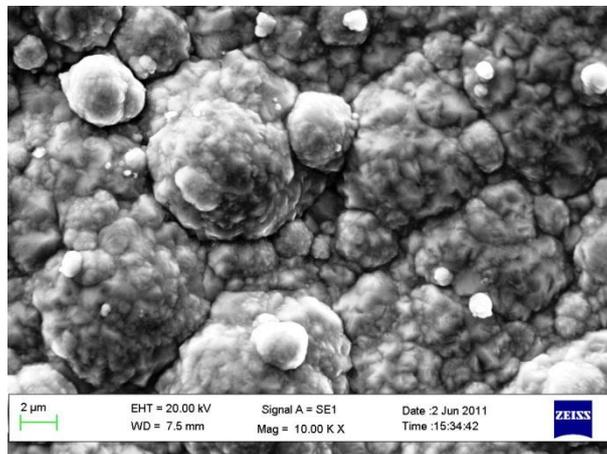
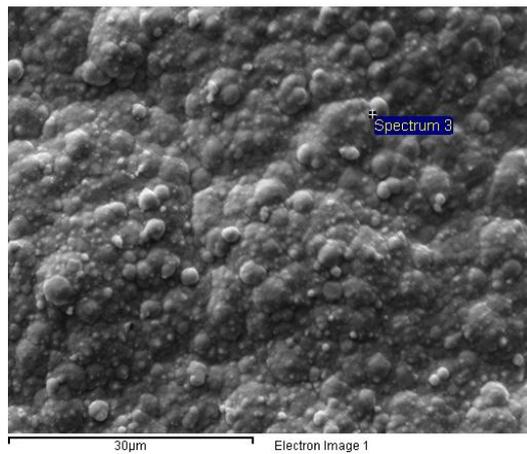


Figure 2.2- 30: Nickel - nSiC deposit under P.C. - 10Hz

Many small globular formations were identified on the nano-SiC composite surface. A composition analysis was made on the surface with EDXS.

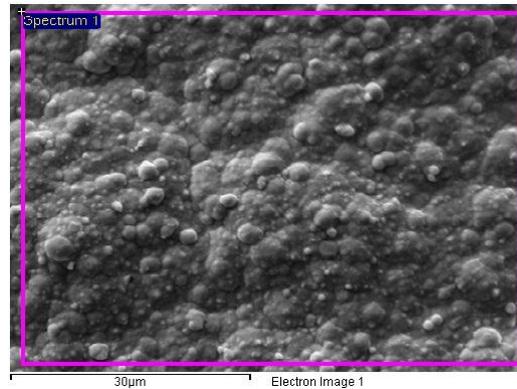
The composition analyses for samples made under D.C. and P.C. at 0,01Hz are reported on figures 2.2-31 - 2.2-34.

The EDXS analyses revealed the presence of Si which leads to the hypothesis that the globular formations consist of SiC particles covered by a first layer of nickel. It could be thus deduced that the SiC nano-particles act as nucleation points for the nickel deposition.



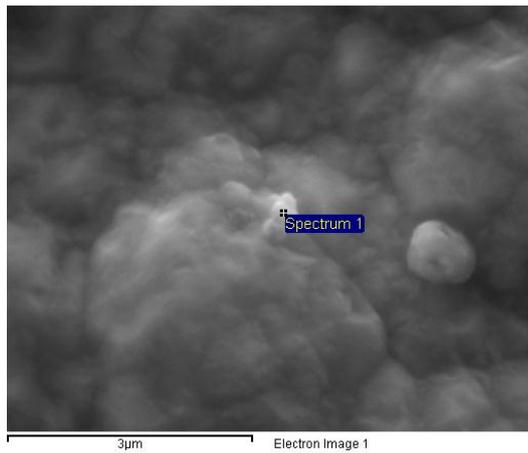
Element	Weight%
C	0.22
Si	1.05
Ni	98.73
Total	100.00

Figure 2.2- 31: Composition analysis under D.C.



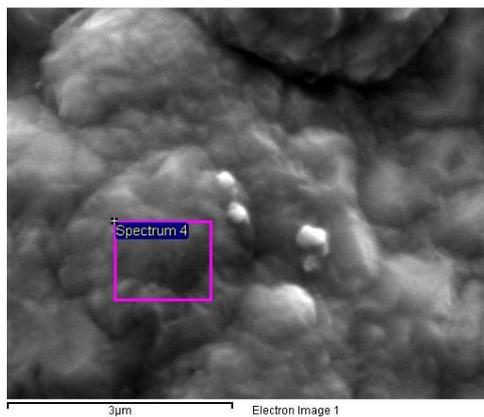
Element	Weight%
Ni	100.00
Total	100.00

Figure 2.2- 32: Composition analysis under D.C.



Element	Weight%
C	0.38
Si	1.23
Ni	98.39
Total	100.00

Figure 2.2- 33: Composition analysis under P.C. at 0,01Hz



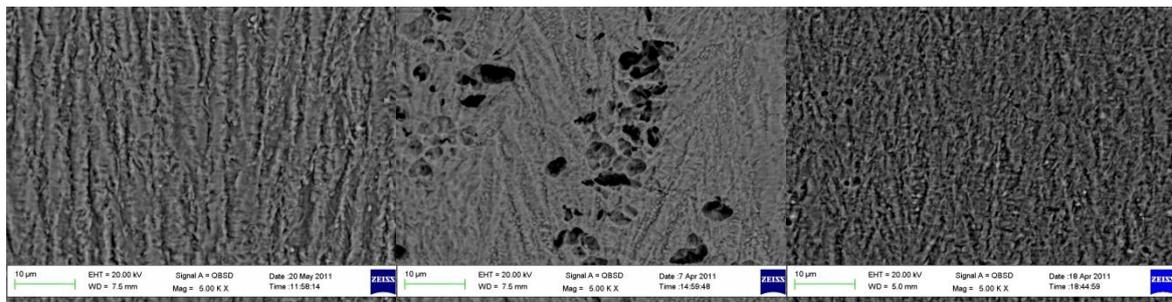
Element	Weight%
Ni	100.00
Total	100.00

Figure 2.2- 34: : Composition analysis under P.C. at 0,01Hz

The cross section micrographs of the obtained deposits produced under D.C. are reported in figures 2.2-35 (a-b-c).

The nickel deposits present a pseudo-columnar structure with the columns oriented on the direction of the electrical field. The codeposition of micro particles leads to the interruption of the columnar growth. The SiC micro particles are distributed randomly in the nickel matrix.

The codeposition of SiC nano particles causes an evident refinement of the columns. The nano composite deposits consist of smaller nickel pseudo-columns not oriented along the direction of the electrical field.



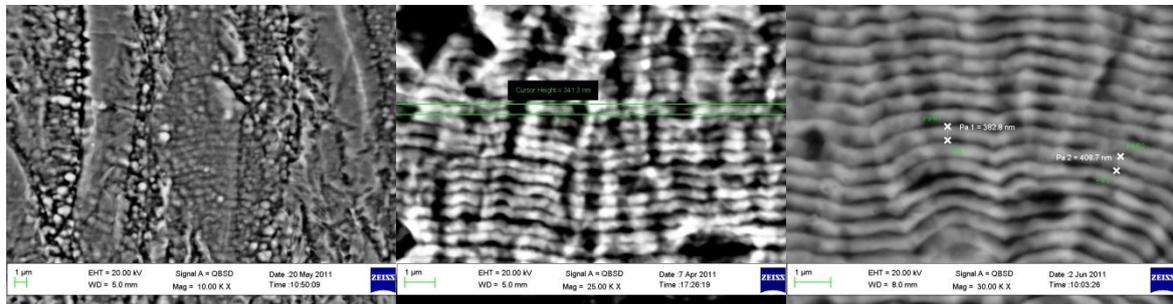
a. Pure Ni DC

b. Ni micro SiC DC

c. Ni nano SiC DC

Figure 2.2- 35: Cross section micrographs of specimens made under DC

The deposits produced under pulse current at 0,01Hz present also a pseudo-columnar structure but at higher magnification it can be observed that the columns consist of lamellas (Fig. 2.2-36 a-b-c). For each frequency cycle a new lamella is deposited. The thickness of those lamellas decreases when the frequency increases, and thus is not observable by SEM.



a. Pure Nickel under PC at 0,01Hz b. Ni + micro SiC under PC at 0,01Hz c. Ni + nano SiC under PC at 0,01Hz

Figure 2.2- 36: Cross section micrographs of different specimens

Could it be that the observable black spots on the cross section micrographs were filled by SiC particles before doing the etching and polishing the surface. The acid of the etching acted to the metal matrix and particles interface, causing their detachment.

On some cross section can be observed that there is non-uniform deposition of the particles in the metal matrix. The particles tend to agglomerate onto the imperfections of the substrate surface.

Many studies^[17,18] have proved that the application of pulsed current in nickel electroplating results in the production of composite deposits with higher percentage of incorporation and more uniform distribution of the particles in the metallic matrix than those attained by direct current technique.

This can be observed clearly on the figure 2.2-37, there are more particles over the imperfections or peaks of the steel surface for the sample made under DC.

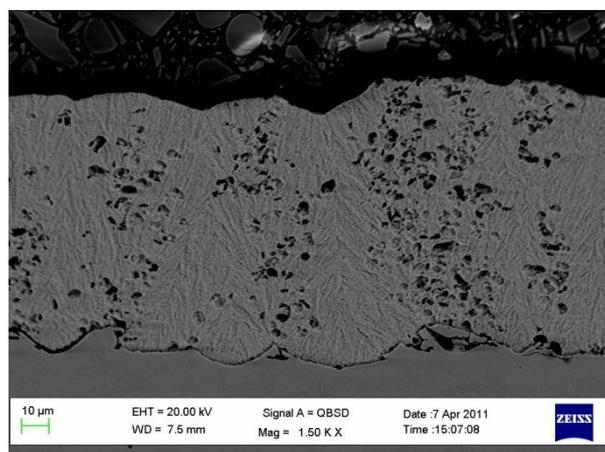


Figure 2.2- 37: Cross section micrograph non-uniform deposition (DC)

2.2.2. SiC content measurements

The amount of SiC incorporated into the metal matrix was studied by Glow Discharge Optical Emission Spectroscopy (GDOES) for the nano SiC composites.

This technique cannot be used for nickel micro SiC composites analysis because the particles dimension in the composite metal/ceramic coatings influences the plasma sputtering. An umbrella effect caused by the ceramic particles leads to a deviation of the electric field lines which creates difficulties on the analysis of these coatings. This effect is probably due to the lower electrical conductivity of SiC particles in comparison to the nickel matrix. [21]

To solve this issue, some micrographs of the cross section of micro SiC composites were used to calculate the SiC amount. Using Photoshop, the area occupied by SiC and nickel were calculated by counting the number of pixels. The percentage of SiC area over the total is easily calculated and using the density of SiC, the weight percentage can be calculated.

Glow Discharge Optical Emission Spectroscopy is one of the most important qualitative and quantitative techniques to determine the chemical composition of a thin film.

During the analysis, due to the high voltage applied between the cathode (the surface of the sample) and the anode, in presence of argon at low pressure, plasma is generated.

Ionized argon atoms cause the sputtering of the area to be tested by spraying excited atoms of the sample surface which are quickly de-excited by emitting photons with characteristic wavelengths for each element.

This basic process can be observed graphically on the figure 2.2-38.

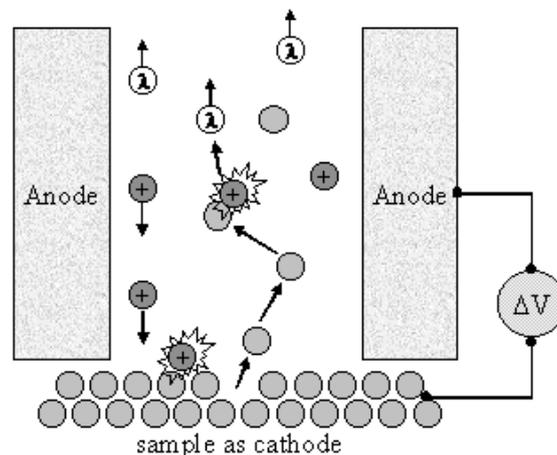


Figure 2.2- 38: Principle of operation

The software of the GDOES instrument gives directly the percentage of each element in front of the coating depth after calibration with standards of known composition. These graphics can be observed on figures 2.2-39 and 2.2-40. The SiC amount of the different specimens of micro and nano composites are reported on the tables 2.2-1 and 2.2-2.

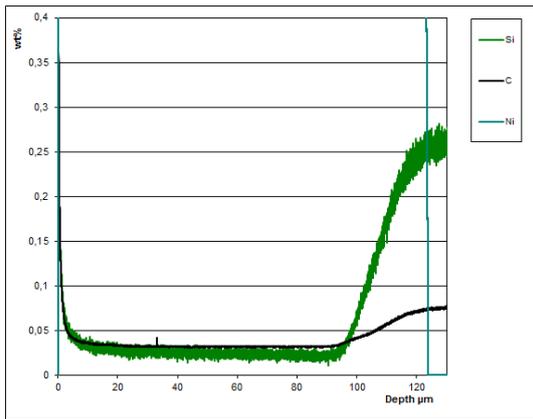


Figure 2.2- 39: nano SiC 0,01Hz

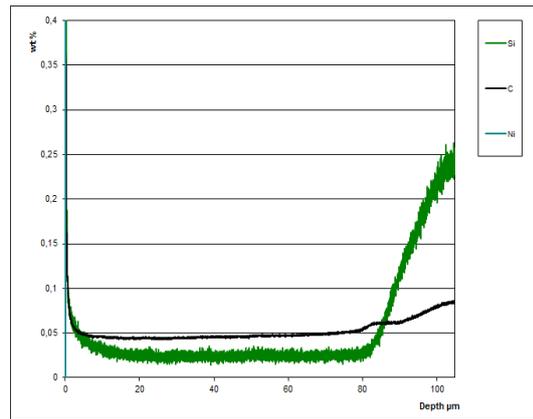


Figure 2.2- 40: nano SiC 1Hz

There is no difference of SiC amount for nano composites when pulse current is used. The nano particles are small enough and do not have any impediment to be deposited on the cathode surface.

Table 2.2- 1: Amount of incorporated SiC in the nickel matrix nano-composite deposits measured by GDOES

Deposit	wt% SiC
Nickel nSiC under D.C.	0,06 ± 0,02
Nickel nSiC under P.C. 0,01Hz	0,04 ± 0,05
Nickel nSiC under P.C. 0,1Hz	0,04 ± 0,06
Nickel nSiC under P.C. 1Hz	0,04 ± 0,01
Nickel nSiC under P.C. 10Hz	0,03 ± 0,01

The particles amount for micro SiC composites increases with the frequency. When pulse current is used, the diffusion layer becomes narrower and thus more particles can be deposited on the cathode surface. When pulsed current is used the amount of deposited particles is greater than when direct current is used. That is because the thickness of the diffusion layer decreases due to its creation and destruction when using pulsed current. The particles which are larger than the diffusion layer have impediments to pass through it, but when the thickness of the diffusion layer decreases the particles can reach more easily the cathode.

Table 2.2- 2: Amount of incorporated SiC in the nickel matrix micro-composite deposits

Deposit	wt% SiC
Nickel mSiC under D.C.	0,8 ± 0,2
Nickel mSiC under P.C. 0,01Hz	2,9 ± 0,2
Nickel mSiC under P.C. 0,1Hz	3,1 ± 0,3
Nickel mSiC under P.C. 1Hz	3,7 ± 0,5
Nickel mSiC under P.C. 10Hz	2,3 ± 0,2

Even though the SiC amount for nano-composites is very low it can change the microstructure of the nickel matrix. As it was seen before, the microstructure of the nano composites is more compact.

Although the weight percentage of the micro composites is greater, does not mean a more number of particles. On the contrary, the nano composite have more number of particles but lower weight due to their smaller size.

2.2.3. Microhardness measurements

The Vickers 0.3 microhardness was measured in cross section to avoid the influence of the substrate. The applied force is 3N and the dwell time is 15s. The values of microhardness are summarized in table 2.2-3 and represented in figure 2.2-41.

Table 2.2- 3: HV 0,3 Microhardness

Deposit	Pure nickel	Micro-composites	Nano-composites
Ni under DC	162 ± 2	245 ± 5	270 ± 9
Ni under PC 0,01Hz	167 ± 5	317 ± 5	315 ± 2
Ni under PC 0,1Hz	177 ± 7	302 ± 5	386 ± 9
Ni under PC 1Hz	172 ± 7	301 ± 8	333 ± 5
Ni under PC 10Hz	180 ± 3	317 ± 9	326 ± 16

As can be observed on figure 2.2-41 the incorporation of SiC particles leads to a noticeable increase of the Vickers microhardness of about 70-80%.

In the case of the micro composite coatings this increase could be mainly attributed to the presence of a high fraction of relatively large particles and to their intrinsic hardness.

In the case of the nano composite deposits the microhardness increase should be mainly attributed to the grain refinement caused by the particles codeposition. The use of pulse current for the production of pure nickel deposits causes a slight increase of the microhardness. In any case the pure nickel deposits present a much lower hardness in comparison to the composite ones.

The micro composite deposits produced under pulse current present higher microhardness than those produced under direct current. This could be attributed mainly to the increase of the SiC content caused by the use of pulse current. Also in this case of nano composite deposits the use of pulse current leads to a noticeable increase of the Vickers microhardness due mainly to the grain refinement. Indeed the nano composite deposits are more fine-grained, the columns are shorter and randomly oriented and thus more difficult to deform.

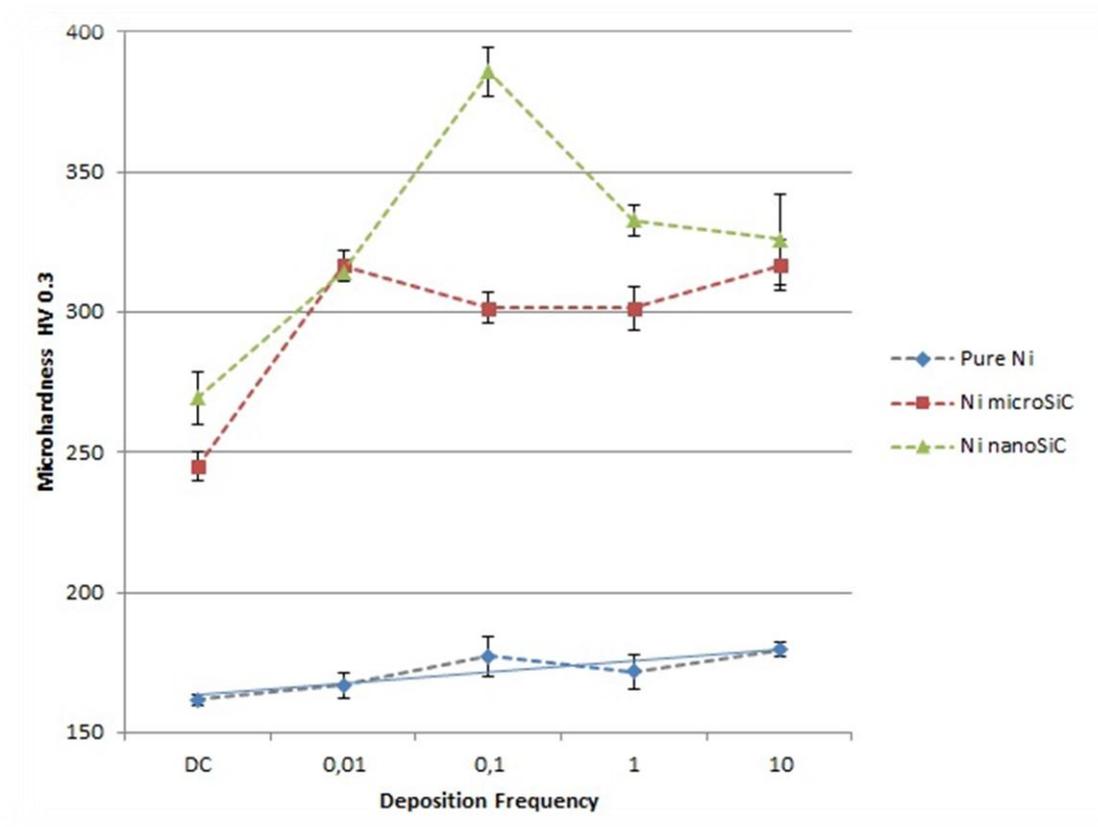


Figure 2.2- 41: HV 0.3 Microhardness as a function of the applied current

2.3. Corrosion resistance of nickel matrix composite coatings

The corrosion resistance in a CO₂ containing media was evaluated by potentiodynamic polarization curves.

After the electrodeposition the panels are cut and embedded into cold epoxy resin in order to expose only the coated surface to the corrosive media. This cold mounting requires the mixing of a crude polymer and a catalyst. This mixture is cast over the specimen within an elastic mould and reacts to form a solid piece.



Figure 2.3- 1: Samples embedded in resin

The potentiodynamic curves for the different coatings produced under DC are reported on the figure 2.3-3. The pure nickel and the nano composites deposits present a similar behavior. The corrosion potential for the micro composite is lower in front of the others. This could be attributed to the presence of voids at the interface between the particles and the metal matrix, which are weak points for the corrosion attack. The corrosive solution can penetrate more easily following this path and reach the substrate.

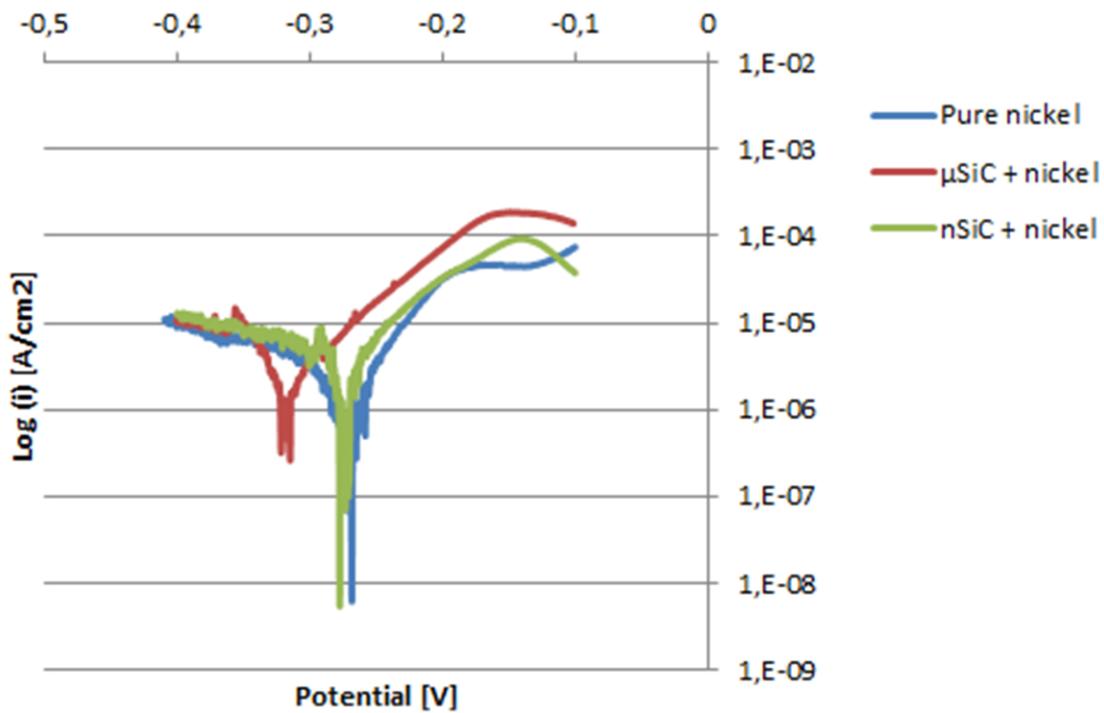


Figure 2.3- 3: Potentiodynamic curves for samples produced under DC

On the figure 2.2-4 can be observed the influence of the frequency when no particles are involved.

There are not many substantial differences between the samples. This can be because the frequency is a secondary factor that influences the corrosion resistance in comparison with the SiC presence.

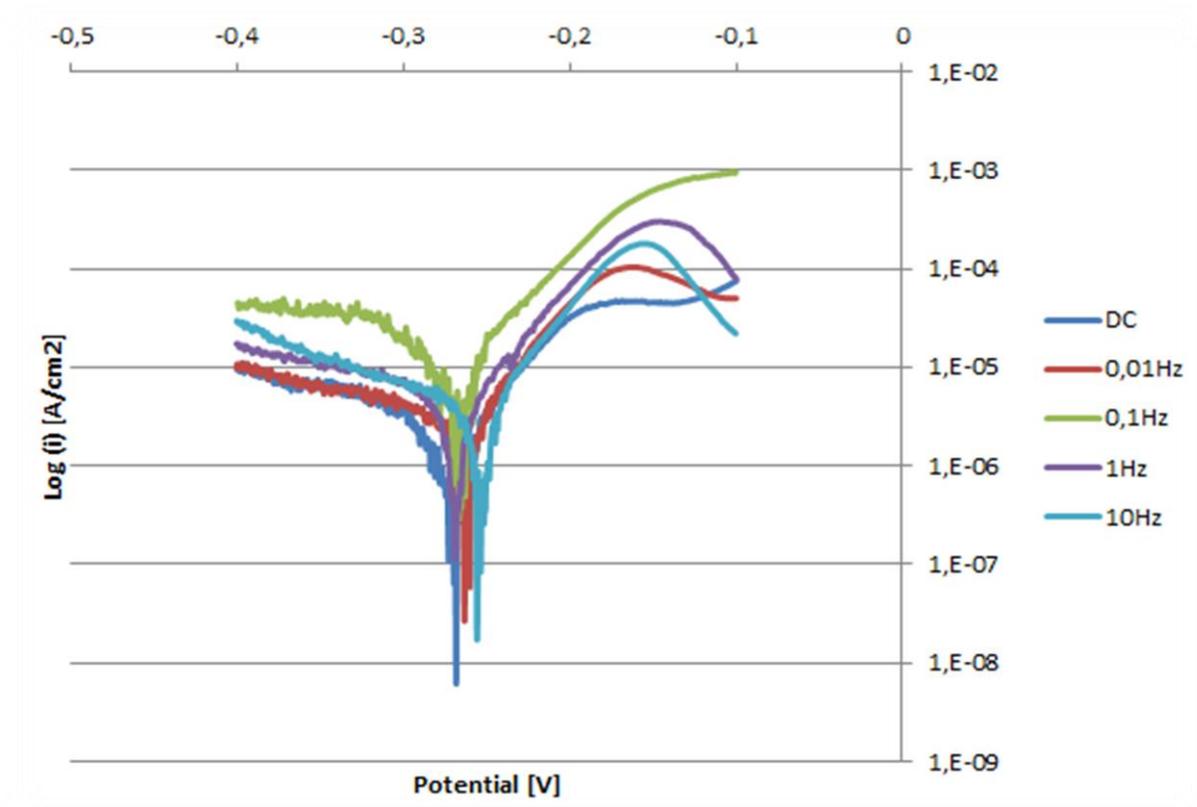


Figure 2.3- 4: Potentiodynamic curves for pure nickel deposits

The potentiodynamic curves for micro composites are reported on figure 2.3-5. As can be observed the specimens present different corrosion potentials. This is attributed to the presence of SiC and to the grain refinement caused by the use of pulse current.

The presence of a high amount of SiC particles increases the amount of voids between the particles and the metal matrix which are a preferential path for the aggressive solution penetration. On the contrary, the use of pulse current causes a grain refinement and the nickel grains better embed the particles leading to the closure of these voids. Anyway these data need further analysis for a complete understanding of the degradation mechanisms.

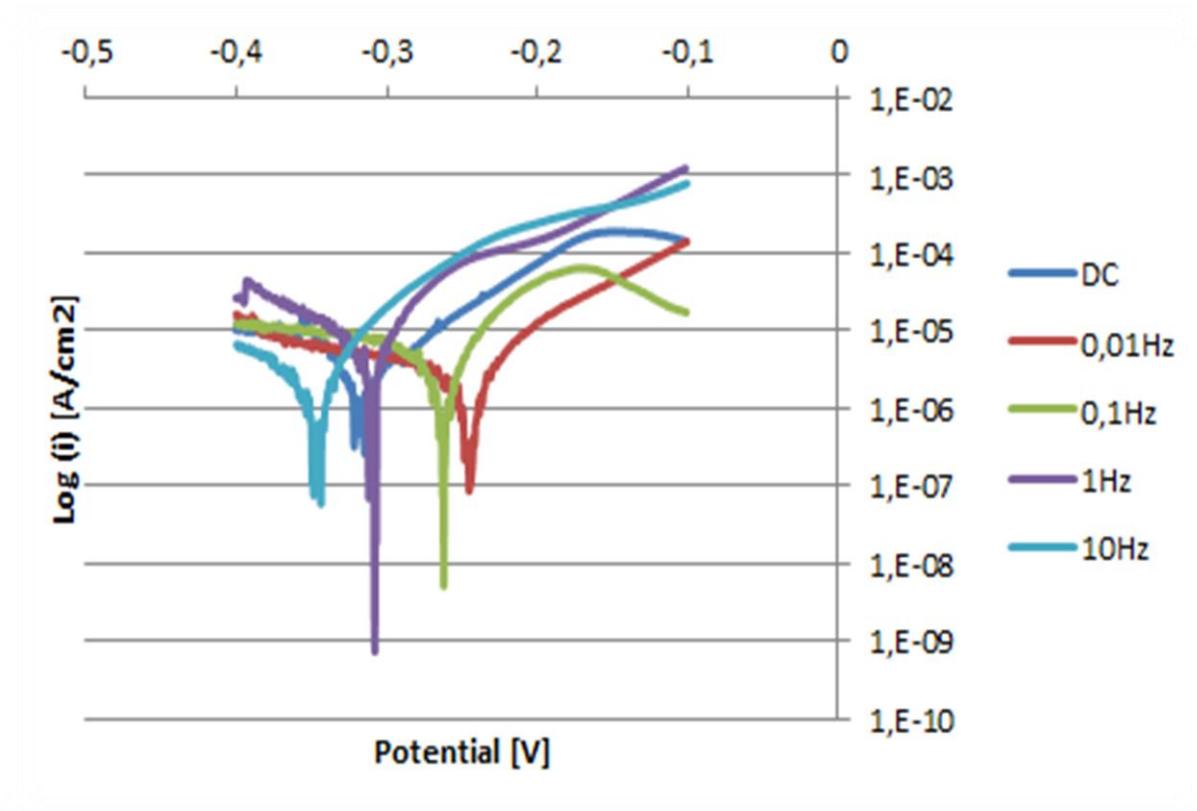


Figure 2.3- 5: Potentiodynamic curves for nickel + micro SiC composites

On the figure 2.2-6 of nano composites, there are no substantial differences between the deposits when using pulse current. All types of nano composites present almost the same corrosion potential. The SiC amount for nano composites is very similar for all types of current conditions and so the microstructure does not present many differences, these may be the reasons for the similar corrosion potentials.

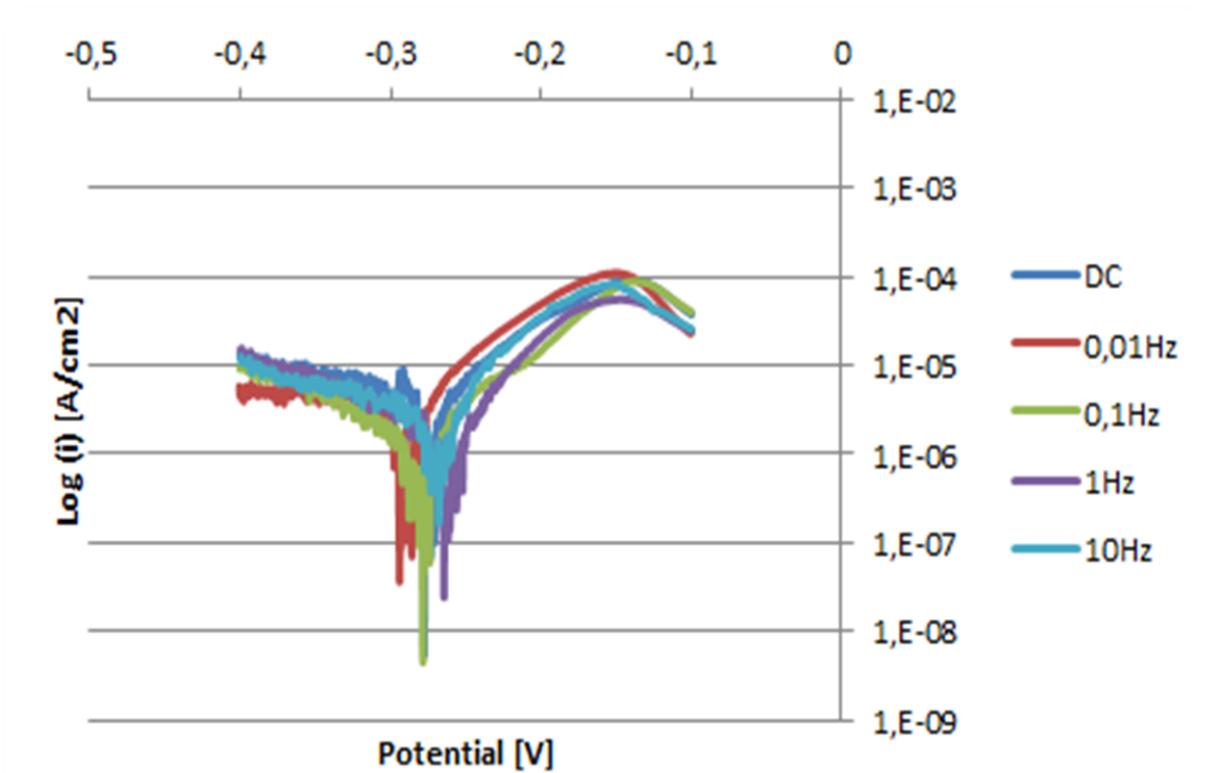


Figure 2.3- 6: Potentiodynamic curves for nickel + nano SiC composites

The corrosion potential is not much different between the nano composites and the pure nickel deposits but is lower for the micro composites. The corrosion resistance is affected by addition of particles and by the current condition. As it is mentioned above, all the specimens present active behavior.

3. Conclusions

This work has been carried out to study the microstructural properties, microhardness and corrosion resistance in acid environment for metals coated with nickel, nickel with micro particles of SiC and nickel with SiC nano particles.

These ceramic-metal deposits are used to cover metal components that normally work in abrasive and corrosive environments.

The work is divided into two parts: the first is the production of different samples in the laboratory and the second one is the microstructural characterization and the study of corrosion resistance into acidic environment with CO₂ gas.

The coatings were made using electrochemical plating bath of nickel with SiC particles in suspension. There were used different types of current; direct current and pulsed current at different frequencies.

The microstructure, microhardness and corrosion resistance was studied for all types of coatings and compared between them.

The microstructure was analyzed with SEM (spectroscopy emission microscope), the microhardness was studied by Vickers microhardness test and the study of corrosion resistance was carried out by electrochemical methods.

In all studies the influence of the added particles and the different current conditions applied were analyzed.

The pure nickel deposits present cauliflower morphology on the top surface and a pseudo-columnar structure in cross section. The columns are oriented on the direction of the electric field. Regarding the deposition under pulse current, during the off-time of the pulse wave the grain growth is stopped and new grains grow on the next cycle. This is evident for the specimens produced under pulse current at 0,01Hz where lamellas are visible in the pseudo-columns in cross section. The grain refinement slightly increases the microhardness of the pure nickel specimens produced under pulse current. On the other hand, the grain refinement does not lead to any evident improvement on the corrosion resistance.

The micro composite deposits present cauliflower morphology on the top surface with the nickel grains forming bigger aggregates in comparison to the pure nickel deposits. In cross section the deposits still present a pseudo-columnar microstructure. The SiC particles are randomly distributed into the metal matrix, interrupt the columnar growth and slightly change the orientation of the columns. The use of the pulse current for the deposition leads also in this case to the formation of lamellas in the columns. Moreover, the deposits produced under pulse current present higher amount of embedded micro particles. This is attributed to the restriction of the diffusion layer which facilitates the particles to reach the cathode and thus embed into the metal matrix. The presence of a high amount of particles and their intrinsic hardness leads to a noticeable increase of the microhardness in comparison to the pure nickel deposits. The use of pulse current for the deposits production further increases the microhardness. The corrosion resistance is mainly influenced by the amount of codeposited SiC and by the grain refinement due to the pulse current. The codeposition of larger particles leads to the formation of gaps between the SiC and the metal matrix which act as preferential points for corrosion attack. The

higher the number of particles, the higher the extent of the interface Ni-SiC. The use of pulse current and the caused grain refinement lead to the partial closure of the gaps and to an increase of the corrosion resistance. The combination of the grain refinement due to the pulse current and the SiC amount are the main factors which control the corrosion resistance, even though the grain refinement is secondary. In all cases the micro composite deposits present a lower corrosion potential than the pure nickel deposits.

The nano composites present a smoother surface compared with the micro composites. The particles act as nucleation points. In this case the SiC amount is lower in weight but is assumed that the number of particles is higher. The nickel columns grow completely randomly, not following the electric field direction as in the case of pure nickel and the micro composites. This change of the structure improves the microhardness. The nano composites present the highest microhardness in front of the pure nickel and the micro composites. In this case, the particle size do not produce voids in the structure of the coating and the corrosion resistance is not affected by the SiC amount, therefore the corrosion potentials are very similar for all the specimens.

In conclusion, nano composites are more suitable than pure nickel and micro composites deposits for applications where corrosion resistance and microhardness are important factors.

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References

- [1] ASM International. Corrosion: Understanding the basics. United States of America, 2000.
- [2] Groysman, A. Corrosion for everybody. Springers Science and Business Media B.V. 2010.
- [3] Palanna, O.G. Engineering chemistry. Tata McGraw Hill Education. 2009
- [4] Putti, R. Vijayasarathy. Engineering chemistry. Prentice-Hall of India Private Limited. New Delhi, 2008
- [5] ASM Handbook. Corrosion: Fundamentals, testing and protection, Volumes 13A and 13B. The Materials information company. 2003
- [6] Plieth, W. Electrochemistry for materials science. Elsevier.2008
- [7] Kanani, N. Electroplating: basic principles, processes and practice. Elsevier. The Neederlands, 2006.
- [8] Dennis, J.K., Such, T.E. Nickel and chromium plating. Woodhead Publishing Ltd. England, 1993.
- [9] Durney, L.J. Electroplating engineering handbook. Chapman and Hall (Reprinted). England, 1998.
- [10] Davis, J.R. Nickel, cobalt and their alloys. ASM International. 2000.
- [11] Stoye, D., Freitag, W. Paints, coatings and solvents. Wiley-VCH.1998.
- [12] Brock, T., Groteklaes, M., Mischke, P. European coatings handbook. 2000.
- [13] Nelis, T., Payling, R. Glow discharge optical emission spectroscopy. 2003.
- [14] Petzow, G. Metallographic etching: techniques for metallography, ceramography and plastography. ASM International. 1999.
- [15] S.K.Kim, H.J.YOO Surfaces and coatings. 1998.
- [16] I.Garcia, J fransaer, Celis. Surface and Coatings. 2001.
- [17] Zimmerman, A.F., Palumbo, G. Science and engineering. 2002.
- [18] L. Benea et al. Solid State Ionics. 2002.
- [19] Malfatti, C.F. et al. Corrosion science. 2005
- [20] Lekka, M. Design, production and performance of metal matrix micro/nano composite electrodeposits. 2008.
- [21] A. Lanzutti, E. Marin, M. Lekka, P. Chapon, L. Fedrizzi. Rf-GDOES analysis of composite metal/ceramic electroplated coatings with nano- to microceramic particles' size: issues in plasma sputtering of Ni/micro-SiC coatings. (2011)

