CONSIDERATIONS ON THE MECHANISM OF ELECTRODEPOSITION OF COMPOSITE MATERIALS

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ABSTRACT: In this study an attempt is made to have a deeper insight in the characterization of thin coatings of composites materials. In this way, we have applied many theotetical models to study the co-deposition phenomenon on composites materials. The small thickness of thin surface coatings may create difficulties in the characterization of their properties so we did this with the help of some mathematical models such as: Saifullin's model, Bazzard and Boden model, Gugliemi model, Celis, Ross, Buelens models.

KEY WORDS: electrodeposition, composites materials, interface fenomena, mathematical model

1. ELECTRODEPOSITION PRINCIPLE

Electrolytic deposition is performed by electrolysis of aqueous solutions of salts, simple or complex containing the metal ion to be deposited. The piece to be coated is the cathode and the anode current source may be an unquestionable inert metal (the insoluble anode electrolysis) or metal coating, which is dissolved in ion form (the soluble anode electrolysis), moving and discarded (submitted) at the cathode, forming protective metal layer. The electrolyte comprises: a metal compound which is decomposed and deposited in well-defined concentration, buffer for maintaining a constant acidity (pH) of the solution, inorganic materials to increase the electrical conductivity, as well as special additives to improve porosity, adhesion, gloss or coating structure.

2. INTERFACE PHENOMENA

To highlight the electro deposition process kinetics are currently using electric model represented by a capacitor called double Helmoltz layer.

It consists of a layer Stern called "transfer" or "fix", which is located near the electrode and has a positive charge ($Mn+$), while the metal surface has a negative charge ($e-$) , and a spread layer Gouy - Chapman. If a current through the electrochemical system then a third layer region is added to the two Helmoltz layers known as spread.

The particles move towards the cathode due to phenomena of:
- Spread, that occurs due to the difference of concentration in the electrolyte;
- Convection due to the hydrodynamics of electrolyte;
- Migration, due to the presence of an electric field.

In the vicinity of the interface cathode/ electrolyte hydrodynamic movement speed is practically null and does not, therefore, material recovery by convection. Also,

migration alone can not fully ensure the transport of matter. There is thus a concentration gradient is established at the

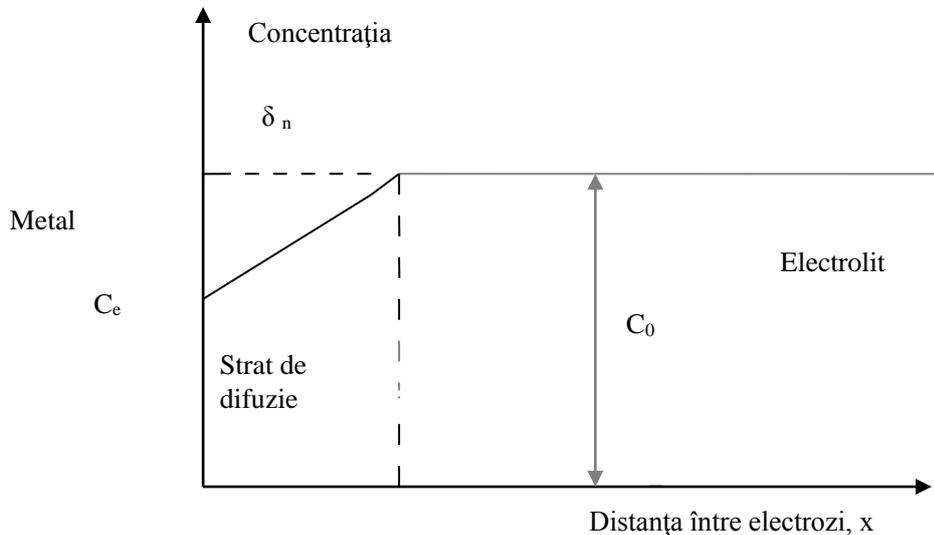interface and which generates the transmission.

Figure 1: Representation gradient concentration diffusion layer

2.1. Interactions and interfaces

Electrodeposition process of the composite materials is complex. It is therefore difficult to establish general laws governing particle deposition. For this you need to study each case and to make a thorough study of electrolyte-particle system.

Between the deposited particles and the layer is established a close connection that requires a knowledge of physicochemical suspension, deposition conditions and precise characterization of the impact of the incorporation of the particles.

2.1.1. Solid interface – solution

Solid interface solution can be represented in Figure 2.

The contact area between solid and liquid interactions occurs which give rise to surface loads q_{solid} noted. The area where the interaction occurs is very small and has the form of a thin

layer called the Stern layer, which may be solid or inert. The potential difference

between the solid surface (Ψs) and limit Stern layer (or externally Helmoltz, OHP) is called the Stern potential. Ions present in the solution tend to isolate the load q_{solid} and to maintain interface electrically neutral. Appears as an area where electrostatic interactions occur which tend to cancel the q_{solid} and broadcast layer is called.

In this region the ions are mobile and have a Brownian motion, and their task canceling the surface, so that:

$$q_{st} + q_d = 0, \qquad (1)$$

q_d is task spread layer.

2.1.2. Metal interface-solution

Metal interaction force depends on the nature of the metal solution: it is very large for transition metals, average for transition metals and small for gold, copper and silver. The task of the solid depends on the charge on the surface of the metal atoms and the charge on the particles adsorbed.
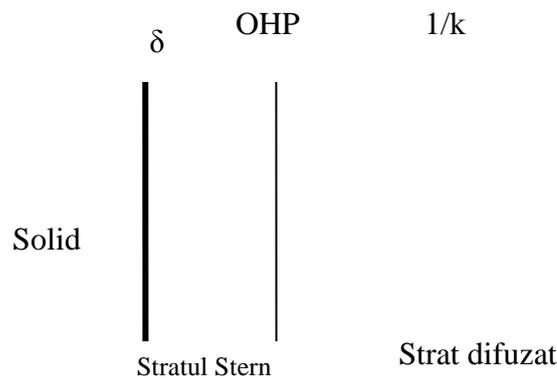
δ   OHP   1/k

Solid

Stratul Stern   Strat difuzat

Figure 2: Solid-liquid interface schematic

In this case we can write the relation:

$$q_{solid} = q^M + q^M_{ad} \qquad (2)$$

where:
q^M - is the task of metal;
q^M_{ad} -charge of adsorbed ions.
As in the previous case, the q_{solid} load tends to be canceled by the spread layer load.
The potential of the metal constituting the electrode can be changed by applying an external generator. Change this potential involves q^M and q^M_{ad} tasks changing, favoring adsorption of ions.
Such potential directly applied influence q^M task. A modification of this task involves a change in q^M_{ad} load that corresponding to the adsorbed tasks that favor ion adsorption. The potential for q^M = 0 is denoted by E_{CN} and is called zero load potential and depends on the structure of the metal that constitutes the electrode and on electrolyte composition.

1.1.3. Particle–electrolyte interface

Since the ratio of the surface electrode (metal) and the volume of the solution is low, putting in contact of the two components (electrode - electrolyte), there will be no changes in the composition of the electrolyte. Electrolytic bath being a concentrated solution composition will not change in the interaction with the metal electrolyte. In addition, the electrolyte bath solution concentrated composition is less influenced by the interaction with the surface of the electrode. In this case, particles in the electrolyte are isolated so that the load is not dependent on the nature of the solid and the composition of the solution. The task of the surface depends on the charge of the q_s solid and of the q^s_{ad} particles adsorbed. Stern layer is formed on the solid surface and the motion of the particles is related to the layer. If the particle is moving in relation to liquid or vice versa, the layer is moved with it and with a shear plane which occurred in the liquid layer is in the air.
The introduction of particulate in the suspension interactions occur between them and the solution, resulting in the appearance of a chain formed from the components of the electrolyte ion.
The movement of ions within the suspension to the electrode occurs due to the turbulence required to suspension.
Respecting the hydrodynamic regime and bustle imposed under suspension, a particle will remain in the vicinity of an electrode, after which it will be adsorbed and formed layer will thus increase.

3. MATHEMATICAL MODELING OF ELECTROLYTE CODEPOSITION

Process for obtaining composite materials is complex, over time many authors have attempted to explain this phenomenon and proposed several models (Saifullin's model, the model proposed by Bazzard and Boden, the model proposed by Gugliemi co-deposition [2] co-deposition model proposed by Celis, Roos and Buelens [2].

3.1. The co-deposition model proposed by Valdes and Cheh

According to this co-deposition model particle velocity is:

$$I_p = k^0 C_s \left[\exp\left(\frac{\alpha z F}{RT} \eta_a \right) - \exp\left(-\frac{(1-\alpha)zF}{RT} \eta_a \right) \right]$$

where:
k^0 = rate constant of the electrochemical reaction,
C_s = electro-absorbed species concentration of surface particles,
η_a = load transfer over voltage (for activation),
α = transfer coefficient,
z = valence of the metal.
The model assumes that all the particles within a critical distance of the surface of the cathode will be embedded in the composite deposit. The model does not take into account all parameters that depend on co-deposition different particles and the effect of current density on the type of particles [1].

3.2. The co-deposition model proposed by Fransaer

This model is based on knowledge of the field around an electrode and consideration of all forces acting on a particle.
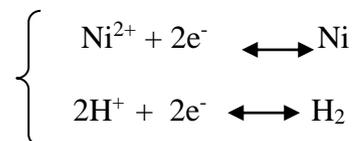The trajectory of a particle motion is described by the equation, studied by

means of a flat cathode as a rotating disk [1]. The model is called co-deposition and it was developed to track the polydisperse particles, spherical polystyrene matrix copper [1]. The disadvantage of this model is that it can not be used at all co-depositions when the cathode is stationary and the agitation is provided by different systems [1].

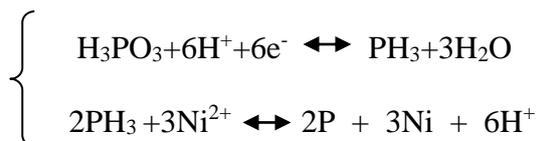## 4. ELECTROLYTIC DEPOSITION OF NIP ALLOYS

The mechanism of incorporation of phosphorus is a complex mechanism and were given more explanation regarding this issue [4].
The mechanism of phosphorus incorporation is a complex mechanism and was given more explanation regarding this issue [4]. One of the more explicit models is the one proposed by Lashmore [5] and has the following chemical reactions:
a) direct chemical reactions:

$$\begin{cases} Ni^{2+} + 2e^- \longleftrightarrow Ni \\ 2H^+ + 2e^- \longleftrightarrow H_2 \end{cases}$$

b) indirect chemical reactions:

$$\begin{cases} H_3PO_3 + 6H^+ + 6e^- \longleftrightarrow PH_3 + 3H_2O \\ 2PH_3 + 3Ni^{2+} \longleftrightarrow 2P + 3Ni + 6H^+ \end{cases}$$

For Ni-P/SiC composite material, the phosphor which is incorporated in the layer depends on the concentration of phosphorous acid in the electrolyte [3]. This dependence is given in Figure 3.

CONCLUSIONS

The processes for obtaining composite materials are complex. In time, many authors have attempted to explain this phenomenon and proposed several models for this (Saifullin's model, Bazzard and Boden model, Gugliemi model, Celis,

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Ross, Buelens, etc). Electro deposition is a complex process for obtaining composite materials. It is therefore difficult to establish general laws governing particle deposition. For this you need to study each case and make a deep study of electrolyte-particles system like we did in this work.
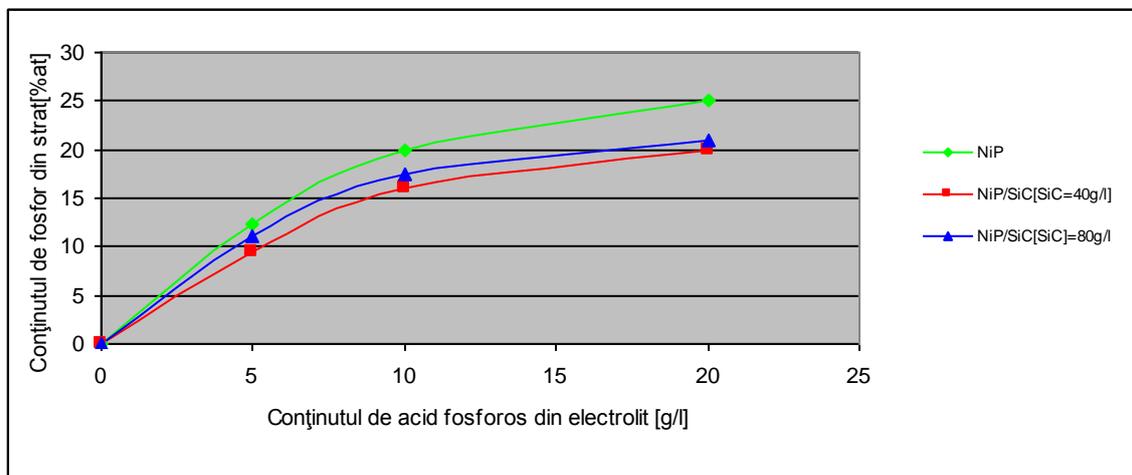

Figure 3: Changes in the phosphorus content of the phosphoric acid based electrolyte

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