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# MATHEMATICAL MODEL FOR OPTIMIZATION OF ZINC-NICKEL ALLOY CO-DEPOSITION PROCESS

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**Abstract:** *In protection against corrosion domain nickel remains the principal metal for coverings, fact which is proved by the dynamics of annual global production. Nickel has an important role in automotive industry and it is used together with zinc. At present the change of electroplating processes with purpose to use with maximum efficiency resources of energy and materials is being focused on. Also for environment protection reasons, it is aknowledged that electroplating processes generate as few polluting substances as possible. In consequence, the processes using heavy metals (as cadmium, intensively used until now) are going to be replaced by processes using alloys. Alloys with superior properties, which are cheaper and have a lower environmental impact have been promoted. The electronic industry is another domain which stimulates development of alloy electroplating processes, because many components are produced through electrochemical procedures. Thorough control of processes is very important in electronic micro-components manufacturing and miniaturization.*

*In this paper a mathematical model describing the nickel and zinc-nickel alloys electrodeposition phenomena is made. It is based on the influence of substratum through deposition and aims to calculate the partial current densities for every species, to predict composition of alloy, if the electrodeposition conditions are known. Corresponding to this mathematical model a software was made to calculate and establish the composition of zinc-nickel alloy.*

**Keywords:** *alloys electrodeposition, anomalous co-deposition, zinc-nickel alloys, mass transfer, electrochemical kinetic*

## 1. Introduction

Any optimization method implies a mathematical model which should meet the quantitative requirements of the problems. This model is based on the substratum effect and aims to calculate the partial current densities and so to give prediction regarding the quantities of metal electrodeposited and the energy involved.

Electrodeposition of a simple metal has also a simpler mathematical model, but the situation is different for alloys deposition. In our model the kinetic parameters are analyzed and we made the supposition that current distribution and mass transport were homogeneous on the working electrode. We also tried to determine the reaction mechanism [1], [2], [3].

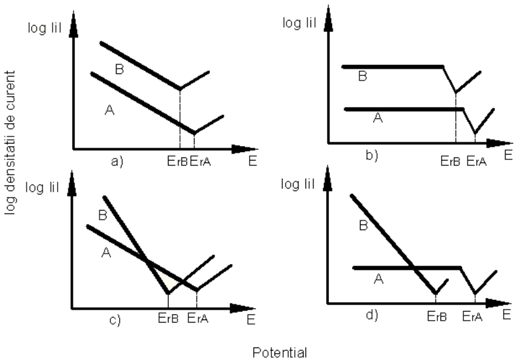


**Figure 1. The scheme which shows partial current densities for A and B components. (a) both components under activation kinetic control, present identic Tafel slopes. (b) both components present limitation of the current. (c) both components under activation control, but with different Tafel slopes. (d) component A presents current limitation, component B under activation control.**

## 2. Theoretical and experimental considerations

### 2.1. Electrochemical process at cathode

In our experiments a zinc-nickel alloy was deposited on gold substratum, previously deposited by sputtering on glass plates. This methode was chosen because it permits to analyze the layers with XRD and SEM-EDX techniques.

The mechanism of electrochemical reactions which occur on the cathode surface has two steps, as Matlosz described [4], [5]. Zinc ions are deposited on their own substratum, on gold substratum and on nickel substratum. Nickel ions are also deposited on their own substratum, on gold and zinc one. More, there are secondary reactions, $Zn^{2+}$ ions are combining with hydrogen to form $ZnH^+$, and similar $Ni^{2+}$ ions are combining to hydrogen to form $NiH^+$. These intermediate species, formed in adsorption process, finally will be decomposed to metallic zinc and nickel respectively.

The mechanism of electrochemical reactions could be written as follow:

$$Ni^{2+} + e^- \rightarrow Ni^+_{ads} \quad (1)$$

$$Ni^+_{ads} + e^- \rightarrow Ni \quad (2)$$

$$Ni + H^+ + \rightarrow NiH^+_{ads} \quad (3)$$

$$NiH^+_{ads} + H^+ + 2e^- \rightarrow Ni + H_2 \quad (4)$$

$$Zn^{2+} + e^- \rightarrow Zn^+_{ads} \quad (5)$$

$$Zn^+ + e^- \rightarrow Zn \quad (6)$$

$$Zn + H^+ \rightarrow ZnH^+_{ads} \quad (7)$$

$$ZnH^+_{ads} + H^+ + 2e^- \rightarrow Zn + H_2 \quad (8)$$

$Ni^{2+}$ and $Zn^{2+}$ are dissolved as metallic ions, hydrolized or not. $Ni^+_{ads}$ and $Zn^+_{ads}$ which could contain or not the group hydroxyl are adsorbed in intermediate reactions. *Ni* and *Zn* are metallic deposits of nickel and zinc respectively [6,7]. The kinetic of mass transfer is supposed to respect Butler-Volmer equation. So far the equilibrium state anodic reactions could be neglected.

### 2.2. Determination of partial current densities

For a binary alloy AB and a thicknes of deposit $\Delta d$, partial current density of *B* element is,

$$i_B = \frac{n_B F}{m_B \Delta t} m_B \quad (9)$$

Here $m_B$ is mass of element B deposited in alloy, $M_B$ is atomic mass of element *B*, $\Delta t$ is deposition time and $n_B$ is number of electrons implied in reaction of element *B*.

### 2.3. Normal and anomalous co-deposition of zinc-nickel alloys

Electrodeposition of zinc-nickel alloys is generally an anomalous co-deposition, after Brenner's definition, because the metal less noble, zinc is deposited preferentialy and its percent in deposit is higher than in electrolyte. Anyway, normal co-deposition of zinc-nickel alloys is possible only under particular experimental conditions. The co-deposition of zinc-nickel alloys from different electrolytic baths was studied potentiostatically and galvanostatically, depending on different variable parameters during electrodeposition [1,2].

### 2.4. Mathematical modelling of zinc-nickel alloy co-deposition. The model of substratum effect

The initial nucleation of adsorbed nickel on the electrode surface acts as a catalyser for zinc deposition, laeding to an inhibition of nickel deposition. It was also shown that pure zinc cannot be deposited from aqueous electrolyte solutions at UPD (*underpotential deposition*), but it could be co-deposited with nickel. These phenomena can be explaine by the fact that nickel nucleation catalizes zinc deposition. At potential more negative than zinc equilibrium potential, zinc deposition rate is enough higher and inhibits nickel deposition leading to an anomalous co-deposition.

The alloy deposition performs a substratum effect. Not only nickel affects zinc deposition, but zinc too affects nickel deposition.

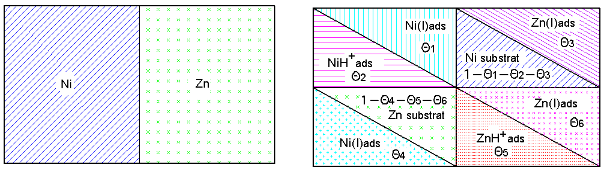


**Figure 2. The diagram of zinc-nickel alloy co-deposition**

Figure 2 shows the diagram of the effects of different substrata during electroplating with zinc-nickel alloys. The initial electrode surface is divided into two parts. The first is corresponding to $\theta_{Ni}$ which is the surface covered by nickel and the second is the surface covered by zinc, $\theta_{Zn}$. Every surface is then divided into four parts. So, for nickel deposition, $\theta_{Ni}\theta_1$ corresponds to the area of Ni substratum surface covered with $Ni(I)_{ads}$. $\theta_{Ni}\theta_2$ corresponds to the area of Ni substratum surface covered with $NiH^+_{ads}$, $\theta_{Ni}\theta_3$ corresponds to the area of Ni substratum surface covered with $Zn(I)_{ads}$. Free surface $\theta_{Ni}(1-\theta_1-\theta_2-\theta_3)$ corresponds to the area of Ni substratum surface non-covered.

For zinc deposition, $\theta_{Zn}\theta_6$ corresponds to the area of Zn substratum surface covered with $Zn(I)_{ads}$. $\theta_{Zn}\theta_5$ corresponds to the area of Zn substratum surface covered with $ZnH^+_{ads}$. $\theta_{Zn}\theta_4$ corresponds to the area of Zn substratum surface covered with $Ni(I)_{ads}$. Free surface $\theta_{Zn}(1-\theta_4-\theta_5-\theta_6)$ corresponds to the area of Zn substratum surface non-covered.

## 2.5. Theoretical model. General mechanism of electrode reactions

A mechanism of reactions was developed as effect of substratum. This model is based on the supposition that every individual component is deposited after a two step-reaction, as Matlosz [4] described. The nickel ions are deposited on their own substratum and on zinc one. Zinc ions are also deposited on their own substratum and on nickel one. Moreover, hydrogenated species $ZnH^+$ and $NiH^+$ are strongly bonded on the electrode surface. $Ni(II)$ will react giving $NiH^+_{ads}$ and these adsorbed species will react afterwards with the nickel deposited. $Zn(II)$ will also react giving $ZnH^+_{ads}$ and these adsorbed species will react afterwards with deposited zinc. [8]

## 2.6. The mass transfer effect

The material balance in equilibrium state through diffusion layer for species $Ni(II)$, $Zn(II)$ and $H^+$, 0<x<d, can be written

$$\nabla \cdot N_{Ni(II)} = 0 \qquad (10)$$

$$\nabla \cdot N_{Zn(II)} = 0 \qquad (11)$$

$$\nabla \cdot N_{H^+} = 0 \qquad (12)$$

$$K_W = C_{OH^-} \cdot C_{H^+} \qquad (13)$$

Supposing a constant diffusion coefficient, $D$, the flow of every species $i$, into diffusion layer is $N_i = -DdC_i / dx$. The values accepted for diffusion coefficients are $4\times10^{-10}\ m^2s^{-1}$ for $Ni(II)$, $5{,}09\times10^{-10}\ m^2s^{-1}$ for $Zn(II)$, and $9{,}3\times10^{-9}\ m^2s^{-1}$ for solvated protons, and $5{,}5\times10^{-9}\ m^2s^{-1}$ for hydroxid ions [3]. Intermediate species, $Ni(I)_{ads}$, $NiH^+_{ads}$, $Zn(I)_{ads}$ and $ZnH^+_{ads}$ exist only on the electrode surface so their concentration is equal to zero in the solution [9].

## 2.7. Electrochemical kinetic

The charge transfer kinetic is supposed to respect Butler - Volmer equation. Far from equilibrium, the anodic reactions could be neglected. A Tafel modified expression describes the electrochemical reactions' rate on the surface and is adapted to calculate the partial current. For example, on the first step of deposition reaction on the nickel substratum, partial current density, $i_{11}$, could be written as:

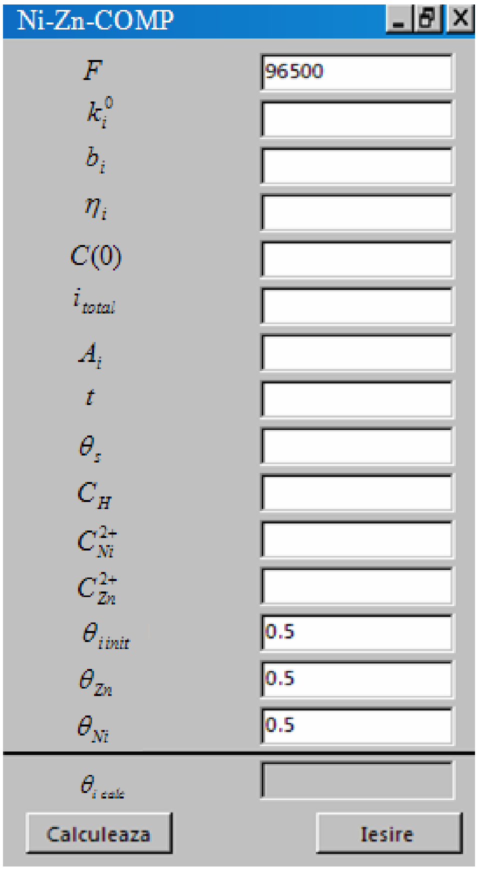
$$i_{11}=-Fk^0_{11}C_{Ni}^{2+}\theta_{Ni}(1-\theta_1-\theta_2-\theta_3)exp(-b_{11}\eta_{11})$$

## 2.8. Software for predictive calculus of zinc-nickel alloy composition

To simulate zinc-nickel alloy deposition, a soft-ware, which uses the calculus relationship from described mathematic model, was elaborated. The calculus stops when the difference between a calculated value and a previous one is smaller than $10^{-5}$ [9], [10], [11].

The program lines are written as follows:

```
using System;
using System.Collections.Generic;
using System.ComponentModel;
using System.Data;
using System.Drawing;
using System.Text;
using System.Windows.Forms;

namespace CalculTETAi
{
  public partial class frmMain : Form
  {
    public frmMain()
    {
      InitializeComponent();
    }

    double F, Ki0, Bi, EtaI, C0, ITotal, Ai, t,
TetaS, CH, CNi, CZn, TetaIInitial, TetaZn, TetaNi;
    double TetaICalculat;
    double Ci, Ii;
    private void m_btnCalculeaza_Click( object
sender, EventArgs e )
    {
      m_tbTetaICalculat.Text = "";

      try
      {
        F = double.Parse( m_tbF.Text );
        Ki0 = double.Parse( m_tbKi0.Text );
        Bi = double.Parse( m_tbBi.Text );
        EtaI = double.Parse( m_tbEtaI.Text );
        C0 = double.Parse( m_tbC0.Text );
        ITotal = double.Parse( m_tbITotal.Text );
        Ai = double.Parse( m_tbAi.Text );
        t = double.Parse( m_tbT.Text );
        TetaS = double.Parse( m_tbTetaS.Text );
        CH = double.Parse( m_tbCH.Text );
        CNi = double.Parse( m_tbCNi.Text );
        CZn = double.Parse( m_tbCZn.Text );
        TetaIInitial          =          double.Parse(
m_tbTetaIInitial.Text );
        TetaZn = double.Parse( m_tbTetaZn.Text
);
        TetaNi = double.Parse( m_tbTetaNi.Text
);
      }
      catch
      {
        MessageBox.Show( "Introduceti valori
corecte", "Atentie", MessageBoxButtons.OK,
MessageBoxIcon.Warning );
        return;
      }
      int Contor = 0;
      int NumarBucle = 1000;
      TetaICalculat = TetaIInitial;
      do
      {
        TetaIInitial = TetaICalculat;

        Ci = C0 * Math.Exp( -Ki0 * Ai * t );
        Ii = -F * Ki0 * CNi * CZn * CH * TetaZn
* TetaNi * ( 1 - TetaIInitial - TetaS ) * Math.Exp( -
Bi * EtaI );
        TetaICalculat = Ii / ITotal;

        Contor++;
        if( Contor > NumarBucle )
          break;
      }   while(   Math.Abs(   TetaIInitial   -
TetaICalculat ) > 1 * Math.Pow( 10, -5 ) );

      if( Contor > NumarBucle )
        MessageBox.Show( "S-a depasit numarul
de bucle!", "Atentie", MessageBoxButtons.OK,
MessageBoxIcon.Warning );
      else
      {
        m_tbTetaICalculat.Text              =
TetaICalculat.ToString();
      }
    }

    private void m_btnIesire_Click( object sender,
EventArgs e )
      {
        this.Close();
```



$F$: 96500

$\theta_{i\,init}$: 0.5

$\theta_{Zn}$: 0.5

$\theta_{Ni}$: 0.5

**Figure 3. User interface with the software for calculus of alloy composition**

## 2.8. Optimization of zinc-nickel alloy co-deposition process

To optimize zinc-nickel alloy electrodeposition process, the Taguchi-type method was used.

The controlled factors will be taken as follows:

- solution type: (1) noted as the solution I (zinc chloride 130g/l, nickel chloride 130g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C) and (2) the second solution II respectively (zinc chloride 130g/l, nickel chloride 65g/l, potassium chloride 230g/l, pH 5-6, t(°C) 24-30°C);
- discharge potential: (1) -850 *mV*, (2) -900 *mV*, (3) -1000 *mV*, (4) -1100 *mV*.

The current density was measured and the current efficiency was calculated. A matrix of experiment was written as follows:

**Table 1.**
**Matrix of zinc-nickel alloy co-deposition experiment**

| Test no. | Controlled factors | | Measured values | |
|---|---|---|---|---|
| | Potential | Solution | Current (Adm$^{-2}$) | Efficiency (%) |
| 1 | 1 | 1 | 7 | 53 |
| 2 | 2 | 1 | 14 | 37.6 |
| 3 | 3 | 1 | 21 | 35.55 |
| 4 | 4 | 1 | 35 | 35.55 (**) |
| 5 | 1 | 2 | 3 | 38.5 |
| 6 | 2 | 2 | 6 | 22.7 |
| 7 | 3 | 2 | 15 | 22.8 |
| 8 | 4 | 2 | 13 | (**) |
| Measured average values | | | | 35.025 |

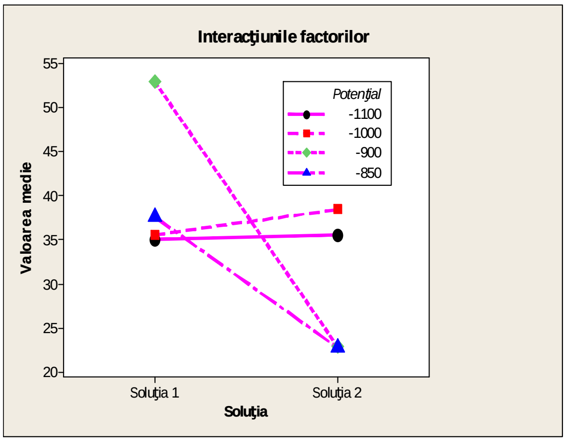


**Figure 4. Interaction of the factors, in this case of discharge potentials for considered experimental conditions (FACTORIAL DESIGN).**

As figure 4 shows (following table 1) for the discharge potential of -900 mV the influence of solution type is the highest. For -850 mV we obtained the 53% energetic efficiency for the first type solution and 38.5% for the second one, which are the highest values. The quality of electrodeposited layers was established by different techniques (optic microscope, SEM-EDX, XRD) [8-11] and was better also for -850 mV discharge potential.

## 3. Conclusions

This model establishes a mathematical apparatus to describe zinc-nickel alloy co-deposition processes, using the substratum effect model for different concentrations of electrolyte and for different applied potentials. There is a good correlation between experimental data and the prediction of this model.

From analyzing the diagrams the following conclusion can be drawn: the discharge potential of -850 mV permits to obtain the best energy efficiency; at this value, the best quality was obtained, too. As regards solutions, superior results are obtained using the solution I.

## 4. Acknowledgments

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