

MATHEMATIC MODEL FOR OPTIMIZATION OF ZINC-NICKEL ALLOY CO-DEPOSITION PROCESS

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Abstract: Any optimization method implies a mathematical model which should resolve the quantitative requires of the problems. This model is based on the substrate effect and has to calculate the partial current densities and so has to give prediction as far as concern the quantities of metal electrodeposited and the energy involved.

Keywords: mathematical model, anomalous co-deposition, zinc-nickel alloys, mass transfer, electrochemical kinetic

1. INTRODUCTION

Electrodeposition of a simple metal has also a simpler mathematical model, but situation is different for alloys deposition. In our proposed model kinetic parameters are analyzed and it was made the supposition that current distribution and mass transport are homogeneous on working electrode. Also we tried to determinate the reaction mechanism.

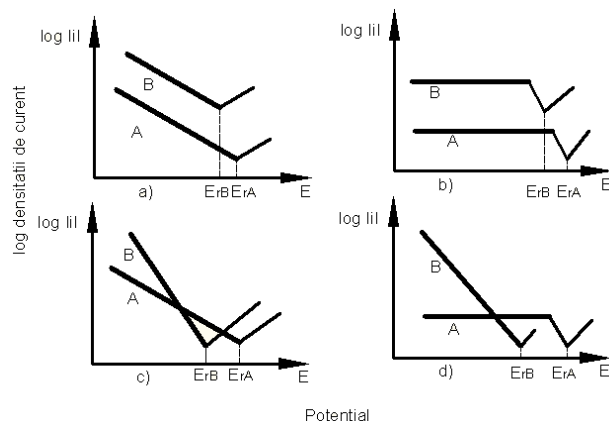


Figure 1. The scheme which shows partial current densities for A and B components. (a) both components under activation kinetic control, present identical Tafel slopes. (b) both components present limitation of the current. (c) both components under activation control, but with different Tafel slopes.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

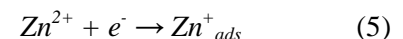
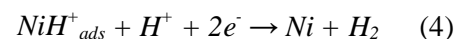
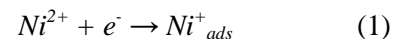
2. EXPERIMENTAL CONSIDERATIONS

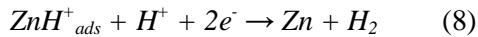
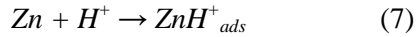
2.1. Electrochemical processes at cathode

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

The mechanism of electrochemical reactions which occur on cathode surface has two steps, as Matloz described Matloz [4], [5]. Zinc ions are deposited on their own substrate, on gold substrate and on nickel substrate. Also nickel ions are deposited on their own substrate, on gold substrate and on zinc substrate. 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+} and Zn^{2+} are dissolved as metallic ions, hydrolyzed 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. In far from equilibrium states anodic reactions could be neglected.

2.2. Determination of partial current densities

For a binary alloy AB and a thickness of deposit Δd , 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, Δt 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 preferential and its percent in deposit is higher than in electrolyte. Anyway, normal co-deposition of zinc-nickel alloys is possible only in particular experimental conditions. Co-deposition of zinc-nickel alloys from different electrolytic bath was studied potentiostatic and galvanostatic, function of different variable parameters during the electrodeposition [1,2].

2.4. Mathematical modeling of zinc-nickel alloy co-deposition. The model of substrate effect

The initial nucleation of adsorbed nickel on electrode surface acts as a catalyser for zinc deposition, resulting an inhibition of nickel deposition. Also it was shown that pure zinc cannot be deposited from aqueous electrolyt solutions at UPD (*underpotential deposition*), but it could be co-deposited with nickel. These phenomena can be explained by the fact that nickel

nucleation catalyze zinc deposition. At potential more negative than zinc equilibrium potential, zinc deposition rate is enough higher and inhibits nickel deposition resulting an anomalous co-deposition.

The alloy deposition performs under substrate effect. Not only nickel affects zinc deposition, but zinc too affects nickel deposition.

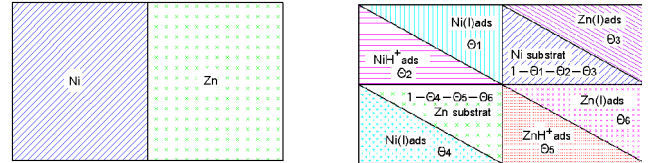


Figure 2. The diagram of zinc-nickel alloy co-deposition

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

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

2.5. Theoretic model. General mechanism of electrode reactions

A mechanism of reactions was developed as effect of substrate. This model is based on the supposition that every individual component is deposited after a two steps-reaction, as Matlosz [4] described. The nickel ions are deposited on their own substrate and on zinc substrate. Also zinc ions are deposited on their own substrate and on nickel substrate. More, hydrogenated species ZnH^+ and

NiH^+ are strongly bonded at electrode surface. $Ni(II)$ will react giving NiH^+_{ads} and these adsorbed species will react after with deposited nickel. Also $Zn(II)$ will react giving ZnH^+_{ads} and these adsorbed species will react after with deposited zinc.

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

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

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

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

$$K_w = C_{OH^-} \cdot C_{H^+} \quad (13)$$

Supposing a constant diffusion coefficient, D , the flow of every species i , into diffusion layer is $N_i = -DdC_i/dx$. Accepted values for diffusion coefficients are $4 \times 10^{-10} m^2 s^{-1}$ for $Ni(II)$, $5,09 \times 10^{-10} m^2 s^{-1}$ for $Zn(II)$, and $9,3 \times 10^{-9} m^2 s^{-1}$ for solvated protons, and $5,5 \times 10^{-9} m^2 s^{-1}$ for hydroxide ions [3]. Intermediate species, $Ni(I)_{ads}$, NiH^+_{ads} , $Zn(I)_{ads}$ and ZnH^+_{ads} exist only on the electrode surface so one their concentration is equal zero in solution [8], [9].

2.7. Electrochemical kinetic

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

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

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

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

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, TetaInitial, 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 );

                    TetaInitial = double.Parse(
                    m_tbTetaInitial.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 deposit
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();
}

```

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

3. CONCLUSIONS

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

4. ACKNOWLEDGMENTS

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