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Influence Assessment of Operating Parameters in Synthesis of Zn-Ni Alloys for Process Electrodeposition

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The influence of the variation of the metallic ions concentrations on the electrodeposition of Zn-Ni alloys on a copper substrate was studied evaluating the Faradaic efficiency. It was used a 2^2 factorial design, with 3 central points. So, fixing the electric current density in 12.5 mA/cm^2, the variables were the concentrations of zinc and nickel. The electrolytic bath was composed by $ZnSO_4$ and $NiSO_4$, salts that were source of zinc and nickel, respectively, ammonium citrate as a complexing agent and sodium borate as an amorphising. The alloys showed good performance at room temperature and the Faradaic efficiency reached 95%. The concentration of zinc was more influential on the deposition efficiency than the concentration of nickel.

1. Introduction

The electrodeposition occurs through the passage of electric current in an electrolytic bath. In order to achieve specific properties, two or more metals may be deposited simultaneously in a metal alloy. These alloys exhibit different properties of those of the single-metal deposits and, by variating the operating parameters, it is possible to maximize an alloy property, thereby obtaining a better material for a given application.
Zn-Ni alloy coatings are expressive in the automotive industry, and are also employed in electronics industries (Riedel, 1988; Crotty, 1996; Brooman, 1993). In addition, Alfantazi (1996), Wright (1994), Lin e Selman (1993) indicate that Zn-Ni alloys have ecological aspects, replacing toxic cadmium alloys. In the chemical industry, this alloy can be applied to control the corrosion of pipes and reactors, where the corrosive environment can be aggressive.
Thus, the study of the Zn-Ni alloy shows to be important and the variation of the zinc and nickel concentrations of the electrolytic bath allows the improvement of its properties. In this work, a two level factorial design was performed in order to define the most important influences on the deposition efficiency.

2. Experimental

For the electrodeposition, copper plates with 8 cm² of area were used as cathodes, where the alloy was deposited. A platinum mesh was used as counter electrode and it was immersed in electrolytic baths with the different concentrations of metals to be studied. The cathode was mechanically treated with systematic sanding with grit 220, 320 and 400 respectively. Then it was chemically treated by submerging it in 10% sodium hydroxide solution to remove the fats, followed by 1% sulfuric acid. The substrate surface was washed with distilled and deionized water and colorless enamel was applied to the rod to prevent external deposition to the square area of 4 cm^2 on each side. The washed substrate was dried in an oven for 5 minutes and cooled in a desiccator for 5 minutes.
The pH of the electrolytic bath was chosen using the open softwares Hydra and Medusa (PUIGDOMENECH, 2004) to identify the pH range in which the species in the bath are optimally complexed in order to allow the best efficiency of the electrolysis. The electric current density used was 12.5 mA/cm^2 and the tests were performed at room temperature (~ 25 ° C).
The composition of the electrolytic bath was evaluated according to the concentrations of $ZnSO_4$ (C_{Zn}) and $NiSO_4$ (C_{Ni}), salts of Zn and Ni, respectively, presented in Table 1. Other compounds were also used for specific purposes such as 0.27 mol/L ammonium citrate ($(NH_4)_2C_6H_6O_7$) for complexing Zn and Ni and

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$3.75x10^{-2}$ mol/L sodium borate ($Na_2B_4O_7$) for bath stability and, for pH correction, concentrates sulfuric acid or ammonium hydroxide. All components of the bath had a high purity level and all the water used in the experiment was distilled and deionized.

Table 1: Concentrations of Zn and Ni for the electrolytic bath

Variables \ Levels	(-1)	0	(+1)
C_{Zn} (mol/L)	0.11	0.17	0.23
C_{Ni} (mol/L)	0.02	0.03	0.04

The Faradaic efficiency of Zn-Ni alloys was calculated according to Equation 1:

$$\varepsilon = \frac{Q_u}{Q} \cdot 100 \quad (1)$$

In which Q_u is the electric charge used to obtain the mass gain at the cathode, Q is the total electric charge applied, both in Coulombs (C) and ε is the Faradaic efficiency in percentage.

The total electric charge Q is obtained by Equation 2, in which i corresponds to the electric current in Ampères (A) and t corresponds to the time in seconds (s):

$$Q = i \cdot t \quad (2)$$

The electric charge used Q_u is obtained by the Equations 3, 4 and 5:

$$Q_{Zn} = \frac{2 \cdot m_{Zn} \cdot F}{M_{Zn}} \quad (3)$$

$$Q_{Ni} = \frac{2 \cdot m_{Ni} \cdot F}{M_{Ni}} \quad (4)$$

$$Q_u = Q_{Zn} + Q_{Ni} \quad (5)$$

In this case m corresponds to the mass in grams (g) of each metal, M to the molar mass (g/mol) and F is the Faraday constant, equal to 96.485,34 Coulomb / mol. The ratio of each metal in the alloy was obtained by Energy-Dispersive X-ray Spectroscopy (EDS).
The copper plate, after being treated and weighed, was coupled to a rotating electrode (AMETEK - Model 616A), responsible for maintaining the angular speed of 45 rpm. Then, the copper plate was submerged in the bath and positioned concentric to the counter electrode, a hollow cylindrical mesh of platinum, as shown in Figure 1. The electric current was forced through the system by a potentiostat (AMETEK - VersaSTAT 3), used galvanostatically. A computer connected to the potentiostat read and stored the process data.

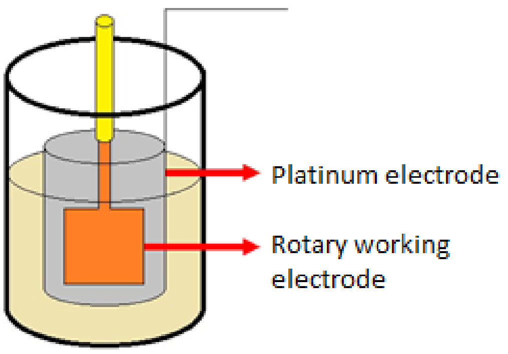

Figure 1: Schematic representation of the electrolytic cell.

3. Results and discussion

3.1 Metallic speciation

The results obtained in the Hydra / Medusa simulator, to determine the possible compounds present in the bath as a function of pH are shown in Figures 2 and 3:

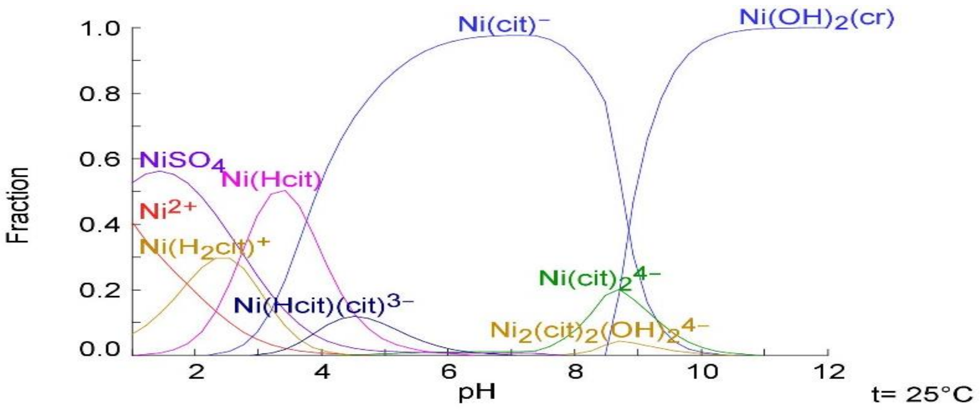

Figure 2: Complexes formed with the Ni^{2+} ion at different pH values.

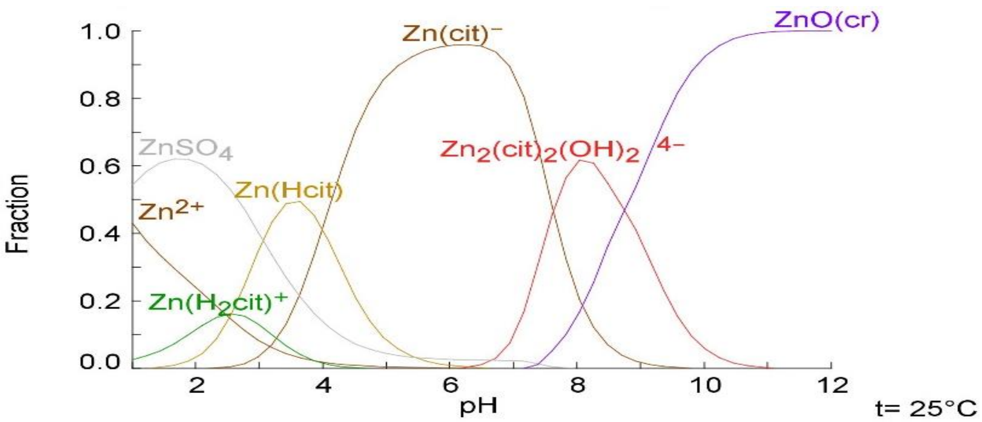

Figure 3: Complexes formed with the Zn^{2+} ion at different pH values.

The complexes formed between the metal ions and the citrate anions are the most favorable to obtain a metal alloy by electrodeposition, thus, by Figures 2 and 3 the pH 6 was determined as the pH in which the chemical species of zinc and nickel Form complexes with citrates.

3.2 Zinc and nickel concentrations effects

The Faradaic efficiencies according to factorial design 2^2 are shown in Table 2 and the Figures 4 and 5 represent the Pareto diagram and the response surface, respectively, obtained from statistics analysis of data.

Table 2: Factorial design 2^2 considering the zinc and nickel concentrations as parameters.

Exp	C_{Zn}	C_{Ni}	ε (%)
1	-1	-1	81.85
2	+1	-1	93.72
3	-1	+1	88.38
4	+1	+1	94.82
5 (C)	0	0	93.06
6 (C)	0	0	91.77
7 (C)	0	0	92.86

The Pareto diagram showed, with 95% confidence, that the statistically significant variable in electrodeposition was the Zn salt concentration, while the Ni concentration and interaction between than weren't significant.

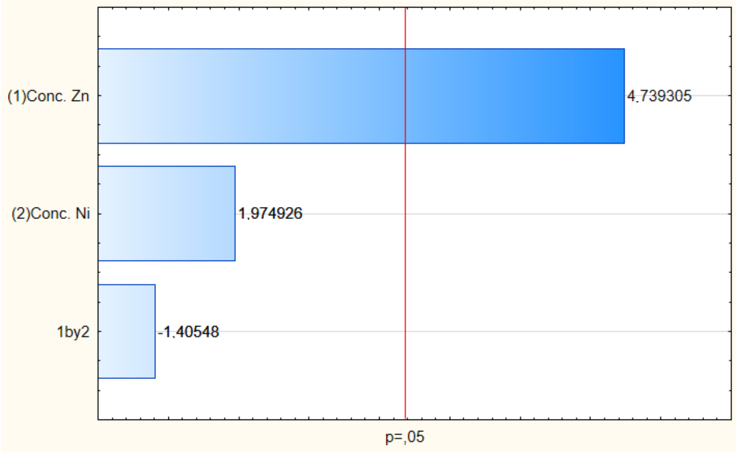

Figure 4: Pareto diagram of effects relating of Faradaic efficiency.

The response surface at Figure 5 also demonstrates the significant influence of Zn concentration on efficiency. It can be notice that the efficiency increases according to the zinc concentration increase, varying little with the nickel concentration. The maximum Faradaic efficiency (94.82%) was obtained at maximum concentrations of zinc and nickel salt concentrations studied.

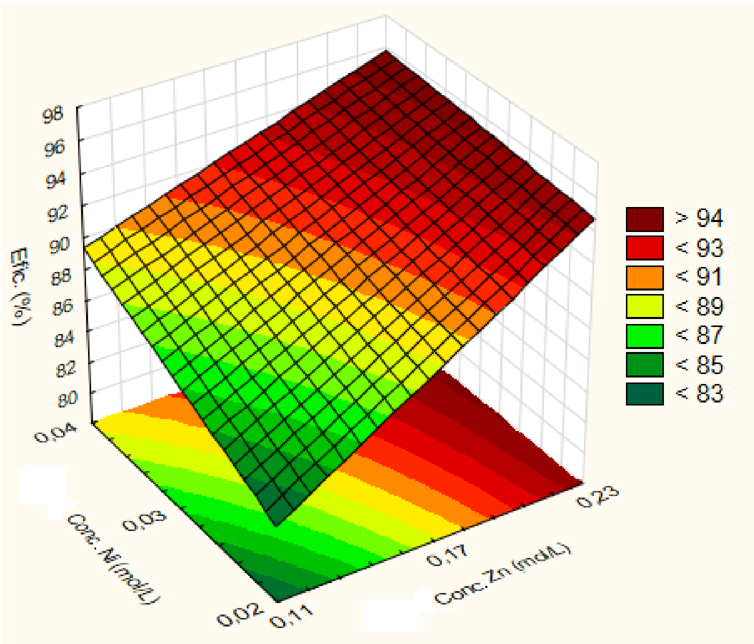

Figure 5: Response surface of Faradaic efficiency as a function of Zn and Ni concentrations.

The Faradaic efficiency decreases when the electric current is used by other reactions but the reduction reactions of interest metals. Among them, the hydrogen evolution reaction is characterized as the main charge sequestrator of the system, leading to the formation of hydrogen bubbles at cathode (Elkhatabi *et al*., 1999; Short *et al.*, 1996; Giridhar and Ooij, 1992).
The Figures 6 and 7 show the micrographs of experiments 1 and 3, respectively, presented in Table 2. It can be observed that under low concentrations of Ni in the bath, the alloy presented larger grains, low porosity and hexagonal morphology of a Zn rich layer (Figure 6) (Ghaziof and Gao, 2014), which are interesting features in

relation to the insulation of substrate against the aggressive medium. However, for high concentrations of Ni in the bath, the alloy presented small grains and porous formation (Figure 7), evidencing the significant influence of Ni concentration on the morphology of the alloy.

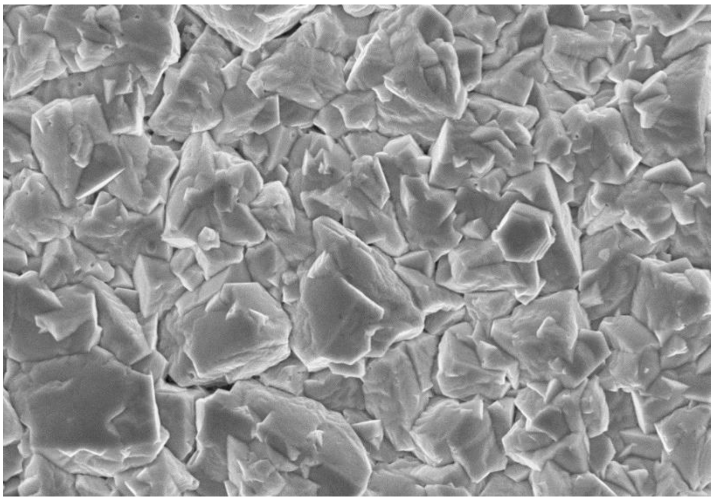

Figura 6: Surface micrograph of alloy Exp 1, enlarged 5000 times.

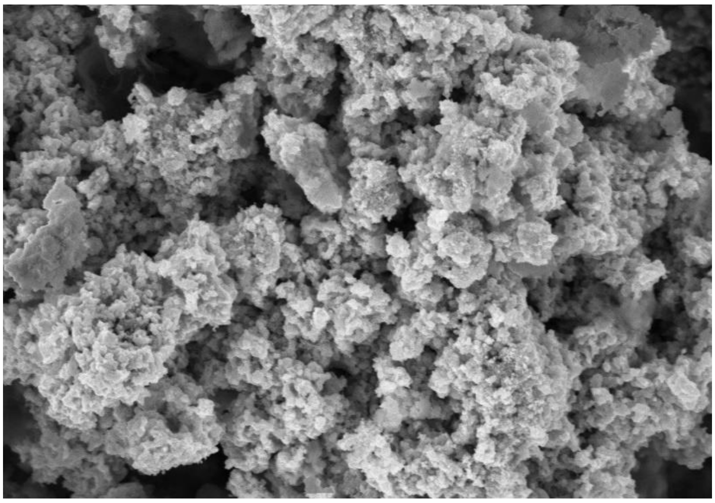

Figura 7: Surface micrograph of alloy Exp 3, enlarged 5000 times.

4. Conclusion

Of all the parameters studied for the Zn-Ni electrodeposited alloy at pH 6 and 45 rpm cathode rotation, the conditions that offered the biggest Faradaic efficiency and adhesion were the concentrations of 0.23 mol/L $ZnSO_4$ and 0.04 mol/L $NiSO_4$. Through the statistical analysis, it was also noticed a significant influence of variations of zinc concentrations on the efficiency.

References

Alfantazi A.M., Page, J., Urb, U., 1996, Pulse plating of Zn-Ni alloy coatings. J. Appl. Eletrochem. 26, 1225-1234.

Brooman, E.W., 1993, Alternatives to cadmium coating for electrical/electronic applications. Plating Surf. Finish. 80, 29-35.

Crotty, D., 1996, Zinc alloy plating for the automotive industry. Met. Finish. 94, 54-58.

Elkhatabi, F.; Benballa, M.; Sarret, M.; Muller, C., 1999, Dependence of coating characteristics on deposition potential for electrodeposited Zn-Ni alloys. Elect. Act. 44, 1645-1653.

Ghaziof, S., Gao, W., 2014, Electrodeposition of single gamma phased Zn-Ni alloy coatings from additive-free acidic bath. Appl. Surf. Scien. 311, 635-642.

Ghiridar, J.; Ooij, W. J., 1992, Study of Zn-Ni and Zn-Co alloy coatings electrodeposited on steel strips I: Alloy electrodeposition and adhesion of coatings to natural rubber compounds. Surf. And Coat. Tech. 52, 17-30.

Lin, Y.P., Selman, J.R.E., 1993, Eletrodeposition of Corrosion-Resistant Ni-Zn Alloy. J. Electrochem. Soc. 140, 1299.

Puigdomenech, I., 2004, Chemical Equlibrium Database and Plotting Software, KTH Royal Institute of Tecnology, freely downloadable software, https://www.kth.se/en/che/medusa accessed 02.22.2016.

Riedel, W., 1988, Proteccion contra la corrosion mediante recumbrimientos de aleaciones de cinc depositados eletrolíticamente, Pinturas y Acabados Industriales. 30 (162), 13-16.

Short, N. R.; Zhou, S.; Dennis, J. K., 1996, Electrochemical studies on the corrosion of a range of zinc alloy coated steel in alkaline solutions. Surf. And Coat. Tech. 79, 218-224.

Wright, D.A., Gage, N., Wilson, B.A., 1994, Zinc-nickel electroplate as a replacement for cadmium on high-strength steels. Plating Surf. Finish. 81, 18-21.