

Nucleation and Growth of Zn, Ni and Zn-Ni Alloys from a Chloride Solution

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1. Introduction

Electrodeposited coatings of zinc alloys, in particular zinc-nickel alloys, are currently the subjects of many studies. Steel sheets electroplated with zinc-nickel alloy, particularly those with composition of 11-14 wt% nickel, are widely used for automotive body panels due to their superior corrosion resistance, even with a light coating weight compared with other types of coated products. This alloys has been used as a substitute for toxic and high-cost cadmium coatings [1].

According to Brenner [1], the electrodeposition of zinc-nickel alloy is classified as anomalous codeposition, because the electrochemically less noble Zn is deposited preferentially. Several mechanisms have suggested for the preferential deposition of Zn.

2. Experimental

A three-electrode Pyrex[®] cell was used to perform the experiments, with an approximate volume of 25 mL. The working electrode was obtained sealing a Pt disk in a Pyrex tube and polishing a aluminum powder. The auxiliary electrode was Pt foil and all potentials quoted in this work were refereed to the saturated calomel electrode (SCE).

The electrolyte bath consisted of a 0.1 M ZnSO₄, 0.1 M de NiSO₄ and mixture of both solution in ratio 1:1, 2:1 and 1:2 Zn:Ni. The electrochemical experiments were performed with an EG&G PARC model 273 potentiostat-galvanostat linked to PC microcomputer. The software used to control the experiments was the M270 from EG&G PARC.

3. Results and Discussion

The Zn, Ni and Zn-Ni electrocrystallization was studied by chronoamperometry. Initially cyclic sweep voltammetry was used as a technique to determine the range potentials for performing the potentiostatic jumps (Zn and Ni:Zn $E_{step} = -1.05$ to -1.15 V and Ni $E_{step} = -0.95$ to -1.09 V). The voltammetric response presents crossover of anodic and cathodic branches, characteristic of the nucleation process.

The figure 1a shows a family transients obtained with different potentials pulses to Zn electrodeposition. Is observed a rising current followed by descending portion that corresponds to linear diffusion to the planar electrode, described by Cottrell equation. The similar behavior was observed from Ni and Ni-Zn chronoamperograms. Current transients present a response typical of a three- dimensional multiple nucleation with diffusion controlled growth [2].

Taking into account the equations for instantaneous and progressive nucleation mechanisms, the transients were normalized representing non-dimensional plots $(I/I_{max})^2$ vs. t/t_{max} . In all cases, experimental results fitting the curve to instantaneous nucleation mechanism

(figure 1b).

The excellent linear relationships of I to $t^{1/2}$ are shown in figure 2, thus indicating, again, an instantaneous 3D nucleation and growth process under kinect control.

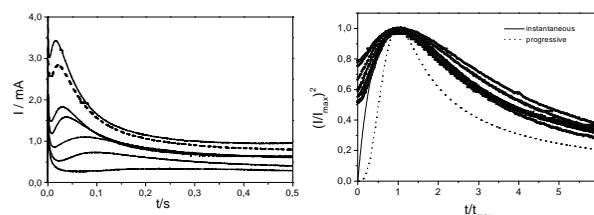


Figure 1: Potentiostatic transients for Zn electrodeposition ($E_{initial} = -0.85$ V and $E_{step} = -1.06$ to -1.12 V (a) and non-dimensional $(I/I_{max})^2$ vs. t/t_{max} plot data in Fig. 1a (b)

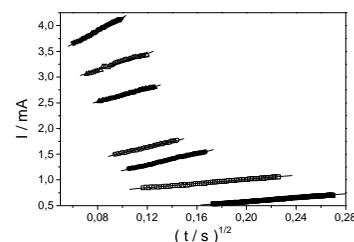


Figure 2: Linear dependence between I and $t^{1/2}$ for the middle, rising sections of the transients in Fig. 1a.

Other diagnostic criteria such as $I_{max}^2 t_{max}$ were calculated and showed a proper concordance with experimental results as presented in Table 1. The same results were observed to Ni and Zn:Ni at different molar ratio.

Table 1: Analysis of the current maximum for deposition of Zn, Ni and Zn:Ni in more cathodic potential step.

Ni:Zn	$i_{max}^2 t_{max} / A^2 cm^{-4} s$		
	Experim.	Calculated (inst.)	Calculated (prog.)
1:1	2.1×10^{-4}	2.0×10^{-4}	3.1×10^{-5}
1:2	6.4×10^{-4}	5.5×10^{-4}	8.7×10^{-4}
2:1	2.8×10^{-4}	2.2×10^{-4}	3.5×10^{-4}
Zn	4.3×10^{-6}	4.6×10^{-6}	1.2×10^{-5}
Ni	3.4×10^{-4}	3.9×10^{-4}	1.4×10^{-3}

Once it is established that the nucleation is instantaneous for all cases studied, the nuclei number at different potentials can be calculated from the current maxima by means Scharifker Models equation. The values obtained were between 0.46 to 4.88×10^{-6} nuclei / cm^2 . To Ni and Ni:Zn alloys 2:1 the nuclei number were lower than Zn or Zn:Ni 1:1 and 1:2.

4. Conclusions

The results pointed that Zn, Ni and Zn:Ni alloys nucleation occurs by instantaneous 3D nucleation and growth process under kinect control. Increasing Ni content in alloys is possible to obtain lower number nuclei.

Acknowledgements

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