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Studies on the Influence of Potential and Electrochemical Conditions on Zinc-Nickel Alloys Electrodeposition

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Abstract: The paper presents studies concerning electrodeposition of zinc-nickel alloys from the point of view of the influence of potential and electrochemical conditions on the composition of the electrodeposited layers. Alkaline systems of Zn^{2+} and Ni^{2+} salts were used. The optimal range of electrical parameter variation, as current density and potential, bath temperature and pH of solution were studied. The SEM-EDX techniques and optical spectroscopy for studies on the composition and structural properties of the layers were used.

Keywords: Electrodeposition; Zinc-nickel alloys; SEM-EDX techniques; Spectroscopy.

Introduction

The interest for zinc-nickel alloys coatings increased during the last decades due to their better corrosion and mechanical properties compared with those of pure zinc or nickel coatings. There is a worldwide tendency in substitution of cadmium intensively used in coating due to its toxicity and high costs industrial processes. The automotive industry was the first in this

general orientation through alloys. The electrolytes for zinc-nickel alloys electrodeposition are a high priority problem, so they are intensively studied.[1-3] Brenner classified zinc-nickel alloys electrodeposition as an anomalous co-deposition because zinc, which is the less noble metal, is preferentially deposited. This phenomenon has been known since 1907, but the mechanism it is not well understood. The anomalous co-deposition of Zn-Ni alloys could be associated with a local increase of the pH, a fact which induces the zinc hydroxide precipitation and so one inhibition of the nickel deposition. Another cause is under-potential deposition of zinc on nickel-rich zinc alloys or nickel nuclei.[4,5]

Experimental

The co-deposition of thin layers of zinc-nickel alloys was performed electrochemically at INCDFM Bucharest-Magurele. With the aim to obtain the target properties it was necessary to search the influence of electrodeposition conditions (co-deposition potential, the bath's composition, the temperature for deposition, mechanical shaking) through the structure, morphology, composition and optical properties, transport properties and magnetic properties of the layers. First aim was to obtain uniform layers. Therefore it was necessary to find the range of potentials which permit to realize the stoichiometric composition of the layer and to find the slowest condition for deposition.

Two recipes were used to prepare the low acid electrolyte for electrodeposition of zinc-nickel alloys.

The first solution: zinc chloride 130 g/L, nickel chloride 130 g/L, potassium chloride 230 g/L, pH 5-6, 24-30°C.

The second solution: zinc chloride 130 g/L, nickel chloride 65 g/L, potassium chloride 230 g/L, pH 5-6, 24-30°C.

As working electrode was used a piece of glass plated with a deposited gold layer, performed using sputtering method (a Hummer 6 installation was used). pH level was maintained between 5 and 6 naturally, without addition of acids, because the used salts were chlorides which by electrolytic dissociation have acid character (excepting KCl). The work temperature was between 24°C and 30°C.[6-9]

For a good adhesion the glass plates were polished first and then gilded in the sputtering installation.

As reference electrode it was used the calomel electrode directly immersed in the electrolyze cell, and the anode was made by platinum.

The chemical reactions which occur on the cathode follow two steps, as Matlosz described them. Zinc ions are deposited on their own substrate, on the gold substrate and on the nickel substrate. Nickel ions are also deposited on their own substrate, on the used gold substrate and on the zinc substrate. In addition it has to take account the secondary reactions when Zn^{2+} ions react with hydrogen to form ZnH^{+}. Similarly, Ni^{+} ions react with hydrogen to form NiH^{+}. These intermediate species, formed in the adsorption process, will decompose finally to form metallic *Zn* and metallic *Ni* respectively.

The electrochemical reactions which occur could be written as follow:

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

$$Ni^{+}_{ads} + e^{-} \rightarrow Ni$$

$$Ni + H^{+} + \rightarrow NiH^{+}_{ads}$$

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

$$Zn^{2+} + e^{-} \rightarrow Zn^{+}_{ads}$$

$Zn^{+} + e^{-} \rightarrow Zn$

$Zn + H^{+} \rightarrow ZnH^{+}_{ads}$

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

Ni^{2+} and Zn^{2+} are dissolved as metallic ions, hydrolyzed or not. Ni^{+}_{ads} and $Zn^{+}_{ads,}$ which contain or not hydroxyl group, are monovalent adsorbed in intermediate reactions. *Ni* and *Zn* are the metallic deposits of nickel and zinc respectively.[4,8,10]

The kinetics of charge transfer is supposed to respect Butler-Volmer equation. In far from equilibrium conditions anodic reactions could be neglected.[11,12]

EDX-SEM analyses were performed by means of a SEM VEGA II LSH scanning electronic microscope (TESCAN, Czech Republic), coupled with an EDX QUANTAX QX2 (ROENTEC, Germany).

Results and discussions

There were obtained many samples in different conditions of temperature and potential, using both solutions (described as above).[8,9]

As we can observe, a uniform deposit was obtained, with micro-cracks, as prove for internal stress. The composition of alloy and the atomic percents are presented in Table 1. The instrument also recorded the relative errors (not shown). The oxygen percent is explained by superficial oxidation of sample due to the time passed through electrodeposition until analysis.

Figure 1. Co-deposition of zinc-nickel alloy on gold plated glass, at -1000 mV, 2 hours and 30°C (optical increase factor 1000×).

Table 1. Composition of the zinc-nickel alloy corresponding to Figure 1.

Element	[norm. wt.-%]	[norm. at.-%]
Nickel	31.10	22.93
Cadmium	4.46	1.72
Chlorine	2.25	2.74
Zinc	35.24	23.32
Gold	9.50	2.08
Oxygen	17.45	47.21
	100	100

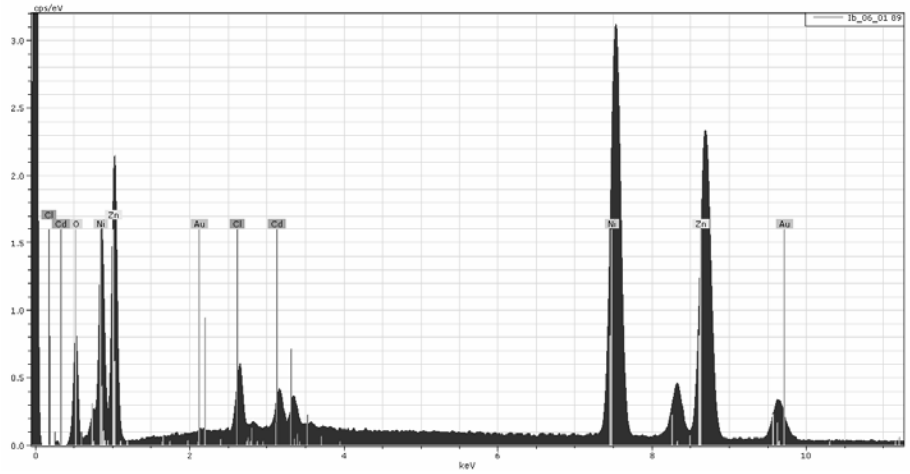

Figure 2. EDX spectrum of a zinc-nickel alloy sample (-1000 mV, 2 hours, 30°C).

In Table 2 is presented the composition of a zinc-nickel alloy sample electrodeposited 2 hours at 30°C and -900 mV. Figure 3 shows a SEM image of the sample. A good quality of the layer is observed and micro-cracks, because of the internal stress.

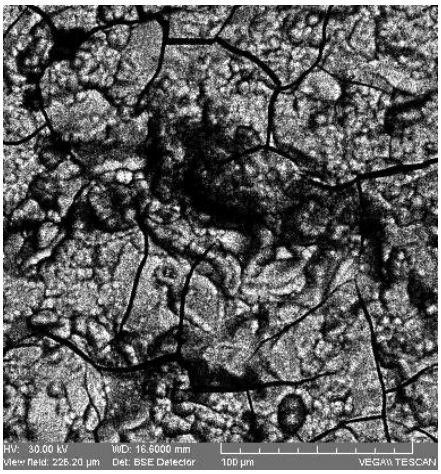

Figure 3. Co-deposition of zinc-nickel alloy on gold plated glass, at -900 mV, 2 hours and 30°C (optical increase factor 1000×).

Table 2. Composition of the zinc-nickel alloy corresponding to Figure 3.

Element	[norm. wt.-%]	[norm. at.-%]
Nickel	36.83	28.20
Gold	4.39	1.01
Chlorine	3.69	4.68
Zinc	40.19	27.63
Cadmium	1.39	0.55
Oxygen	13.51	37.93
	100	100

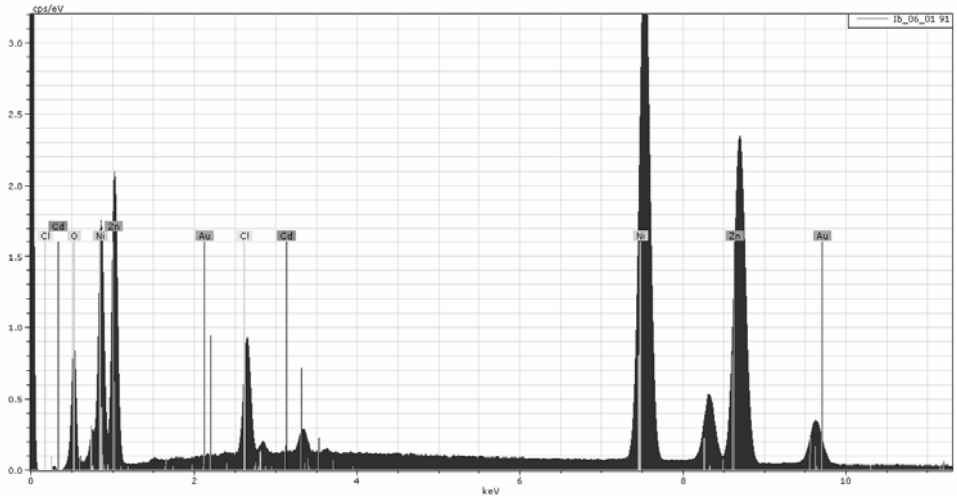

Figure 4. EDX spectrum of a zinc-nickel alloy sample deposited at -900 mV, 2 hours and 30°C.

Figure 5. Co-deposition of zinc-nickel alloy on gold plated glass, at -1050 mV, 2 hours and 30°C (optical increase factor 1000×)

Table 3. Composition of the zinc-nickel alloy corresponding to Figure 5.

Element	[norm. wt.-%]	[norm. at.-%]
Nickel	30.94	24.44
Chlorine	2.03	2.65
Zinc	37.88	26.86
Gold	11.19	2.63
Cadmium	3.47	1.44
Oxygen	14.49	41.98
	100	100

Table 3 presents the composition of a zinc-nickel alloy deposited at 30°C, -1050 mV and 2 hours. A good quality of the co-deposition is also observed with minor micro-cracks.

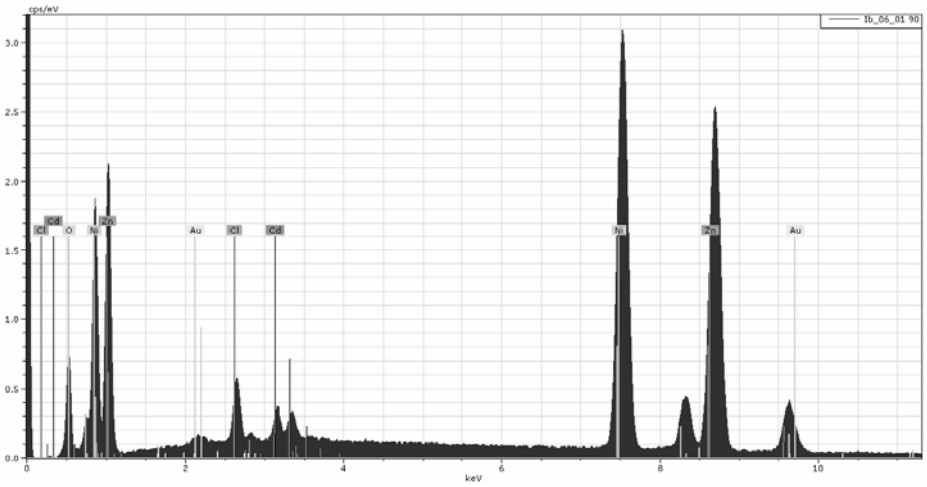

Figure 6. EDX spectrum of a zinc-nickel alloy sample deposited at -1050 mV, 2 hours and 30°C.

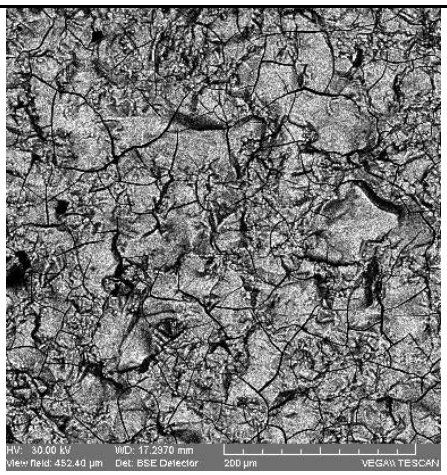

Figure 7. Co-deposition of zinc-nickel alloy on gold plated glass, at -950 mV, 2 hours and 30°C (optical increase factor 1000×).

Table 4. Composition of the zinc-nickel alloy corresponding to figure 7.

Element	[norm. wt.-%]	[norm. at.-%]
Nickel	33.31	27.55
Gold	11.93	2.94
Zinc	37.24	27.64
Chlorine	1.06	1.44
Potassium	0.23	0.29
Cadmium	3.49	1.51
Oxygen	12.74	38.63
	100	100

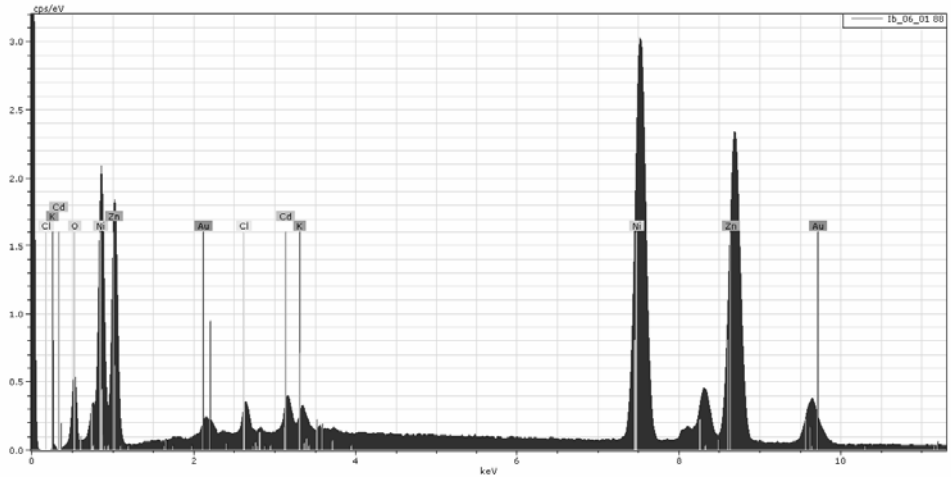

Figure 8. EDX spectrum of a zinc-nickel alloy sample deposited at -950 mV, 2 hours and 30°C.

In the sample deposited at -950 mV, there are micro-cracks and the alloy was also formed.

Conclusions

Zinc-nickel alloys were formed in all cases. The properties of the layers depend on the electroplating conditions and the composition of the electrolytic bath. For the highest applied potential (-1050 mV) a high quality deposited layer was obtained. At -900 mV the greatest micro-cracks were observed and consequently the higher internal stress during electrodeposition.

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