

Electrochemical Mechanism of Nickel and Zinc-Nickel Alloy Electrodeposition

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Abstract: The mechanism of electrochemical deposition of nickel and zinc-nickel alloy was described as in actually science literature. To prove practically the proposed mechanism, it was used as interesting effect which consists in an increase of the deposited mass more than Faraday law predicts. Nickel was deposited and zinc-nickel alloy was co-deposited using a potentiostat-galvanostat Parstat 2273 coupled with an Electrochemical Quartz Crystal Microbalance (EQCM). The mass distribution of deposited metal and alloy was monitored during the process, together with electrochemical parameters (potential, current density, and temperature). The electrodeposited layers were characterized with SEM-EDX techniques. A mathematical relation referring to the process was proposed in order to describe the evolution of mass electrode versus time in the first step of the electrodeposition.

Keywords: Nickel, Zinc-Nickel alloy, Electroplating, EQCM, SEM-EDX.

1. INTRODUCTION

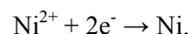
Because it offers a very good quality of covered surfaces, nickel electroplating has a great commercial and industrial importance. This importance is proved by increased annual global consumption of nickel. The applications of electroplating could be divided into three great categories: decorative, functional and electroforming [1-13].

This work studies the process of nickel electrodeposition using the electrochemical quartz crystal microbalance (EQCM) for recording the mass evolution versus time, also SEM-EDX techniques to measure the composition of the samples and optical microscopy [5, 6, 14, 15].

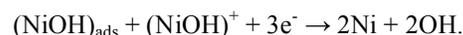
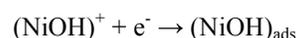
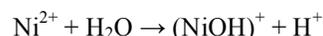
Electroplated zinc coatings are considered as one main way for the corrosion protection of steel. Recently, the interest of zinc-nickel alloy coatings has increased due to their better mechanical and corrosion properties as compared to pure zinc coatings. Developing and studying electrolytes for electrodeposition of zinc-nickel alloys it is a high-priority problem in electroplating. The use of zinc and its alloys for improving the corrosion resistance of coated steel, has been growing worldwide and as a substitute for toxic and high-cost cadmium coatings. In the automotive industry, for example, it has been growing in search of increasing corrosion resistance of chassis. The Zn-Ni alloys obtained by electrodeposition processes, with the amount of nickel varying between 8% and 14% by weight, give corrosion

protection five to six times superior to that obtained with pure zinc deposits [5-9]. Many studies have attempted to understand the characteristics of deposition process of Zn-Ni alloy. The electrodeposition of zinc-nickel alloys was classified by Brenner as an anomalous co-deposition where zinc, the less noble metal is preferentially deposited. Although this phenomenon has been known since 1907, the co-deposition mechanism of zinc and nickel is not well understood. There are some propositions to explain the anomalous co-deposition of Zn-Ni alloys. The first attributes the anomalous co-deposition to a local pH increase, which would induce zinc hydroxide precipitation and would inhibit the nickel deposition. Another proposition is based on the under-potential deposition of zinc on nickel-rich zinc alloys or on nickel nuclei [4, 5, 8, 16-20].

The electrochemical reactions which occur in nickel electrodeposition process on the cathode could be written generally as:



and the proposed mechanism evolves after the next steps:



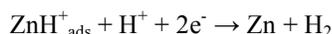
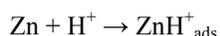
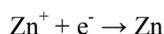
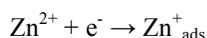
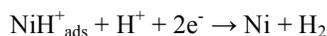
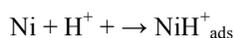
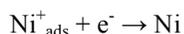
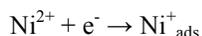
This mechanism was proposed after the studies about inductive impedance loops with the method of electrochemical impedance spectroscopy, but all steps were not identified and elucidated yet [21, 22].

Regarding zinc-nickel alloy co-deposition, the chemical reactions which occur on the cathode follow two steps, as

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they were described by Matlosz [1, 8]. Zinc ions are deposited on their own substrate, on the gold substrate and on the nickel substrate. Also, nickel ions are 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 ions Zn^{2+} combine with hydrogen to form ZnH^+ , in the same way Ni^+ ions combine with hydrogen to form NiH^+ . These intermediate species, formed in the process of adsorption, will decompose finally to form metallic Zn and metallic Ni, respectively.

The electrochemical reactions which occur 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 or not contain hydroxyl group, are monovalent adsorbed in intermediate reactions. Ni and Zn are the metallic deposits of nickel and zinc, respectively [5-8, 16, 23-25].

2. EXPERIMENTAL

The nickel layers and zinc-nickel alloy layers were electrochemically obtained. We performed the electrodepositions at INCDFM Bucharest-Magurele. For nickel electrodeposition, we used additive polyvinylpyrrolidone, as wetting agent. The solution for electroplating had the next composition: nickel sulfate ($NiSO_4 \cdot 6H_2O$) – $240g \cdot L^{-1}$, nickel chloride ($NiCl_2 \cdot 6H_2O$) – $45g \cdot L^{-1}$, boric acid (H_3BO_3) – $30g \cdot L^{-1}$, poly-

vinylpyrrolidone (PVP) – $5g \cdot L^{-1}$, temperature $65^\circ C$, pH 2,5-4 (maintained naturally, without additives for pH correction).

Composition of electroplating solution for alloy electrodeposition was: zinc chloride ($ZnCl_2$) – $130g \cdot L^{-1}$, nickel chloride ($NiCl_2$) – $130g \cdot L^{-1}$, potassium chloride (KCl) – $230g \cdot L^{-1}$, pH 5-6 (naturally, without pH correctors), operation temperature $24-30^\circ C$.

The electrodeposition was made by using an Electrochemical Quartz Crystal Microbalance Parstat 2273, designed to be a comprehensive electrochemical tool. The Parstat 2273 is also a potentiostat-galvanostat that consists of hardware capable of ± 10 V scan ranges, 2 A current capabilities. The interface to the PC or laptop is Universal Serial Bus (USB).

The EQCM device (Fig. 1) usage is described in many other articles [26, 27, 29].

The cathode was a thin gold layer deposited on Teflon (standard cathodes for described model of EQCM), having $0.2826cm^2$ surface (3mm radius).

3. RESULTS AND DISCUSSIONS

For nickel electrodeposition, we found the next values for resonance frequencies of the device: $f = 8.95$ MHz, $f' = 8.90$ MHz. Deposition time was fixed on 2 minutes.

As regarding zinc-nickel alloy electrodeposition, measured frequencies were: $f_1 = 8.968$ MHz, $f_2 = 8.920$ MHz, $f_3 = 8.900$ MHz. For these depositions we used 60 s fixed time.

During the nickel and zinc-nickel electrodeposition process the current intensity was recorded, as it is presented in Figs. (2, 3). This behavior is similar to other experiments made without adding polyvinylpyrrolidone, but with other agents, like sodium saccharine (as brightness agent) or/and sodium lauryl sulfate (as wetting agent) [5-8]. A slow increase of current after 20 seconds is observed commonly.

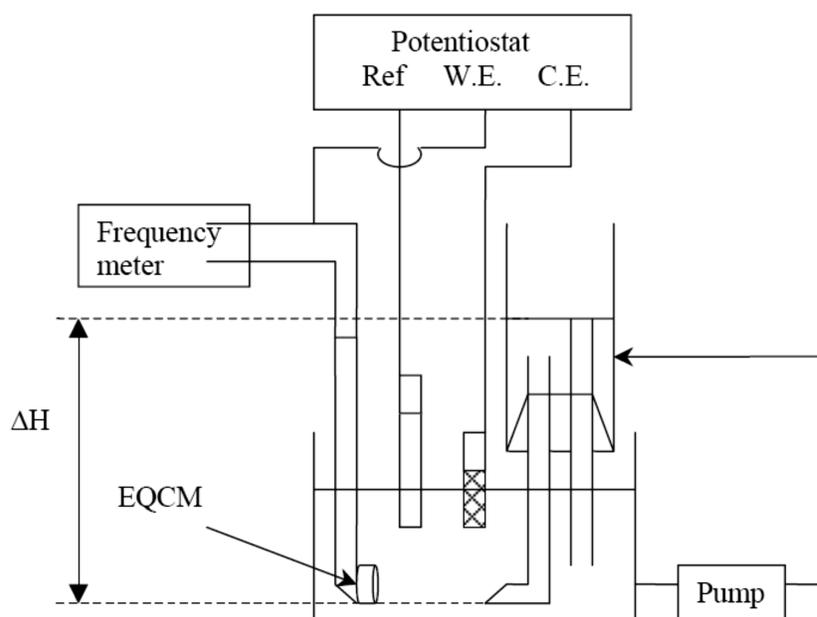


Fig. (1). Working scheme of an EQCM used for electrochemical studies.

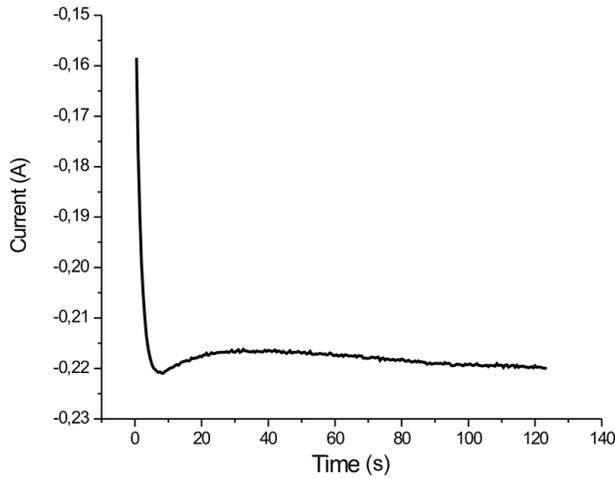


Fig. (2). Current vs time chart recorded during electrodeposition of nickel at 65°C and -1000 mV from the solution described as above and using Electrochemical Quartz Crystal Microbalance with a potentiostat-galvanostat PARSTAT 2273.

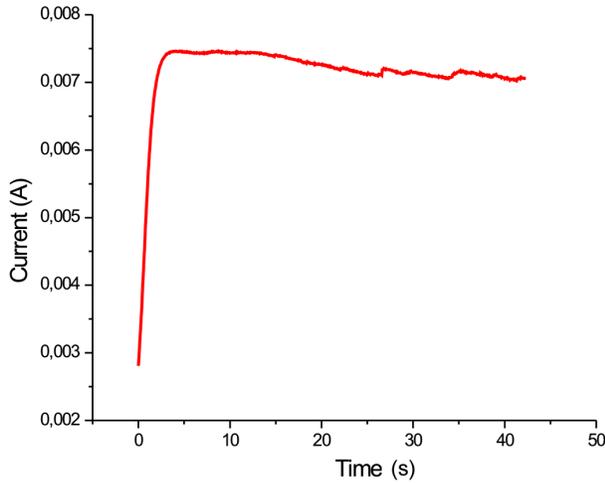


Fig. (3). Current vs time chart recorded during electrodeposition of a zinc-nickel alloy at 30°C and -1000 mV from the solution described as above and using Electrochemical Quartz Crystal Microbalance with a potentiostat-galvanostat PARSTAT 2273.

Using the recorded data and the relation between frequency and thickness of the layer $f = \frac{k}{d}$, where, k is the apparatus constant ($k = 1666 \text{ m} \cdot \text{s}^{-1}$ for this EQCM) and d is the thickness of the deposited layer, it was found:

$$d = \frac{k}{f} = \frac{1666}{8.95 \cdot 10^6} = 0.186 \text{ mm} \text{ For the initial thickness, and}$$

$$d' = \frac{f \cdot d}{f'} = 0.187 \text{ mm} \text{ For the final thickness, after electrodeposition.}$$

It results for the electrodeposited mass

$$m = (d' - d)\pi R^2 \rho = 0.001 \text{ mm} \cdot 3.14 \cdot 9 \text{ mm}^2 \cdot 8.9 \text{ g/cm}^3 = 0.251514 \mu\text{g}$$

That means on the other hand $8.9 \cdot 10^{-4} \text{ g cm}^{-2}$ the surface density of the deposited layer.

The calculated mass after Faraday law is $0.2371 \mu\text{g}$, and we could consider a good correlation, inside limits of experimental errors.

As regard zinc-nickel alloy, it is necessary to find the composition of the layer first. The analyses SEM-EDX were performed at INCDFM Bucharest-Magurele and also at A.I.I. Cuza University of Iasi (Figs. 4, 5). The investigation was performed by means of a SEM VEGA II LSH scanning electron microscope manufactured by TESCAN for the Czech Republic, coupled with an EDX QUANTAX QX2 detector manufactured by ROENTEC Germany. The microscope, entirely computer operated, contains an electron gun with tungsten filament that may achieve a 3nm resolution at 30KV, with a magnifying power between 13 and 1,000,000 X in the resolution mode, a gun potential between 200 V and 30 kV, a scanning speed between 200 ns and 10 ms per pixel. The working pressure is lower than $1 \times 10^{-2} \text{ Pa}$. Quantax QX2 is an EDX detector used for qualitative and quantitative micro-analysis in industry, research and education, which performs quantitative measurements without using specific calibration standards.

A percent of 42.32% was found for nickel and 57.68% for zinc. From these results an average density of the layer 7.88 g cm^{-3} .

After similar calculus on found $d_1 = 0.1857 \text{ mm}$, $d_2 = 0.1867 \text{ mm}$ and $d_3 = 0.1871 \text{ mm}$. On the first step a mass m_1 was deposited as follow:

$$m_1 = (d_2 - d_1)\pi R^2 \rho = 0.2228 \mu\text{g}, \text{ and on the second step}$$

$$m_2 = (d_3 - d_2)\pi R^2 \rho = 0.0891 \mu\text{g}.$$

For total we found a mass of $0.3119 \mu\text{g}$, which means more than Faraday law predicts for the same conditions ($0.19 \mu\text{g}$). Also we found a first step with rapid increase of the mass deposited and a second one with a smallest slope. Similar results were found by Volotkiene and co. [28].

A possible explanation for the mass increase more than Faraday law predicts, could be the precipitation of zinc hydroxide on the electrode surface. The hydrogen evolution which occurs in the vicinity of the cathode conducts to an increase of the value of pH. So it results in an increase of zinc hydroxide precipitation rate because this is less soluble than nickel hydroxide.

For mass evolution Faraday law could be modified in a manner to consider the processes which occur in the first step of the electrodeposition, for example:

$$m = [1 + f(t, \mu, \dots)] \frac{1}{F} \frac{A}{n} It, \text{ where,}$$

$f(t, \mu, \dots)$ is a special function which takes values

$f(t, \mu, \dots) = 0$ for $t \geq t_{\text{equilibrium}}$ and $f(t, \mu, \dots) \neq 0$ for $t \leq t_{\text{equilibrium}}$. In these relations μ is chemical potential of species which could affect chemical reactions, m is the deposited mass during time t of the process, F is the Faraday constant, A the atomic mass of the deposited metal, I the current intensity and n the electrovalence of the metal.

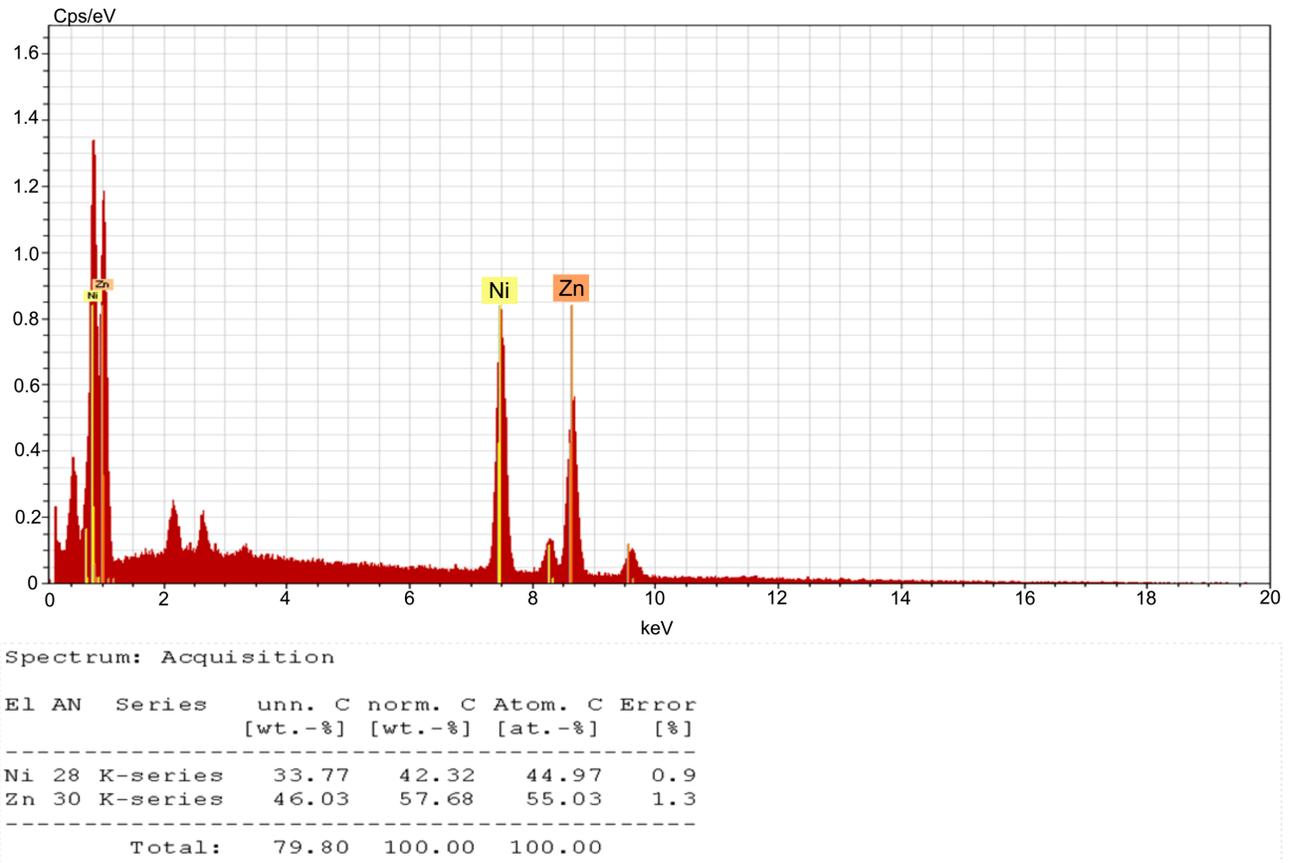


Fig. (4). Results of EDX analyses for zinc-nickel alloy deposited at 30°C and -1000 mV.

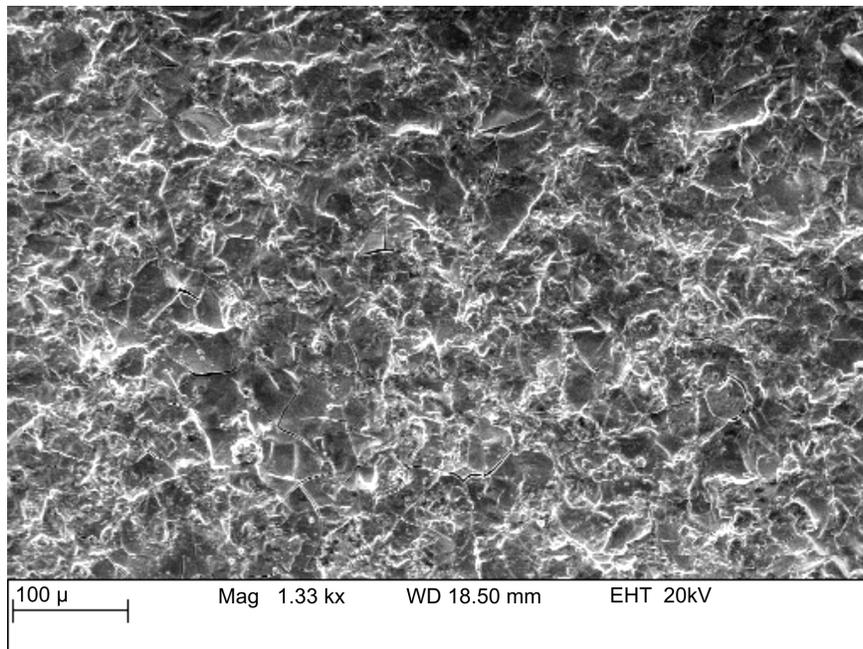


Fig. (5). SEM image of the zinc-nickel layer electrodeposited at 30°C and -1000 mV, 13300X.

4. CONCLUSIONS

Zinc-nickel alloy electrodeposition was studied using electrochemical quartz crystal microbalance. An increase in the mass rate deposited was observed, much more than Faraday law predicts. The precipitation of zinc hydroxide on the cathode surface occurs due to a local increase of pH and this could be a satisfactory explanation. Similar results were found for zinc-nickel alloy anomalous co-deposition and are coming to prove hydroxide suppression mechanism which could explain this type of electrodeposition for the iron group metals.

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