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Ph.D. Thesis

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# A study on pulse electrodeposition of Ni-Co alloys: physical and electrochemical characterisation

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## Introduction

In the past few years, the synthesis and the characterisation of nanostructured materials, chains of atoms and atomic clusters on the surface or even bulk materials, such as multilayers, and nanocomposites, was an important duty of material science. Applying the so-called nanoscience, a very important tool of future technologies, it is possible to produce nanosize mechanical machineries, manipulators and sensors in the range of few angstroms to several nanometers. Therefore, nanotechnology shows real benefits upon micro and macro techniques in the field of microelectronics, specially making chips and small devices.

Many techniques have recently become available for the production of nanostructured coatings. In addition to Physical Vapour Deposition (PVD), Chemical Vapour Deposition (CVD) ball milling and sol-gel techniques, electrochemical deposition is an efficient technique for the fabrication of such layers. Adhesive and compact surfaces including metals or alloy coatings can be electrodeposited in nanosize dimensions using the Pulse Electrodeposition (PED-technique).

In this work, I pulse plated well-adsorbed, compact Ni-Co coating in controlled film thickness. In any electrodeposition process, several parameters such as bath composition, pH, agitation, temperature as well as the applied current waveform, can govern the quality and composition of the deposited alloy. Unless the influence of these parameters on deposit properties is clearly understood, deposit quality and properties cannot be obtained systematically or reproducibly. Therefore, the purposes **of this work** were the followings:

- Investigations of three different baths that are commonly used in galvanotechnics for the production of Ni-Co alloys,
    - examine the morphology of the Ni-Co alloy layers deposited in different electrolytes;
    - examine the passive layer formation on Ni-Co alloys in different electrolytes;
- investigations of the surface morphology, composition and metallic phases of the pulse plated Ni - Co alloys, deposited from chloride containing solution, in the frame of the variation of the pulse deposition parameters, namely the on-time, off-time, peak current density and the temperature;
- to study the passivity of the pulse plated alloys in alkaline solution and find the best alloy composition and morphology for the most stable passive layer formation.

## Experimental

This work is divided onto three parts. In the first part of the experimental work, I examined the deposition kinetic of Ni, Co and Ni-Co in different baths (sulfamate, Watts, Chloride-containing baths) that are commonly used for the production of nanostructured materials in the galvanic industry. Then, I studied the proneness for passivity in the baths that are used for the electrodeposition by the means of cyclic voltammetry (potential range: –700 mV - -100 mV) and chronoamperometry on Ni-Co samples that were deposited from the different baths by the pulse parameters peak current densitiy of 0.05 A $cm^{-2}$, on-time and the off-time at a value of 5 ms, at 35$^{o}$C. Following, I compared the cross section morphology and the microhardness of the different layers. Transmission Electron Microscope were used for the morphological characterisations and the cross sections of samples for TEM were made by $Ar^{+}$ ion milling.

In the second part of this work, I presented the effect of the variation of the pulse parameters (peak current densitiy of 0.5 – 1 A $cm^{-2}$, on-time of 1-3 ms and the off-time 50-250 ms) and of the temperature ,25-35$^{o}$C on the morphology of the Ni-Co alloy coating, deposited from chloride containing bath. The influence of pulse parameters on the composition, morphology and the crystal structure of the alloy were examined by scanning electron microscope and X-ray diffraction measurements.

In the third part of the experimental work, electrochemical tests were carried out on Ni-Co samples, deposited from chloride solution by different pulse parameters (peak current densitiy of 0.5 – 1 A $cm^{-2}$, off-time 50-250 ms, on-time of 1ms) at the temperature of 35°C. Based on cyclic voltammetry experiments carried out in the potential range of –300 mV-+450 mV, I deduced the type of the oxide that formed on the surface in the function of the potential and I allocated the range of the passive state. Then, I examined the kinetics of passive layer formation on Ni-Co at the potential of + 0.43 V and estimated the thickness of the oxide layer.

## Results

According to the outcome of this work, hereby, I state the main results of the electrochemical preparation and testing of pulse plated nanostructured Ni-Co alloys.

1, Production of Ni-Co alloys, was successfully completed from chloride, Watts and sulfamate bath by applying rotating disc voltammetry. *I obtained from the measured potential shift in the different baths that the probability for a kinetic control was the highest in the chloride bath and decreased in Watts and sulfamate bath, respectively. The formation of the coating with the less stress* *would be possible the most likely using the sulfamate bath induced by a lower hydrogen evolution for a given potential or current.*

2, Production of Ni-Co alloys by pulse reverse plating is a promising technology. However, for the successful application of this technique, it is crucial to examine the passive layer formation in the different baths that are usually used for the production of nanostructured materials in the galvanic industry. *Based on my experimental work, I pointed out that those alloys that were deposited from the chloride containing electrolyte revealed a lower proneness to passivation.* The ability for passive layer formation increased from chloride to Watts and sulfamate bath, respectively.

3, The deposited coatings were homogeneous throughout the whole cross section of a Ni - Co alloy layer. Notable difference in the microstructure between the different Ni – Co samples related to the electrochemical nature of the plating baths and the difference in the hydrogen overpotential in different electrolytes. According to my hardness measurements, the highest hardness was achieved in the case of the deposit pulse plated from chloride bath. *I allocated that different microhardness could be achieved for a fixed composition by obtaining different microstructures; nevertheless, changing the amount of Co in the alloy has a pronounced effect on the microhardness of the Ni-Co alloy, too.*

4, According to the previously demonstrated results, achieved by electrochemical and physical testing methods, *I proved that out of the three different baths, the most suitable solution for pulse plating the most homogeneous and hardest Ni-Co alloy was the chloride bath.*

5, Since I stated that the best solution for pulse plating is the chloride bath, my attention was focused on the microscopic and EDX studies of the alloys deposited from chloride bath. Therefore, I examined the influence of the pulse deposition parameters on the microstructure and the composition of the deposited alloys. *My result pointed out that the pulse parameters influenced both the structure and the composition of the alloy. The most compact layer was obtained by applying pulse deposition parameters of lower current densities and longer off-time.*

6, According to my electrochemical tests carried out in 1 M NaOH solution, both the alloy morphology and the Co content of the alloy determine the rate of the dissolution and the stability of the formed oxides of Ni-Co alloy. The anodic peaks, ascribing to the formation of Ni and Co oxides, reduced dramatically in the second cycle of the cyclic voltammetry indicating the passivity of the Co-sites. *Therefore, I stated that the lowest dissolution rate* *was found on the sample that was deposited by lower current density and longer off-time.*

7, I used chronoamperometry measurements for the examination of the kinetics of the oxide layer formation of the Ni-Co alloy. Oxide layer growth calculation showed that the Co content of the alloy strongly influenced the film formation and the type of the oxide layer. It was likely that Co blocked the oxide layer growth. *Based on my experiments, I predicated that the most compact and stable oxide layer formed on the sample that were deposited by lower current density and longer off-time.*

**Applications**

Nickel-based alloys are used in a wide variety of applications for aerospace industry, energy generation and corrosion protection, especially in environments where materials have to withstand high temperatures and oxidizing conditions. Ni-Co alloys have been gaining popularity because they have been found to have a range of uses other than corrosion resistance; for example, they are used as electro-catalysts, as magnetic materials or have applications in hydrometallurgy.

## Publications

*Papers in national and international journals*

1. **B. Tury**, M. Lakatos-Varsányi and S. Roy, Ni-Co Alloys Plated by Pulse Currents Surface and Coatings Technology, accepted for publication
2. **B. Tury**, M. Lakatos-Varsányi and S. Roy, Effect of Pulse Parameters on the Passive Layer Formation on Pulse Plated Ni-Co alloys submitted for Applied Surface Science (under publication)
3. **Barbara Tury**, Martina Halmdienst, Wolfgang E.G. Hansal, Magda Lakatos Varsányi, Wolfgang Kautek: Electrochemical characterisation of nickel cobalt electrolytes -for pulse reverse plating, submitted for Electrochimica Acta (under publication)
4. **B. Tury**, G. Z. Radnóczi, G. Radnóczi, M. L. Varsányi, Microstructure properties of pulse plated Ni-Co alloy, Electrochemistry Communications (under publication)
5. Lakatosné Varsányi Magda, Mikó Annamária, **Tury Barbara**, Papp Katalin, Kálmán Erika Nanostructured coatings in the field of corrosion protection (in Hungarian): Korróziós Figyelő 2002, XXXXII, 4, p. 107-112

6. **Tury B.**, Electrochemical Deposition and characterisation of nanostructured Ni layers, *Technika Műszaki szemle,* 2001*,* 44,12, p.43-45 (in Hungarian)

*National and international conferences, seminars*

1. Magda Lakatos Varsányi, A. Miko, **B Tury**, L.K. Varga, Pulse Electrodeposition of Nanocrystalline Layers, EDNANO, Dresden, Germany,16-18 Március, 2006.
2. Magda Lakatos Varsányi, A. Miko, **B Tury**, L.K. Varga, Pulse Electrodeposition of Nanocrystalline Layers, 1st European Pulse Plating Seminar, Vienna, Austria Március 10-12, 2006
3. **B. Tury**, S. Roy, M.Lakatos Varsányi: Pulse plating of Ni-Co alloy, ELECTROCHEM 2004, Leicester, United-Kingdom, 12-15 September, 2004
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6. M. Lakatos Varsányi, **B. Tury**, A. Miko, E. Kálmán Production and characterisation of nanostructures Second International Conference on Advanced Materials and Structures 19-21 September 2002, Timisoara, Romania
7. Á. Kriston, M. Lakatos-Varsányi, **B. Tury**, E. Kálmán: Study the corrosion properties of nanostructured coatings by noise measurement, International Workshop on Nanochemistry, Vienna, Austria, 26-29 September 2002 (Poster P51)
8. M. Lakatos Varsányi, **B. Tury**, A. Mikó and E. Kálmán: Electrochemical Deposition and Examination of nanostructured Ni layers, Segovia, Spain, September 03-07, 2001 (Poster PB-48)