Barbara Tury

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

Supervisor: prof. Dr. Magda Lakatos Varsányi
Senior lecturer
Bay Zoltán Foundation for Applied Research, Institute of Material Science and Engineering
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1. Introduction

There are several motivations for producing pure metal and alloy coatings, e.g., improving the lifetime of a base metal, production of electromechanical devices, or enhancing the catalytic properties of a material. Therefore, an important duty of the plating industry is to develop layers in a controlled thickness with excellent corrosion protection, high strength, formability, coating uniformity, and appearance.

One method of fabricating pure metal and alloy coatings is electrodeposition. Electrodeposition from aqueous media is a relatively cheap, room temperature and atmospheric pressure process and requires low capital expenditure, which makes it an attractive method. However, the widely used direct current (DC) technique is not entirely perfect for the production of smooth, adhesive and poreless coating surfaces. In order to improve the previously mentioned surface properties, a new technique, namely pulse plating electrodeposition (PED), was developed. In addition, pulse plating has been identified as a means to lower residual stress, avoid incorporation of other bath components, and to control the deposit composition and morphology [1].

In this work, the pulse electrodeposition of nanostructured Ni-Co alloys was carried out in order to obtain adhesive and compact surfaces with controlled film thickness. Despite the large volume of nickel-cobalt alloy co-deposition studies available using DC-technique, only a preliminary study has been carried out on the pulse plating of these alloys [2]. Although some workers have used pulse plating to deposit Ni-Co alloy multilayers and sandwiches, the focus of their studies was mainly to examine the magnetic properties [3,4]. Therefore, the aim of this work is to examine the changes of the qualitative and quantitative parameters of the alloy coating with the variation of the pulse parameters and the temperature.
1.1. Main aims

Nickel-based alloys are used in a wide variety of applications for aerospace, energy generation and corrosion protection, especially in an environment where materials have to withstand high temperatures and oxidizing conditions [5,6]. 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 [7-11].

The development of the scientific and technological tendencies in the past few decades made claims on introducing more effective production processes or required the development of new types of materials. The main aspects that should take into consideration in both cases are the structure and the functional application of the materials produced. Electrodeposition is an atmospheric pressure process and requires low capital expenditure, which makes it even more attractive. However, 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 galvanotechnique for the production of Ni-Co alloys,
  - examine the morphology of the deposited Ni-Co alloy layers
  - examine the passive layer formation on Ni-Co alloys in the 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.

2. Background and literature review

2.1. Nanomaterials and pulse plating

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. (Nanoparticles are considered to be in the range of 10 nm < d < 50 nm, beyond 100 nm one talks about bulk materials.) Therefore, nanotechnology shows real benefit upon micro and macro techniques in the field of microelectronics, specially making chips and small devices. Some of these units are coated by thin layers, which enhance their physical and mechanical properties.

A variation in the particle size determines the density of the surface sites of special activity as well as the surface energy and so the new material’s thermodynamic properties.
One of the effects of a decrease in the grain size is the narrower bonds in the clusters sitting on the surface, affecting a change in the crystallographic geometry and in the electronic structure, which results in better catalytic properties compared to micro or macro structured materials. Another effect of the reduced grain size appears in the mechanical properties of the layers: if a crack is initiated on the outside, it is unable to move further inside, since the nanostructured bricks stop them. The above mentioned property variations are important tools both for as an elementary point of view and for developing new technologies [12,13]

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 [8] and sol-gel techniques [14], electrochemical deposition is an efficient technique for the fabrication of such layers. The main advantages of the electrochemical deposition are the low operating costs, the easy control of the film thickness by charge transfer and high efficiency. However, those coating layers that are produced at a high electrode potential or current by the commercially used direct current technology may become spongiest and porous.

Adhesive and compact surfaces including metals or alloy coatings can be electrodeposited in nanosize dimensions using the Pulse Electrodeposition (PED-technique). Main motivations for applying this method over DC plating [15,16] are as follows:

- better current distribution
- controlled mass transfer conditions
- controlled microstructure of deposits
- controlled composition of the alloy deposition
- reduced porosity and stress in the deposit
- improved uniformity of the layers
- lower hydrogen embrittlement in the coating
It was first discovered in the early 1950s that direct current pulse deposition conferred important benefits to 24 K acid gold, which were unobtainable with standard DC. It was obvious to many that pulse depositing might be useful for controlling the physical properties of electrodeposits [17]. An example that presents the enhanced properties of the deposit produced by PED technique is the deposition of Co-W coating. This alloy’s brittlement was reduced, when it was produced by PED technique, and a similar effect was found in the case of chromium and palladium deposits [18]. The principle of pulse plating method is based on the periodical change or stop of the direct current/potential, which results surface properties that cannot be achieved with continuous DC electrodeposition. Of the several pulse waveforms that are applied in PED the simplest one is the square wave current waveform [19]. A schematic view of the different forms of the pulses is shown in Fig. 1.

The main application area of the waveforms b-e in Fig. 1 is mainly for the deposition of multilayers and sandwiches, in the case of the electrodeposition of alloys and pure metals the waveform in Fig. 1a is usually used. In the period of the galvanostatic pulse in Fig. 1 the peak current \((j_{p,1})\) is the cathodic current during time portion, when current output is on, other words: \(\text{on-time} (t_{on})\), and \(j_{p,2}\) the cathodic or anodic current during the electrolysis. The period, when there is no current flow between the two electrodes is the \(\text{off-time} (t_{off})\).
Fig. 1: Different types of pulse waveforms: a: pulse; b: superimposed pulse; c: pulsed pulse; d: duplex pulse; e: pulse-on-pulse. $j_{p1}$: cathodic peak current, $j_{p2}$: anodic / cathodic peak current.
When a current, which is supplied by the generator, is changed abruptly from one value to another, the electrode potential and the state of the double layer also change. In this case, the electrode behaves like a capacitor, where the charging of the double layer requires certain time, which depends on the current density and on other physicochemical parameters of the system. For particular reasons, the charging time should be much shorter than the pulse duration; otherwise, the current pulse is strongly distorted. Moreover, the time required for discharge of the double layer should be much shorter than the on-time and the off-time between the pulses. Pulses in the frequency range, where capacitive effects are relevant do not significantly influence the current efficiency, but affect the amplitude of the pulses and hence, the structure and the properties of the deposit [20].

However, the limitations of on- and off-time due to the mass transport effects cannot be too strict. In the immediate vicinity of the cathode, the concentration decreasing during the pulses and relaxing in the interval between them. In the case of a very short off-time, the diffusion layer does not time to extend very far to the solution and therefore, does not extend to the region, where convection takes over the mass transport. Therefore, in the case of pulse plating, two distinct diffusion layers exist, which affect the deposition conditions (a) the pulsating diffusion layer and (b) the outer diffusion layer. Through the outer diffusion layer, cations are supplied towards the cathode during the off-time limiting the average current density. The maximum pulse duration is called transition time. In the case of pulse deposition, the pulse duration should not exceed the transition time and the average current density cannot exceed the DC limiting current density [21].

According to the enhancement of mass transport, in the case of pulse electrodeposition, the range of the applied current density is as high as A/cm² and the pulse duration time is in 1-300 ms range. PED technique can be described by the following parameters:
The active time ratio of the cycles in a deposition period, the so-called duty cycle ($\gamma$) is defined by equation:

$$\gamma = \frac{t_{on}}{t_{on} + t_{off}}$$  \hspace{1cm} (1)

Then, the average value of the current, which is a comparative value of DC current, is given by:

$$j = j_p \cdot \gamma$$  \hspace{1cm} (2)

2.2. Electrodeposition of alloys

By applying pulse-plating technique, it is possible to produce adhesive and dense layers of pure metals and alloys in nanosize. Since the purpose of this work is pulse electrodeposition of alloys, in the next paragraph a short introduction into the alloy electrodeposition is given. According to the New International Dictionary [22] an alloy is

“Substance composed of two or more metals intimately mixed and united, usually by being fused together and dissolving in each other when molten”

However, this definition is very narrow, since it assumes that alloys can be formed only when they are molten and dissolve in each other. If this were so, the formation of many common alloys (e.g. Ag-Ni) would not be possible, though it is produced by powder metallurgy. Therefore, practically it can be said that a metallic alloy is a material that has metallic properties and is composed of two or more chemical elements of which at least one is a metal and the individual constituents cannot be seen by the unaided eye [23].
The scope of the alloy electrodeposition and, therefore, the reason for its wide application is that metal / alloy properties vary over a wide range. These properties can be tailored for a certain purposes. (eg. cobalt is added to gold or iridium to platinum in order to make it harder). Furthermore, alloy production costs are much lower than those of the pure metals.

In the case of alloy electrodeposition, at least one of the metals should be able to deposit individually and their deposition potentials must be reasonably close enough [24]. This requirement is based on the fact that the more noble metal deposit preferentially. During the alloy electrodeposition the current must be altered, that can be achieved at high current densities.

Alloys can be grouped in many ways, but one of the most important groupings is weather they are homogenous or heterogeneous. The homogenous, one phase alloys can be *solid solutions*, when a homogeneous crystalline phase contains two or more chemical phases. Both interstitial and substitution solutions are possible. *Intermetallic compounds* refer to when two metals have a distinct chemical formula, making a compound. Phase diagrams will show that they exist only in a narrow range. Heterogeneous or two-phase alloys are the mixture of a solid solution, an intermetallic compound, or virtually unalloyed elements. The alloys produced through electrodeposition belong to the first group.

For many applications, a certain composition of the alloy is required for reaching the relevant physical, chemical or mechanical phenomena. In the case of electrochemical deposition, the composition of the alloy clearly depends on the deposition kinetics of the alloy elements. According to Landolt [7], if the Tafel slopes of electrode reactions of the two components are the same, then the (pulse) deposition parameters have no influence on the alloy composition, however, if their slopes are dissimilar or the electrode reactions are of different kinetics, then (pulse) deposition parameters have a strong effect on the alloy
composition. Therefore, polarisation curves are of special interest reflecting to the nature of
the whole deposition process and providing information on the deposition mechanism. One
relation between current density and potential curves of the individual metals of the
electrodeposited alloy is illustrated in Fig. 2. The reduction of metals of \( M_1, M_2, M_3 \) in the
electrolyte are symbolised by the curves named 1, 2, 3.

![Fig. 2. Polarization plot of the metal ions reduction in the case of metal alloy deposition](image)

The curves must overlap for co-deposition to take place, so alloy formation
supposedly does not occur until potential B is exceeded. In the potential range of BC, at a
constant potential, a binary alloy composed of \( M_1 \) and \( M_2 \) is deposited, passing the potential
value of C, a three-component alloy is expected. The composition of a metal alloy is assumed
to be given by the ratio of the current densities e.g. the ration of one metal to the other in the
alloy deposited at the potential D is assumed to be \( DF / DE \) [25,26].
The type relation between the quantity of the current and the potential is essential, when the kinetics of the electrochemical reaction is studied. Generally, two types of deposition kinetics exist. If the element follows kinetic controlled deposition then the Tafel–equation describes the rate of the electrode process as a function of $\eta$ and as it is stated in Eq. 3:

$$\log \left( I \right) = \log I_0 - \frac{\alpha n F}{2.3 R T} \eta$$

(3)

where $I$ is the current density, $I_0$ is the exchange current density, $\alpha$ is the transfer coefficient, $\eta$ is the overpotential, $n$ the number of electrons exchanged, $F$ the Faraday constant, $R$ the gas constant and $T$ the temperature.

If the deposition process is under mass transport control then a thin layer of thickness, $\delta$, exists near the electrode, which is called Nerst diffusion layer and which is assumed to be completely stationary. Through this layer, transport takes place only by diffusion and by the transport of electric field. The latter contribution can be negligible by adding to the solution large concentrations of an electrolyte that does not participate in the electrode reaction. In all cases, in which diffusion occurs, the concentration profile and the thickness of the stagnant layer depend on the rate of the stirring in the solution. On the other hand, even without any forced convection, a limiting current is found, due to the natural convection based on the density differences caused by the electrode reaction. The limiting current in the Nerst diffusion layer can be determined as (Eq. 4):

$$I_l = \frac{n F D C_0^\infty}{\delta}$$

(4)

where $I_l$ is the limiting current density, $D$ is the diffusion coefficient, $C_0^\infty$ is the bulk concentration and $\delta$ is the diffusion layer thickness.
As can be seen from Eq. 4, the limiting current depends on the thickness of the diffusion layer, thus it is necessary for any measurements to apply well-controlled conditions. Considerable information can be obtained about the kinetics of the electrode reaction of the alloy and its constituent by using rotating disc electrode (RDE). Levich analysed the hydrodynamics near the interface of rotating disc electrode and obtained that the thickness of the diffusion layer is given by Eq. 5:

\[ \delta = 1.61 D^{1/3} \nu^{1/6} \omega^{-1/2} \]  \hspace{1cm} (5)

where \( \nu \) is the kinematics viscosity and \( \omega \) is the angular velocity. Substituting Eq. 5 in Eq. 4, Eq. 6 expresses the Levich-equation:

\[ I_l = 0.62 nFD^{2/3}C_0^{1/6} \nu^{-1/6} \omega^{1/2} \]  \hspace{1cm} (6)

According to Eq. 6, the ratio between the square-root of the rotation speed and the limiting current is linear. Overall, based on the Levich equation, it can be stated that if the intersection of a \( I - \omega^{1/6} \) plot is zero, then the electrode reaction is mass transport controlled. In any other cases, the electrode reaction is under mixed or kinetic control.

2.3. Ni-Co alloys

A large number of investigations have been carried out on the required electrolytes, mostly sulphate and sulfamate baths and the additives used for the electrodeposition of Ni-Co alloys. The main electrolyte compositions are summarised in Table 1.

Experimental studies on the electrodeposition of Ni-Co alloy were carried out by a number of researchers [27-34]. C. Fan and co-workers investigated the effect of trisodium
citrate (Na$_3$C$_6$H$_5$O$_7$ · 6 H$_2$O) on the deposition kinetics of Ni(II), Co(II) and the Ni-Co alloy [27]. They used two types of electrolytes, one with only metal chlorides in solution and another one with trisodium citrate. They applied two different currents to plate Ni-Co alloys and found that whereas in the chloride-only-solution the alloy deposition was anomalous, it was not so in the solution containing trisodium citrate. They discussed this as a consequence of the formation of Co-citrate complex, which inhibited Co(II) reduction. A model for sulphate electrolytes by Zech et al. [3] showed that under kinetic deposition the higher Co deposition rate suppressed the deposition rate of the Ni.

An extensive voltammetry study by Bai et al. [28] was performed to examine the effect of temperature and potential range on the composition and the morphology of the alloys. The authors observed that if the applied potential range in the cyclic voltammetry experiments included the anodic oxidation region, anomalous deposition did not occur. They attributed this to the behaviour of adsorbed mono-hydroxides of cobalt and nickel. They explained that Co(II) and (Ni(II)) ions react with OH$^-$ resulting in the formation of metal mono-hydroxides which adsorb on the deposit surface.
Table 1. Different electrolyte compositions for Ni-Co alloy deposition

<table>
<thead>
<tr>
<th></th>
<th>Citrate bath (mol dm⁻³)</th>
<th>Sulfamate bath (mol dm⁻³)</th>
<th>Acetate bath (mol dm⁻³)</th>
<th>Sulphate bath (mol dm⁻³)</th>
<th>Sulphate-Chloride bath (mol dm⁻³)</th>
<th>Chloride bath (mol dm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NiSO₄</td>
<td>1</td>
<td>0.17</td>
<td>0.05</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiSO₄·7H₂O</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-acetate</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ni-sulfamate</td>
<td>0.50-1.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCl₂</td>
<td></td>
<td></td>
<td></td>
<td>0.05-0.2</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiCl₂·6H₂O</td>
<td></td>
<td></td>
<td></td>
<td>0.84</td>
<td>0.7-1</td>
<td></td>
</tr>
<tr>
<td>CoSO₄</td>
<td>0.02</td>
<td></td>
<td></td>
<td>0.01-0.16</td>
<td>0.09</td>
<td></td>
</tr>
<tr>
<td>CoSO₄·7H₂O</td>
<td></td>
<td></td>
<td></td>
<td>0.007-0.02</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Co-sulfamate</td>
<td>0.044-0.07</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>CoCl₂</td>
<td></td>
<td></td>
<td></td>
<td>0.068</td>
<td>0.01-0.16</td>
<td></td>
</tr>
<tr>
<td>CoCl₂·7H₂O</td>
<td></td>
<td></td>
<td></td>
<td>0.10-0.40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Na₃C₆H₅O₇₇</td>
<td>0.20</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃Citrate</td>
<td></td>
<td></td>
<td></td>
<td>0.12</td>
<td></td>
<td></td>
</tr>
<tr>
<td>H₃BO₃</td>
<td>0.35-0.64</td>
<td>0.65</td>
<td>0.40</td>
<td>0.40</td>
<td>0.40-0.50</td>
<td></td>
</tr>
<tr>
<td>NaAc</td>
<td></td>
<td></td>
<td></td>
<td>0.5</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Saccharin</td>
<td></td>
<td></td>
<td></td>
<td>0.0075</td>
<td>0.0003</td>
<td>0.0075</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td></td>
<td></td>
<td></td>
<td>0.10-0.70</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NaCl</td>
<td>0.70</td>
<td></td>
<td></td>
<td>0.70</td>
<td>0.10-0.70</td>
<td></td>
</tr>
</tbody>
</table>

Normally, due to the greater adsorption of Co(OH)⁺, the Co content in the alloy was higher, which led to anomalous deposition. The formation mechanism of metal hydroxide ions during the electrolysis is expressed in the following equations:
The tendency for OH⁻ inclusion in the coating is the highest in chloride solutions and is lower in sulfate and sulfamate solutions. However, when the electrode potential is kept in the anodic region, the adsorbed mono-hydroxides dissolved and the deposition of the Ni(II) on the coating surface became dominant, so the anomalous deposition kinetics were not observed.

Correia et al. [30], on the other hand, studied the effect of changing electrolyte formulation on deposit composition. They used different metal ion ratios of Ni(II) and Co(II), ranging from 1-5 and examined its effect on alloy composition and morphology. They found these alloy properties to be strongly dependent on the electrolyte formulation and applied deposition potential. By increasing the content of Ni(II) in the electrolyte, the morphology of the deposit changed from fibrils to a nodules, as would be expected when the alloy composition changed from cobalt-rich to nickel-rich phase.

Myung et al. [31] investigated the relationship between the crystal structure, phases and the corrosion resistance of the alloy. They found three different crystal structures, controlled by the Co-content. At low cobalt content, pure face centred cubic structure (fcc) (which would exist for pure nickel) was found. As the content of cobalt increased, both fcc and hexagonal (hcp) phases appeared, and for a Co-rich alloy pure hcp was observed. The appearance of these phase structures controlled the grain size, and hence, the corrosion
properties of the alloy. Since the highest grain size was found for the pure fcc phase, better corrosion resistance was also observed for this alloy.

Generally, investigations on Ni – Co alloys with different composition and microstructure show that physical and electrochemical properties strongly depend on the Co – content of the alloy. Myung at al [31] showed the coexistence of hcp and fcp phase between 70 – 80 % of Co content. In this region the grain size is reduced and the corrosion resistance decreased. Wang et al. observed that [35] the microhardness of the Ni – Co alloy represent a maximum at a Co – content of 49% in the alloy. Applying different plating technique but obtaining a constant Co content, the hardness of the Ni-Co alloy is increased with 20 % in the case of pulse current and with 70 % in the case of pulse reverse electrodeposition [36]. Similar trend was observed by Wattson [37].

Under certain conditions a metal alloy coating builds up a thin oxide layer on their surface that is usually energetically more stable than the coating itself; therefore, it performs less chemical activity [5,6]. From corrosion protection view, the formed oxide film fulfils the requirements if it is dense, has good adherence to the coating and insoluble in the adequate electrolyte media [38].

Numerous works have examined the anodic-cathodic behaviour of Co oxide / hydroxide [39,40], Ni oxide / hydroxide [41,42] and Ni-Co oxide / hydroxide layers [14,43-48]. When subjected the Ni-Co surface to anodic polarisation, a single-phase mixed metal hydrous oxide formed, in which the Co$^{3+}$ occupied the Ni$^{3+}$ and the Ni$^{2+}$ sites in the lattice [46]. Co content up to 10 atomic % in the alloy does not affect the structure of the nickel hydrous oxide. It was also observed that, however the $\alpha$-Ni(OH)$_2$ film completely oxidised, Co ions did not participate in the electrochemical reaction since the oxidation state of Co did not change during the potential scan.
Serebrennikova et al. [47] doubted the Co inactivity during the electrochemical reaction. Using maximum film charge density measurement on Ni-Co oxide, that was correlated with the complete Co and Ni content in the films, they stated that Ni and Co oxidation / reduction process occurred, which resulted in the precipitation of a mixture of Ni(OH)$_2$ and Co(OH)$_2$ on the surface.

The possible general oxidation process for Ni [48] and Co [40] is

\[ 3H_2O + Me \rightarrow Me(OH)_2 \cdot (H_2O) + 2H^+ + 2e^- \quad (11) \]

and

\[ Me(OH)_2 \cdot (H_2O) + OH^- \rightarrow MeOOH \cdot (H_2O)_{1+x} + e^- + (1-x)H_2O \quad (12) \]

where Me symbolises the Co and Ni species.

A model was proposed for the mass transport of OH\(^-\) ions in the oxide film during its formation, based on mass changes measurement monitored by Electrochemical Quartz Crystal Microbalance (EQCM), for the duration of the charging / discharging reaction on 50:50 Ni-Co films in alkaline solution [14]. According to this model, water expelled from the oxide film in the period of the oxidation process and injected to the oxide film during the reduction process [49], therefore, the redox reaction for Ni-Co oxide materials in alkaline solution could be written as:

\[ Me^{2+} \text{oxide} + 2OH^- \leftrightarrow Me^{3+} \text{oxide} \cdot 2OH^- + e^- \quad (13) \]

Pulse plated coatings form more compact layers and perform less stress in the surface coating than that of in the case of direct current deposited coatings, therefore, the oxide films, which are developed on pulse-plated coatings, is expected to exhibit more stable form over direct current plated coatings.
To prove this assumption it is essential to get knowledge on the properties and the kinetic characteristics of the oxide film that forms on the pulse plated coating surface. Therefore, in this study, the deposition kinetic of the Ni-Co alloy and its constituent, the morphological characterisation, the electrochemical behaviour and the growth mechanism of the oxide layer during the oxide layer growth on pulse plated Ni-Co alloy are presented.

3. Experimental results

3.1. Materials and methods

3.1.1. Electrolytes

For the examination of the deposition kinetics of the single alloy elements, pure Ni solution was prepared from sulfamate, Watts, chloride plating baths respectively, and pure Co solution, prepared from chloride salt, were used. The electrodeposition of Ni-Co alloys was carried out from sulfamate, Watts, chloride types of baths using analytical reagent grade chemicals in order to exam the passive layer formation in the above mentioned three electrolytes. The temperature of these baths was kept constant at 35°C for all experiments.

Electrodeposition of Ni-Co alloys for studying the morphology as well as the electrochemical properties and the passive oxide layer formation in alkaline solution in the frame of pulse parameters was carried out from the chloride-based electroplating bath. The composition of the different baths and their nomenclature are shown in Table 2.
### Table 2. Different electrolyte compositions for Ni-Co alloy deposition

<table>
<thead>
<tr>
<th>Bath type</th>
<th>Chemicals</th>
<th>Composition</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfamate bath</td>
<td>Ni-sulfamate 1.5M</td>
<td>1.5M</td>
</tr>
<tr>
<td></td>
<td>Ni-bromide 0.04M</td>
<td>0.04M</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·6H₂O 0.06 M</td>
<td>0.06 M</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃ 0.6M</td>
<td>0.6M</td>
</tr>
<tr>
<td></td>
<td>C₁₀H₅(NaSO₃)₃·H₂O 0.01 M</td>
<td>0.01 M</td>
</tr>
<tr>
<td>Chloride bath</td>
<td>NiCl₂·6H₂O 0.6 M</td>
<td>0.6 M</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·6H₂O 0.06 M</td>
<td>0.06 M</td>
</tr>
<tr>
<td></td>
<td>NH₄Cl 0.7 M</td>
<td>0.7 M</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃ 0.1M</td>
<td>0.1M</td>
</tr>
<tr>
<td></td>
<td>C₁₀H₅(NaSO₃)₃·H₂O 0.01 M</td>
<td>0.01 M</td>
</tr>
<tr>
<td>Watts type bath</td>
<td>NiSO₄·6H₂O 0.170 M</td>
<td>0.170 M</td>
</tr>
<tr>
<td></td>
<td>NiCl₂·6H₂O 1.250 M</td>
<td>1.250 M</td>
</tr>
<tr>
<td></td>
<td>CoCl₂·6H₂O 0.06 M</td>
<td>0.06 M</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃ 0.650 M</td>
<td>0.650 M</td>
</tr>
<tr>
<td></td>
<td>C₁₀H₅(NaSO₃)₃·H₂O 0.01 M</td>
<td>0.01 M</td>
</tr>
<tr>
<td>Co bath</td>
<td>CoCl₂·6H₂O 0.06 M</td>
<td>0.06 M</td>
</tr>
<tr>
<td></td>
<td>H₃BO₃ 0.650 M</td>
<td>0.650 M</td>
</tr>
<tr>
<td></td>
<td>C₁₀H₅(NaSO₃)₃·H₂O 0.01 M</td>
<td>0.01 M</td>
</tr>
</tbody>
</table>

### 3.1.2. Deposition parameters

*Comparison of sulfamate, Watts and chloride baths*

For comparison of the voltammograms for the Ni-Co alloys deposited in the three different plating electrolytes peak current densities of up to 0.05 A cm⁻² were applied using a computer controlled PE86 Plating Electronic pulse reverse power supply system. Both the on-time (t_on) and the off-time (t_off) were kept constant at a value of 5 ms in each experiment. A Pt-Ti basket, filled with nickel pellets acted as a counter electrode.
Electrodeposition from chloride bath to study the physical and the electrochemical properties

An Axel Akerman computer controlled system with peak current densities of up to 1 A cm$^{-2}$ were applied to prepare the Ni-Co layers for the morphology and passive oxide layer studies. In these cases, the on-time ($t_{on}$) was kept at values of 1 and 3 ms, whilst the off-time ($t_{off}$) was set to either 50 or 250 ms. Applied current density altered between 0.5 – 1 A cm$^{-2}$. A Pt sheet acted as the anode material, which was kept 3 mm distance from the cathode material. Copper and steel discs, with an area of 0.5 cm$^{2}$ were used as substrates. Before each experiment, they were polished with emery paper and washed in isopropyl alcohol in an ultrasonic bath. Relatively thick (4µm) alloy deposits were used for the physical and electrochemical characterisation of the alloy layers that were pulse plated by a constant deposition period of 1800s.

Electrodeposition from chloride bath to study the kinetic of passive layer formation

In these cases, the on-time ($t_{on}$) was kept at values of 1 ms, whilst the off-time ($t_{off}$) was set to either 50 or 250 ms. Applied current density altered between 0.5 – 1 A cm$^{-2}$. Thin layer (a few atomic layer) alloy coatings were deposited by applying constant charge of 187 mC cm$^{-2}$ in order to test the passive layer formation on the Ni-Co alloy coatings deposited at different pulse deposition parameters.

3.1.3. Different testing methods

Linear sweep voltammetry, cyclic voltammetry and chronoamperometric measurements were carried out in order to examine the kinetic of the electrodeposition of Ni, Co and Ni-Co and to compare their passivity in the different plating baths investigated. For these experiments a Jaissle PGU-20V-2A potentiostat connected with an electronic rotating
EXPERIMENTAL RESULTS

disc electrode was used. The current/potential plots were recorded at a scan rate of 2mVs\(^{-1}\) at different rotation speeds, altering between 100 – 3000 rpm, on steel rotating disc electrodes with a surface area of 1 cm\(^2\). The potential was swept 500 mV relative to the open circuit potential to the cathodic direction. In these experiments, a mercury sulphate electrode (0.5M sulphuric acid) was used as reference for all the rotating disk voltammetry measurements.

Depth profile analysis of the electrodeposited alloys were performed by Glow Discharge Optical Emission Spectrometry (GDOES) using JY Quantum 2000 RF glow discharge spectrometer equipped with a 4 mm diameter anode and operated at 15 W in an argon atmosphere. The glow discharge produces energetic Ar\(^+\) ions, which are sputtering the sample surface with a nm/second rate on the exposed diameter. The sputtered metal atoms are immediately excited in the plasma and emit their characteristic spectral lines with an intensity proportional to their actual concentration in the sputtered surface. Recording the selected line intensities vs. sputtering time, this operation can provide the exact alloy composition function up to 50-100 µm total depths. Here we applied this technique only to show the qualitative composition profile within the layers.

A JEOL 5300LV Scanning Electron Microscope (SEM) fitted with a Roentee analysis system (EDX), with an accelerating voltage of 25 kV in a high vacuum mode and Transmission Electron Microscope using a Philips CM20 electron microscope, operated at 200kV and equipped with a NORAN Ge detector EDS spectrometer were used for the morphological characterisations. The cross sections of samples for TEM were made by Ar\(^+\) ion milling using the Technoorg Linda made ion millers at 10 keV ion energy were used to analyse the morphology and the composition of the deposits [50]. X-ray Diffraction (XRD) measurements were carried out with a Philips X'Pert Pro diffractometer, fitted with an X'Celerator and a secondary monochromator using Cu K-alpha radiation to determine the phases.
Experimental Results

Microhardness of the deposit was measured using a Zeiss Durimet Vicker’s microhardness indenter using a load of 50g for 20 s. Indentions were made on approximately 15µm thick deposits.

Cyclic voltammetry was used to study the passive oxide layer formation on Ni-Co samples pulse plated by different pulse parameters. The studies were carried out in 1 mol dm$^{-3}$ NaOH solutions. A Radiometer potentiostat PG201 with a typical three-electrode cell was used in these experiments. A Pt sheet acted as a counter electrode, while the reference was a saturated calomel electrode (SCE), placed about 0.5 cm away from the Ni-Co surface layer. In all experiments, the potential was swept at a rate of 10 mVs$^{-1}$. Pure nitrogen was bubbled through the solution throughout the experiments and provided a means for de-aeration as well as stirring.

Potential step measurements were carried out and current-time curves were recorded in 1 mol dm$^{-3}$ NaOH solution in order to examine the passive layer formation in alkaline solution. Initially, the potential was fixed at – 0.32 V for 60 s in order to stabilize the surface and remove the possible oxide layers from the coating surface and than the potential was stepped to + 0.43 V that had been determined from a previous study on cyclic voltammetry measurements. The lengths of the potential step experiments were 5, 10 and 15 minutes, respectively.

To determine the amount of the dissolved Ni-Co from the coating UNICAM 701 ICP-OES Inductively Coupled Plasma Optical Emission Spectroscopy (ICP-OES) was used and all the applied standards were Aldrich certified aqueous standards. For this purpose, three samples were prepared analogue with the same deposition parameters (see 3.1.2) and after the potential step measurements the coatings were dissolved in cc. HNO$_3$ and diluted to 25 ml in order to determine the Ni-Co amount remained on the substrate.
3.2. Results and discussions

In the case of the pulse electrochemical deposition three main parameters influence the deposit characteristic, namely the composition and the surface morphology of the alloy as well as the formed metallic phases in the alloy:

- Type and composition of the electrolyte (pH, complex forming agent, additives)
- Temperature of the electrochemical process
- Pulse parameters (\(j_p\); on-, off-time)

The following sections present the effect of these parameters. All the deposition experiments were repeated three times to verify the reproducibility of the results. Less than \(\pm 1.5\%\) variation in composition was observed in the plated deposits.

3.2.1. Effect of different electrolytes on deposition of Ni-Co alloy

3.2.1.1. Rotating disc voltammetry

Ni-Co alloys can be easily produced by electrodeposition from aqueous media in a broad variety of alloy composition. Typical plating baths that are used for the electrodeposition of such alloys are sulfate, sulfamate, Watts and chloride type baths [26].

Fig. 3a. compares the polarisation graphs of individual nickel and cobalt depoositions from different electrolytes (concentrations were the same as in the baths) and the correlations between the rotating speed and the limiting current. We observed an anomalous behaviour of Co deposition as, up to the potential value of \(-1000\) mV, the limiting current of Co is the highest while its concentration is at least ten times less in each of the plating baths than the concentration of Ni. Independently from the type of the bath the intersections of the Levich plots for Co are zero, it shows diffusion control.
Intersections of Ni plots are above zero value, however the differences are not significant and it is possible that both kinetic and mass transport interplay at the electrode reactions. On the other hand, it was stated [3] that nickel is only kinetically controlled during the deposition, whereas the cobalt is rather mass transfer controlled during the electrochemical deposition of the Ni-Co alloy. According to the results of this work, the probability for a kinetic control is higher in the chloride bath and decreases in Watts bath and sulfamate bath, respectively.
Fig. 3. Polarisation graphs measured with sweep rate of 2 mV s\(^{-1}\) at the rotation speed of 100 rpm and the corresponding Levich plots measured at \(E = 900\) mV of (a) Co in chloride, Ni in different electrolytes. Ni, Co, Ni-Co in (b) sulfamate -, (c) Watts- and (d) chloride bath. Reference electrode: \(\text{HgSO}_4/\text{H}_2\text{SO}_4\)

It is also seen from Fig 3a, that hydrogen evaluation, as a side reaction, starts from the potential value of \(-950\) mV in Watts bath and its reduction potential shifts to the more negative potentials in the case of chloride and sulfamate bath, respectively. The highest reduction potential of hydrogen was found in the case of Co.
Polarisation graphs recorded on pure Ni, Co and Ni-Co alloy in different plating baths are illustrated in Fig 3. b, c, d. In each bath, up to the potential value of -1050 mV, Co has significantly higher limiting current and more positive deposition potentials than that of Ni and Ni-Co. At lower potential values, Ni-Co cathodic polarisation plots are close to be overlapped by that of Ni, which leads to the assumption that the kinetics of the Ni-Co electrodeposition is probably determined by the Ni deposition kinetic. This phenomenon, however, changes, at higher potential values in the chloride bath, when Ni-Co cathodic polarisation graph is close to be overlapped by the Co deposition. This might be due to the higher hydrogen evaluation, which increases the local pH. That might result in a different deposition kinetic [28].

The comparison of the cathodic polarisation graphs of the Ni-Co alloys deposited from the different plating baths is shown in Fig. 4. Similarly, to the polarisation plots for the pure Ni deposition in Fig.3a, the limiting current is the smallest for the sulfamate bath and the highest for the chloride bath. The values of the deposition potential of hydrogen are the lowest for the Watts bath and increases for the chloride and the sulfamate bath, respectively. It is likely, that in sulfamate bath, a complex is formed shifting the deposition potential of hydrogen.

From the measured potential shift of hydrogen in the different baths, the formation of the most stress free coating will be most likely observed using the sulfamate bath. While in the case of sulfamate and Watts bath the graphs show clearly the limiting current region, in the plot recorded for the chloride bath an additional shoulder is visible following the limiting current region. This might be explained by a preliminary adsorption reaction of the reactive species before the integration into the deposit matrix.
3.2.1.2. Alloy composition in dependence of the plating bath

According to the rotating disc electrode measurements (Fig 3.d), in the chloride bath at higher potential values, the alloy deposition is closer to Co that may result in a higher Co content in the alloy [26] compared to the other electrolytes. In the case of higher Co content, voltammetric peaks show higher anodic currents that result in a higher dissolution rate of the metal. Also, a shift in the anodic peak position shows a Co-like behaviour, leading to a higher dissolution of the components rather than to the passivity of the alloy.

Conducting alloy composition measurements using ICP analysis proofed these derivations. According to the industrial demands, nickel cobalt alloy layers were deposited from all three electrolytes using the same 0.05 A cm\(^{-2}\) pulse current densities. As it was stated...
based on the electrochemical measurements, the cobalt content varied in dependence of the electrolyte used. In this current density, the highest cobalt content was found for the chloride type electrolyte system. The sulfamate type electrolyte led to the lowest cobalt content in the deposits. These results are in a remarkable accordance with the results of the electrochemical measurements.

The cobalt content in the deposits clearly follows the deposition potentials of the alloy forming metals for all three types of electrolytes. At lower current densities (and thus potentials), the nobler cobalt is preferably deposited, leading to higher cobalt content in the alloy. A higher current density enriches the nickel content in the deposit.

### 3.2.1.3. Cyclic voltammetry and chronoamperometry

Under certain conditions a metal alloy coating builds up a thin oxide layer on its surface that is usually energetically more stable than the coating itself [5,6]. However, in the case of pulse reverse plating, this phenomenon is undesired as a forming oxide layer hinders the dissolution during the anodic phase and transforms the general (electrochemical) behaviour of the deposited alloy towards that of a multilayer. Therefore, it is important to clarify the conditions of passivity in different plating electrolytes. In order to compare the passive layer formation on Ni-Co alloy deposited from the different plating electrolytes, cyclic voltammetry measurements were carried out with a scan rate of 10 mVs$^{-1}$. For these tests, the Ni-Co alloys were pulse deposited by applying the deposition parameters of $t_{on} = t_{off} = 5$ ms, $j = 0.05$ Acm$^{-2}$ $T = 35^\circ$C.

A comparison of the voltammograms for the Ni-Co alloys previously pulse deposited in the three different plating electrolytes is presented in Fig. 5. The voltammograms of the alloys have a similar shape: there are no separated Ni and Co peaks and the rather wide peaks
indicate the dissolution of Ni-Co as an alloy. However, there is a considerable difference between the anodic peak positions as they occur at –520mV in Watts bath, –460 mV in sulfamate and –300mV in chloride bath. Significantly lower current was measured in the case of the layers in the sulfamate and Watts bath, respectively. The potential range of the passive state is the widest in the case of Watts bath and it is decreased in sulfamate and chloride bath, respectively. This indicates a significant difference both in the morphological and electrochemical properties of the alloy.

Fig. 5. Plots of cyclic voltammetry recorded on Ni-Co layers in the solution used for their deposition. Sweep rate is 10 mVs\(^{-1}\). Deposition parameters of Ni-Co samples \(t_{on} = t_{off} = 5 \text{ ms}, j = 0.05 \text{ Acm}^{-2}, T = 35^\circ \text{C}.\)
Fig. 6a-d. represents the logarithmic form of the time-current transients recorded on previously pulse deposited Ni-Co samples in their parent solution. Based on the results of the cyclic voltammograms, the potential was stepped from –700 mV to –430 mV in sulfamate and Watts bath. In chloride bath the potential was stepped to –160 mV. It can be clearly seen from the plots that the highest tendency for the dissolution at the selected potential is shown by the chloride bath sample. Passive layer formation starts almost immediately in the case of the sulfamate system but it needs more time to develop at the Watts and chloride systems. A decrease in the current shows the formation of a passive layer on the Ni-Co surfaces in each bath. However, this passive layer is not stable, and the current starts to increase again, representing the dissolution of the alloy.

Fig. 6. Potential step measurements on Ni-Co layer in the solution used for their deposition. 
(a), (b) from –700 mV to -430 mV; (c) from –700 mV to -160 mV. Deposition parameters of Ni–Co samples: \( t_{on} = t_{off} = 5 \) ms, \( j = 0.05 \) \( Acm^{-2} \), \( T = 35^0C \).
Comparing the results of the cyclic voltammetry with the potential step measurements in all three types of electrolytes investigated, it was found that those alloys that were deposited from the chloride electrolyte have lower proneness to passivity [30], however the possibility for pit formation is higher. The formation of pits on the alloy surfaces decreases and the ability for passive layer formation increases by decreasing the Cl⁻ content in the type of bath used for deposition from chloride to Watts and sulfamate bath, respectively.

3.2.1.4. Morphology and phase structure of Ni-Co alloys deposited from different electrolytes

Typical cross-sections of Ni-Co alloys deposited from sulfamate, Watts and chloride baths by applying pulse deposition parameters of $t_{on} = t_{off} = 5$ ms, $j = 0.05$ Acm⁻² $T = 35^{\circ}$C are shown in Fig. 7 a-c, respectively. The bright-field and dark-field TEM images of the electrodeposited Ni–Co alloys illustrate a homogeneous and granulated microstructure for the deposits form sulfamate and Watts bath. In contrary, the crystal structure of the coatings deposited from chloride bath represents heterogeneity, which can be denote to the presence of the mixture of columnar and granulated grains.

Film growth is a process in which two processes, namely, the growth of existing crystals and the formation of new ones are in competition and can be influenced by different factors [19]. Perpendicular to the substrate surfaces the following structures can be identified [51]: a, Field oriented (FT) crystals (whiskers, dendrites); b, basis reproduction (BR) structure when crystals are obtained by 2D nucleation only and become larger in the direction of the growth of the coating; c, field orientated texture type (FI) possess also 2D nucleation, but with a constant diameter and d, unoriented dispersion type (UD) that is a 3D nucleation resulting in always new crystals on the surface. The transition between these structures is possible (e.g.:BR-FT or UD-FT) according to the nature of the 3D nucleation. In our cases, the
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deposits of sulfamate and Watts baths can be characterised by the UD structures, as globular grains can be clearly observed. However, in the case of the chloride bath, a mixture of FI and UD structure is found.

The nature of the solution may be the cause of the difference in the structure of the deposited alloy. (Note, that during the off-time, as the current stops mainly dissolution and recrystallisation happens) It can be clearly seen from the cyclic voltammetry and the chronoamperometry measurements that the tendency is the highest for the dissolution of the freshly deposited layer at a selected potential in chloride bath [52]. Passive layer formation starts almost immediately in the case of the sulfamate system but it needs more time to develop at the Watts and chloride systems.

There is a considerable difference in the average grain size in the examined cases. The grain size is about 50 nm in the case of Watts bath and increases in chloride and sulfamate baths, respectively. A crystal grows, while an extraneous species that can be hydrogen bubble, additive molecule, or even a very thin oxide layer sit on the crystal surface. When these species adsorb on the crystal surfaces, they close the mass and electron transport of the ions and act as a barrier, which retain the growth of the existing crystal. When the freshly arrived Ni and Co ions reach the surface, they cannot fix to the old crystal because of the previously formed barrier layer, therefore, new seed appears and a new grain starts grow [53, 54].

Numerous works [31, 35] attribute the decline of grain size to the variation in Co content of the alloy. However, in our case, we cannot clearly declare this observation as the Co content of the alloy deposited from Watts and chloride baths is nearly the same. A possible explanation for the grain size reduction can be found in the deviation of hydrogen overpotential and the tendency for passive layer formation in the different baths.

In one hand, it was presented in section 3.2.1.1 that the value of the deposition potential of hydrogen is the lowest for the Watts bath and increases for the chloride and the
sulfamate bath, respectively. Parallel, we also observed that the decline of grain size of the Ni-Co alloy deposited from these baths follow similar trend, that is the higher the hydrogen evolution the reduced the grain size (see Table 3.). This correlation suggests that the deposited hydrogen may adsorb on the surface of the freshly deposited alloy grains, causing a decrease in the crystal growing which, in turn, increases the possibility of formation of new seeds on the substrate.

Also, the adsorbed hydrogen keeps the surface from the oxidation, which increases the possibility of the formation of columnar structure. The tendency for passivity, as it was declare before, the highest in sulfamate bath and decreases in Watts and chloride bath. The formation of even a monolayer of oxide on the freshly deposited alloy surface blocks the further growth of the existing crystals, resulting in repeated nucleation of small new crystals with a 3D nucleation, as it is detectable in the case of the deposits from sulfamate and Watts bath. Tendency for oxide layer formation on the top of the crystals deposited from chloride bath is minor [55,56], therefore the active sites remained open for the 2D nucleation add up to a columnar structure with an UD character among the columns.
3.2.1.5. GDOES experiments

Jayaganthan reported an enrichment of Ni atoms at the initial stage of deposit formation in different Ni-Me bimetallic alloy depositions when the particle size decreases [57]. Our observations, based on depth profiles received from GDOES investigations of electrodeposited Ni-Co alloys on steel substrates from different bath, do not show this behaviour on steel substrates as it can be clearly seen Fig. 8. The deposited coating had uniform alloy composition along their cross-section. It has to be added that the transition between the substrate and the layer is not staged due to the minor roughness of the substrate surface.
3.2.1.6. Microhardness measurements on Ni–Co alloys

As shown in Table 3, the hardness-test results exhibit the lowest hardness for the samples deposited from sulfamate bath and the highest from chloride bath. The remarkable diversity of the hardness values for the deposits of sulfamate and Watts baths relates to the variation in the Co content of the alloys as the correlation of the layer hardness and the Co content was already observed by others [35, 37].
Table 3. Hardness, morphology and Co content of Ni-Co alloy coatings. Deposition parameters: $t_{on} = t_{off} = 5 \text{ ms}$, $j = 0.05 \text{ Acm}^{-2}$, $T = 35^\circ \text{C}$.

<table>
<thead>
<tr>
<th>Bath type</th>
<th>Hardness (HV$_{50}$)</th>
<th>Co content (wt %)</th>
<th>Average grain size (nm)</th>
<th>Morphology</th>
</tr>
</thead>
<tbody>
<tr>
<td>Steel substrate</td>
<td>130 ± 5</td>
<td></td>
<td>100</td>
<td>Granulated (UD)</td>
</tr>
<tr>
<td>Sulfamate</td>
<td>340 ± 40</td>
<td>5</td>
<td>50</td>
<td>Granulated (UD)</td>
</tr>
<tr>
<td>Watts</td>
<td>470 ± 70</td>
<td>14</td>
<td>75</td>
<td>Mixed (FI and UD)</td>
</tr>
<tr>
<td>Chloride</td>
<td>600 ± 30</td>
<td>16</td>
<td>75</td>
<td></td>
</tr>
</tbody>
</table>

Average thickness ≈ 15 µm

The difference in the hardness values is even more considerable in the case of the deposits of Watts and chloride baths. The compositions were measured by the ICP analytical method after peeling and dissolving the deposited layers. Note that the Co – content of the two alloys are almost the same, therefore the change in microhardness cannot be achieved through the control of composition. These data are fairly fitting to the composition values of same layers found in the same baths, however the XRF method was used there to the surface analysis. In this case, a reasonable explanation to the diversity can be obtained by the dissimilarity in the morphology. As it was stated in the previous paragraph, in the case of the deposits of chloride bath a mixed structure can be observed: between the mainly columnar structured grains some granulated grains are visible. As it is known, columnar structures possess higher hardness than globular ones [54] due to the reduced deformation mechanism in these structures.
3.2.2. Effect of the temperature and the pulse parameters in chloride bath

Studying the effect of the deposition parameters, out of the three examined plating electrolytes, the chloride bath was used with always the same composition but systematically varied deposition temperature and pulse parameters. Table 4. summarises the deposition parameters as well as the measured physical characteristics of the Ni-Co alloys. In this table, the composition of the alloy was measured by EDX, the grain size was determinated by XRD and the roughness values were recorded by using profile analyser. The obtained SEM micrographs can be seen in Fig 9-10.

Table 4: Deposition parameters (at electrode distance of 3 mm) and some physical characteristic of the Ni-Co alloy layers

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Deposition current density (A cm⁻²)</th>
<th>On-time (ms)</th>
<th>Off-time (ms)</th>
<th>Co (%wt)</th>
<th>Ni (%wt)</th>
<th>Grain size (nm)</th>
<th>Roughness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RT</td>
<td>0.5</td>
<td>1</td>
<td>250</td>
<td>65</td>
<td>35</td>
<td>21.2</td>
<td>466</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
<td>50</td>
<td>61</td>
<td>39</td>
<td>25.2</td>
<td>699</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>250</td>
<td>59</td>
<td>41</td>
<td>24.5</td>
<td>637</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>41</td>
<td>59</td>
<td>19</td>
<td>1037</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3</td>
<td>250</td>
<td>52</td>
<td>48</td>
<td>26.2</td>
<td>632</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3</td>
<td>50</td>
<td>42</td>
<td>58</td>
<td>20.8</td>
<td>978</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>250</td>
<td>43</td>
<td>57</td>
<td>18.6</td>
<td>605</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>50</td>
<td>30</td>
<td>70</td>
<td>14.3</td>
<td>990</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
<td>250</td>
<td>61</td>
<td>39</td>
<td>16.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>1</td>
<td>50</td>
<td>41</td>
<td>59</td>
<td>21.4</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>250</td>
<td>62</td>
<td>38</td>
<td>21.2</td>
<td></td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>1</td>
<td>50</td>
<td>24</td>
<td>76</td>
<td>18.8</td>
<td></td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3</td>
<td>250</td>
<td>55</td>
<td>45</td>
<td>22.3</td>
<td>998</td>
</tr>
<tr>
<td></td>
<td>0.5</td>
<td>3</td>
<td>50</td>
<td>29</td>
<td>71</td>
<td>22.6</td>
<td>1608</td>
</tr>
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<td>250</td>
<td>44</td>
<td>56</td>
<td>21.5</td>
<td>1688</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>3</td>
<td>50</td>
<td>24</td>
<td>76</td>
<td>17.5</td>
<td>5500</td>
</tr>
</tbody>
</table>
Fig. 9. Surface morphology at 35°C
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**Fig. 10. Surface morphology at 25°C**

### a, \( t_{on} = 1\text{ms} \)

- 1
  - 0.5 A cm\(^{-2}\), 250 ms
- 3
  - 1 A cm\(^{-2}\), 250 ms
- 5
  - 0.5 A cm\(^{-2}\), 250 ms
- 7
  - 1 A cm\(^{-2}\), 250 ms

### b, \( t_{on} = 3\text{ms} \)

- 0.5 A cm\(^{-2}\), 50 ms
- 1 A cm\(^{-2}\), 50 ms
EXPERIMENTAL RESULTS

3.2.2.1. Morphological characterisation at 35°C

The microstructure of Ni-Co surfaces showed similarity both at higher and lower temperature. It can be seen in Fig. 9a that at a lower current density and a longer off-time, the surface was smooth, coherent and the grains had nodular shapes with smaller and bigger grain size. As the off-time was reduced, the surface became rough and possessed a dendrite-like structure. The size of the grains remained mixed as the smaller grains sat on the bigger grains. An increase in peak current density did not resulted in any changes at a higher off-time, however, the formation of fibril shape grains with enlarged grain size was typical at shorter off-time.

At an increased on-time, at lower current densities and at a longer off-time the shape of the grains was nodular, the surface was still coherent, though, some pits could be seen. As the off-time reduced, the shape of the grains changed from nodular to fibril. Also, fibril shape formation was typical at high current density both at longer and shorter off-time. The grain size was the smallest at a high current density and at a shorter off-time. The summary of changes in the microstructure can be seen in Fig. 11.

![Graphs showing changes in microstructure with varying parameters](image-url)
Fig. 11. Variation in a, structure b, grainsize and c, roughness for the different pulse plated Ni-Co alloy at the temperature of $T = 35\,^\circ C$

3.2.2.2. Morphological characterisation at 25°C

Fig. 10 a, b illustrates the surface morphologies of Ni – Co alloy deposits obtained at pulse off-time 250 ms and 50 ms, at pulse on-time 1 ms and 3 ms, at two different peak current densities of 0.5 A cm$^{-2}$ and 1 A cm$^{-2}$. At an on-time of 1 ms the shape of the grains were nodular at a lower current densities and at a longer off-time. The form of the grains represented similar feature at a reduced off-time. At a high current density and at a longer off-time the grains were fibril shaped with rather large grain size. The surface became more compact and owned smaller grain size at a reduced off-time.

Also, fibril structure could be observed at 3 ms on-time, at a lower current density both longer and shorter off-time, but the grain size reduced at a shorter off-time. Similar morphology was visible at a higher current density and a shorter off-time. The surface structure completely changed with the reduction of off-time. In the case of a short off-time, a very low grain size formed, however, cracks on the surface became clearly visible.
EXPERIMENTAL RESULTS

Fig. 12. Variation in a, structure b, grainsize and c, roughness for the different pulse plated Ni-Co alloy at 25°C

To sum the above described microstructure in Fig 12: at lower temperature, three different formations are visible: columnar structure form at a lower off-time but higher on-time and current density. Either increasing the off-time or decreasing the on-time and the current density the shape of the grains change to fibril. Nodular structure appears only at a higher off-time and a lower on-time, independently from the current density. While at a lower temperature the dominant formation is the fibril structure, an increase in the temperature results in the formation of more grains that are nodular and less fibril one.
It is well known that in the case of the direct current deposition, the Co deposits are characterised by fibril shapes, therefore a higher Co-content in the alloy results in a rather fibril grain shape.\cite{33,34}. According to Bai et al.\cite{28} during the electrodeposition, Co(II) and Ni(II) ions react with OH$^-$ resulting in the formation of metal mono-hydroxides, which adsorb on the deposit surface. Normally, due to the greater adsorption of Co(OH)$^+$, the Co content in the alloy was higher, which led to the formation of bigger grains and fibril (Co-like) structure.

![Graphs showing variation in Co content and changes in structure for different pulse plated Ni-Co alloy at temperatures](a, b)

Fig. 13. Variation in Co content and changes in the structure for the different pulse plated Ni-Co alloy at the temperature of a, $T = 25^\circ C$; b, $T = 35^\circ C$

Surprisingly, in the case of the pulse current deposition, a change in the Co-content in the alloy, not always causes a change in the shape of the grains, furthermore, different surface
morbidity can be obtained at the same alloy composition (image 1 in Fig. 9a-image 2 in Fig. 10a). This phenomenon indicates that they are mainly the pulse parameters that determine the morphology of the alloy deposit.

Usually, an increase in off-time and on-time as well as a decrease in peak current density results in an increase in grain size, as the bigger grains are thermodynamically more stable than the small ones [19]. However, in our case, an increase in the off-time and a decrease in the peak current density results in smaller grain size in the case of low on-time and low peak current density, at both temperature. Furthermore, as the on-time is increased at lower temperature and at lower off-time, the grain size also reduced. This phenomenon was not observable either at higher temperature or at longer off-time.

If the pulse off-time is considered as the period when surface diffusion as well as (anodic) dissolution takes place then one can expect the re-arrangement of atoms and nuclei, which may induce re-crystallisation and hence, an increase in the grain size. In the case of Ni–Co alloy deposition, the previously adsorbed Ni(OH)\(^+\) and Co(OH)\(^+\) mono-hydroxides are thought to block the growth centres of Ni and Co species during the off-time and retaining their diffusion [19]. Therefore, in the case of the next pulse, new nuclei form, resulting in smaller grain size and granulated structure in the coating. This is also supported by the fact that increasing the off-time forms a more compact deposit.

3.2.2.3. XRD measurements

Crystallographic structures of some pulse-plated alloy were examined by XRD measurements. The obtained patterns of samples, deposited at higher temperature at an on-time of 1 ms, are presented in Fig 14, in the order of increasing film thickness. In spectra 1 – 4, the intensity of Cu substrate diffraction peaks decreased as the deposited film thickness
increased (e.g.: (111)). Lines marked by closed symbols show where Ni and Co phases are expected to appear.

Fig. 14 illustrates the influence of pulse parameters on the metallic phases that appear in the coating at a constant on-time. The deposited film was mainly composed of face-centred cubic (fcc) phases and their orientation was strongly determined by the pulse parameter off-time. It can be observed that the peak intensity of the Cu substrate decreased as the coating layer thickened.

![XRD pattern of Ni-Co alloy deposited by applying different pulse parameters at a constant $t_{on} = 1$ ms. 1: $j = 0.5$ A cm$^{-2}$, $t_{off} = 250$ ms; 2: $j = 0.5$ A cm$^{-2}$, $t_{off} = 50$ ms; 3: $j = 1$ A cm$^{-2}$, $t_{off} = 250$ ms; 4: $j = 1$ A cm$^{-2}$, $t_{off} = 50$ ms](image)

**Fig. 14.** XRD pattern of Ni-Co alloy deposited by applying different pulse parameters at a constant $t_{on} = 1$ ms. 1: $j = 0.5$ A cm$^{-2}$, $t_{off} = 250$ ms; 2: $j = 0.5$ A cm$^{-2}$, $t_{off} = 50$ ms; 3: $j = 1$ A cm$^{-2}$, $t_{off} = 250$ ms; 4: $j = 1$ A cm$^{-2}$, $t_{off} = 50$ ms
According to the binary phase diagram of Ni and Co [58] and their similar atomic diameter, the Ni-Co alloy forms a substitution solid solution. Usually, in the case of a solid solution, a concentration change in alloy causes a shift in line position to the element that has the higher concentration in the alloy. Comparison of diffraction peaks correspond to Ni – Co deposits with different Co concentration indicates that the crystalline structure of alloys with different composition is similar. Pulse plated Ni – Co alloy films build up from fcc Ni and hcp Co, which was also observed by several authors [31, 32].

In the case of nanostructured materials, the crystallographic structure may differ from the geometric structure of micro- or macrostructured materials. Based on this statement, the formation of a mixed structure is possible [59, 60], in which either a hexagonal Co cluster contains cubic structured Ni or a hexagonal Co is built in the cubic structured Ni (sample 1,3,4) as can be seen in Fig 15.

**Fig. 15. Theoretical crystal structure for Ni – Co alloy deposit: a, cubic structured Ni built in the hexagonal Co cluster; b, hexagonal Co is built in the cubic structured Ni**
3.2.3. Electrochemical characterisation of thick layers

Cyclic voltammetry experiments were carried out in 1 mol dm\(^{-3}\) NaOH solution at a scan rate of 10 mV s\(^{-1}\) in order to examine the passive layer formation on Ni-Co alloy coating. In these experiments, four samples were examined, of which deposition parameters are listed in Table 5. Contrary to my previous work [56], in this case, the Ni-Co coatings were deposited at an electrode distance of 3 mm, because application of shorter electrode distance led to more compact surface. The thickness of the deposited layers was approximately 4 µm. During these electrochemical experiments, the potential was referenced against Saturated Calomel Electrode (SCE). The stability of the oxide layer formed during this cycling was calculated from the anodic and cathodic charge ratios (\(Q_a/Q_c\)) of the second cycle of the cyclic voltammogram.

Table 5. Deposition parameters of Ni – Co alloys and their characteristics.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Peak current density (A cm(^{-2}))</th>
<th>Off-time (ms)</th>
<th>Co %wt</th>
<th>Ni %wt</th>
<th>Morphology</th>
<th>Phases</th>
<th>(Q_a/Q_c) (NaOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>0.5</td>
<td>250</td>
<td>65</td>
<td>35</td>
<td>Compact, fine granulated</td>
<td>hcp in fcc</td>
<td>9.27</td>
</tr>
<tr>
<td>2</td>
<td>0.5</td>
<td>50</td>
<td>61</td>
<td>39</td>
<td>Porous, cauliflowers-like</td>
<td>fcc in hcp</td>
<td>3.65</td>
</tr>
<tr>
<td>3</td>
<td>1</td>
<td>250</td>
<td>59</td>
<td>41</td>
<td>Compact, fine granulated</td>
<td>hcp in fcc</td>
<td>9.21</td>
</tr>
<tr>
<td>4</td>
<td>1</td>
<td>50</td>
<td>44</td>
<td>56</td>
<td>Dense, fibril</td>
<td>hcp in fcc</td>
<td>3.85</td>
</tr>
</tbody>
</table>

Fig. 16. represents the comparison of the first cycle of voltammograms measured in 1 mol dm\(^{-3}\) NaOH solution on Ni-Co layers deposited by different pulse parameters at an electrode distance of 3 mm. The first cycle of the positive potential scan started from an initial
voltage of – 0.32 V and an oxidation peak at – 0.15 V appeared that corresponds to the formation of Co(OH)\textsubscript{2}. At this potential, the anodic oxidation peak current density of “2” was significantly lower than that of the other voltammograms. Another oxidation peak was seen at around 0.20 V that is attributed to oxidation of Co(II) to Co(III) in the form of CoOOH [40, 61,62]. Increasing the potential to more positive potential values, the current density rose again, due to the formation of Ni-oxide (see insert fig). This oxide was reduced during the reverse scan.

Fig. 16. First cycle plots of cyclic voltammograms measured on Ni-Co alloy deposit in NaOH.

Sweep rate: 10 mVs\textsuperscript{-1}. Deposition parameters: \( t_{on} = 1 \text{ ms}, T = 35 \degree C \).
The comparison of the first and second cycle of voltammograms on Ni-Co layers deposited by pulse parameters $j_p = 0.5 \text{ mA cm}^{-2}$ and $t_{\text{off}} = 250 \text{ ms}$ is shown in Fig 17. In the second cycle, the outward scan shows the lowering of oxidation peaks of Co(OH)$_2$ and CoOOH, mainly due to cobalt-oxides, which had been formed previously. A further difference with the first cycle was the lower Ni anodic oxidation current.

![Comparison of first and second cycle of cyclic voltammograms on Ni-Co alloy.](image)

**Fig. 17. Comparison of first and second cycle of the cyclic voltammograms on Ni-Co alloy.**

*Sweep rate: 10 mVs$^{-1}$. Deposition parameters: $t_{\text{on}} = 1 \text{ ms}, t_{\text{off}} = 250 \text{ ms}, j_p = 0.5 \text{ A cm}^{-2}$*

Comparison of the second cycle of the voltammograms for the different Ni-Co layers is presented in Fig. 18. The shapes of the voltammograms labelled “1”, ”2” and “3” are similar; they showed similar oxidation peaks. All these voltammograms can be described by
rather large shoulders, which indicate the dissolution of a Ni-Co solid solution. For the voltammogram labelled “4”, two distinct oxidation peaks for nickel and cobalt were observed.

Fig. 18. Comparison of the second cycle of the voltammograms for the different Ni-Co layers in NaOH. Sweep rate: 10 mVs⁻¹. Deposition parameters: tₜₐₖ = 1 ms, T = 35 °C

As observed in the voltammograms in Fig 18, Ni oxidation and the formation of Ni-oxides dominated the voltammograms (during the anodic polarisation), for the coatings with nodular shapes and high nickel contents (Fig. 9, 1-3). A deposit with a fibril structure showed distinct Co and Ni oxidation peaks both in the cathodic and anodic parts of the cycle. The voltammetric behaviour of Ni-Co films seems to be depended on the morphology of the deposit.

Table 5. shows the comparison of Qₐ and Qₑ values for Ni-Co layers electrodeposited by different pulse parameters. It can be seen that the highest ratio is obtained in the case of those samples, which were plated using a long off-time (Fig 9, graph “1”, ”3”). This shows
that the oxide film is more stable for these two samples. Such behaviour indicates a decrease in the reversibility of the redox systems, which can be associated the reducing solubility of Ni-Co-oxides formed anodically in that medium.

If the coating deposition is taken place at a high current density, as it is happening in the case of direct current alloy deposition, not even the deposited coating, but also the oxide layer, that formed on the deposited coating, becomes sponges, porous and poor adhesive, so the coating loses its adequate to the practical usage. Despite a huge volume of studies on nickel cobalt oxide produced by different methods being available, none of these works deals with the electrochemical characterisation and the modelling of the growth mechanism of the oxide layer.

3.2.4. Kinetics of the passive layer formation

Examination of the oxide layer is possibly by e.g. XPS, AES methods. Among these techniques, a cheap and simple way is the examination of the passive layer formation by using electrochemistry. **For these testing methods a thin layer (few atomic layer) is more advantageous, therefore, beside the characterisation of thick layers, the thin layer deposit was required for the aimed technical applications.**

3.2.4.1. Cyclic voltammetry in the case of thin layer deposit

In Fig. 19, the second cycle of the cyclic voltammetry on thin layered Ni-Co alloy that were deposited with a charge of 184 mC cm\(^{-2}\) can be seen. Deposits were obtained at pulse off-time 250 ms and 50 ms, at pulse on-time 1 ms at two different peak current densities of 0.5 A cm\(^{-2}\) and 1 A cm\(^{-2}\), at 35 °C. Similarly to the previous discussed results in alkaline
solution, an anodic peak appeared at 0.35 V vs. SCE at each sample that was correspond to the formation of Ni-hydroxide. However, a second oxidation peak, that is attributed to the oxidation of Co(II) to Co(III) in the form of CoOOH at 0.10 V, was seen only at sample 2. Shifting the potential to more positive values, the formation of a Ni-oxide is observable in all the cases that oxide is reduced during the reverse scan.

Fig. 19. First cycles of cyclic voltammogram plots recorded in 1 mol dm$^{-3}$ NaOH on the Ni-Co layers deposited by different pulse parameters. Sweep rate: 10 mVs$^{-1}$. Deposition parameters: $t_{on} = 1$ ms, $T = 35$ °C. **Insert plot:** second cycles of the cyclic voltammogram plots
In the second cycle (see insert Fig), the outward scan shows the reduction of anodic currents that is mainly due to previously formed oxides. The anodic charge ratio is the highest in the case of sample 2. The difference of the other samples can be explained both by the increased amount of CoOOH that is more porous [40, 61, 65] than Co(OH)$_2$, and also by the lowering Co-content of the alloy. This leads to the conclusion that the dissolution of the metal film at a selected potential is strongly determined by the Co content of the alloy and the type of the Co oxide/hydroxide, which forms on the alloy coating.

3.2.4.2. Chronoamperometry experiments

Time-current transients of Ni-Co surfaces can be seen in Fig. 20 and 21.

![Graph showing time-current transients with different pulse parameters](image)

Fig. 20. Time-current transients recorded in 1 mol dm$^{-3}$ NaOH on Ni-Co samples pulse plated by different pulse parameters. Deposition parameters: $t_{on} = 1$ ms, $T = 35$ °C. Potential step from -0.32V to +0.43V.
Fig. 21. Logarithmic form of time-current transients recorded in 1 mol dm$^{-3}$ NaOH on Ni-Co samples pulse plated by different pulse parameters. Deposition parameters: $t_{on} = 1$ ms, $T = 35^\circ$C. Potential step from -0.32V to +0.43V.

Plotting the current-time data in double log scale (Fig. 21), nearly constant correlation between the elapsed time and the measured current can be observed between log $t = -1.5$ and - 0.5. This can be related both to the initial oxide thickness of samples and to the restriction introduced by the oxide film resistance [64] of a poorly conducting Ni (II) (III) /Co(II) oxide [66,67]. If a new oxide layer forms, ions may have to go over a barrier in order to move from one point to another. The insufficient potential results in low ion mobility in the film or the slow charge transport. At the same time, electric field lowers the potential barrier for the motion of ions and increases their probability for the movement, resulting in the thickening of the oxide layer [68]. Then, all the plots show a decrease from log $t = -0.5$, however their gradients are different. The slope is $-1$ in the case of sample 1 and 2, while, at sample 3 and 4 reduces to $-0.7$ from log $t = -0.2$. The decrease in the slope can be explained by the change in the kinetic of the oxide layer formation.
3.2.4.3. ICP results

The ratio of Co : Ni in the deposited coating before the potential step measurement was about 1.3 in the case of sample 1 and 2 (Fig. 22.), while this was 0.6 at samples 3 and 4. Following the potential step to a constant potential, at those alloys with higher Co content, the slope of the change in Co : Ni ratio vs., time was negative, which could be attributed to the higher dissolution rate of Co than that of Ni. This slope was almost constant in the case of lower Co content in the alloy coating that represented a similar dissolution rate of Co and Ni in time.

![Graph showing Co/Ni atomic ratio vs. time](image_url)

*Fig. 22. Co and Ni atomic ratio. Potential step from -0.32V to + 0.43V.*
3.2.4.3. Calculation for oxide layer thickness estimation

Different experimental processes such as choronoamperometry, chronoculomerty, chronopotentiometry and linear sweep voltammetry were used to examine the oxide growth mechanism on steel [62, 69-71], Cr [72] and other metallic phases [73-75]. In this work, the formation mechanism of a passive layer on the Ni-Co surfaces was examined by chronamperometry measurements, combined with solution analysis.

Generally, the first step of the oxide film growth mechanism on coatings is the oxygen ion and/or hydroxyl as well as water adsorption on the metal surface. As the monolayer of adsorbed oxygen is forming on the metal surface, atoms from the metal pass through it and at the same time, oxygen ions diffuse into the metal. Therefore, the first monolayer of oxide is this monolayer [5]. Two main theories are applied for modelling the growing mechanism of the first monolayer: (1) rate limiting reaction model [76,77] and (2) high field electron (HFM) model [68].

Zhang et al [78] suggested that if the anodic passive film thickness depended on the electric field (as it was in the case of HFM model) than the plot of

$$\frac{\sqrt{-i'}}{i} \text{ vs. ln} i \quad (14)$$

in a chronoamperometric record of anodic potential step study was linear with a positive slope. In this equation $i$ is the current and $i' = di / dt$. If the electric field in the oxide layer is independent of the thickness (rate limiting reaction model) than the curve of Eq. 14 shows a slope with 0 value.
Alternatively, we use another method to determine which out of the two oxide growth mechanisms describes the kinetic of the oxide formation. In the detailed description of Cabrera and Mott [68], the oxygen atoms dissociate to oxygen ions on the account of the electrons that rapidly arrives from the metal surface, resulting in 1-2 V potential differences in the oxide film. The potential difference between the metal / oxide and the oxide / electrolyte interfaces leads to the formation of a strong electric field that proportionally determines the transport rate of both ions and electrons through the oxide layer. This electric field becomes the driving force to the further oxide growth process.

However, in steady state, both ion- and electrontransfer can be supposed in the oxide film and the numbers of ions and electrons are equal; therefore, the current can be expressed by the number of atoms crossing unit area per unit time, which then gives the following derivate:

$$\sqrt{-\frac{i'}{i}} \text{ vs. } \ln i$$ at the different pulse plated Ni-Co alloy
where $X$ is the oxide layer thickness, $A$ is a constant and $t$ is the time. This equation principally reflects that the electric field in the film is inversely proportional to the thickness. Integrating Eq. 15, the oxide layer growth for thick films shows parabolic law that can be describe by the

$$X^2 = 2At$$

(16)

equation and the current – time function can be expressed by:

$$i \sim t^{-\frac{1}{2}}$$

(17)

Plotting this current function in log $i$ – log $t$ scale, the slope of the plot gives $–0.5$.

For thin layers, (at the first region of the plot) the growth law may be linear

$$X = At$$

(18)

which in turn gives

$$i \sim t^{-1}$$

(19)

This current function gives a slope of $–1$ in log $i$ – log $t$ scale.

In our cases, all of the four graphs show the expected behaviour of HFM (see Fig 21 and Fig 23), however, the gradients of the plots with high Co content in the alloy are less steep than that of at lower Co content (Fig 23).

Based on the previously presented criteria, the high field model was adopted to describe the oxide film formation in our experiments. The applied calculation method based on the mass transport of the species through the oxide layer during their formation [72].
According to the work of Landolt’s group [72], we assumed that all the oxidation took place at the oxide / metal interface and no other electrontransfer reaction occurred in the solution.

In this case, the following mass balance can be expressed:

$$ m_{\text{film}} = m_{\text{ox}} + m_{\text{oxygen}} $$  \hspace{1cm} (20)

Where $ m_{\text{film}} $ can be related to the total mass of oxide film and $ m_{\text{oxygen}} $ is the mass of oxygen in the oxide film, which can be defined as the oxygen uptake in the oxide layer. This is in stochiometric relation with the metal in the oxide layer. For the calculation of the amount of metal in the oxide layer ($m_{\text{ox}}$) we assumed that total mass balance during the potential step reaction could be expressed:

$$ m_{d} = m_{c} + m_{\text{ox}} + m_{i} $$  \hspace{1cm} (21)

$m_{d}$ is the total mass of the deposited Ni-Co alloy coating; $m_{c}$ is the metal in the coating, $m_{\text{ox}}$ is the metal in the oxide after the potential step and $m_{i}$ the dissolved metal in ionic form.

During the potential step experiments, a thin layer of metal oxide forms on the top of the alloy coating. Then, the sum of metal in the oxide and the in underlaying coating ($D$) can be determined by ICP analysis.

$$ D = m_{c} + m_{\text{ox}} $$  \hspace{1cm} (22)

At the same time, the charge ($Q$), measured during the potential step experiment, is the sum of the amount of oxidised metal and the amount of the dissolved metal:

$$ \frac{Q}{F} M_{\text{metal}} = m_{\text{ox}} + m_{i} $$  \hspace{1cm} (23)
where F is the Faraday constant and M is the atomic mass of the metal.

Inserting Eq. 22 and Eq. 23 into Eq. 21, the metal mass remained in the oxide is:

$$m^{m} = Q - m^{d} + D \quad (24)$$

Estimations for the metal oxide thickness formed on the alloy layer during potential step experiments were performed and the results were presented in Fig. 24. Based on our CV measurements and other author’s works [44, 14] the formation of Me(OH) (Me = Ni, Co) was assumed at the selected + 0.43 V potential. Having no quantitative information on the composition of the oxide layer, for each oxide layer thickness calculations a value averaged from the pure Co(OH)₂ and Ni(OH)₂ density values upon the actual metal layer composition was used. This average density (ρ) value is ranged between 3.84 and 3.95 g cm⁻³. The oxide layer composition was taken same as the composition of the metal layer.

![Fig. 24. Calculated thickness of the oxide layer for the different pulse plated Ni-Co alloy](image-url)
It can be seen in Fig. 24 that depending on the Co content of the alloy (see Fig 22), there is a significant difference in the oxide layer thickness. In the case of those alloys, which have lower Co content in the coatings, the formed oxide layer thickness is in the range of 30 – 90 nm and presumably, the formed oxide matrix is a Ni-matrix, in which some of the Ni sites are occupied by the Co ions [78]. At higher Co content, the oxide thickness is between 0 – 20 nm; in this case, the oxide film probably builds up from mainly Co-ions or the oxide has a Co based matrix in which the Ni ions occupy the Co sites [46]. The difference in the oxide film thickness of alloys due to the Co content leads to the assumption that Co hinders the oxide layer growth [79].

Plot 2 in Fig 24. indicates deviation from others, since it shows negative oxide layer thickness, which practically means that no or a very thin, porous oxide layer formed during the experimental time. This is in accordance with our cyclic voltammetry results, which shows the highest anodic dissolution at this sample. In addition, the formation of the porous CoOOH can also be discovered at this alloy. Kim [46] pointed out that if the Co is present in Co$^{3+}$ form in the Ni / Co films then the absence of Co$^{2+}$ provides less proneness to the passivity and the formation of a well protecting oxide layer [39], leading to a higher alloy dissolution. Therefore, in this case, Co plays a minor role in oxide layer formation and this is in agreement with results of Y. Bo at al. [48].
4. Summary

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.
References


REFERENCES


NYILATKOZAT

Alulírott Tury Barbara kijelentem, hogy ezt a doktori értekezést magam készítettem és abban csak a megadott forrásokat használtam fel. Minden olyan részt, amelyet szó szerint, vagy azonos tartalomban, de átfogalmazva más forrásból átvettem, egyértelműen, a forrás megadásával megjelöltem.


Tury Barbara