Microstructure and mechanical properties of disperse Ni–Co alloys electrodeposited on Cu substrates

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1. Introduction

The recent interest in the electrodeposition of iron-group metals (Ni, Co and Fe) and their alloys is due to their unique magnetic and thermophysical properties [1,2]. Electrodeposition is a process which is capable for depositing nanocrystalline metals and alloys [3] onto recessed and non-uniform surfaces, and therefore has found a role in microelectromechanical systems (MEMS) [2,4–7]. The hardness and strength of the electrolytic deposits are better than alloys prepared by conventional metallurgical processes [2]. One of the most important aspects of electrodeposition process is possibility for production of nanocrystalline materials which exhibit unique properties compared to the microcrystalline counterparts [3].

A metal powder represents a loose deposit which can spontaneously fall off from the electrode or can be removed by tapping or by other similar way [8–10]. The electrodeposition of the powders from the solutions, established by the work of Calusaru [11] possesses significant advantages over other methods for synthesis of nanocrystalline materials [3]. This method usually yields products of requested chemical composition and high purity, which can be well pressed and sintered [12–14]. The effect of operating conditions, electrolyte composition, temperature and pH on the Ni–Co composition and properties of obtained deposits are widely investigated [15–18]. On the other hand, electrodeposition at very high current density and high overpotential is only investigated for the case of the obtaining of powders [19–21].

However, electrochemical synthesis of disperse deposits on the substrate is insufficiently investigated [8]. Investigations of such Cu deposits formed at high current densities characterized by open and very porous structures with extremely high surface areas were initiated recently [22]. It has been stated that the open and porous structures of copper deposits obtained at high current densities were ideally suited for use as electrodes in electrochemical devices such as fuel cells, batteries and chemical sensors [22], while the extremely high surface area is relevant for evaluating

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some electrochemical reactions [23]. Surface microstructure plays a crucial role in application such as a magnetic storage, printing devices and all other similar technological procedures, but correlation between surface morphology and roughness structure with deposition parameters is still open topic [24]. Three-dimensional (3D) characterization seems more adapted for applied research. Therefore, the aim of this study is investigation of the influence of deposition current density on microstructure of disperse Ni–Co deposits and correlation between electrolysis conditions for formation of such rough deposits on the substrates with morphology, surface roughness and mechanical properties.

2. Experimental

The deposits were obtained in an open glass electrochemical cell with a volume of 1 dm³, thermostatically controlled at a temperature of 298 K. A Ti-plate covered with RuO₂/TiO₂ (10 cm² geometric area), placed close and parallel to the Cu plate, was used as an anode (DSA). The solutions were made from analytical grade chemicals and triple distilled water. The alloys were electrodeposited from mixed ammonium sulfate-chloride solutions of different Ni²⁺/Co²⁺ ions concentration ratios of 0.25, 0.5, 1, 2 and 4 (total concentration of NiSO₄ + CoSO₄ was 0.12 mol dm⁻³ using 0.5 mol dm⁻³ NH₄Cl and 3.5 mol dm⁻³ NH₄OH as a buffering agent and a supporting electrolyte at pH 10. The electrodeposition was performed with a constant current regime ranging from 65 to 400 mA cm⁻². The deposition time was adjusted to the same quantity of electricity (43 mA cm⁻²). Polarization diagrams were recorded with the three-compartment standard electrochemical cell at a temperature of 298 K. The platinum foil counter electrode and the reference—saturated calomel electrode (SCE) were placed at separate compartments connected to the working electrode by a Luggin capillary positioned at a distance of 0.2 cm from the working electrode surface. The working electrode was a copper electrode rod (d = 0.4 cm). Before each experiment the working electrode surface was polished using 0.05 μm alumina impregnated polishing cloths. The Ni–Co alloys were electrodeposited with same quantity of electricity (43 mA h cm⁻²).

Polarization curves for the cathodic process of Ni–Co deposition on copper cathode for different composition of the electrolyte: (○) Ni²⁺/Co²⁺ = 0.25; (©) Ni²⁺/Co²⁺ = 0.5; ( ▲) Ni²⁺/Co²⁺ = 1, (□) Ni²⁺/Co²⁺ = 2 and ( ■) Ni²⁺/Co²⁺ = 4, corrected for IR drop. Scan rate 1 mV s⁻¹.

Fig. 1. Polarization curves for the cathodic process of Ni–Co deposition on copper cathode for different composition of the electrolyte: (○) Ni²⁺/Co²⁺ = 0.25; (©) Ni²⁺/Co²⁺ = 0.5; ( ▲) Ni²⁺/Co²⁺ = 1, (□) Ni²⁺/Co²⁺ = 2 and ( ■) Ni²⁺/Co²⁺ = 4, corrected for IR drop. Scan rate 1 mV s⁻¹.  
3. Results and discussion

3.1. Current efficiency

Fig. 1 shows the polarization curves for different compositions of the electrolyte performed on a Cu cathode. The polarization curves for different current densities and compositions of the electrolyte: (○) Ni²⁺/Co²⁺ = 0.25; (©) Ni²⁺/Co²⁺ = 0.5; ( ▲) Ni²⁺/Co²⁺ = 1, (□) Ni²⁺/Co²⁺ = 2 and ( ■) Ni²⁺/Co²⁺ = 4.

The hydrogen evolution during the deposition of the alloys diminishes the current efficiency, depending on the electrolyte composition as well as on the current density. These results are in agreement with polarization measurements where alloys with less nickel content have lower hydrogen overpotential and consequently a lower current efficiency. In the current density range, where the disperse deposits were obtained, the current efficiency decreases with the increase of the current density and with the decrease of the Ni²⁺ concentration in the electrolyte.
3.2. Composition of the Ni–Co alloys

In order to define the influence of the electrolyte concentration on composition of the obtained disperse Ni–Co deposits, the electrodeposition from five electrolytes of different compositions at current density of 65 mA cm$^{-2}$ was performed. The chemical composition of the alloys galvanostatically deposited was determined for alloy samples as an average of 3 measurements with surfaces of $10^{-2}$ m$^2$ with an error of ±2%. Afterwards, current densities of 220 and 400 mA cm$^{-2}$ were selected to define the effect of the current density on deposit composition for a chosen electrolyte composition.

According to the EDX analysis, the electrolyte composition (Ni$^{2+}$/Co$^{2+}$ ions ratio) as well as the current density, affects the composition of the electrodeposited alloys remarkably, Figs. 3 and 4.

However, the percentage of Ni in the deposit, especially for the deposit obtained from the electrolyte with [Ni$^{2+}$]/[Co$^{2+}$] = 0.25 was lower than in the electrolyte solution, Fig. 3. This indicates that the electrochemical alloying leads to an increase in the reaction rate of Co at relatively low current density of $j = 65$ mA cm$^{-2}$ resulting in the higher content of cobalt in the alloy than in the electrolyte. Such behavior is in accordance with the term “anomalous co-deposition” as introduced by Brenner [25] which refers to the preferential deposition of the less noble metal, i.e. Co. Besides, with the increase of the Ni$^{2+}$ concentration in the electrolyte, the Ni content in the alloys almost reaches its content in the electrolyte.

The difference between the electrolyte composition and the deposit composition (Fig. 4) is much less pronounced at high current density, i.e. $j = 400$ mA cm$^{-2}$. The composition of the obtained deposit is almost similar to the concentration of the metal ions in the electrolyte. In this case, the composition of the deposits is dependent on the current density, indicating that an increase of the current density is accompanied by a decrease of the cobalt content in the deposit. An increase of the current density leads to an increase of the overpotential which is combined by an increase of the activation of the electrode reaction. This results in an increase of the nickel content in the deposits.

3.3. Microstructure of deposits-Influence of chemical composition of the electrolyte on microstructure

Fig. 5 shows a series of XRD patterns for all five alloys electrodeposited from different bath compositions at a selected current density of $j = 65$ mA cm$^{-2}$ with same quantity of electricity and with an average sample thickness of $(25 ± 5)$ μm.

The X-ray analysis of the deposits shows the presence of solid solutions of Ni and Co with a structure which changes progressively with the change of their chemical composition depending on the used electrolyte. For the lowest content of Ni, a single phase deposit involves the hexagonal close-packed (HCP) phase also known as α-phase (Fig. 5a). With the increase of nickel content in the deposit ranging to 30–40 at%, the mixture of face centered cubic (FCC) also known as ε-phase and the HCP phase was found (Fig. 5b–d). With the further increase of Ni content in Ni deposit, only a single FCC phase is observed (Fig. 5e). The noticed diffraction peaks of Cu with low intensity belong to the substrate material. Deposits rich in Co and deposits rich in Ni (Fig. 5a and e) exhibit cell volumes comparable to the theoretical values of Co (22.1 Å$^3$) and Ni (43.8 Å$^3$), cf.
Table 1
Phase composition, grain size and cell parameters of the electrodeposited alloys.

<table>
<thead>
<tr>
<th>Ni²⁺/Co²⁺ concentration (%)</th>
<th>Crystal structure/concentration (%)</th>
<th>Grain size (nm)</th>
<th>a (Å)</th>
<th>c (Å)</th>
<th>Cell volume (Å³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni²⁺/Co²⁺ = 0.25/65 mA cm⁻²</td>
<td>HCP/100</td>
<td>20</td>
<td>2.596</td>
<td>4.069</td>
<td>22.126</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 0.5 65 mA cm⁻²</td>
<td>FCC/27 HCP/73</td>
<td>11/9</td>
<td>3.533/2.505</td>
<td>4.076</td>
<td>44.114/22.153</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 1/65 mA cm⁻²</td>
<td>FCC/28 HCP/72</td>
<td>19/15</td>
<td>3.529/2.505</td>
<td>4.072</td>
<td>43.955/22.127</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 1/220 mA cm⁻²</td>
<td>FCC/71 HCP/21 amorphous phase/8</td>
<td>13/11</td>
<td>3.530/2.499</td>
<td>4.077</td>
<td>43.971/22.043</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 1/400 mA cm⁻²</td>
<td>FCC/82 HCP/3 amorphous phase/15</td>
<td>11/10</td>
<td>3.533/2.455</td>
<td>4.096</td>
<td>44.096/22.100</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 2.65 mA cm⁻²</td>
<td>FCC/87 HCP/13</td>
<td>14/5</td>
<td>3.528/2.480</td>
<td>4.057</td>
<td>43.901/21.610</td>
</tr>
<tr>
<td>Ni²⁺/Co²⁺ = 0.25/65 mA cm⁻²</td>
<td>FCC/100</td>
<td>13</td>
<td>3.526</td>
<td></td>
<td>43.833</td>
</tr>
</tbody>
</table>

Fig. 6. SEM micrographs of Ni–Co deposits obtained at a current density 65 mA cm⁻² from an electrolyte with different Ni²⁺/Co²⁺ concentration ratio: (a) 0.25, (b) 0.5, (c) 1, (d) 2 and (e) 4.
The morphology of all Ni–Co deposits strongly depended on the chemical composition of the alloy deposit, i.e. the chemical composition of the electrolyte, Fig. 6. For the chosen current density of 65 mA cm\(^{-2}\) with a size varying from 5 to about 50 µm composed of fine nanosized crystallites of different morphology were obtained.

The morphology of the alloy deposited from electrolyte with the highest concentration of [Co\(^{2+}\)] ions in the electrolyte, at current density of 65 mA cm\(^{-2}\) is shown in Fig. 6a. This deposit possesses the platelet structure.

For the concentration ratio [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 1 in the electrolyte, the morphology of the deposit is slightly changed and consists of cauliflower particles exhibiting a surface morphology based on preferred oriented platelets (Fig. 6c). Fig. 6b and d show enhanced dendritic growth with more dispersed deposits obtained from the baths with the concentration ratio [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 0.5 and 2, respectively. At one and the same current density of 65 mA cm\(^{-2}\), more developed structures are formed leading an increase of the mean surface roughness. Finally, the particles deposited from the electrolyte with the highest content of Ni show cauliflower structure, Fig. 6e. The morphology of the deposits is similar to the morphology of the pure Ni obtained from the Wath’s bath without addition of a surfactant substance [8,20].

The SEM micrographs show that the surface morphology of the deposit is determined by the nature of the electrochemically active ions or complexes and the kinetics of the electrocrystallization process.

### 3.4. Phase analysis of deposits—Influence of current density on microstructure

A detailed Rietveld’s analysis revealed that the phase composition of the deposited Ni–Co solid solutions depends on the composition of the electrolyte bath as well as on the applied current density (Fig. 7). Rietveld’s refinement procedure [26] is able to simulate the XRD pattern from given starting parameters. The purpose of this simulation is to refine individual parameters, e.g. phase fraction, grain size, and crystal lattice parameters, to obtain a good fit. For this purpose Rietveld’s refinement program TOPAS V3.0 (Bruker AXS GmbH, Germany) was used [27]. The quality of the refinement progress was controlled by monitoring the fit parameter \(R_{wp}\), the goodness of fit (GOF), and the Durbin–Watson factor.

The deposits obtained from an electrolyte with a equal ion metal concentration ratio, [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 1, have shown the formation of a mixture of both phases, HCP and FCC. The formation of solid solutions is a consequence of the mutual miscibility of Ni and Co in the range of concentration in the obtained deposits (Table 1) which is in accordance with the phase diagram [28]. The decrease of the current density results in pronounced crystallization and an increase of the size of crystallites as well as a higher HCP content in the alloys. Evolution of the FCC phase content from the same bath was achieved by the increase of current density (Fig. 8).

If the kinetics of the deposition process is fast, a disperse deposit can be obtained at low driving force, while a much larger driving force is needed for kinetically slow processes such as Ni and Co deposition [8] resulting in an electrodeposition process far from equilibrium conditions, i.e. at high overpotentials, and in the formation of the FCC phase. At low overpotentials, a higher amount of Co as the HCP phase is formed.

### 3.5. Grain size of Ni–Co alloy deposits

The electrolyte composition and the current density have a great effect on the grain size of the deposits. Average grain sizes were calculated from the peak broadening from XRD according to the Scherrer relation with the Rietveld refinement method [26]. Obtained alloy deposits were composed of fine nanosized crystallites (cf. Table 1).

The alloy electrodeposited at selected current density of 65 mA cm\(^{-2}\) from the electrolyte with the ratio [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 0.25 (Fig. 5a), contains the \(\varepsilon\)-Co phase with hexagonal close-packed lattice and with an average grain size of 20 ± 2 nm. The average grain size in the deposits consisting single FCC phase was 13 ± 2 nm (Fig. 5e). In general, deposits with finer grain sizes are obtained with increasing [Ni\(^{2+}\)] concentrations in the electrolyte. With increasing Co content in the alloys (Table 1) the average size of crystallite increases ranging from 13 to 19 nm for the FCC phase and from 15 to 20 nm for the HCP phase. The mixture of two phases leads to a further grain size refinement of deposits.

A reduction of the grain size was also achieved by an increase of the current density. Increasing the current density leads to the increase of the overpotential, and therefore increases the nucleus formation probability resulting in smaller critical radii and the number of atoms constituting the nucleus. Hence, the increase of current density decreases the grain size of the Ni–Co deposits (Table 1). The formation of electrochemical deposits from electrolytes with a higher [Ni\(^{2+}\)]/[Co\(^{2+}\)] ratio is accompanied by higher overpotential values, therefore deposit with finer grains is formed.
from a bath containing a higher Ni\(^{2+}\) ions concentration (Table 1.). For the deposition of more disperse deposits composed from fine nanosized crystallites, the use of the overpotentials higher than 1.3 V are requested, specifically in the case of the deposits obtained from electrolyte with concentration ratio [Ni\(^{2+}\)]/[Co\(^{2+}\)] > 0.5.

3.6. Surface roughness of Ni–Co alloy deposits

The 3D dataset was deduced from two stereoscopic images obtained by tilting the sample stage in the ESEM at the eucentric point with an angle of 5\(^{\circ}\), Fig. 9a–c. The calculated roughness parameters are shown in Table 2.

The concentration ratios [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 0.25 and 4 corresponding to a single-phase systems, led to a surface with similar mean roughness values in spite of different morphology, (Fig. 6a and e), respectively. In the case of a ions concentration [Ni\(^{2+}\)]/[Co\(^{2+}\)] = 1, involving more than one phase, the Ra values are almost 3 times higher, and the active surface increases in comparison to the specimens with ratios of 0.25 and 4. An increase in the current density results in a decrease in the mean roughness (Table 2), since at higher current densities the amount of crystal nuclei on the surface is enhanced. The larger the nucleation rate, the more homogenous is the grain size distribution leading to the formation of smoother deposits (see also, Fig. 6a and e). 3D SEM reconstruction experimental results confirmed the beginning of disperse deposits formation in galvanostatic deposition using current density, \(j \geq 65 \text{ mA cm}^{-2}\).

3.7. Mechanical properties of Ni–Co deposits

Nanoindentation test were performed to investigate the mechanical properties of the deposited samples. A load of 50 \(\mu\)N was applied on the cross-section of the samples (deposits on copper substrate). The low applied load is needed to make penetration depths small enough to avoid the influence of the substrate on the hardness measurements. The nanoindentation test demonstrated that nanocrystalline deposits have a higher hardness with an increase of the Ni content in the sample (Fig. 10). The hardness of the Ni–Co alloys deposited from the same bath composition but at different current densities shows a reduction of the hardness, not as significant as in the case of the hardness measured on the samples prepared from the different bath compositions.

<table>
<thead>
<tr>
<th>Ni(^{2+})/Co(^{2+}) concentration ratio</th>
<th>Current densities (mA cm(^{-2}))</th>
<th>(Ra) ((\mu)m)</th>
<th>(Rz) ((\mu)m)</th>
<th>RS</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.25</td>
<td>65</td>
<td>0.7</td>
<td>4.7</td>
<td>1.64</td>
</tr>
<tr>
<td>0.5</td>
<td>65</td>
<td>1.3</td>
<td>5.2</td>
<td>1.34</td>
</tr>
<tr>
<td>1</td>
<td>65</td>
<td>3.0</td>
<td>13.1</td>
<td>1.98</td>
</tr>
<tr>
<td>1</td>
<td>220</td>
<td>1.1</td>
<td>5.2</td>
<td>1.38</td>
</tr>
<tr>
<td>1</td>
<td>400</td>
<td>1.0</td>
<td>6.5</td>
<td>1.62</td>
</tr>
<tr>
<td>2</td>
<td>65</td>
<td>2.1</td>
<td>9.2</td>
<td>1.37</td>
</tr>
<tr>
<td>4</td>
<td>65</td>
<td>1.0</td>
<td>4.7</td>
<td>1.64</td>
</tr>
</tbody>
</table>

\(Ra\), mean roughness, \(Rz\), the difference between the highest and the lowest point in the picture of defined scan, RS, active surface, the ratio of the real surface including topography to a projected surface of the measurements (a square with dimensions of 23 \(\mu\)m x 15 \(\mu\)m).
In contrast to some authors [29], the hardness is increased with an increase of the Ni content in the deposits. According to the optical micrographs of the cross-sections of the deposits obtained on the Cu substrate presented in Fig. 11, two possible reasons can cause such behavior. One is the grain size and the second is porosity inside the deposit with high Co content (Fig. 11a). The release of hydrogen in the layer surrounding the electrode also affects the properties of the obtained deposits, causing the formation of craters in the deposit (Fig. 11c). The deposit obtained from the electrolyte with the highest concentration of Ni$^{2+}$ are compact (Fig. 11c), while the deposits obtained at the same current density from the bath with the concentration ratio Ni$^{2+}$/Co$^{2+}$ = 1 show a dendritic structure (Fig. 11b). It should be indicated that when the grain size is smaller than 10 nm, the grain refinement may cause softening of the nanocrystalline metals. In these measurements, differences in the grain size have not been so significant, but they still affect the large difference in the hardness value (Fig. 12).

The nanograin size did not affect the softening of the deposits formed from electrolytes with equal ion compositions, Ni$^{2+}$/Co$^{2+}$ = 1 at different current densities, considering grain sizes of the deposits were in the range of 10 nm. Although the more dendritic deposits performed at higher current densities, are characterized by a reduce...
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grain size, the formation of the deposits with a very disperse dendritic structure has a decisive influence on the measurements.

4. Conclusions

The microstructure as well as the morphology of the Ni–Co alloy deposits electrochemically obtained from an ammonium sulfate-chloride solution depends on the deposition current density and the bath composition. With a decrease in the deposition current density the volume fraction of the HCP phase in the deposits increases accompanied by the crystal grain growth. The increase of HCP phase content in the nanocrystalline deposits appears as a result of both an increase in the Co²⁺ ions concentration in the bath and a decrease of the deposition current density. The increase of the current density and the decrease of the Co²⁺ ions concentration in the bath results in finer grain deposits. Surface morphology and mean roughness of the deposits depend on the concentration ratio in electrolyte; in the case of equal ions concentration of Ni²⁺/Co²⁺ in the electrolyte, the mean roughness of the deposit is the highest. It is possible to achieve variety of microstructural properties by choosing the current density or the electrolyte composition appropriately.

Acknowledgments

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