Study of the Dendritic Growth of Ni–Co Alloys Electrodeposited on Cu Substrates

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Ni–Co alloy deposits and their parent metals were formed on Cu substrates by electrolysis under different current densities applied in the galvanostatic regime. A quantitative scanning electron microscopy technique was employed to study the morphology and surface roughness of the obtained deposits. The structure of the deposits is governed by the nature of depositing ions and quantity of evolved hydrogen. The cauliflower morphology and the highest mean surface roughness values are the results of electrodeposition from the Ni containing bath. The structure of the Co deposits formed under the same conditions and determined by the formation of the hexagonal close-packed phase results in a more uniform grain size distribution and formation of smoother platelet deposits. The mean surface roughness values of the parent metals are independent of the current density. The dendritic growth is a special case of a structure formed only in the Ni–Co alloy deposition at selected, high current densities of 220 and 400 mA cm⁻². The dendrites obtained at a higher current density of 400 mA cm⁻² have shown more developed structures with smaller dendrites that have more pronounced secondary branch and high order branches.

The electrodeposition is one of the well-known approaches developed in recent years for the preparation of the nanostructured pure metals and alloys. The Ni–Co alloys have been widely investigated due to their unique magnetic and electrical properties, which have found a potential application in different computer read/write heads and microelectromechanical systems.

In general, electrolytic deposits can be compact or disperse. The disperse deposits are formed under electrolysis conditions, which favor a complete diffusion control of the process. The electrodeposition represents an excellent tool for the formation of metal disperse deposits with a highly developed surface area, which can be successfully used as electrodes in electrochemical devices such as fuel cells, batteries, and sensors.

The basic characteristics of these electrodes, which should be fulfilled to be used for these purposes are the open porous structure, which enables the rapid transport of gas and liquid, and the extremely high surface area, which is desirable for electrochemical reactions. According to this, in the galvanostatic powder deposition, the initial deposition current density must be larger than the limiting diffusion current density. The electrodeposition at overpotentials belonging to the plateau of the diffusion-limiting current density leads to the formation of dendritic deposits.

The strong hydrogen codeposition leads to a stirring of the solution and changes the mass-transfer limitations at the electrode surface. At the same time, the evolved hydrogen affects the mass- and heat-transfer, limiting the current density and ohmic resistance, leading to the formation of the open porous deposit structures with a high surface area.

In this work, Ni–Co nanoscaled deposits were prepared and characterized using different techniques, with respect to elucidating the effect of the current density and electrolyte composition on the formation of the dendritic deposits.

**Experimental**

The Ni, Co, and Ni–Co nanostructured deposits were obtained in the galvanostatic regime at a current density range of 65–400 mA cm⁻². The electrolytes were performed from ammonium sulfate–chloride solutions for the concentration ratio Ni²⁺/Co²⁺ = 1 of a solution composition as follows: total concentration 0.12 M (NiSO₄ + CoSO₄), 0.5 M NH₄Cl, and 3.5 M NH₄OH at pH 10. The parent metal deposits were prepared from the same supporting electrolyte with a total metal ion concentration of Co²⁺ or Ni²⁺ being 0.12 M. The reagents of the analytical purity and deionized water were used for the bath preparation. The temperature of the bath during deposition was maintained at 298 K. The Ni, Co, and Ni–Co deposits were prepared at the constant current density with a quantity of electricity of 0.043 Ah cm⁻² and an average sample thickness of (25 ± 5) μm. The Cu electrodes placed in the center of the cell with a 1.0 cm² surface area and a 0.2 cm thickness were used as working electrodes. A Ti plate covered with RuO₂/TiO₂ (10 cm² geometric area), placed close and parallel to the Cu plate, was used as an anode [dimensionally stable anode (DSA)]. The schematic representation of the electrochemical cell used for the deposition is presented in Fig. 1.

The polarization measurements were carried out by a computer-controlled electrochemical system (PAR M 273A, software PAR M352/252, version 2.01) with a sweep rate of 1 mV s⁻¹. For the correction of the IR drop, the current-interrupt technique was used with a time of current interruption of 0.5 s. The polarization curves were measured in a three-electrode electrochemical cell at (298 ± 1) K (Fig. 1), where the DSA was replaced by a large-area platinum mesh. The Luggin capillary connecting the reference electrode [saturated calomel electrode (SCE)] to the electrolyte was positioned at a distance of 0.2 cm from the working electrode (copper rod embedded in resin, d = 4 mm). Before each experiment, the working electrode was highly polished with an alumina-paste (0.05 μm)-impregnated polishing cloth.

The average current efficiency for the hydrogen evolution reaction is determined by the measurement of the quantity of evolved hydrogen based on Faraday’s law. The overall electrodeposition current was calculated as a function of the electrodeposition time. The thickness of the deposits was estimated based on their cross-section images.

The surface morphology was analyzed by XL 30 environmental scanning electron microscope (ESEM) with field emission gun (FEI Co., Netherlands). The profile and roughness measurements, as well as three-dimensional (3D) area analyses, directly from the stereoscopic images of the specimen surface were carried out using MeX software from Alicona (A). The cross-section alloy composition...
analyses of the deposited samples embedded in the resin were performed by ESEM using the energy dispersive X-ray analysis (EDX) technique (Genesis).

X-ray powder diffraction (XRD) analysis was carried out using an MPD diffractometer (Philips, NL) with Cu Kα radiation (40 kV/30 mA) in Bragg/Brentano geometry. The step scan mode was utilized with 0.03° in a 2θ/1.15 s step. The angular 2θ range investigated was 20–110°.

Results and Discussion

Cathode polarization and efficiency.— During the cathodic electrodeposition of the iron group metals from aqueous solutions, a competitive cathodic hydrogen evolution reaction occurs.12 Because the formation of the disperse and powder deposits is enhanced by a small metal ion concentration and high deposition current density, polarization curves were measured with a correction for the IR drop. In this case, the plateau corresponding to the limiting current density cannot be established, as in the case for the electrodeposition performed from aqueous solutions containing an electropositive metal such as Cu due to the intensive hydrogen evolution reaction almost from the beginning of the deposition. At the end of this plateau and at larger overpotentials, the intensive hydrogen evolution takes place. Therefore, the polarization curves for the electrodeposition of Ni, Ni–Co, and Co are complex with the appearance of the limiting current density in a wide range of potential values (Fig. 2a), characterized by the electrodeposition currents that grew (Fig. 2b) with the increasing of the overpotential. The corresponding overpotential needed for the deposition is most positive for the deposition of Co, followed by the deposition of Ni–Co alloy and Ni.

The electrodeposition potentials of Ni, Ni–Co, and Co are very similar with the values of about −0.5 V vs SCE. The range of potentials of −0.6 to −1.0 V is the activation control region of the metal and alloy electrodeposition. The deposition at overpotentials higher than −1.1 V is characterized by a sharp increase in the current density, most probably as a consequence of the formation of dendritic deposit with more developed structures.

The hydrogen evolution reaction in the alkaline solution proceeds according to the three reaction mechanisms13 resulting in the release of OH− ions in the layer surrounding the electrode and, therefore, an increase in pH. However, the bath for the electrodeposition consists of NH₄Cl/NH₄OH used as a buffering agent for pH 10, and no significant increase in pH during deposition was observed.

The hydrogen overpotential can manifest itself through the cathodic current efficiency (Fig. 3). The hydrogen evolution during the deposition of the alloys diminishes the current efficiency, depending on the electrolyte composition and on the current density. These results agree well with the polarization measurements where the electrodeposition performed from bath with Co bath has a lower hydrogen overpotential and consequently a lower current efficiency.
Also, the evolution of hydrogen provides some additional stirring effect and enhances the formation of disperse deposits with more developed structures. Deposition becomes dependent on hydrogen evolution because at current densities, \( j = 200 \, \text{mA cm}^{-2} \), the hydrogen evolution is predominant in the overall cathodic process. The current efficiencies for the Ni-containing electrolyte and for the Co-containing electrolyte at a current density of 200 mA cm\(^{-2} \) were found. The hydrogen method used for the calculation of the current efficiency of the Ni, Co, and Ni–Co alloys results in slightly higher values in comparison with the current efficiency data obtained by the gravimetric method. An explanation is attributed to the fact that the formation of dendritic deposits at higher current densities can cause the fall of some amount of deposit into the solution, resulting in less weight values and, consequently, diminished values of the calculated current efficiency.

**Growth of Ni, Co, and dendritic Ni–Co deposits on Cu substrates.**—The needlelike deposits known as dendrites are usually obtained by electrodeposition at low cation concentrations. By definition, dendrite represents a skeleton of monocrystals and consists of stalk and branches resembling a tree.

The scanning electron microscopy (SEM) of the Ni–Co deposit cross sections obtained on copper substrates has shown the gradual evolution of the dendritic formation (Fig. 4a–c). With an increasing current density, a detailed investigation of the deposits morphology has shown a formation of primary dendrites, which further grows with increasing current density. The sample obtained at a current density of 65 mA cm\(^{-2} \) revealed the formation of a rough deposit (Fig. 4a). The propagation of this structure by branching produces dendrites, as shown in Fig. 4b. The dendrites obtained at a higher current density of 400 mA cm\(^{-2} \) (Fig. 4c) have shown more developed structures with smaller dendrites that have more pronounced secondary branch and high order branches. A comparison with deposits obtained from pure Ni baths revealed a formation of a rough deposit only (Fig. 5a). In contrast, electrodeposition performed at the lowest value of the current density, i.e., 65 mA cm\(^{-2} \), from a pure Co bath has shown a formation of dendritic growth (Fig. 5b). In the particular case of anisotropic Co deposition when the hexagonal close-packed (hcp) lattice is formed, the growth along the high index axis does not lead to a formation of low index planes. Therefore, the hcp lattice serves as a growth site for the dendrite formation because the development of protrusions along some axis in the direction of the increasing concentration is more favorable. Repeated nucleation results in the dendrite formation. Although deposits produced from simple solution salts without additives are often dendritic or treelike, real dendritic structures are formed only from Ni–Co baths (\( \frac{\text{Ni}^{2+}}{\text{Co}^{2+}} = 1 \)), whereas with increasing current density, the dendritic growth is even more pronounced (Fig. 4b and c).

In this range of concentrations, Ni and Co exhibit a mutual solid solubility. The deposition from bath with different \( \frac{\text{Ni}^{2+}}{\text{Co}^{2+}} \) concentration ratios, i.e., 0.25, 0.5, 2, and 4, results in more disperse than the dendritic growth.\(^{14} \)

**EDX composition analysis of Ni–Co deposits.**—The cross-section composition analysis of the alloys galvanostatically deposited from the solution containing the total concentration of...
0.12 mol dm$^{-3}$ of ion metal with a ratio Ni$^{2+}$/Co$^{2+} = 1$ is presented in Table I. The composition of the dendritic deposit samples near the electrode surface and in some distance is different.

An EDX analysis revealed that at higher current densities, i.e., 220 and 400 mA cm$^{-2}$, the deposition of Co is enhanced near the electrode surface due to the lower overpotential for the Co electrodeposition (Fig. 4b and c), reaching values of the corresponding ions in the solution (Fig. 4b and c). An explanation can be attributed to the fact that at high current densities, the hydrogen evolution is higher (Fig. 3), providing some stirring effect and leading to the more uniform distribution of Ni$^{2+}$ and Co$^{2+}$ ions in the diffusion layer and therefore resulting in a more uniform composition of the deposit. At high current densities, high growth velocities deplete the cations in the double layer, and the growth is controlled by mass transfer in the electrolyte. However, for a lower current density of 65 mA cm$^{-2}$ (Fig. 4a), the deposition comes more under the activation control, so the deposition of Co is enhanced compared to Ni.

At a current density of 65 mA cm$^{-2}$, the content of Co in the deposit is higher than in the electrolyte, as a consequence of the lower overpotential for the Co$^{2+}$ reduction compared to Ni$^{2+}$, as can also be seen from the polarization curves (Fig. 2). In the current density range 65–400 mA cm$^{-2}$, the current density increase results in an increase in the nickel content in the deposits. The phenomenon

![Figure 5](image-url) Cross section of Ni deposit galvanostatically obtained from the solution containing 0.12 M NiSO$_4$ at current density of 65 mA cm$^{-2}$. (b) Cross section of Co deposit galvanostatically obtained from the solution containing 0.12 M CoSO$_4$ at current density of 65 mA cm$^{-2}$.

![Figure 6](image-url) XRD of Ni–Co deposits galvanostatically obtained on Cu substrate from the solution containing 0.12 M (NiSO$_4$ + CoSO$_4$), Ni$^{2+}$/Co$^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm$^{-2}$ (S-reflection attributed to the Cu substrate).

### Table I. Cross-section composition analysis of Ni–Co alloys galvanostatically deposited at different current densities.

<table>
<thead>
<tr>
<th>Atom % Ni</th>
<th>Atom % Co</th>
<th>j (mA cm$^{-2}$)</th>
<th>Spot position</th>
</tr>
</thead>
<tbody>
<tr>
<td>40</td>
<td>60</td>
<td>65</td>
<td>Interface</td>
</tr>
<tr>
<td>22</td>
<td>78</td>
<td>65</td>
<td>Bulk</td>
</tr>
<tr>
<td>39</td>
<td>61</td>
<td>220</td>
<td>Interface</td>
</tr>
<tr>
<td>49.5</td>
<td>50.5</td>
<td>220</td>
<td>Bulk</td>
</tr>
<tr>
<td>37</td>
<td>63</td>
<td>400</td>
<td>Interface</td>
</tr>
<tr>
<td>49.5</td>
<td>50.5</td>
<td>400</td>
<td>Bulk</td>
</tr>
</tbody>
</table>

### Table II. Phase composition, grain size, and cell parameters of the Ni–Co deposits galvanostatically obtained from solution containing 0.12 mol dm$^{-3}$ (NiSO$_4$ + CoSO$_4$), ratio Ni$^{2+}$/Co$^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm$^{-2}$.

<table>
<thead>
<tr>
<th>Current density (mA cm$^{-2}$)</th>
<th>Content of the phases (atom %)</th>
<th>Grain size (±3 nm)</th>
<th>Lattice parameters</th>
<th>Cell volume (Å$^3$)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Amorphous</td>
<td>fcc/hcp</td>
<td>a (Å)</td>
<td>c (Å)</td>
</tr>
<tr>
<td>65</td>
<td>72</td>
<td>28</td>
<td>19</td>
<td>3.5291</td>
</tr>
<tr>
<td>220</td>
<td>20</td>
<td>71</td>
<td>13</td>
<td>3.5296</td>
</tr>
<tr>
<td>400</td>
<td>5</td>
<td>80</td>
<td>11</td>
<td>3.5329</td>
</tr>
</tbody>
</table>

Figure 6. XRD of Ni–Co deposits galvanostatically obtained on Cu substrate from the solution containing 0.12 M (NiSO$_4$ + CoSO$_4$), Ni$^{2+}$/Co$^{2+} = 1$ at current density: (a) 65, (b) 220, and (c) 400 mA cm$^{-2}$ (S-reflection attributed to the Cu substrate).
of the anomalous codeposition (characteristic of the electrodeposition of iron group metals) is very pronounced in the production of compact deposits. In the disperse deposits, the anomalous codeposition is much less pronounced, so that the composition of the deposits obtained at high current density is almost similar to the concentration of the metal ions in the electrolyte (Fig. 4c). Increasing the current density shifts the ratio of Ni and Co in the alloys closer to the value of the concentration of the corresponding ions in electrolyte.

Structural analysis of Ni–Co deposits.— The nanostructured dendritic deposits were analyzed by XRD (Fig. 6). The Rietveld refinement procedure was used to determine the structure and the grain size of the deposits. For this purpose, Rietveld’s refinement program TOPAS V3.0 (Bruker AXS GmbH, Germany) was used. The quality of the refinement process was controlled by monitoring the fit parameter $R_{wp}$, the goodness of fit, and the Durbin–Watson factor.

A detailed Rietveld’s analysis revealed that Ni–Co alloys obtained by the galvanostatic deposition using the same electrolyte at different current densities consist of a mixture of solid solutions. The crystal structure obeys the phase diagram because the obtained bulk deposits are in the range of concentrations where Ni and Co exhibit solid solubility (see Table I).

The face-centered cubic (fcc) phase, whose structure is defined by the $Fm\bar{3}m$ space group, and hcp, whose structure is defined by the $P6\bar{3}mc$ space group, were identified. By increasing the current density, the structure and composition of the obtained deposits is progressively changed. The increase in the current density leads to the increase in the content of the fcc phase, as well as the formation of significant amounts of the amorphous phase (Table II). Furthermore, the cell volume of the fcc phase increases slightly with increasing current density (Table II).

At a current density of 65 mA cm$^{-2}$, mainly the hcp phase, the equilibrium phase of Co stable at room temperature is generated, and it is in good correlation with the EDX results of the bulk material (Table I). At higher electrode polarization, i.e., far from equilibrium, at a current density of 220 mA cm$^{-2}$, the fcc phase growth preferentially on the polycrystalline FCC-structured Cu substrate. Still, an amount of 20% hcp phase (Co) calculated by the XRD Rietveld refinement is present (Table II). Taking into account the amount of an amorphous phase of 9%, this means that approximately 70% of the deposit is composed of the fcc solid solution.

In the deposition at a current density of 400 mA cm$^{-2}$, even further from equilibrium in comparison with deposits obtained at 220 mA cm$^{-2}$, the growth of the fcc phase is more pronounced (Table II). As determined by TOPAS using the Rietveld method, the disperse deposits with more developed structures obtained at a high current density, i.e., 400 mA cm$^{-2}$, also contained an up to 15% amorphous phase. The amorphous phase content, attributed to the enhanced background intensity, was estimated by the determination of the integral area of the broad diffuse diffraction halo, which cannot be assigned to distinct diffraction maxima correlated with crystalline phases and by comparing with samples without an amorphous phase.

The classical expression for the steady-state nucleation rate $J$ is given by

$$J = K_1 \exp \left( - \frac{K_2}{\eta} \right)$$  \hspace{1cm} [1]

where $K_1$ and $K_2$ are practically overpotential-independent constants. The nucleus probability formation $J$ is enhanced by the increase in the overpotential $\eta$. The electrochemical deposit formation at higher current densities is accompanied by higher overpotential values. Based on the equation, obviously, a further increase in the current density decreases the grain size of the deposits down to 10 nm (Table II).

Surface morphology of Ni–Co deposits.— The nature and magnitude of the applied electric field across the counter-working electrode arrangement determines (i) grain size, (ii) surface roughness, and (iii) dendritic electrodeposition growth.

The surface roughness of the Ni–Co deposits was determined by the 3D SEM reconstruction of the specimen surface (Fig. 7a-c). Such a characterization gives quantitative results of the mean sur-
face roughness: $\sigma = 3$ $\mu$m in the deposit obtained at current density 65 mA cm$^{-2}$ (Fig. 7a) and $\sigma = 1$ $\mu$m in the deposits obtained at current densities 220 and 400 mA cm$^{-2}$ (Fig. 7b and c). The value $\sigma$ represents a picture of local surface irregularities and gives the height deviation of the surface from the mean level. An increase in the current density results in a decrease in the mean roughness because at higher current densities, the amount of crystal nuclei on the surface is enhanced, causing a more homogeneous grain size distribution and, therefore, formation of a smoother deposit.

The effective surface roughness increases due to the increase in the coarseness of the deposit with increasing current density (Fig. 7b and c). This surface amplification leads to the initiation of the preferential growth of protrusions or dendrites. The Ni deposits obtained from simple solution salts are characterized by a cauliflower surface morphology and mean surface roughness values of $\sigma = 4$ $\mu$m for all analyzed deposits obtained at current densities of 65, 220, and 400 mA cm$^{-2}$. A typical 3D SEM reconstruction of the surface of the Ni deposit is presented in Fig. 8.

Co deposits have shown mean $\sigma$ values of 1 $\mu$m, and the result of the deposition is the appearance of smoother deposits compared to the Ni deposits (Fig. 9). One of the consequences of hydrogen evolution is that H$_2$ bubbles are attached to the surface during deposition and therefore can cause growth of the deposit around the bubbles before they are released. Such impact of hydrogen during the codeposition of Ni can cause larger mean surface values of Ni deposits. The confirmation of these is the presence of craters or holes in the Ni deposit (Fig. 10a), clearly visible on the surface of one typical SEM micrograph. The bottoms of the holes consist of small Ni particles, while around them during codeposition, larger cauliflower particles are formed. A faster growth of the deposit around bubbles is caused by increasing current density because the overall current is concentrated around the bubbles, which are not conductive. This directly results in the formation of high surface area disperse deposit confirmed by 3D SEM results and the value of surface roughness of $\sigma = 4$ $\mu$m. A typical SEM micrograph of particles of the Co deposit (Fig. 10b) separated by boundaries is characterized by the platelet morphology with very fine nanosized crystallites growing on the surface during codeposition from the Co-containing bath. In both cases, the particles consist of smaller agglomerates of grains.

The surface morphology of the Ni–Co deposit is characterized by the formation of dendrites. Figure 10c shows the cauliflower-shaped
particles with dendrites growing on its surface. Increasing the overpotential under a strong hydrogen codeposition leads to the dendritic deposits formation in the Ni-Co alloy deposition.

The basic cause of dendritic growth is the formation of the diffusion field of depositing ions that favors the development of protrusion in the direction of increasing concentration. Dendrite exhibits a highly ordered structure and grows and branches in well-defined directions.

The motion of the growing interface is controlled by a concentration of the diffusing particle and electric potential. According to Fick’s law, which satisfies the equation for a nonlocal growth process, such as electrodeposition, the low value of the growth velocity and the large value of the diffusion length enhance the deposition preferentially on protrusions.

Well-defined organizations, such as dendritic, are formed under such conditions. A schematic representation of the common effect of hydrogen and electrolysis conditions, which favor the dendrite formation, is shown in Fig. 11.

Apart from decreasing the concentration of the depositing ion, the formation of a dendritic deposit can also be enhanced by increasing the concentration of the supporting electrolyte, increasing the viscosity of the solution, decreasing the temperature, and decreasing the velocity of motion of the solution.

**Conclusion**

The grain size of Ni-Co deposits is determined by the applied overpotential. Increasing current density results in finer grain deposits. The structure of Ni-Co deposits is characterized by a solid solution formation; increasing current density results in an increase in the volume fraction of the cubic phase. The morphology of Ni-Co is affected by conditions applied during electrolysis. Morphology is determined by the nature of depositing ions. The Ni deposit exhibits a spherical growth during deposition, which manifests itself by a typical cauliflower structure; the surface pattern of the Co deposit is characterized by a platelet structure. The composition of the alloy deposit is determined by the hydrodynamics conditions in the near electrode layer; with increasing current density, the hydrogen evolution is predominant, leading to the more uniform distribution of Ni and Co ions in the double layer, and, therefore, the composition of the deposits reaches the real value of the corresponding ions in the solution. The whole process determines the density of nucleation sites and the final morphology of the deposit. The formation of the dendritic Ni-Co alloy deposits is enhanced by increasing the current density and leads to a decrease in the mean roughness. The number of atoms in the nucleus having the critical radius declines with the overpotential square, resulting in a more rapid nucleation at higher current density and the formation of smaller crystals with the average grain sizes of 10 nm. The increase in the current density leads to an increase in the volume fraction of the cubic phase in the nano-crystalline alloy deposits with a corresponding decrease in the grain size.

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