

FINAL REPORT – OTKA NN 79846

The major goal of the project carried out in collaboration with TU Freiberg (Germany) is to correlate the giant magnetoresistance (GMR) properties of electrodeposited magnetic/non-magnetic multilayers with their structural features. It was planned to investigate the following three systems:

- (i) Ni/Cu with unlimited mutual solubility in an fcc structure;
- (ii) Co/Cu with very limited mutual solubility in stable phases (hcp-Co, fcc-Cu) but with the possibility of the formation of a metastable alloy by incorporating Cu in fcc-Co; and
- (iii) Co/Ru with unlimited mutual solubility in the hcp structure.

Although the domestic project of the partner institute in Germany could not be extended for the second year of the project period, the original goal was fulfilled. Besides the study of the three key element pairs, multilayers have been also prepared for magnetocaloric studies and the element distribution of several electrodeposited alloys has been studied with a novel method (the latter fields were studied independently of the foreign partner).

The report below accounts for all results achieved in the framework of the present project.

1. Microstructure formation in electrodeposited Co-Cu/Cu multilayers

The influence of the current density applied during the deposition of the magnetic layers on the microstructure formation in electrodeposited Co-Cu/Cu multilayers and on their GMR was investigated. The key parameter in this study is the ratio of the deposition current density of the magnetic layer (j_{mag}) to the diffusion limited current density of the non-magnetic Cu spacer metal (j_{Cu}). When the current density is increased from j_{Cu} to higher values, the deposit becomes more and more Co-rich as long as a moderate current density is applied. At very high current densities ($|j_{\text{mag}}| > 100 \text{ mA/cm}^2$ in our case), the high rate of the hydrogen evolution destroys the sample structure. During our study, the current density always fell in the region where compact deposits could be obtained without the impact of the hydrogen evolution.

The Cu content of the samples increased as the current density for the deposition of the magnetic layers decreased from -84 mA/cm^2 to -9.6 mA/cm^2 . Concerning the decrease of the current density, the change in the deposit composition is analogous to the case when the Cu^{2+} concentration in the electrolyte is increased and a constant current density is applied (see, e.g., an earlier paper of our group: Liu et al., *J. Electrochem. Soc.* **152** (2005) C316-C323), but the deposition conditions for the Cu layer are identical when the current density is modulated.

The magnetoresistance measurements revealed that a reduction of the current density stimulates a transition from a predominantly ferromagnetic character to the formation of superparamagnetic (SPM) regions (see Figure 1; next page). Based on electrochemical considerations and also on the composition analysis, this change in the magnetoresistance properties is the result of the increased amount of Cu codeposited with Co at low current densities. It turned out from the structural studies that a pronounced segregation of Co and Cu occurs at low current densities. In accordance with their very low mutual solubility at room temperature, no atomic scale intermixing of Co and Cu could be detected in spite of the common fcc lattice of both constituents at this nanoscale level. The segregation of Cu and Co was related to the fragmentation of the magnetic layers, to the enhancement of the local lattice strains, to the increase of the interface corrugations, to the partial loss of the multilayer periodicity and finally to the formation of separated Co grains in a Cu matrix.

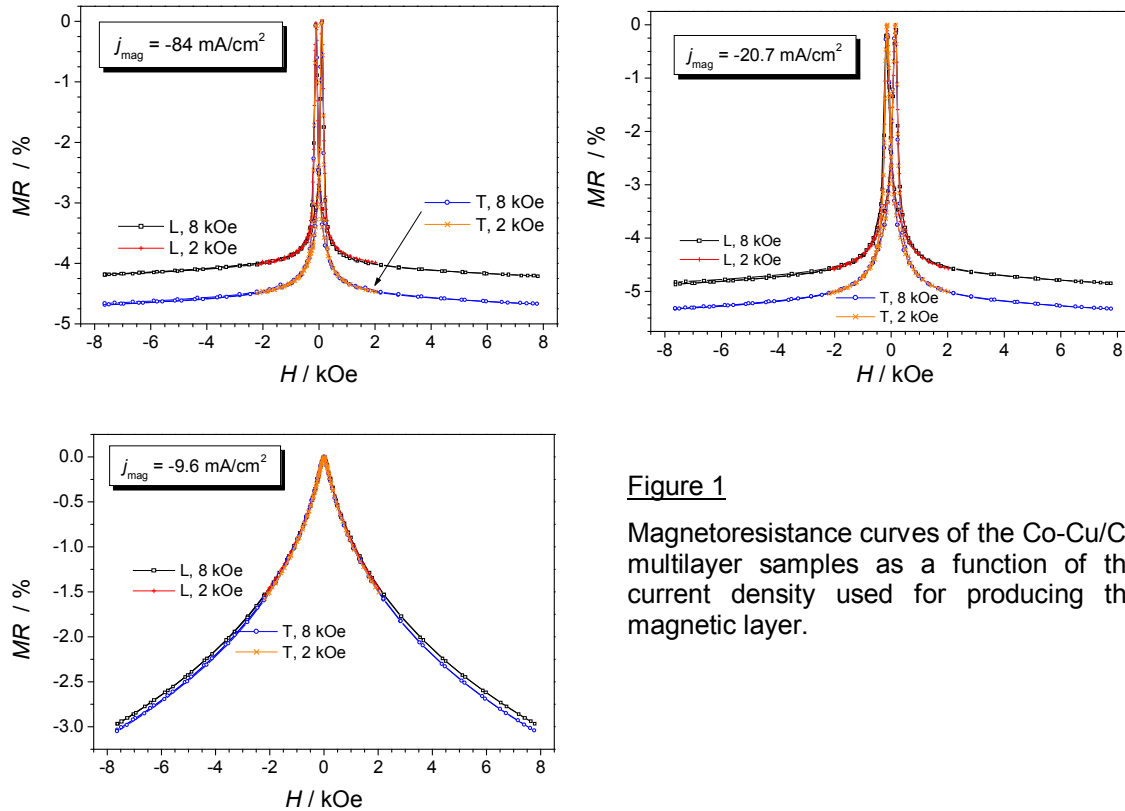


Figure 1

Magnetoresistance curves of the Co-Cu/Cu multilayer samples as a function of the current density used for producing the magnetic layer.

The wide-angle X-ray diffraction data obtained for the same samples were in accord with the composition change. As the Cu content of the deposit increased, the mean position of the main XRD line was shifted to the lower diffraction angles (see Figure 2).

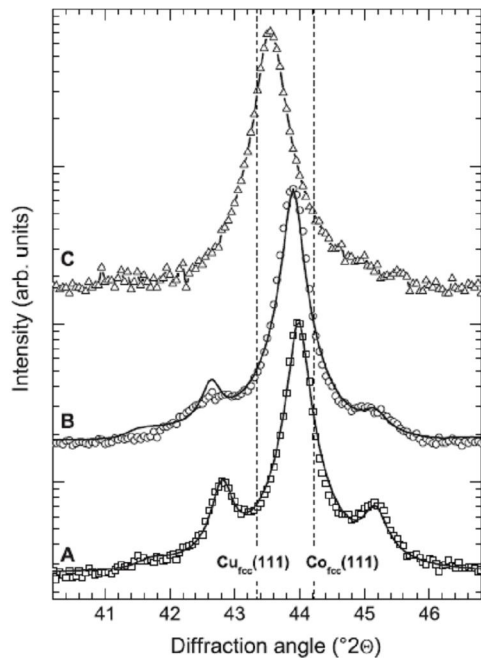


Figure 2

Wide-angle X-ray diffraction pattern of the multilayer samples studied.

Deposition current densities are:
 A, -84 mA/cm^2 ; B, -20.7 mA/cm^2 ;
 C, -9.6 mA/cm^2

As the Cu content of the deposit increased, the mean position of the main XRD line was shifted to the lower diffraction angles (see Figure 2). The fit of the X-ray diffractograms resulted in the same multilayer periodicity than that calculated from the deposition parameters by using Faraday's law. The satellite reflection due to the multilayer periodicity disappeared at high Cu content of the magnetic layer. The loss of the layer-like periodicity was also confirmed by transmission electron microscopy.

The results of the structural study have shown that the microstructure formation in Co-Cu/Cu multilayers is controlled by the competition between the codeposition of Cu with Co during the deposition of magnetic layers and by their segregation. High current density ($j_{\text{mag}} = -84 \text{ mA/cm}^2$) facilitated the growth of laterally continuous, periodic multilayers with large but highly correlated interface corrugations. A decrease of the current density to $j_{\text{mag}} = -20.7 \text{ mA/cm}^2$ led to the formation of columnar grains separated from each other by Cu domains. Other consequences of the segregation of the codeposited elements were a partial loss of the multilayer periodicity, an enhancement of the

interface corrugations and an increase of the lattice strain in both the non-magnetic and magnetic layers. A further reduction of the current density to $j_{\text{mag}} = -9.6 \text{ mA/cm}^2$ resulted in a preferential deposition of Cu at the expense of Co, which caused the formation of Co grains embedded in a Cu matrix. In general, decreasing j_{mag} led to the loss of the periodicity of the multilayers and to the fragmentation of the magnetic layers that enhanced the superparamagnetic contribution to the total magnetoresistance. The ferromagnetic contribution to the total magnetoresistance declined with increasing discontinuity of the magnetic layers.

The atomic distances in the samples parallel and perpendicular to the growth direction were determined mainly by the strain field. As long as the samples have a coherent structure (i.e., for those with low Cu content and having a layered structure), the atomic distances are determined by the strain equilibrium. As a consequence of the strain field within the samples, a very high twin density is observed when the strain is high; i.e., for samples with high Cu content. The tensile stress in the Co (or Co-rich) layer is partly compensated by the lattice defects.

The results of this part of the joint work have been published[#] (*Acta Materialia* **59**, 2992-3001 (2011)).

2. Magnetoresistance and structural study of electrodeposited Ni-Cu/Cu multilayers

Electrodeposition was used to produce Ni-Cu alloys and Ni-Cu/Cu multilayers by direct current (dc) and two-pulse plating, respectively, from two sulfate/sulfamate electrolytes: one with analytical grade Ni-sulfate (impure electrolyte) and one with highly purified Ni-sulfate (ultrapure electrolyte) and their magnetoresistance (MR) was investigated.

The Ni-Cu alloys grown from both impure and ultrapure electrolytes exhibited anisotropic magnetoresistance (AMR). The difference between the two alloy series was explained by the presence of a few at.% of Co in the deposits from impure electrolyte. While GMR was observed on Ni-Cu/Cu multilayers deposited from the impure electrolyte, formally identical multilayers grown from ultrapure electrolyte exhibited anisotropic magnetoresistance (AMR) only. The trace element analysis of the starting Ni-sulfates did not yield a satisfactory explanation. The main impurity in the analytical grade Ni-sulfate was Co, Na and Mg (the latter two has neither electrochemical activity nor an influence on the deposit structure at the few hundred ppm level). Even though the impact of the Co impurity was simulated by adding an appropriate amount of the Co-sulfate to the ultrapure Ni-sulfate, no GMR was seen for the samples produced with this chemical. We have not found a satisfactory explanation for the difference in the properties of the sample produced with the various chemicals. Although the ultrapure Ni-sulfate contained some impurities in a higher concentration than the analytical grade one, their concentration was less than 100 ppm and it is believed that they cannot significantly influence the electrodeposition process. Due to this unknown effect, the samples studied in detail were all obtained with the analytical grade chemical and hence contained a few percent of Co as well.

The GMR as a function of the Cu layer thickness was studied first. The optimum Cu layer thickness was 4.2 nm. For samples deposited at $j_{\text{mag}} = -50 \text{ mA/cm}^2$, the character of the GMR curves was dominantly ferromagnetic, with an essentially negligible superparamagnetic contribution (see Figure 3; next page).

[#] All accepted papers and manuscripts mentioned in this report have also been indicated in the OTKA homepage in the publication summary sheet.

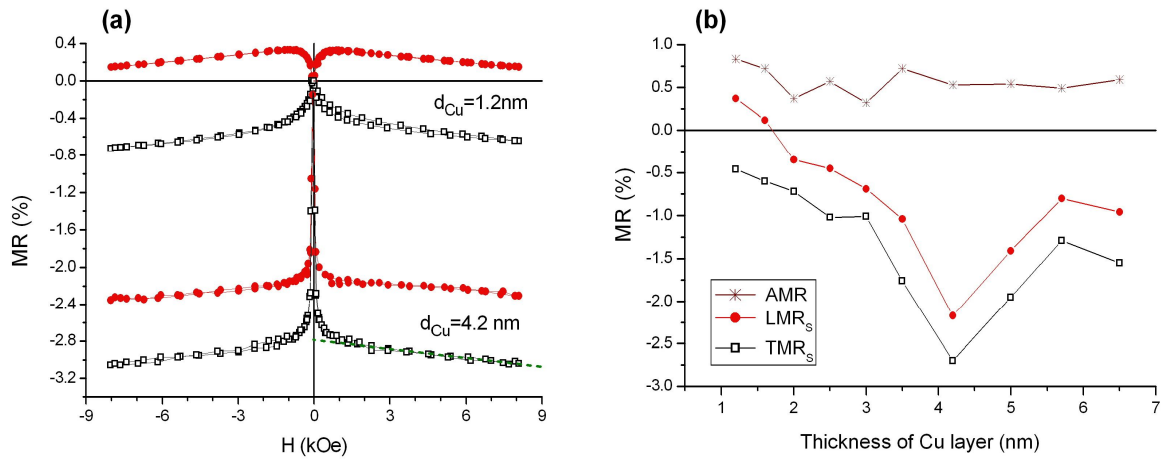


Figure 3

(a) Magnetoresistance curves for Ni-Cu/Cu multilayers with small (1.2 nm) and high (4.2 nm) Cu layer thickness, exhibiting AMR and GMR, respectively. (b) Magnetoresistance of the Ni-Cu/Cu samples as a function of the Cu layer thickness.

All samples were deposited at $j_{mag} = -50\text{ mA/cm}^2$, where the Cu content of the magnetic layer was about 6 at.%; $d_{Ni} = 3\text{ nm}$.

When the Ni layer thickness was varied at the optimum Cu layer thickness ($d_{Cu} = 4.2\text{ nm}$), the magnetoresistance properties of the deposit varied from superparamagnetic (at low Ni layer thickness, $d_{Ni} = 1\text{ nm}$) through ferromagnetic (at medium Ni layer thickness, $d_{Ni} = 3\text{ nm}$) to anisotropic magnetoresistance (at high Ni layer thickness, $d_{Ni} = 5\text{ nm}$). This is illustrated in Figure 4.

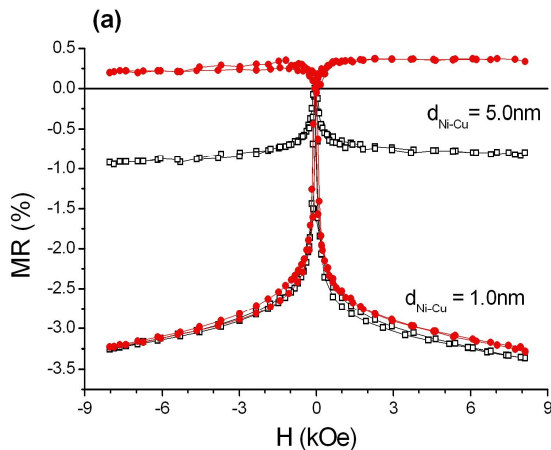


Figure 4

Magnetoresistance curves obtained for Ni-Cu/Cu multilayer samples with different Ni layer thickness.

The magnetoresistance properties of the samples were in accord with the results of the structural studies. Whenever the thickness of either of the layers was small enough to be discontinuous or at least containing pinholes, the XRD pattern did not show satellite peaks. This was observed for small Cu layer thickness (for $d_{Cu} < 2\text{ nm}$ where AMR occurred due to the pinholes in the Cu layer) or for small Ni layer thickness (for $d_{Ni} < 2\text{ nm}$ where the MR curves showed SPM character due to the discontinuous magnetic layer).

The room-temperature magnetoresistance study of the samples deposited from electrolytes with increasing Cu content drew our attention to an interesting feature of the Ni-Cu system. With the increase of the Cu^{2+} concentration, the increase of the Cu content of the magnetic layer is expected also for the Ni-Cu layer, and the ferromagnetic character of the Ni layer should disappear when the Ni content drops below about 60 at.% as it is well-known for homogeneous bulk Ni-Cu alloys, and the GMR can also be expected to drop to zero. However, a ferromagnetic character of the samples was observed also at such high Cu contents in the magnetic layer where the Curie temperature of the homogeneous Ni-Cu alloys is already much below room temperature. This can be understood only by taking into account

the segregation of large Ni-rich zones within the magnetic layer. This phase separation tendency observed is not at all governed by the degree of mutual solubility of the two components codeposited, as one might naively think. Instead, either the random nature of the electrodeposition process during the formation of an alloy or some other hidden kinetic factor of the electrocrystallization process may be responsible for the behavior observed. According to the relevant literature, this phase segregation for Ni-based systems is quite common for electrodeposited samples.

The GMR was investigated for the Ni-Cu/Cu multilayers from the impure electrolyte as a function of the Ni-Cu and Cu layer thicknesses and also at low temperatures down to 18 K. An increase of the GMR was obtained at low temperatures by conserving the ferromagnetic character of the magnetoresistance curves. This is in full agreement with the expectations.

The paper containing the results of this part of the joint work will soon be published (*Journal of The Electrochemical Society* **159**, D1-D10 (2012)).

3. Electrochemical study of the Co-Ru system

Codeposition of Ru and Co was studied from various baths containing CoSO₄, MgSO₄, NaCl, H₃BO₃ and RuCl₃. Some experiments were performed at room temperature only, but the great majority of the study was done with solutions with varying Co²⁺ to Ru³⁺ ion concentration ratios at both room temperature and 50 °C.

The electrodeposition of Co, Ru and Co-Ru alloys was first studied with electrolytes containing one of the metals only or both Co and Ru. It was found that the current observed for the mixed solution is not simply the sum of the current recorded for solutions containing one of the metal ions only. This indicated that the deposition of the two metals is not an independent process. Codeposition at the potentials more positive than the Co²⁺/Co equilibrium potential led to an incomplete substrate coverage and to a very low deposition efficiency. Nevertheless, once the deposit appeared, it was never pure Ru but always contained Co as well. Therefore, the codeposition of Co and Ru proved to be anomalous since no pure Ru could be obtained, but Co was incorporated into the deposit at potentials where the deposition of pure Co was not possible. This prevented us from depositing magnetic/non-magnetic multilayer samples with pure Ru as a spacer layer since the deposition of pure Ru did not prove to be possible.

The rest of the experiments was performed with a fixed total metal ion concentration of 0.1 mol/liter and with a varying ratio of Co²⁺ and Ru³⁺ concentrations. The composition of the deposits varied monotonously with the change of the concentration ratio of Co²⁺ and Ru³⁺. The deposition of Ru was very hindered and the current efficiency was a few percent only when the Co concentration in the deposit was low. Such samples were obtained at low current density (typically with a cathodic current density smaller than 2 mA/cm²). Continuous deposits could be obtained when the molar fraction of Co in the deposit was at least 40 at.%, and the typical current density required to deposit high Co-content samples was 5 mA/cm² or higher. The deposit composition as a function of the deposition parameters is shown in Figure 5 (next page).

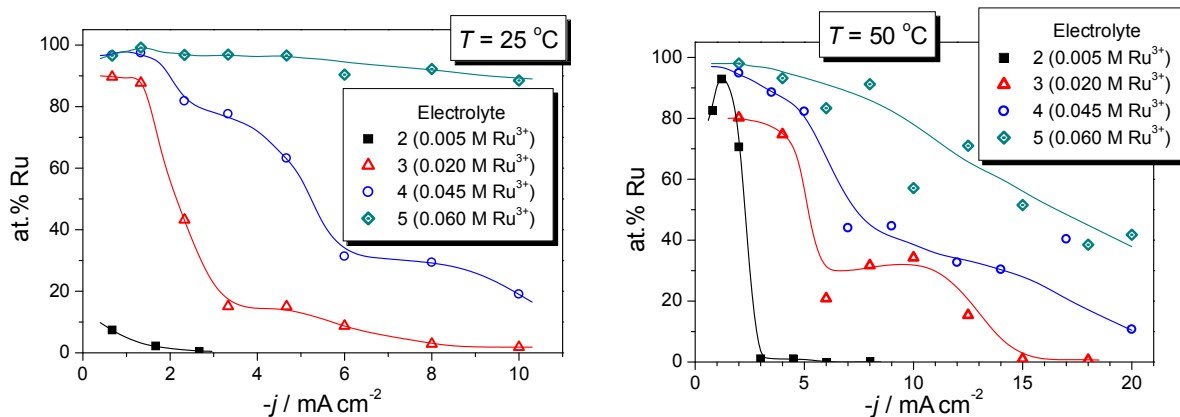


Figure 5

Composition of the Co-Ru alloys deposited at 25 °C (left) and 50 °C (right) as a function of the electrolyte composition and the current density. Total metal ion concentration: $c(\text{Co}^{2+}) + c(\text{Ru}^{3+}) = 0.1 \text{ mol/liter}$

The morphology of the deposits was related to the molar fraction of Co in the deposit but it was mostly independent of either the temperature of the deposition or the current density.

At low current density, where the deposit contains a few percent of Co only (2 to 8 at.%), the coating was discontinuous. There were round-shaped voids in the thin deposit that corresponded to surface spots where the hydrogen bubbles prevent the formation of a continuous coating. As the current density increased and, consequently, the Co concentration in the deposit was higher, the pits from the surface gradually disappeared, and the continuous coating became decorated with small hemispherical grains. At high Co content ($y(\text{Co}) > 60$ at.%), the coverage of the substrate surface was complete and the number of extra grains decreased, but at the same time the stress in the deposit led to fractures.

Very few samples could only be prepared by using a substrate with thin metallic layers. Namely, experiments performed with Si/Cr(5nm)/Cu(20nm) substrates led to the result that the thin metallic coating of the substrate peeled off from the Si wafer during the deposition, hence preventing us from growing a thick enough layer for electrical transport studies. Transport measurements were possible only for a few samples prepared with very high Co content in the electrolyte ($c(\text{Co}^{2+}) = 1 \text{ mol/liter}$) but in this case the Ru content of the deposit was less than 2 at. %. The MR studies performed for these samples revealed an AMR behaviour. The lack of GMR even in the case of the pulse-plated samples is in agreement with the fact that according to the electrochemical studies no pure Ru layer could be formed under the experimental conditions explored.

The results of the study related to the Co-Ru system have been submitted to *Journal of Solid State Electrochemistry*. The paper was accepted in May 2011 (issue and page number are yet to be assigned).

4. Composition depth profile studies

In the last years, a new method was developed in our laboratory to analyze the composition of the near-substrate zone of electrodeposited samples. In this method, the substrate is a pre-coated Si wafer with the typical structure of Si/Cr(5nm)/Cu(20nm). The layer of interest is deposited onto this substrate. The thickness of the first electrodeposited layer is at least 300 nm. After the deposition of the first layer is completed, a Ni supporting layer is also plated on top of the first layer by using another electrolyte.

After the deposition sequence is completed, the samples are cut from the Si wafer along their edges. Then, the back side of the Si wafer around the central region of the deposit was scratched along its crystallographic axis in order to define the breaking line. The sample was bent in a manner so that the ED layers were at the concave side; hence, they were never exposed to a tensile stress. The Si wafer was thus broken, but the deposit remained intact. Hereupon, the deposits could be detached from the Si wafer and samples with a very smooth surface were obtained.

The samples prepared according to the above described procedure were examined with secondary neutral mass spectrometric depth profile analysis. New results were obtained for alloys in which the preferentially deposited metal (Cu, Cd, Sn or Co) is the minority component besides Ni.

In the first group of samples, the concentration ratio of the precursor compounds in the electrolyte was in the range of 100 to 20 ($c(\text{Ni}^{2+}) = 1 \text{ mol/liter}$ while the concentration of the ions of the preferentially deposited metal was much lower). For these samples, it was shown that the preferentially deposited metal is always accumulated in the near-substrate zone. A typical example for the Cd-Ni alloys is presented in Figure 6.

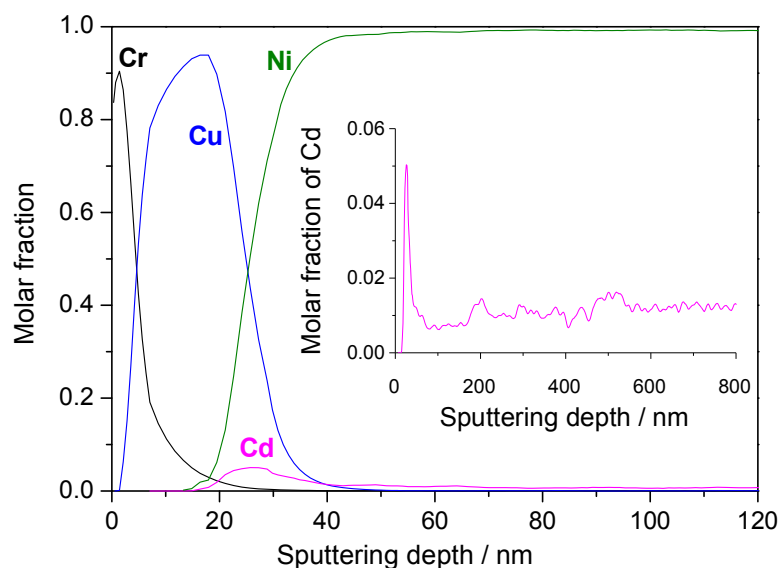


Figure 6

Reverse composition depth profile curve measured for a Ni-Cd sample deposited at -19.5 mAcm^{-2} from an electrolyte with 10 mM Cd^{2+} concentration.

Particularly interesting composition depth profile functions were measured when two preferentially deposited metals were present besides Ni. When Co and Cu were both present, an Ag-covered substrate was used for a sensitive detection of both alloying elements in the near-substrate zone. It was found that the order of the accumulation of the alloying metals is in agreement with the order of deposition preference. A maximum in the Cu molar fraction was found first, which was followed by the molar fraction maximum of Co (see Fig. 7.a, next page). After the initial zone, a decay in the molar fractions of the minority components was found and the steady-state alloy composition was achieved at a deposit thickness of about 200 nm.

It was also confirmed that the change in the molar fractions of the preferentially deposited metals are correlated in the steady-state deposition zone (Fig. 7.b). This was attributed to the instability of the diffusion field and to the spontaneous flow of electrolyte due to the density difference of the bulk and depleted electrolytes.

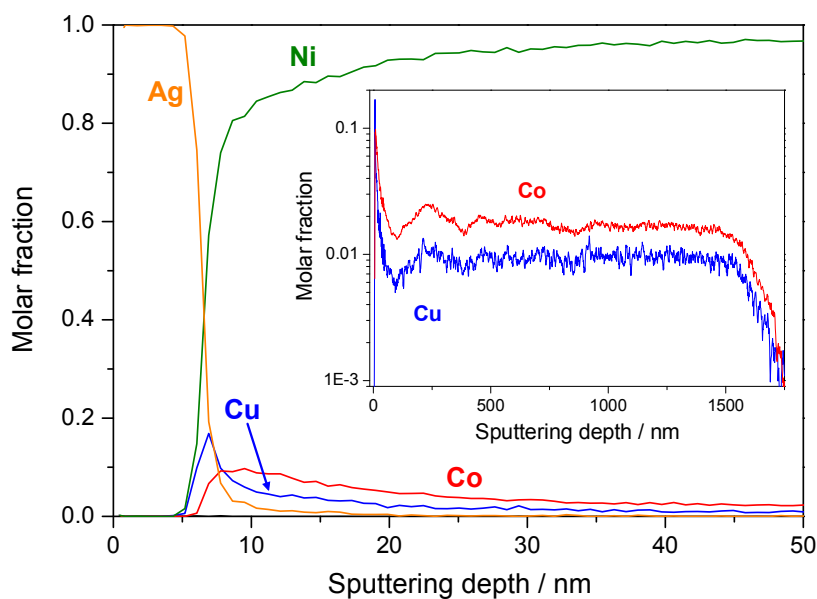
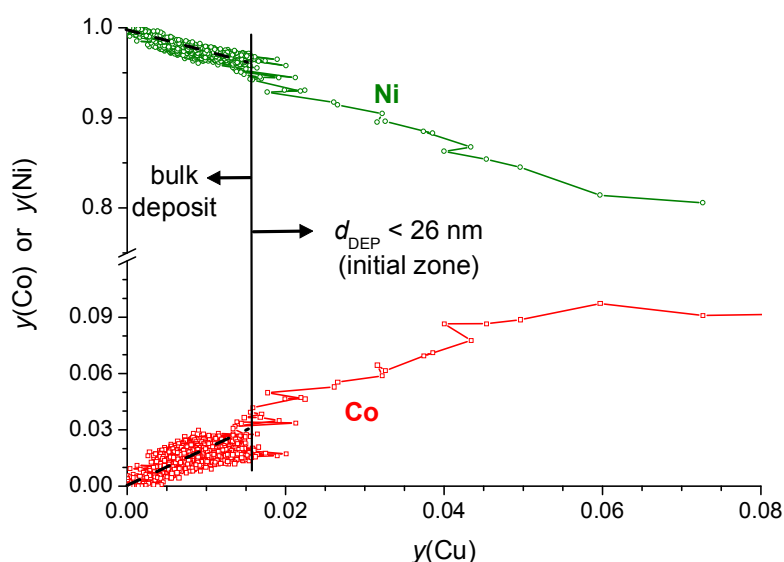


Figure 7

a,
Reverse composition depth profile curve measured for a Cu-Co-Ni sample deposited at -20 mAcm^{-2} . Electrolyte concentrations:
 $c(\text{Ni}^{2+}) = 200 \text{ mmol/liter}$
 $c(\text{Co}^{2+}) = 25 \text{ mmol/liter}$
 $c(\text{Cu}^{2+}) = 10 \text{ mmol/liter}$



b,
Molar fraction of Co and Ni, displayed as a function of the molar fraction of Cu. The complete composition depth profile for the same Cu-Co-Ni sample can be seen in Fig. 7.a

The results found for the Cu-Co-Ni alloys were in a good agreement with our earlier results achieved for the Fe-Co-Ni system (see our earlier papers: A. Csik et al., *Electrochem. Commun.* **11**, 1289 and L. Péter et al., *Electrochim. Acta* **55**, 4734 (2010)). In both ternary alloys, the accumulation of the alloying elements in the near-substrate zone followed the order of the deposition preference, and the fluctuations in the molar fractions of the minority components were correlated in the steady-state deposition zone.

The results of this part of the work have been published in a review paper (*Journal of Solid State Electrochemistry* **15**, 2523-2544 (2011)).

5. Electrodeposition of magnetic multilayers for magnetocaloric applications

The magnetocaloric effect (MCE) is the reversible temperature change of a magnetic material due to the application of an external magnetic field change under adiabatic conditions. Its energy-efficient and environment-friendly features are the prominent advantages over conventional gas compression-expansion refrigeration technology that is used nowadays.

MCE-based experimental devices are operated with various homogeneous magnetic alloys that are either crystalline or amorphous. The maximum magnetocaloric efficiency is expected around the Curie temperature of the heat exchanger magnetic material.

In order to produce tunable materials for MCE devices, we suggested that magnetic multilayers can be made by electrodeposition. The layer thicknesses were around 100 nm and the composition of the layers were modulated so that each layer exhibited a different Curie temperature.

A new electrochemical bath was developed for depositing Ni-Cu alloys of various composition and hence with varying Curie temperature. The new bath formulation was based on available literature data on citrate-based Ni-Cu electrolyte, but the metal ion concentrations were adjusted to the desired alloy composition and the bath pH was stabilized with nickel acetate. The Curie temperature range of the layers deposited was designed to be in the range of 192 to 449 K.

The samples produced fulfilled the expectation that due to the wide range of Curie temperature of the various layers, the magnetic entropy change showed a much wider distribution than the same function for a homogeneous material. The results obtained indicated that such nanostructured systems are good candidates to control the field dependence of the magnetocaloric response of the materials used in magnetic refrigeration near room temperature.

The results of this study are to be published in a conference paper. The revised version of the manuscript has been accepted for publication in a special issue of the *Journal of Nanoscience and Nanotechnology*.

List of publications resulting from the present OTKA project:

1. D. Rafaja, C. Schimpf, T. Schucknecht, V. Klemm, L. Péter, I. Bakonyi: Microstructure formation in electrodeposited Co-Cu/Cu multilayers with GMR effect: influence of current density during the magnetic layer deposition. *Acta Mater.* **59**, 2992-3001 (2011).

[IF(2010) = 3.781; independent citation: 1]

2. K. Neuróhr, A. Csik, K. Vad, A. Bartók, G. Molnár, L. Péter: Composition depth profile analysis of electrodeposited alloys and metal multilayers: the reverse approach. *J. Solid State Electrochem.* **15**, 2523-2544 (2011).

[IF(2010) = 2.234]

3. M. Jafari Fesharaki, G.R. Nabiyouni, J. Dégi, L. Pogány, I. Bakonyi, L. Péter: Anomalous codeposition of cobalt and ruthenium from chloride-sulfate baths. *J. Solid State Electrochem.* (in press); DOI: 10.1007/s10008-011-1416-6.

[IF(2010) = 2.234]

4. M. Jafari Fesharaki, L. Péter, T. Schucknecht, D. Rafaja, J. Dégi, L. Pogány, K. Neuróhr, É. Széles, G. Nabiyouni, I. Bakonyi: Magnetoresistance and structural study of electrodeposited Ni-Cu/Cu multilayers. *J. Electrochem. Soc.* **159**, D1-D10 (2012)

[IF(2010) = 2.420]

5. R. Caballero-Flores, V. Franco, A. Conde, L.F. Kiss, L. Péter, I. Bakonyi: Magnetic multilayers as a way to increase the magnetic field responsiveness of magnetocaloric materials. *J. Nanosci. Nanotechnol.* (accepted for publication)

[IF(2010) = 1.351]