

Electrochemical deposition of cobalt-nickel coatings in a constant magnetic field

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Abstract: The electrochemical deposition of Co-Ni coatings on gold-disc electrode with and without of constant magnetic field (CMF) has been investigated using cyclic voltammetry (CV), scanning electron microscopy (SEM), and energy dispersive X-ray spectroscopy (EDX). The EDX results showed that CMF applied during the electrodeposition of Co-Ni coatings affects their composition. In particular, an increase by 17% in the content of cobalt in coating, i.e. the main component, with a simultaneous decrease of nickel content has been observed when magnetic induction B of 1200 mT was applied compare to this without of CMF. Moreover, it has been supposed that the increase of internal stresses in electrodeposited Co-Ni coatings under CMF can be attributed to a decrease in their thickness.

Keywords: cobalt-nickel coatings, constant magnetic field, electrochemical deposition

1. Introduction

Development of functional metallic and metal alloy coatings with the specific mechanical, electrical, and magnetic properties is one of the main directions of research in electrochemistry (Kołodziejczyk et al., 2018; Louki et al. 2021; Mieszkowska et al., 2021; Mishra et al., 2020; Shapouri et al. 2021; Soegijono et al., 2020). Among them, Co-Ni alloys coatings are of special interest as they display such favorable features as high coercive forces, very low residual stresses and high surface abrasion resistance (Sinha et al., 1990). Due to those properties, Co-Ni alloys can be used as soft magnetic materials, surface protection and decoration coatings, and catalysts.

Both metals alone and metal alloys can be obtained by the electrodeposition in the presence of CMF which affects the morphology of deposits. In fact, the grains of electrodeposited Fe under CMF were rounded with a smooth surface and a small size distribution, however, those obtained without CMF were a sharp-edged with a large size distribution (Matsushima et al., 2004). Similarly, Ni-Fe alloys electrodeposited in the presence of CMF exhibited a lower surface roughness, the more uniform structure, and preferential grain orientation compare to those electrodeposited without CMF (Msellak et al. 2004). It is assumed that in electrochemical processes in the presence of external magnetic field the Lorentz force causes a magnetohydrodynamic effect on fluid convection (Tacken et al., 1995). These phenomena localized near a surface of a ultramicroelectrode has been successfully visualized using the scanning electrochemical microscope (Ragsdale et al., 1999). The magnetic forces have also been taken into account in electrochemical dissolution of copper, nickel, and silver under CMF (Bund et al., 2003; Bund et al., 2005).

In this article, we present the results of our investigations on electrochemical deposition of Co-Ni binary coatings on gold-disc electrode with and without of CMS using CV, EDX, and SEM methods. CV has been used to determine the electrodeposition potential. EDX spectra have allowed to determine the composition of the electrodeposited Co-Ni coatings, and their surface morphology has been examined with SEM.

2. Materials and methods

The solutions for electrodeposition of Co-Ni coatings have been prepared with $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ (cobalt(II) sulfate heptahydrate, Chempur, Poland), $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ (nickel(II) sulfate heptahydrate, Chempur, Poland), and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ (trisodium citrate dehydrate, Chempur, Poland) which were used as received. The concentration of $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ was varied in the range of 0.025-0.500 M, whereas the concentrations of $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ and $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ were constant and equal to 0.100 and 0.600 M, respectively. Trisodium citrate has been added as the Co(II) and Ni(II) complexing agent, the supporting electrolyte, and the inhibitor of hydrogen evolution (Berkh et al., 2011). The constant pH of solutions has been maintained with H_2SO_4 (Chempur, Poland) at a concentration of 0.010 M. All the solutions have been made using triple distilled water. The composition of deposition solutions and magnetic inductions B used in electrodeposition of Co-Ni coatings are given in Table 1.

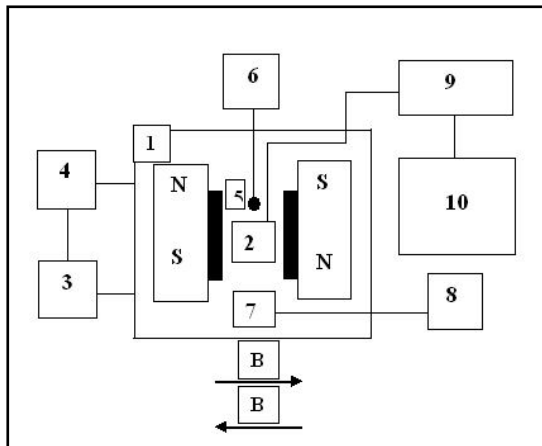
Table 1. Composition of deposition solutions and magnetic inductions B used in electrodeposition of Co-Ni coatings

Deposition solution	Co(II) [M]	Ni(II) [M]	$\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ [M]	H_2SO_4 [M]	B [mT]
1	0.025	0.100	0.600	0.010	0
2	0.050	0.100	0.600	0.010	0
3	0.100	0.100	0.600	0.010	0, 200, 600, 1200
4	0.200	0.100	0.600	0.010	0
5	0.300	0.100	0.600	0.010	0, 600, 1200
6	0.400	0.100	0.600	0.010	0
7	0.500	0.100	0.600	0.010	0

CV measurements and electrodeposition of Co-Ni coatings have been performed using the home-made three-electrode electrochemical cell with the polycrystalline gold disc electrode with surface area of 0.1 cm² as a working electrode, the saturated calomel electrode as a reference electrode, and the platinum mesh as an auxiliary electrode. The working electrode has been prepared mechanically using a sandpaper with a grit size of 2000, then treated chemically with a chromic acid, followed by electrochemical pretreatment through its polarization in the potential range from -1.5 V to +1.5 V vs. SCE with a scan rate of 50 mV/s in the stock solution of 0.010 M H_2SO_4 . The potentiostat ATLAS 99 equipped with Electrochemical Interface 9933 has been used which was operated with a PC computer using dedicated software POL-99 (Atlas-Sollich, Poland). The electrodeposition of Co-Ni coatings has been performed under potentiostatic conditions at potential of -1.30 V vs. SCE (-1.053 V vs. SHE) without stirring of deposit solution, and the time of electrodeposition was equal to 3500 s.

The water-cooled laboratory electromagnet ER-2505 (RadioPAN, Poland) has been used to generate CMF with the induction B equal to 200, 600, and 1200 mT. The electrochemical cell with a three-electrode system has been placed between N and S poles which were interchanged. To achieve the maximum of the Lorentz force, the magnetic induction vector was perpendicular to the surface of the gold disc working electrode. The measuring station were also equipped with the controlling device PZP-80, the regulated power supply SZP, the permanent magnetic field Hall sensor, and the digital temperature controller CMR-02. The constant temperature of 20.0 °C has been maintained using the air thermostat. The block diagram of the measuring system for electrodeposition of Co-Ni coatings in CMF is shown in Fig. 1. The electrodeposition of Co-Ni coatings has been carried out at the Department of Inorganic and Analytical Chemistry of the University of Lodz.

The morphology of cathodic deposits has been analyzed using the Vega 5135 MM scanning electron microscope (TESCAN, Czech Republic) (Fig. 2). The qualitative and quantitative chemical composition of the coatings have been determined using the EDX method with EDX Link 300 ISIS X-ray microanalyzer (Oxford Instruments, UK). Both SEM and EDX measurements have been made in the Material Research Laboratory of the Department of Solid State Physics at the University of Lodz.



- 1 - laboratory electromagnet ER-2505 with poles N and S
- 2 - measuring cell with the three-electrode system
- 3 - laboratory electromagnet control device PZP-80
- 4 - regulated power supply of electromagnet type SZP
- 5 - permanent magnetic field Hall effect sensor
- 6 - Hall effect teslameter TH-26
- 7 - air thermostat
- 8 - digital temperature controller CMR-02
- 9 - potentiostat ATLAS 99
- 10 - PC computer with POL-99 software
- B - orientation and direction of magnetic induction

Fig. 1. The block diagram of the measuring system for electrodeposition of Co-Ni coatings in CMF



Fig. 2. Tescan Vega 5135 MM scanning electron microscope

3. Results and discussion

The potential of electrodeposition of Co-Ni coatings on gold-disc electrode has been determined using CV. The CV curve of solution with composition of 0.100 M Co(II) + 0.100 M Ni(II) + 0.600 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 0.010 M H_2SO_4 is presented in Fig. 3.

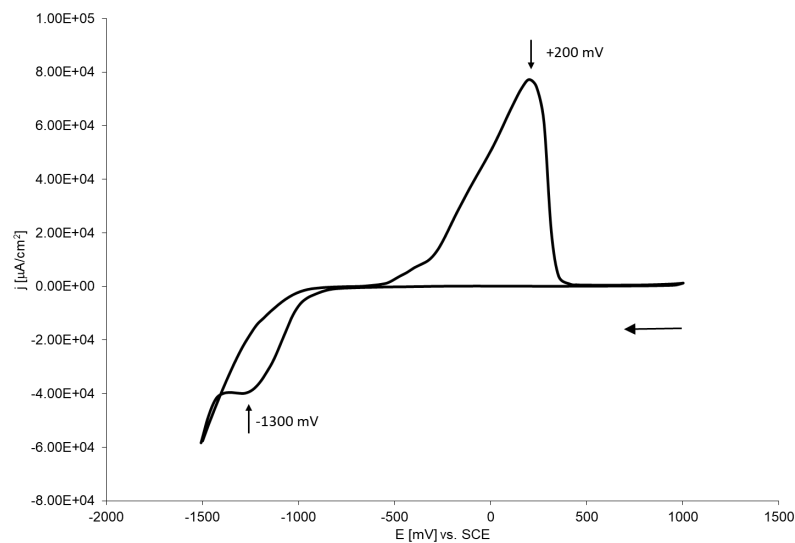


Fig. 3. CV curve of solution 0.100 M Co(II) + 0.100 M Ni(II) + 0.600 M $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ + 0.010 M H_2SO_4 .
Potential scan rate: 50 mV/s; initial potential: +1300 mV

On this CV curve there are two peaks at -1300 and +200 mV vs. SCE. The cathodic peak at -1300 mV vs. SCE is related to the electroreduction of Co(II) and Ni(II) to Co(0) and Ni(0), respectively. On the other hand, the anodic peak at +200 mV vs. SCE refers to the electrooxidation of the cathodic electrodeposited Co(0) and Ni(0) to Co(II) and Ni(II), respectively. Thus, all electrodepositions of Co-Ni coatings described in this paper, both with and without of CMF, have been performed under the potentiostatic condition at potential of -1.30 V vs. SCE in non-stirred solutions.

3.2. Electrodeposition of Co-Ni coatings with and without CMF

Firstly, the potentiostatic electrodeposition of Co-Ni coatings has been performed on gold-disc electrode without CMF. The recorded cathodic current density-time curves for electrodeposition time of 3500 s and its first 100 s are presented in Figs. 4 and 5, respectively. When CMF is not applied and the concentration of Co(II) increases from 0.025 to 0.500 M, the cathodic current density is stable with time for all deposition solutions. Obviously, the higher concentration of Co(II) in deposition solution, the higher cathodic current density is observed.

As the next step, the potentiostatic electrodeposition of Co-Ni coatings has been performed on gold-disc electrode under CMF with magnetic induction B of 0, 600, and 1200 mT. The deposition solution 5 was used in which the concentration of Co(II) was equal to 0.300 M. The recorded cathodic current density-time curves for electrodeposition time of 3500 s and its first 100 s are presented in Figs. 6 and 7, respectively. Compare to the electrodeposition without CMF (Fig. 4), the course of cathodic current

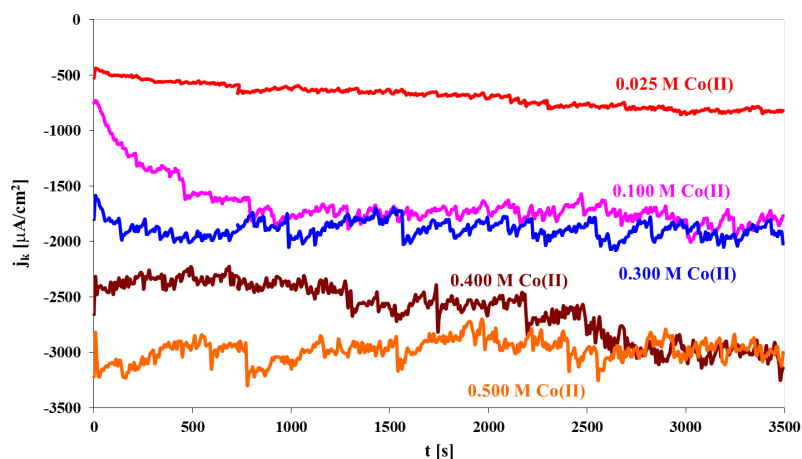


Fig. 4. Cathodic current density-time curves for electrodeposition of Co-Ni coatings without CMF from deposition solutions 1, 3, and 5-7. Time of electrodeposition: 3500 s

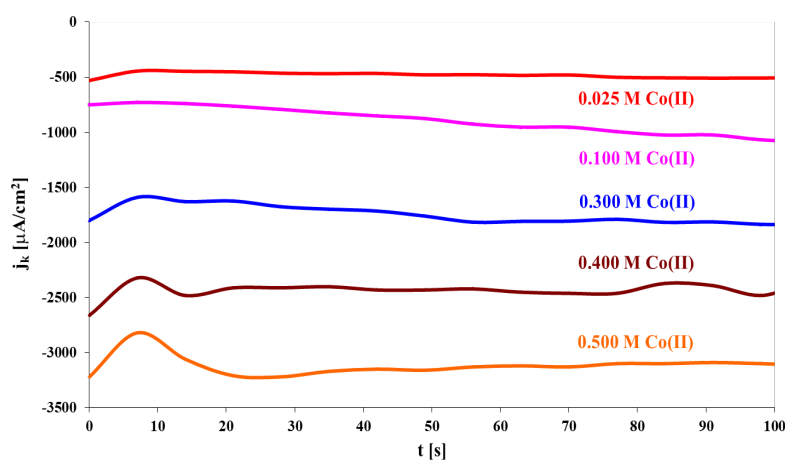


Fig. 5. Cathodic current density-time curves for the first 100 s of electrodeposition of Co-Ni coatings without CMF from deposition solutions 1, 3, and 5-7

density with time is different. Namely, the higher magnetic induction B , the higher cathodic current density at the beginning of the electrodeposition followed by its stabilization with time.

Using the EDX method both qualitative and quantitative analysis of the deposited Co-Ni coatings have been carried out. EDX spectra of Co-Ni coatings electrodeposited without CMF from the solutions 1, 3, and 6 where concentration of Co(II) was equal to 0.025, 0.100, and 0.400 M, respectively, are presented in Figs. 8-10, respectively.

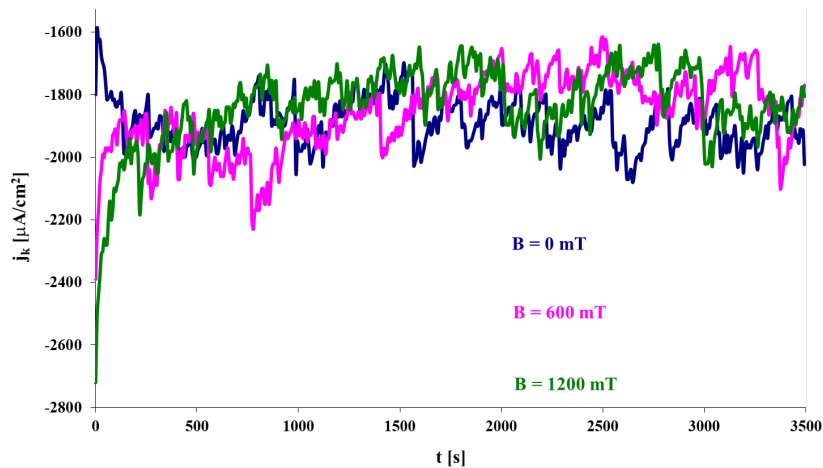


Fig. 6. Cathodic current density-time curves for electrodeposition of Co-Ni coatings in CMF with magnetic induction B of 0, 600, and 1200 mT from deposition solution 5. Time of electrodeposition: 3500 s

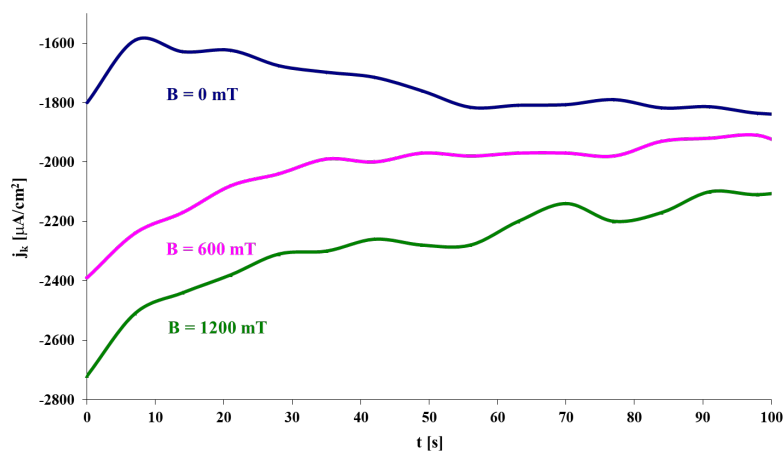


Fig. 7. Cathodic current density-time curves for the first 100 s of electrodeposition of Co-Ni coatings in CMF with magnetic induction B of 0, 600, and 1200 mT from deposition solution 5

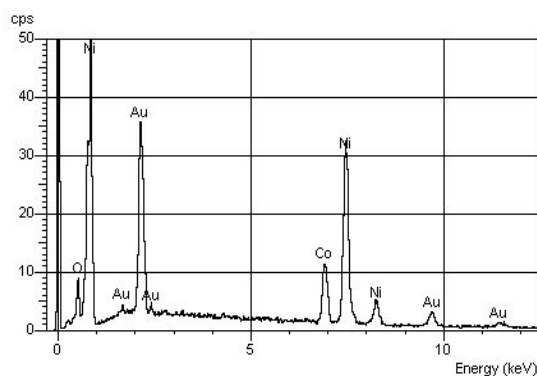


Fig. 8. EDX spectrum of Co-Ni coating electrodeposited from deposition solution 1 without of CMF. Coating composition: 22.6% Co and 77.4%Ni (Au from the working electrode has not been taking into consideration)

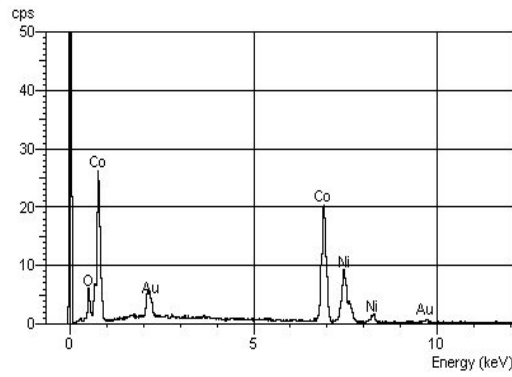


Fig. 9. EDX spectrum of Co-Ni coating electrodeposited from deposition solution 3 without of CMF. Coating composition: 66.7% Co and 33.3% Ni (Au from the working electrode has not been taking into consideration)

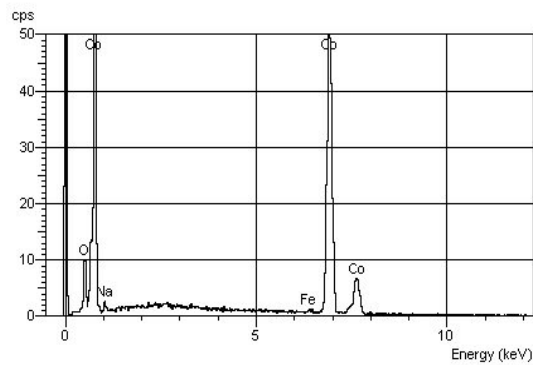


Fig. 10. EDX spectrum of Co-Ni coating electrodeposited from deposition solution 6 without of CMF. Coating composition: 100% Co and 0% Ni (Au from the working electrode has not been taking into consideration)

Based on EDX results, the chart of cobalt and nickel content in electrodeposited coatings without CMF as a function of concentration of Co(II) in deposition solutions has been made (Fig. 11). It can be seen from the Fig. 11 that when the concentration of Co(II) in deposition solutions is lower than 0.200 M, the higher concentration of it, the higher content of cobalt in deposits along with the lower amount of nickel. However, when concentration of Co(II) is equal to 0.200 M, or higher, only cobalt is present in the deposits.

In order to study the impact of CMF on deposit content, the deposition solution 3 with the composition of 0.100 M Co(II) and 0.100 M Ni(II) has been chosen as this from which Co-Ni coating with the highest content of cobalt has been obtained, namely 66.7% Co and 33.3% Ni. During the electro-

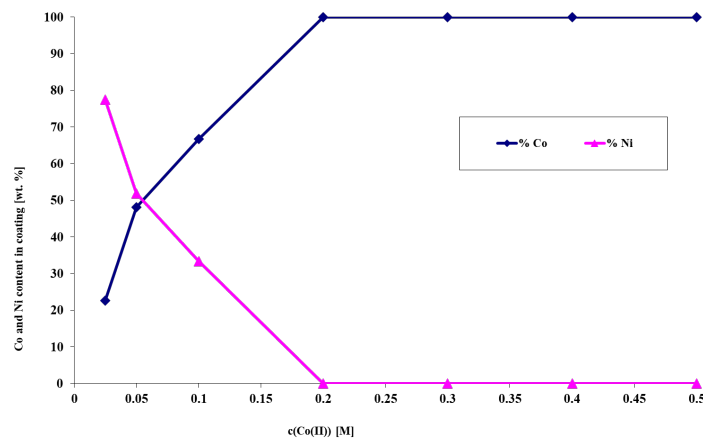


Fig. 11. Cobalt and nickel content in electrodeposited coatings without CMF determined using EDX method as a function of concentration of Co(II) in deposition solutions

deposition, CMF with the magnetic induction B of 0, 200, 600 and 1200 mT has been used. The illustrative EDX spectra of Co-Ni coatings electrodeposited at magnetic induction B of 0 and 1200 mT are presented in Figs. 12 and 13, respectively, and the composition of Co-Ni coatings as a function of the magnetic induction B is showed in Fig. 14.

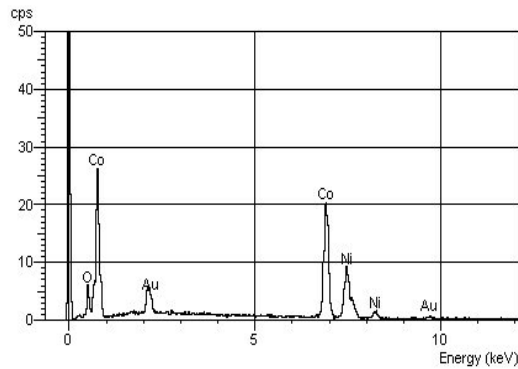


Fig. 12. EDX spectrum of Co-Ni coating electrodeposited from the deposition solution 3 at magnetic induction B of 0 mT. Coating composition: 66.7% Co and 33.3% Ni (Au from the working electrode has not been taking into consideration)

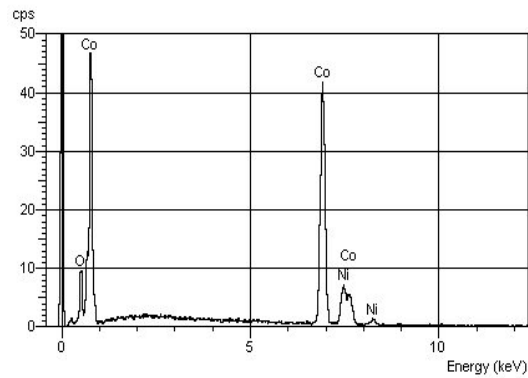


Fig. 13. EDX spectrum of Co-Ni coating electrodeposited from deposition solution 3 at magnetic induction B of 1200 mT. Coating composition: 83.9% Co and 16.1% Ni (Au from the working electrode has not been taking into consideration)

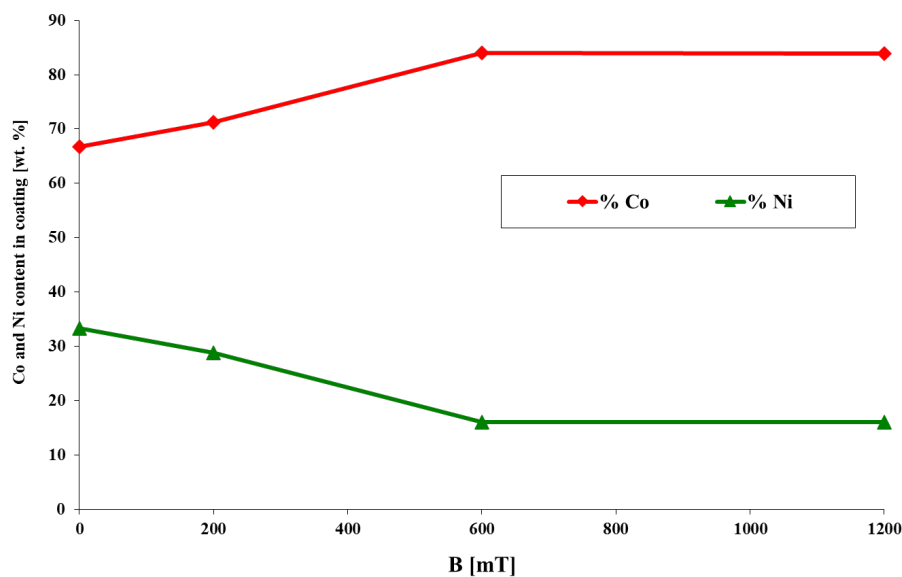


Fig. 14. Cobalt and nickel content in coatings electrodeposited under CMF from deposit solution 3 determined using EDX method as a function of magnetic induction B

From Fig. 14 one can conclude that in the case of the deposit solution 3 with composition of 0.100 M Co(II) and 0.100 M Ni(II), the higher magnetic induction B up to 600 mT, the higher content of cobalt in the coating. However, the increase of magnetic induction B to 1200 mT does not increase the content of cobalt. Moreover, it is noteworthy that in the case of coatings electrodeposited at magnetic inductions B of 0 and 1200 mT, the increase by 17% in the content of cobalt is observed.

Using SEM method the surface morphology of electrodeposited Co-Ni coatings has been analyzed. In particular, if the concentration of Co(II) in the deposit solution was as low as 0.025 M (deposit solution 1), the gold working electrode was not fully covered by coating when the electrodeposition time was equal to 3500 s (Fig. 15).

On the other hand, if the concentration of Co(II) was as higher as 0.400 M (deposit solution 6), the electrodeposited coating tend to drop away from the gold working electrode or to break in the most thickest fragment (Fig 16.). Moreover, when CMF with magnetic induction B of 600 and 1200 mT has been applied during the electrodeposition from solution 3, the fractures on the coatings surface were observed (Fig. 17). This can be attributed to the increase of the residual stresses in coatings which, in turn, are related to the decrease of the thickness of electrodeposits (Socha et al., 2001; Zieliński, 2013; Żak et al., 1979).

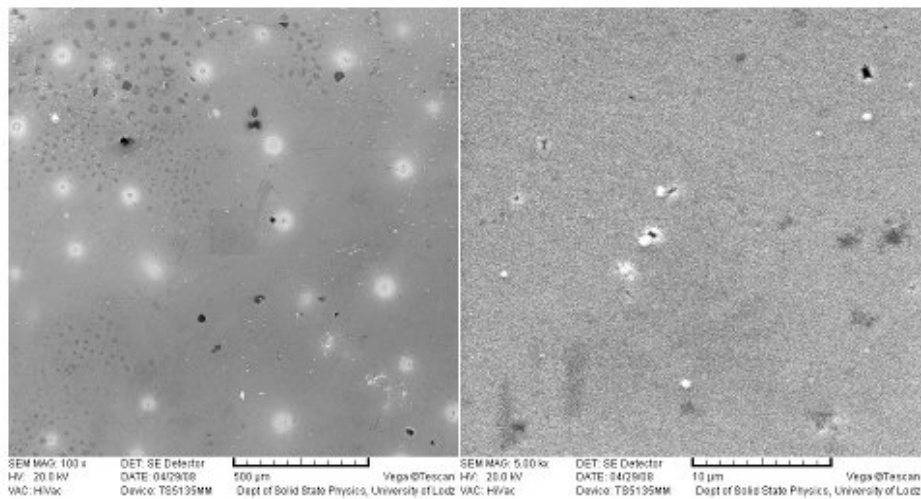


Fig. 15. SEM images of Co-Ni coating electrodeposited from deposit solution 1 at magnetic induction B of 0 mT. Coating composition: 22.6% Co and 77.4% Ni. Magnification: 100x (left) and 500x (right)

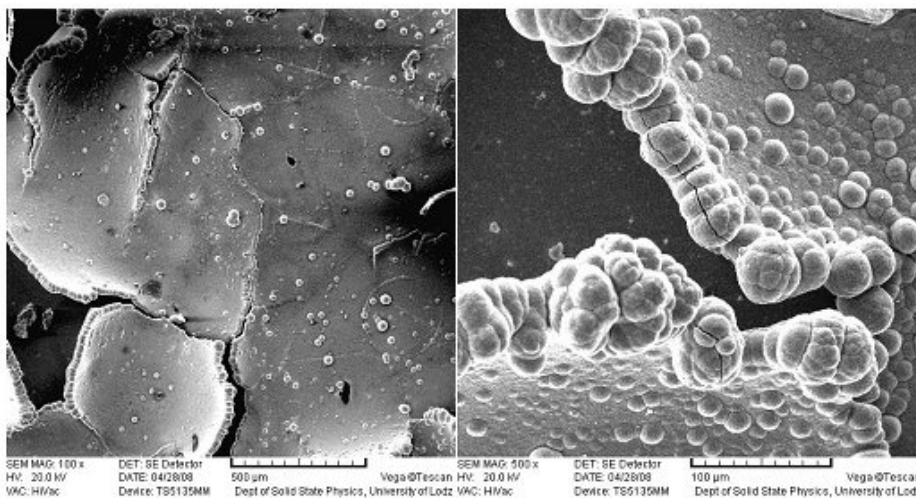


Fig. 16. SEM images of Co-Ni coating electrodeposited from deposit solution 6 at magnetic induction B of 0 mT. Coating composition: 100.0% Co and 0.0% Ni. Magnification: 100x (left) and 500x (right)

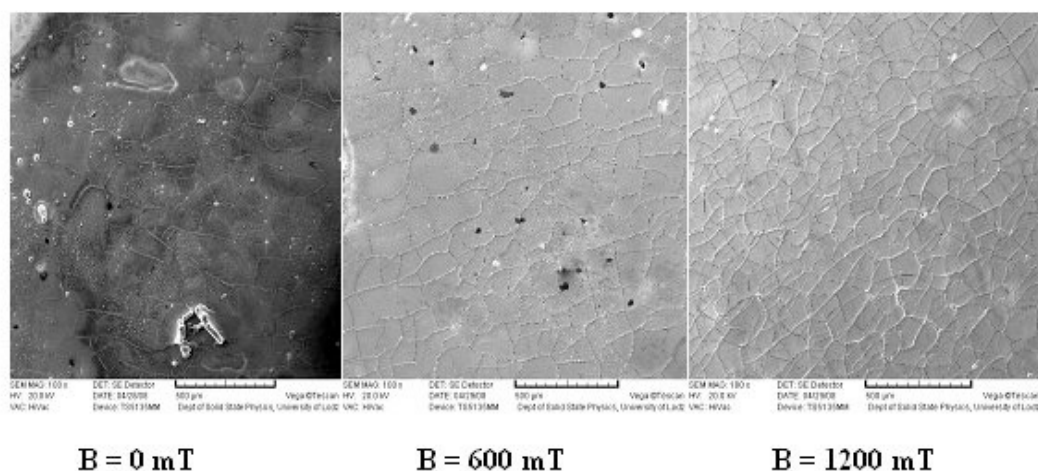


Fig. 17. SEM images of Co-Ni coatings electrodeposited from deposit solution 3 at magnetic induction B of 0, 600, and 1200 mT. Magnification: 100x

4. Conclusions

The potential of electrodeposition of Co-Ni coatings on gold-disc electrode has been determined using CV method. When CMF has not been applied during the electrodeposition of Co-Ni coatings, the cathodic current density increased with increasing content of Co(II), and at a given concentration of Co(II) it was stable with time. On the other hand, the electrodeposition of Co-Ni coatings under CMF revealed that the higher magnetic induction B , the higher cathodic current density at the beginning of the process followed by its lowering and stabilization with time. Using EDX method the highest content of cobalt in the deposit equal to 66.7% has been found which were obtained from solution with the composition of 0.100 M Co(II) and 0.100 M Ni(II). In addition, the increase by 17% in the content of cobalt in Co-Ni electrodeposit has been observed under magnetic inductions B of 1200 mT compare to this without of CMF. The SEM method revealed that under CMF the increase of internal stresses in electrodeposited Co-Ni coatings has been observed which can be attributed to a decrease in the thickness of deposit.

Acknowledgments

This work has been supported by the University of Lodz.

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