# MAGNETIC FIELD EFFECT ON PROPERTIES OF GALVANOSTATICALLY DEPOSITED Co–Pd ALLOYS

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**Abstract** : The results of studies on the influence of magnetohydrodynamic effect (MHD), paramagnetic and magnetic field gradient force on properties of an electrochemically synthesized Co-Pd alloys. The electrolysis was performed at constant current conditions. An attention was mainly dedicated to the influence of the magnetic field on the process efficiency, composition, structure and morphology of the synthesized Co-Pd alloys.

## 1. Introduction

External magnetic field during deposition of an alloy causes additional convection at the electrode surface coming from magnetohydrodynamic effect (MHD), paramagnetic force and magnetic field gradient force. The additional convection results in changes of the alloy composition, structure and morphology and by this way on the further properties of obtained alloys. In the literature there can be found that Pd-Co alloys are characterized by better electrocatalytic properties for ORR than pure palladium [1]. In catalysers composed of two metals, of which one has poorly occupied (Co) and the second (Pd) completely occupied d orbitals, the result of their interactions might be lowering of Gibbs free energy for the process of electrons transport [2].

The properties of Co – Pd alloys deposited in the magnetic field of parallel and perpendicular orientation of the magnetic field forces lines vs working electrode were described. Particular attention was focused on the influence of current density, direction and value of magnetic field induction vector on composition, structure and morphology of Co – Pd alloys.

## 2. Results

The composition of electrodeposited alloys depends on many factors, including the concentration of individual components of electrolyte, presence of complexing agents, pH, temperature, a substrate material as well as the WE potential or the value of applied cathodic current density. The first step of the tests was performed to determine the value of cathodic current density enabling deposition of coatings well adhesive to the substrate. The electrolysis was performed in different times depending on applied current density. Coatings were deposited for 120 min for i = 10, 20 [mA/cm$^2$], and 60 min for i = 50, 100, 250 [mA/cm$^2$] from the electrolyte containing 0.01 M Pd(NH$_3$)$_4$Cl$_2$ and 0.005 M CoCl$_2$ 6H$_2$O. Significant differences were noticed in the composition of alloy coatings and in cathodic current efficiency depending on the applied current intensity (Fig. 1). The lowest content of Co (28 at. %) was featured by an alloy obtained at i = 50 [mA/cm$^2$], for which the highest current

efficiency (6.4 %) was achieved simultaneously. However, the coating was characterized by high internal stresses manifested by micro cracks and lack of cohesion of deposits with the material of substrate. Therefore, the further alloys deposition was performed at current intensity of 10 [mA/cm$^2$].
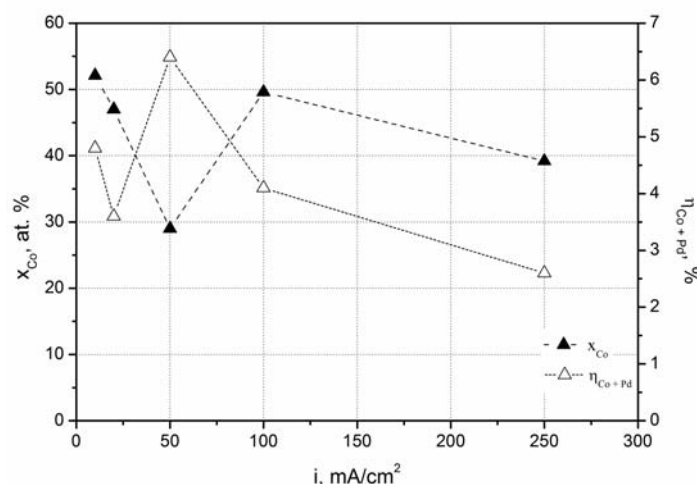


Figure 1: Influence of cathodic current density on Co content in alloys ($x_{Co}$) and current efficiency ($\eta_{Co+Pd}$) (0.01 M Pd(NH$_3$)$_4$Cl$_2$, 0.005 M CoCl$_2$ 6H$_2$O, 1.68 M NH$_4$Cl, pH = 9.5, T = 25 °C).

Electrolysis performed at different concentrations of Pd(NH$_3$)$_4$Cl$_2$ allowed determination of the bath composition effect on Pd content in the obtained alloys (Tab). The highest current efficiency was achieved for 0.1 M Pd(NH$_3$)$_4$Cl$_2$ and it is connected with an increase of rate of the [Pd(NH$_3$)$_4$]$^{2+}$ complex reduction reaction. The electrolyte of such concentration of Pd(NH$_3$)$_4$Cl$_2$ was used for tests on the MF influence. The increase of Pd(NH$_3$)$_4$Cl$_2$ concentration from 0.01M to 0.1M caused an increase of current efficiency from 4.8 % to 75.2 % as it can be seen in Table 1.

Table 1. Alloys composition and cathodic current efficiency depending on the content of Pd(NH$_3$)$_4$Cl$_2$ in electrolyte (0.005 M CoCl$_2$ 6H$_2$O, 1.68 M NH$_4$Cl, pH = 9.5, T = 25 °C).

| Pd(NH$_3$)$_4$Cl$_2$ [mol/dm$^3$] | $x_{Co}$ [% at.] | $x_{Pd}$ [% at]. | $\eta_{Co}$ [%] | $\eta_{Pd}$ [%] | $\eta_{Co+Pd}$, [%] |
|---|---|---|---|---|---|
| 0.001 | 94.9 | 5.1 | 6.3 | 0.2 | 6.5 |
| 0.01 | 52.1 | 47.9 | 3.2 | 1.6 | 4.8 |
| 0.1 | 2.5 | 97.5 | 3.3 | 71.9 | 75.2 |

Further studies were performed at different orientation of MF lines: parallel and perpendicular. Parallel orientation was applied to induce additional convection following the Lorentz force action. Whereas, perpendicular orientation aimed to generate paramagnetic force action and magnetic field gradient force. As it is visible in Fig. 2, the applied MF, regardless of its configuration, caused significant lowering of current efficiency in relation to alloys deposited without a MF and an increase of cobalt content in the obtained coatings.

The diffraction patterns registered for the obtained alloy coatings are visible in Figs. 3a–d. An increase of grain size with an increase of cathodic current density was noticed. The XRD diffraction pattern in Fig. 3a, shows, regardless of current intensity, three repetitive peaks indicating the presence of phase CoPd$_x$ with FCC structure whose location changes with the relation of content of Co and Pd in alloys (Fig. 3) [3-5].
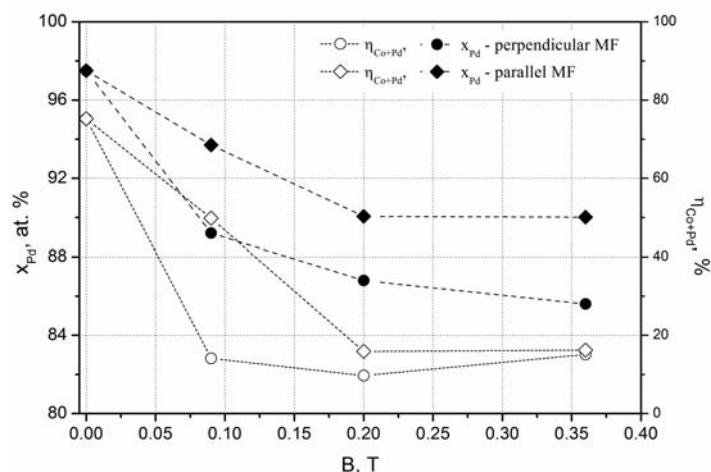
Figure 2: Influence of magnetic field induction vector on Pd content in deposited alloys and cathodic current efficiency (0.1 M Pd(NH$_3$)$_4$Cl$_2$, 0.005 M CoCl$_2$ 6H$_2$O, 1.68 M NH$_4$Cl, pH = 9.5, T = 25 °C).
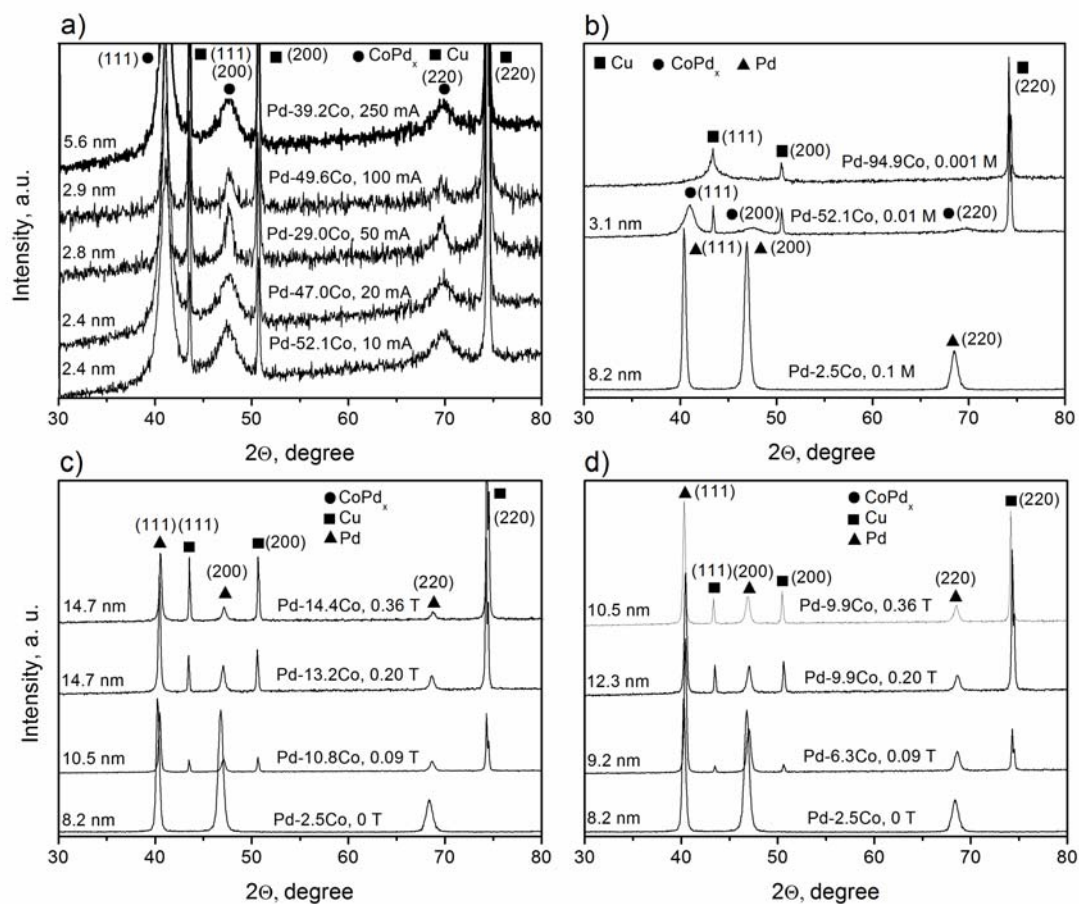


Figure 3: XRD diffraction patterns of alloys deposited at different current density (a), Pd(NH$_3$)$_4$Cl$_2$ concentration (b) and in MF of different magnetic field induction vector value and orientation: perpendicular (c) and parallel (d).

The influences of Pd salt concentration on structural changes in the obtained alloys are visible in Fig. 3b. XRD diffraction pattern of an alloy deposited from electrolyte containing

0.001 M $Pd(NH_3)_4Cl_2$ shows three peaks coming from the Cu substrate. After increasing the concentration of $Pd(NH_3)_4Cl_2$ from 0.01 M to 0.1 M, there are a visible shifts of peaks coming from planes (111), (220) and (200) of the phase $CoPd_x$ to a location typical for the FCC structure of pure Pd ($2\Theta = 40.12°$, $2\Theta = 46.66°$ and $2\Theta = 68.12°$).

The applied MF regardless of configuration did not cause, apart from an increase of grain size with an increase of the value of magnetic induction vector, changes in the deposit structure (Figs. 3c,d). It was observed that regardless of the orientation, an increase of the value of magnetic induction vector resulted in an increase of the grain size. The perpendicular MF also caused higher than for parallel one decrease of current efficiency which is manifested by increased intensity of peaks coming from the substrate material with an increase of MF intensity (Fig. 3c,d).
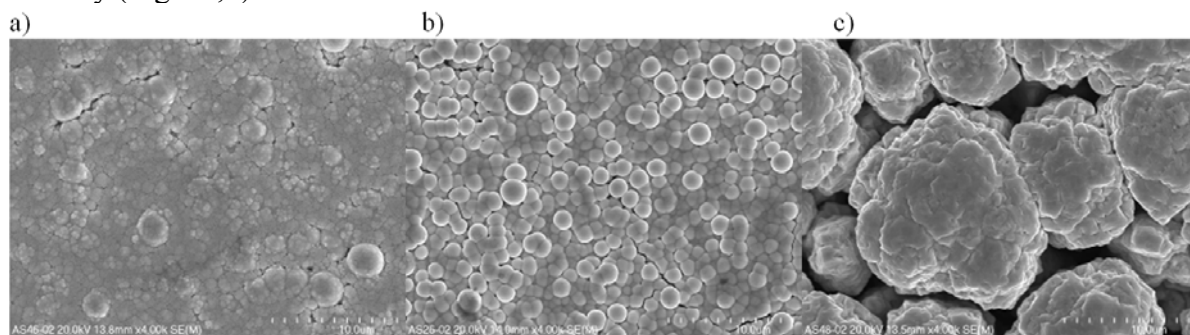


Figure 4: Microphotographs of alloys deposited form electrolytes of different $Pd(NH_3)_4Cl_2$ concentration: a) 0.001 M, b) 0.01 M, c) 0.1 M (0.005 M $CoCl_2$ $6H_2O$, 1.68 M $NH_4Cl$, pH = 9.5, T = 25 °C, res. 4000 X).

Observations of alloys morphology with the use of SEM microscope showed, similarly to XRD analysis, that the size of cathodic deposit grain increased remarkably with an increase of $Pd(NH_3)_4Cl_2$ concentration which can be seen in Fig. 4.

## 3. Conclusion

The best adherent coatings were deposited from electrolyte containing 0.1 M $Pd(NH_3)_4Cl_2$ at cathodic current intensity at i = 10 [$mA/cm^2$]. The magnetic field, regardless of configuration, caused a decrease of current efficiency of the electrolysis process. It can be also concluded, based on XRD measurements that MF influencing crystallisation process. An increase of the value of magnetic induction vector independently on MF orientation increased the deposits grain size.

## 4. References

[1] Suo Y.; Zhuang L.; Lu J.: First-principles considerations in the design of Pd-alloy catalysts for oxygen reduction. Angewante Chemie - International Edition. 46 (2007) 2862-2864.
[2]. Wang Y. X.; Balbuena P. B.: Design of Oxygen Reduction Bimetallic Catalysts: Ab initio-Derived Thermodynamic Guidelines. Journal of the Physical Chemistry B. 109 (2005) 18902-18906.
[3]. Heibel M.; Kumar G.; Wyse C.; Bukovec P.; Bocarsly A. B.: Use of sol-gel chemistry for the preparation of cyanogels as ceramic and alloy precursors. Chemistry of Materials. 8(7) (1996) 1504-1511.
[4]. Matsuo Y.: Ordered Alloys in Cobalt-Palladium System. Journal of Physical Society Japan. 32(4) (1972) 972.
[5]. Buschow K. H. J.; Vanengen P. G.; Jongebreur R.: Magneto-Optical Properties of Metallic Ferromagnetic Materials. Journal of Magnetism and Magnetic Materials. 38(1) (1983) 1-22.