

## Effects of Constant Magnetic Field on Electrodeposition of Co-W-Cu Alloy

Marek Zieliński\*, Ewa Miękoś, Dominik Szczukocki, Radosław Dałkowski, Andrzej Leniart, Barbara Krawczyk, Renata Juszczyk

Department of Inorganic and Analytical Chemistry, Faculty of Chemistry, University of Lodz, Tamka 12, 91-403 Lodz, Poland

\*E-mail: [zielmark@chemia.uni.lodz.pl](mailto:zielmark@chemia.uni.lodz.pl), [magnet@toya.net.pl](mailto:magnet@toya.net.pl)

Received: 8 February 2015 / Accepted: 11 March 2015 / Published: 23 March 2015

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The paper presents a study of the effect of constant magnetic field (CMF) on the basic processes of Co-W-Cu alloys electrodeposition. The alloys electrodeposited in the presence of CMF were more homogeneous and smooth than those obtained without CMF. The reason for these changes was the fact that the Lorentz force, generated in CMF, caused the magnetohydrodynamic (MHD) effect. Electrolyte motion under the influence of CMF caused an increase of cobalt and tungsten content with a simultaneous decrease of copper content in the alloy. The presence of the magnetic field during plating leads to significant greater corrosion resistance and smaller roughness.

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**Keywords:** Alloys, Electrodeposition, Constant magnetic field, Magnetohydrodynamic effect.

### 1. INTRODUCTION

Understanding the magnetic phenomena influences the development of technologies based on new magnetic materials. The demand for alloy films possessing specific properties has increased in the recent years. They demonstrate much better resistance to corrosion than single metal ones. Obtaining binary, ternary alloys and those with higher numbers of components, among which cobalt is the basic one must involve introduction of other metals with physical properties superior to cobalt. Daniluk et al. [1] analysed CV curves obtained during the electrodeposition of Cu in a magnetic field of  $B = 0 - 0.178$  T. They attributed the phenomenon to the MHD effect, which intensifies the convection process (as well as the motion of ions and molecules) in the electrolyte, leading to an increase in both the Faradaic and limiting current. It had been observed earlier that magnetic field may affect electrochemical processes [2-9]. The obtained data indicated that such changes are due to

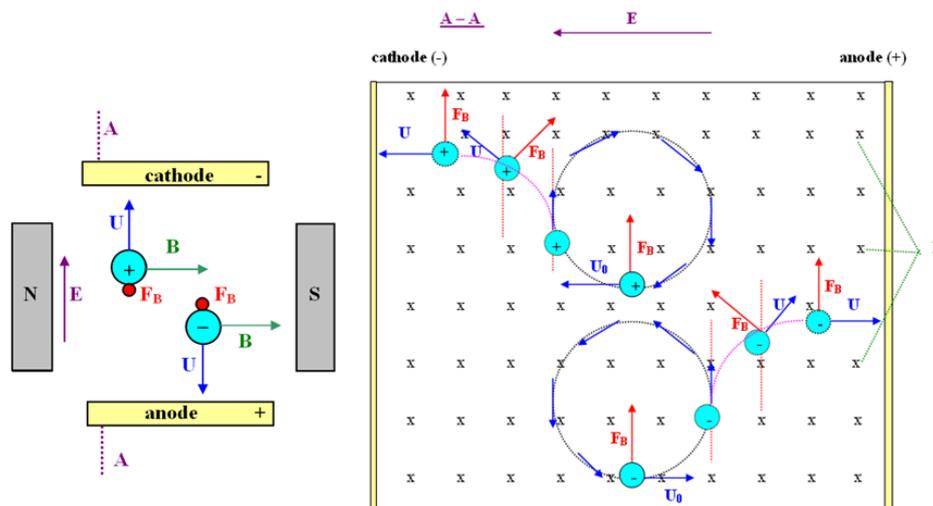
magnetohydrodynamic (MHD) effect. The MHD effect is based on the Lorentz force, inducing movements of the electrolyte and increasing or decreasing transport of the electroactive molecules to the electrode [5]. Coey and Hinds [10] confirmed that CMF increased significantly copper electrodeposition rate. Then, they observed increased transport of cationic mass, both diamagnetic ( $\text{Ag}^+$ ,  $\text{Zn}^{2+}$ ,  $\text{Bi}^{3+}$ ) and paramagnetic ( $\text{Cu}^{2+}$ ,  $\text{Ni}^{2+}$ ) under CMF conditions. Lioubashevski et al. [11,12] developed a theoretical hydrodynamic model demonstrating the influence of a magnetic field on electrochemical processes. Because of high content of ferromagnetic cobalt (60 – 70%), the studied alloys could be classified as so-called magnetics. Magnetics are materials whose thermodynamic system properties could be described exclusively by thermodynamic equations – without taking into account their microscopic structure [13]. Owing to Maxwell's thermodynamic equations we can calculate the functional correlations of the variables whose values cannot be modified in the experiment. In the presence of CMF (at  $V$ ,  $T$ ,  $P = \text{const.}$ ) the internal energy of a diamagnetic decreases parabolically with the increase of CMF, whereas the internal energy of a paramagnetic is not affected by CMF. Diamagnetic enthalpy increases parabolically with the increase of CMF, whereas paramagnetic enthalpy demonstrates a linear decrease with the increase of CMF. An increase of CMF does not cause any heat exchange with the environment in a diamagnetic (heat is transmitted into the environment – the magnetic entropy decreases). In contrast, in paramagnetics and ferromagnetics an increase of CMF induces the release of heat.

In this paper, the effect of CMF on electrodeposition of Co-W-Cu alloy has been studied. To the author's knowledge, such research has been performed for the first time for Co-W-Cu alloy. The results obtained show that the application of CMF causes changes in the kinetics of alloy deposition reactions, as well as changes in the chemical composition of the alloy.

## 2. EXPERIMENTAL PART

Electrochemical measurements were performed using Potentiostat (Atlas 0531 Electrochemical Unit). Co-W-Cu alloy was prepared by electrodeposition using three-electrode system. The three-electrode electrochemical cell, in which the alloys were deposited, consisted of a working electrode (gold, disc-shaped) with  $0.1 \text{ cm}^2$  surface area, an auxiliary electrode (platinum, mesh) and a reference electrode (saturated, calomel) [5]. The galvanic solution prepared to obtain Co-W-Cu alloy contained 0.2 M cobalt sulfate ( $\text{CoSO}_4 \cdot 7\text{H}_2\text{O}$ ), 0.05 M sodium tungstate ( $\text{Na}_2\text{WO}_4 \cdot 2\text{H}_2\text{O}$ ), 0.02 M copper sulfate ( $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ), 0.4 M sodium citrate ( $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7 \cdot 2\text{H}_2\text{O}$ ) and 0.1 M sulfuric acid ( $\text{H}_2\text{SO}_4$ ). The alloys were deposited at potential  $-1,3 \text{ V}_{\text{SCE}}$  (as related to the saturated calomel electrode) for 300 seconds. The Co-W-Cu alloy electrodeposition potential was determined on the basis of the dependence of current on potential.

The Co-W-Cu alloy was deposited without and in CMF produced by the N and S pole pieces of an ER 2525 laboratory electromagnet [5]. The magnetic induction  $B$ , used in the study within the value range from zero to 1.0 T, was directed either parallel to the surface of the working electrode [i.e. perpendicular to the current density  $j$  direction (electric field intensity  $E$ ),  $B \perp j$  ( $E$ ) configuration], as presented in Figure 1.



**Figure 1.** Diagrams of the origination of force  $F_B$  as a result of the action of constant magnetic field in the process of electroreduction and electrooxidation of a paramagnetic positive and negative ion, in the settings of magnetic induction direction  $B \perp E$  (A–A is the cross-section view is selected in the left figure), where: N, S-pole pieces of a laboratory electromagnet,  $F_B$ -Lorentz force, B-magnetic induction, E-electric field intensity,  $U_0$ , U-initial and final velocity of ions.

The morphological structure of the Co-W-Cu alloys was studied by Scanning Electron Microscopy (SEM) using a Nova Nano SEM 450 manufactured by FEI instrument company and by Atomic Force Microscopy (AFM) using a AFM Dimension TMI com manufactured by Bruker Nano Surfaces. The chemical composition of the alloys was determined by Energy Dispersive X-ray Spectroscopy (EDS) using a DEPR spectrometer.

### 3. RESULTS AND DISCUSSION

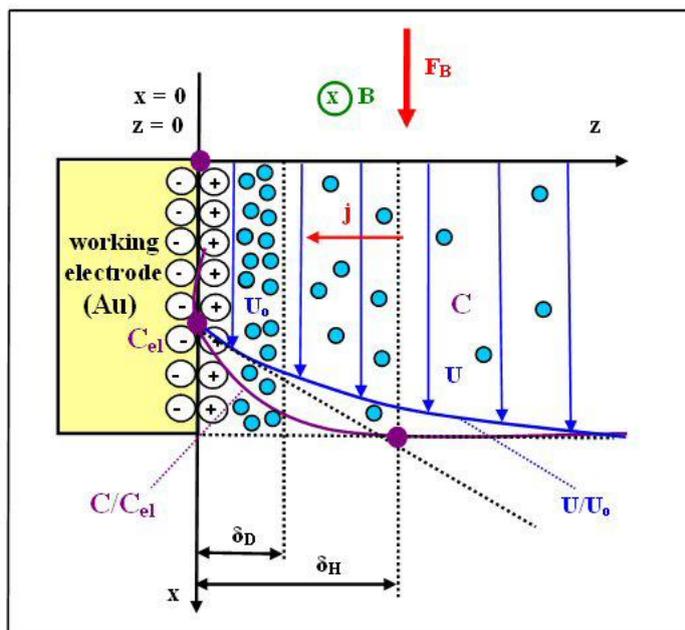
The main objective of the study was to answer the question what is the effect of CMF on the fundamental processes involved in electrodeposition of Co-W-Cu alloy, transport of the mass towards the cathode and kinetics of electrode reactions. During electrodeposition of Co-W-Cu alloy, as a result of exposure to CMF, Lorentz force  $F_B$  was generated. The Lorentz force is described as the cross product of the electric current density  $\mathbf{j}$  and the magnetic induction  $\mathbf{B}$ :

$$F_B = \mathbf{j} \times \mathbf{B} \tag{1}$$

In the transition state for the ongoing processes, concentration changes in time should be taken into consideration. The mass transport equation can be expressed as follows [5]:

$$\frac{\partial C}{\partial t} = uC\nabla^2\phi + D\nabla^2C - v\nabla C \tag{2}$$

here  $u$  is the ion mobility,  $C$  is the concentration of electroactive ions,  $\phi$  is the internal potential (electrical) phase and  $v$  is the bulk flow velocity.



**Figure 2.** Reduction in the Nernst diffusion layer thickness  $\delta_D$  near the working electrode surface under the influence of CMF, and formation of the Navier-Stokes hydrodynamic layer  $\delta_H$  [7].

Eq. (2) is the Navier-Stokes equation, describing the motion of fluid substances. Eq. (2) and hydrodynamic continuity equation (3) are the basic differential equations describing convective mass transport [5]:

$$\frac{\partial \rho}{\partial t} + \nabla(\rho v) = 0 \tag{3}$$

where  $\rho$  is the fluid specific density and  $t$  is the mass transfer time.

Eq. (2) for steady-state convection diffusion can be expressed as follows:

$$\frac{\partial C}{\partial t} = D \nabla^2 C - v \nabla C = 0 \tag{4}$$

where  $D$  is the electrolyte diffusivity.

There is a gradient of concentrations  $(C - C_{el})$  in the aforementioned diffusion layer  $\delta_D$ ; thus, the mass diffusion transfer  $J_{diff}$  can be written as:

$$J_{diff} = D(C - C_{el}) / \delta_D \tag{5}$$

where  $C_{el}$  is the concentration of electroactive ions near the working electrode surface.

The force  $F_B$  generated as a result of the exposure to CMF caused electrolyte movements. The Nernst diffusion layer  $\delta_D$  was depleted, while a new Navier-Stokes hydrodynamic layer  $\delta_H$  appeared (Figure 2).

It caused magnetohydrodynamic (MHD) effects in the solution, resulting in movement of the electrolyte. Consequently, the Nernst diffusion layer ( $\delta_D$ ), was reduced, which could be described by equation (6) [5-7]:

$$\delta_D \approx 1.59(\rho R v^{2/3} D^{1/3})^{1/3} (n F C B)^{-1/3} \tag{6}$$

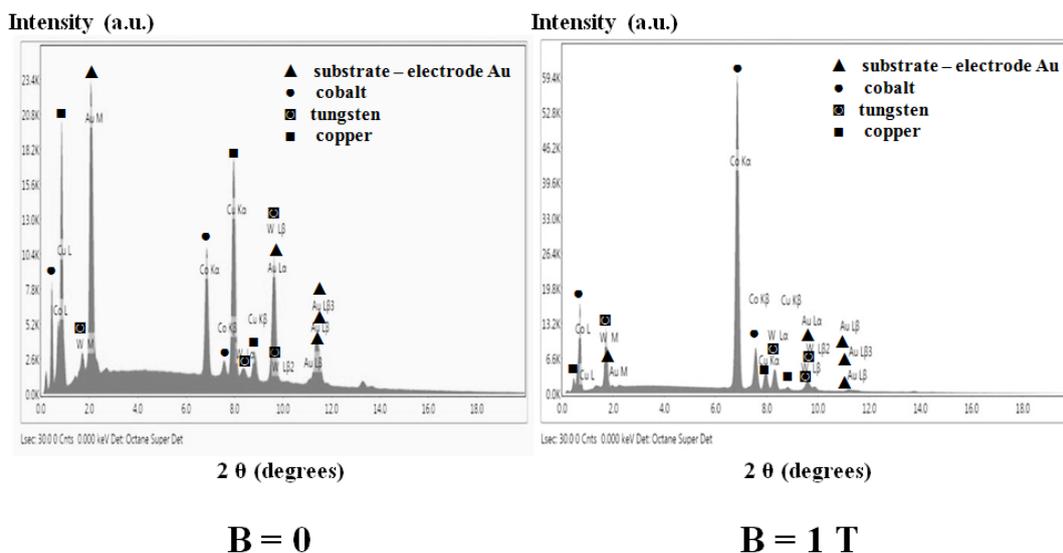
where  $\rho$  electrolyte density,  $R$  radius of the working electrode,  $\nu$  kinematic viscosity of the electrolyte,  $D$  electrolyte diffusion,  $n$  number of electrons involved in the electrochemical process,  $F$  Faraday’s constant,  $C$  concentration of electroactive ions in the solution and  $B$  magnetic induction.

The decrease of Nernst diffusion layer thickness ( $\delta_D$ ) consequently increased the concentration of molecules ( $C$ ) near the solid phase and resulted in deposition of a higher number of molecules according to the following equation (7) [6,7]:

$$m \approx 0.63(\rho R)^{-1/3} \nu^{-2/9} D^{8/9} (nFCB)^{1/3} \tag{7}$$

in which  $m$  denotes the mass of the molecules.

A new hydrodynamic Navier-Stokes layer ( $\delta_H$ ) appeared, which determined the flow velocity of electroactive molecules to the working electrode [5]. Energy values corresponding to the characteristic of test lines of the spectrum (Figure 3) led to the identification of the type of the chemical elements which were Co-W-Cu alloy components.



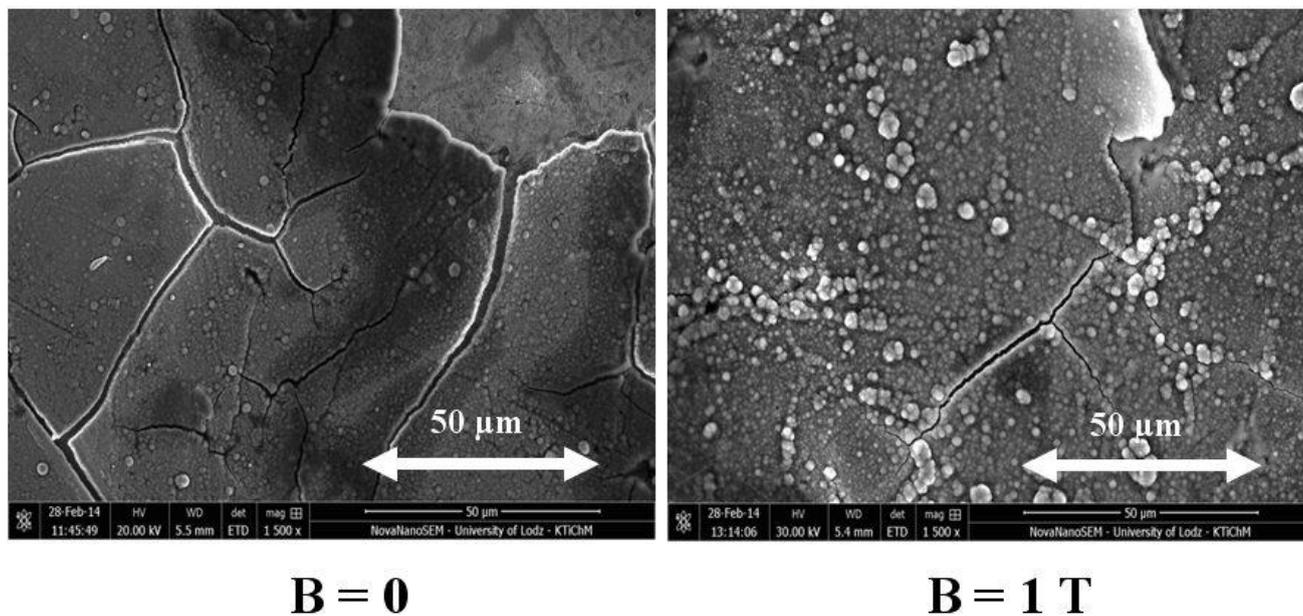
**Figure 3.** Qualitative analysis. X-ray spectra of Co-W-Cu alloys obtained in the CMF of the magnetic induction  $B=1T$  and without magnetic field. The peak (Au) means that the substrate is made of gold (gold working electrode, disc).

The size of the area under the peak allowed to calculate the percentage of the alloy chemical element in the region penetrated by the electron beam. The effect of CMF involved also an increase of cobalt (ferromagnetic) and tungsten (paramagnetic) content with a simultaneous decrease of copper (diamagnetic) content (Table 1).

**Table 1.** EDS method. The quantitative analysis of the chemical elements contained in the resulting Co-W-Cu alloys.

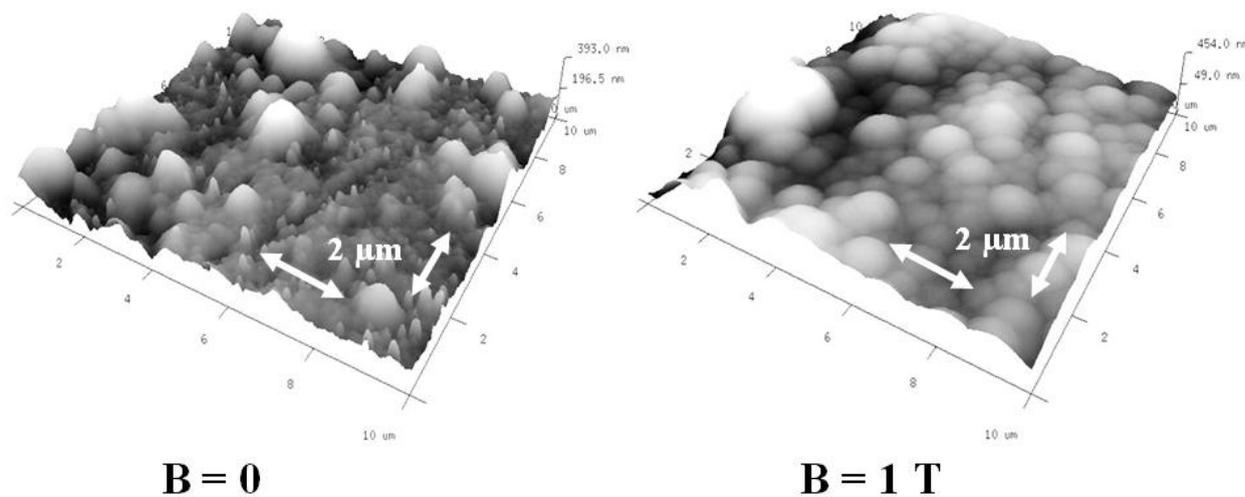
The chemical element in the Co-W-Cu alloy	Magnetic induction B (T)	
	B = 0	B = 1
Co	18,47 wt %	69,55 wt %
Cu	70,33 wt %	12,53 wt %
W	11,20 wt %	17,92 wt %

The morphology of the alloys was studied using SEM (Figure 4). The Co-W-Cu alloys were obtained electrochemically either with no exposure to magnetic field or under CMF conditions.



**Figure 4.** SEM images of Co-W-Cu alloy samples, obtained with no exposure to magnetic field and in CMF with magnetic induction value  $B=1\text{ T}$  ( $B \perp j$  configuration).

We observed a significant effect of CMF on the morphology of metallic films Co-W-Cu (Figure 5).



**Figure 5.** AFM method. Topography of Co-W-Cu alloy surface electrodeposited on a plateshaped gold electrode in CMF with magnetic induction  $B=0$  and  $B=1\text{ T}$ .

The alloys electrodeposited in the presence of CMF were more homogeneous and smooth than those obtained without CMF.

The surface texture was confirmed by studies of roughness of the deposited Co-W-Cu alloy. The AFM method was used in the study. The roughness was expressed as the surface development coefficient (SDC), root mean square deviation of the profile of surface roughness (RMS) and the maximum height of the electrochemically deposited alloy ( $h_{max}$ ). SDC and RMS were described by the following correlations:

$$SDC = \frac{S_A}{S_G} \tag{8}$$

where  $S_A$  stands for the actual surface area and  $S_G$  is the geometric surface area,

$$RMS = \left[ \sum_i (Z_i - Z_a)^2 / N \right]^{1/2} \tag{9}$$

where  $Z_i$  is the distance of  $i$  – the point from the average  $Z_a$  level and  $N$  is the number of measurement points.

Exemplary studies of roughness are shown in Table 2:

**Table 2.** Alloy roughness (scan area 1 x 1  $\mu\text{m}$ ).

Magnetic induction B (T)	SDC	RMS (nm)	$h_{max}$ (nm)
B = 0	1,06	15,3	117
B = 1 T	1,02	10,1	95,4

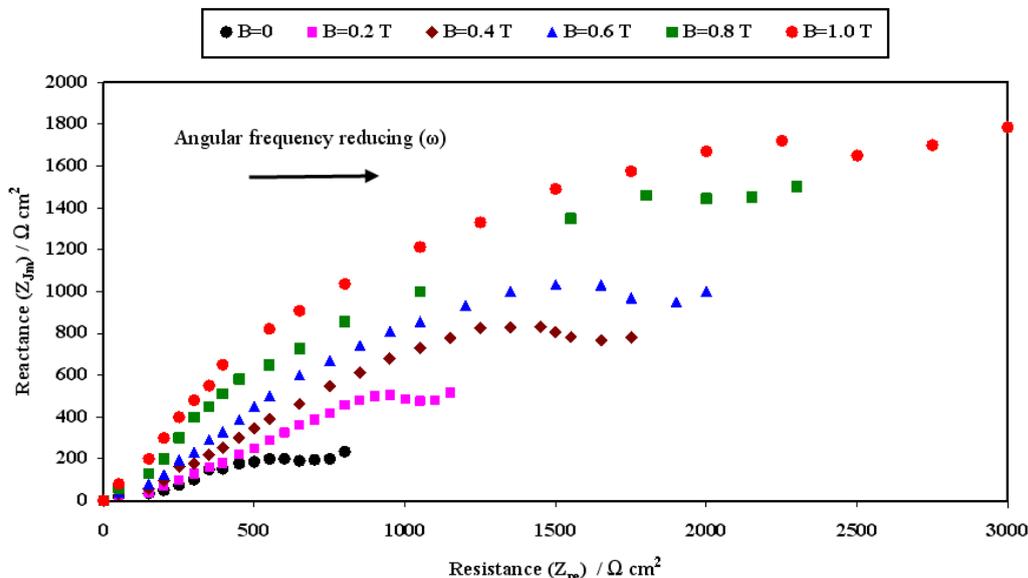
Reducing the surface roughness of Co-W-Cu alloy in constant magnetic field results in a surface less developed and less susceptible to chemical reactions (e.g. oxidation). The access of reagents (e.g. oxygen) to the active sites is reduced. As a result, the alloy is more resistant to corrosion.

The thickness of coating Co-W-Cu in constant magnetic field it decreased. It was observed that the thickness of the coatings and direct dependency with strength of applied B and is more pronounced in case of perpendicular magnetic field as shown in Table 3. Decrease in the thickness in case of perpendicular orientation of magnetic field is due to MHD effect induced by Lorentz force. Been written this also in the article [14]. The decrease in thickness of Co-W-Cu alloy coatings are due to the changed MHD convections.

**Table 3.** Effect of magnetic field on thickness Co-W-Cu.

Magnetic induction B (T)	Thickness ( $\mu\text{m}$ )
0.00	9.10
0.10	8.95
0.20	7.90
0.40	7.55
0.60	6.85
0.80	6.40
1.00	5.95

Electrochemical impedance spectroscopy (EIS) technique is very powerful tool for characterizing inorganic coating of all types.



**Figure 6.** EIS response of Co-W-Cu coatings under different field intensity, deposited from same bath in the frequency range of 100kHz-10mHz using  $\pm 10\text{mV}$  perturbing voltage.

The Nyquist plots corresponding to the coatings, developed at perpendicularly induced  $\mathbf{B}$  is shown in Figure 6. Increase of polarization resistance,  $R_{jw}$  with field intensity clearly indicates that the capacitive behavior of the coatings increases. This is confirmed by the conclusions of the article [14].

As presented by the magnetic field theory [15] the energy of each particle ( $\varepsilon$ ) and its velocity ( $v$ ) in the magnetic field is constant. A charged particle moves in constant magnetic field (CMF) along the helical line, the axis of which is parallel to the direction of magnetic field strength vector ( $H$ ) or magnetic induction vector ( $B$ ). According to this theory, the particle movement in CMF can be described with equation (10) as follows:

$$\frac{\varepsilon}{c^2} \frac{dv}{dt} = \frac{e}{c} v \times H \tag{10}$$

where:  $e$  – charge value,  $c$  – light velocity,  $t$  – time.

When a charged particle is exposed at the same time to a constant magnetic and electric field, the direction of its movement is perpendicular to the plane of the magnetic field strength vector ( $H$ ) electric field strength vector ( $E$ ). The particle will be moving along the line referred to as trochoid or cycloid. Its mean velocity can be expressed in the form of the following equation (11):

$$\bar{v} = \frac{cE \times H}{H^2} \tag{11}$$

If vectors ( $H$ ) and ( $E$ ) are parallel to each other, the magnetic field will have no effect on the movement of the particle.

We used CMF to modify the physical and chemical parameters of the materials developed within the framework of the research. CMF affected not only chemical and electrochemical reactions, physical and chemical properties of the final products. In the liquid, magnetic fields acting both on electrons and on ionized atoms caused dynamic effects, including volumetric motion of the medium.

#### 4. CONCLUSION

The results obtained in the study indicated that the use of CMF resulted in changes of Co-W-Cu alloy deposition kinetics, chemical composition and surface morphology. It is currently presumed that the effects of magnetic fields in electrochemical processes are associated with the electrolyte mass transport. That force induced magnetohydrodynamic effects in solutions, which caused electrolyte movement. Consequently, the Nernst diffusion layer ( $\delta_D$ ) was reduced and a new Navier-Stokes hydrodynamic layer ( $\delta_H$ ), determining the velocity of electroactive ions flow towards the working electrode, appeared. The effect of CMF involved also an increase of cobalt (ferromagnetic) and tungsten (paramagnetic) content with a simultaneous decrease of copper (diamagnetic) content. The presence of the magnetic field during plating leads to significant greater corrosion resistance and smaller roughness. The thickness of coating alloys in constant magnetic field it decreased. The alloys electrodeposited in the presence of CMF were more homogeneous and smooth than those obtained without CMF.

#### ACKNOWLEDGEMENTS

This work was supported by the Lodz University.

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