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ELECTROCHEMICAL DEPOSITION OF RUTHENIUM AND COBALT-RUTHENIUM ALLOYS FROM ACIDIC CHLORIDE IONS CONTAINING BATHS

The article presents results of tests on potentiostatic electrodeposition of ruthenium and Co-Ru alloys.
The tests applying the method of cyclic voltammetry with the use of gold disk electrode (RDE) allowed to define a potentials range in which it is possible to obtain ruthenium and its alloys with cobalt from acid chloride electrolytes.
The influence of electrodeposition parameters and the electrolyte composition on the composition, morphology and structure of the obtained deposits was determined. Co-Ru alloys underwent XRD tests, an analysis with the XRF method and observations using scanning electron microscopy (SEM).

Keywords: Co-Ru alloys, Electrodeposition, Thin Films, Chloride baths

1. Introduction

An essential part of a continuous development of the fuel industry is improvement of technological processes and obtaining higher and higher efficiency of energy carriers. A necessary condition to achieve it is working out better and better catalytic materials of higher degree of conversion, better structure and longer operation time. [1] The best catalytic properties are found in metals from the platinum group [2-3], but due to their high prices it is impossible to commercialise production of hydrogen as a common energy carrier. A solution to the problem can be application of alloy or composite catalysers of catalytic properties close to those of the platinum metals though much less expensive [4-11].

The problem of catalysis is widely analysed, and particularly, development of materials featuring high catalytic activity is a challenge for contemporary engineering and the fuel industry. Catalytic properties of materials are analysed in a nanoscale, e.g. nanoparticles of precious metals in processes of electro-oxidation of glucose, designated for fuel cells [12-13]

For example the Tropsch-Fischer synthesis uses cobalt oxides and irons deposited on alumina matrix of highly developed surface as the catalytically active material [14-17]. Cobalt catalysers of the latest generation feature in their composition a slight addition of ruthenium [18] introduced in the form of nanoparticles, which allows a local increase of gaseous CO concentration as a result of its strong adsorption on its surface.

Obtaining alloy coatings designated for catalysis can be conducted through electrolytic deposition. It is a fast and inexpensive method allowing to obtain coatings of desired composition and morphology. In regard, the literature on cobalt – ruthenium alloys is relatively poor, especially obtained by electrochemical method, the subject taken at work will be a valuable source of information in this field.

Mech et al. described in their work a mechanism of creating Co-Ru alloy coatings during electrolysis from chloride solutions [19]. The coatings were deposited on copper within potentials range from -0.5 to -0.9 V. The concentration of Ru(III) and Co(II) ions in a complexed form amounted at, respectively, 10 mM and 10-100 mM. Additional parameters of the process were temperature (25-70°C) and the electrolyte pH (1-3).

Electrodeposition of Co-Ru coatings was also investigated by Fesheraki et al. [20]. They deposited cobalt-ruthenium alloys from chloride-sulphate baths in acid environment (pH = 1.5). The additives to the electrolyte were $MgSO_4$ or H_2SO_4, KCl and H_3BO_3. As a result of galvanostatic deposition on polycrystalline copper or Cr-Cu coatings sputtered on glass, alloys of cobalt content from 2 to 8% were obtained at low current intensity ($J = 2$ mA/cm²). At higher current density ($J = 20$ mA/cm²) it was possible to obtain coatings containing from 0 to 40 % at. Ru. Juzikis et al. [21] also used chloride-sulphate solutions for electrodeposition of multilayer coatings on platinum, however, they applied higher concentrations (0.08 mol/dm³ Ru(IV), 1.5 mol/dm³ Co(II)). The measurements were performed in increased temperature (60°C).

Multilayer coatings Co(Ru)/Ru were obtained by Bakonyi et al. [22] Galvanostatic deposition was conducted from solutions of $CoSO_4$ (0.36 M), $RuCl_3$ (0.04 M), Na_2SO_4 (100 g/L) and HCOOH (46 mL/L) in temperature 50°C. The working electrode was a titanium plate. The work comprises analyses of the coatings.

Previous work was mainly focused on the mechanism of electrode reactions and magnetic properties of obtained coatings. In our work, emphasis has been placed on the influence of process parameters on the elemental composition

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and phase alloys. The results may allow expansion of knowledge of cobalt – ruthenium alloys to be used in future work related to the effects of phase composition of these alloys on the electrocatalytic properties.

2. Experimental section

The electrolyte was prepared by dissolving $CoCl_2 \cdot 6\,H_2O$ (Lach-ner), $RuCl_3 \cdot xH_2O$ (35-40% Ru) (POCH S.A.) and 36% HCl (POCH) (analytical grade reagents) in deionized water. The alloys were potentiostatically deposited from electrolytes of $CoCl_2$ concentration range from 10 to 100 mM and constant $RuCl_3$ concentration of 10 mM. The pH of the electrolyte was adjusted by the addition of NaOH (pH = 1). Tests were performed in a Teflon electrochemical cell. The working electrode (WE) was chemically polished Cu substrate. The counter electrode (CE) was platinum sheet (Pt). The working electrode was placed at the bottom of the cell. The saturated calomel electrode was used as the reference electrode in deposition process as well as in woltammetry research. The measurements were conducted at constant temperature of 298 K. Elemental analysis was performed using the XRF (Rigaku Primini) and SEM technique (Hitachi Su–70). Phase analysis was performed using the XRD method (Rigaku MiniFlex II). All electrochemical measurements were performed with the use of potentiostat/ galvanostat AutoLab PGSTAT30.

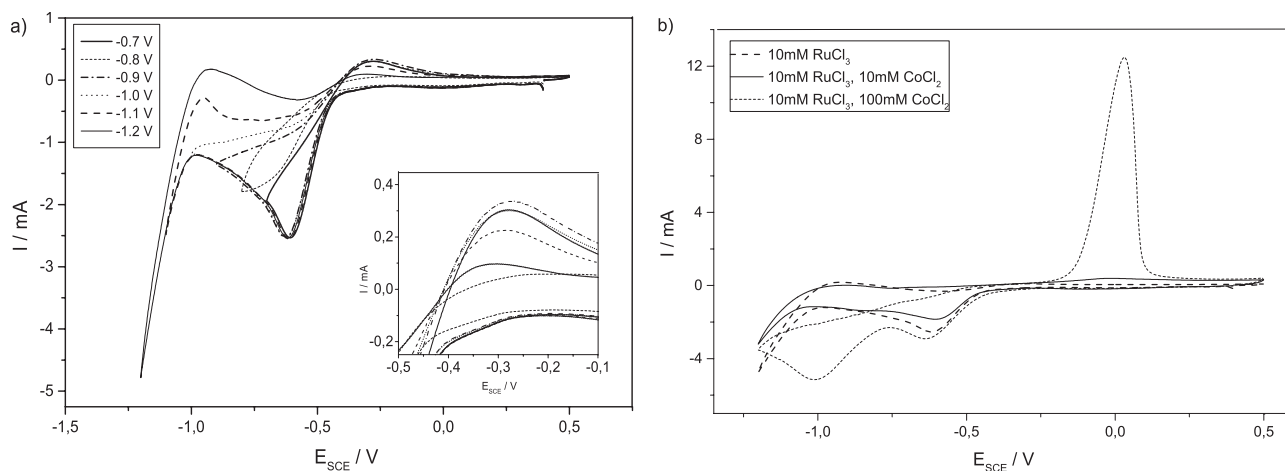## 3. Results and discussion

Electrochemical tests:

An introduction of cobalt to the electrolyte of 10 mM concentration (Fig. 1b) slightly changes the shape of voltammetric curves. A similar course of cathodic curve is observed with insignificantly increased current maximum for a peak observed at potential -0.6 V as well as a larger anodic peak. The changes can result from anomalous co-deposition of cobalt following the reactions:

$$Co^{2+} + 2e^- = Co$$
$$Ru^{3+} + e^- = Ru^{2+}$$
$$Ru^{2+} + 2e^- = Ru$$
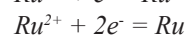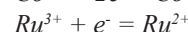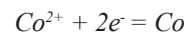
An increase of cobalt concentration in the electrolyte changes the course of anodic curve. There is an additional peak observed coming from the process of metallic cobalt deposition which begins at potential -0.8 V. It has a corresponding anodic peak, much higher than in the previously discussed cases.

Electrodeposition:
On the basis of voltammetric curves the potentials range at which it is possible to obtain coatings from cobalt-ruthenium baths was determined.

Increases of cathodic deposits mass (Fig. 2a) obtained from the electrolyte containing only ruthenium chloride were slight and insignificantly grew following application of more negative potentials. Addition of 10 mM cobalt chloride made the obtained coatings mass higher than in case of ruthenium baths containing ions of one metal only. A linear tendency of the deposit mass increase is observed in a function of potential. It should be emphasised that this case pertains to anomalous alloy deposition. Obtaining cobalt coatings from acid solutions is not possible above potential – 0.7 vs SCE.

Fig. 1. Voltammetric curve made for solutions: a) 10 mM RuCl3, 1M [Cl-], pH = 1 at different scanning range, b) 10 mM RuCl₃, 10 mM CoCl₂ and 10 mM RuCl₃, 100 mM CoCl₂, 1M [Cl⁻], pH = 1

Cyclic voltammetry implemented for the electrolyte containing only Ru^{3+} ions (Fig. 1a) demonstrated that on the copper surface the Ru^{3+} ions reduction to metallic form takes place.

At potentials from -0.5 to -0.9 V an increase of the anodic peak height is observed. For more electro-negative potentials the process of the Ru^{3+} ions electroreduction is likely to be inhibited due to strong hydrogen evolution on the electrode which decreases the anodic peak.

In case of 10-times higher increase of cobalt concentration in the solution, a sharp change of mass is clearly seen. It can result from altered mechanism of co-deposition of cobalt with ruthenium and occurrence of cobalt deposit in an oxide form.

The XRF analysis allowed to determine the sizes of intensity of peaks coming from the elements contained in the alloy that were subsequently converted to the mass of ruthenium and cobalt.
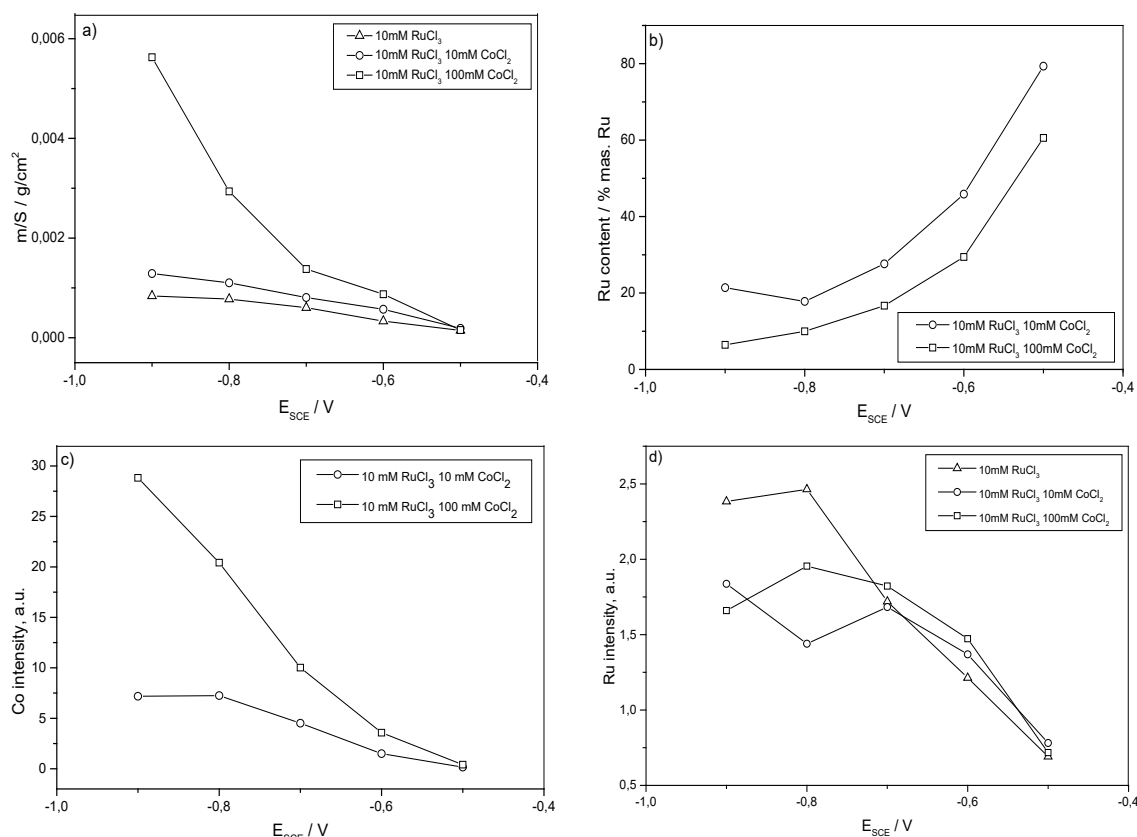
Fig. 2. Dependencies: a) mass increase, b) percentage content of ruthenium in the coatings, c) intensities of peak characteristic for cobalt, d) for ruthenium obtained for different composition of electrolyte and electrolysis potentials

The XRF analysis allowed assessment of cobalt and ruthenium percentage content in the obtained coatings. It proves anomalous character of Co-Ru alloys co-deposition. Applying more electro-negative potentials is accompanied by an increase of cobalt content in coatings. An increase of Co: Ru concentrations ratio from 1:1 to 10:1 allows to obtain coatings richer in a more electro-negative metal. The difference of ruthenium content in the coating at each of the potentials is on average 12-15 %.

The amount of ruthenium in an alloy determined based on intensity of a peak characteristic for ruthenium (Fig. 2d) in deposit obtained from electrolyte not containing cobalt achieves maximum at potential -0.8 V and remains stable. Electrolytes containing cobalt show very similar values
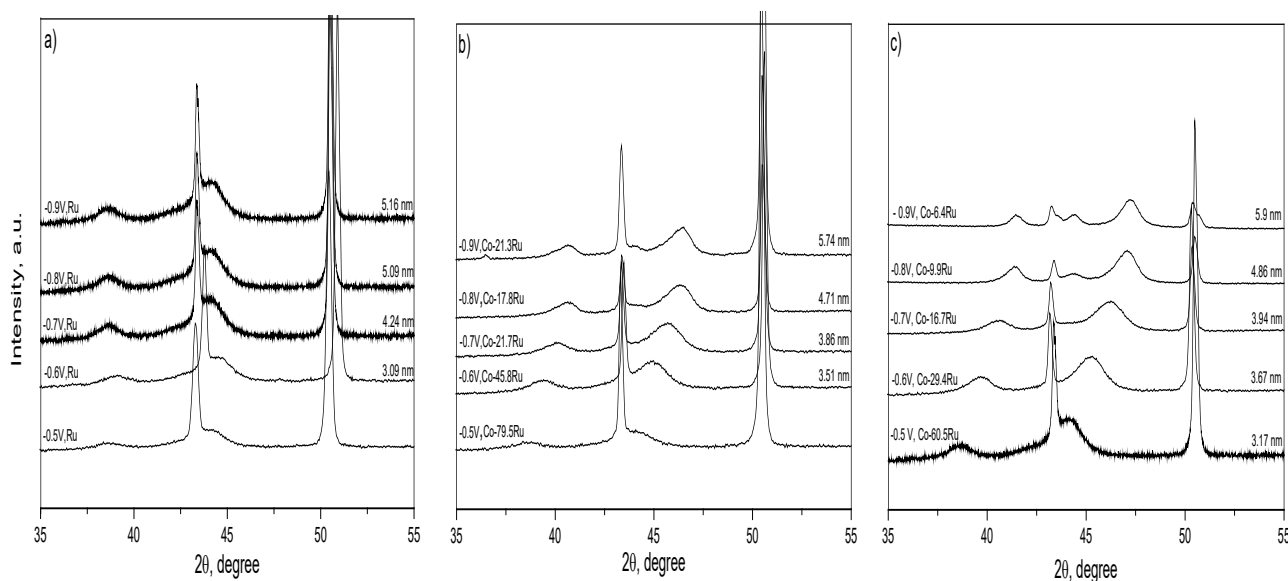

Fig. 3. X-ray diffraction patterns of coatings obtained from electrolytes composed of a) 10 mM $RuCl_3$ b) 10 mM $RuCl_3$ + 10 mM $CoCl_2$ c) 10 mM $RuCl_3$ + 100 mM $CoCl_2$ and deposition potential ranges from -0.5 to -0.9 V vs SCE. The diagram also includes composition of a Co-Ru alloy and sizes of crystallites

of intensity for peaks characteristic for ruthenium within potentials -0.5 to -0.7 V, but their maximum is higher than for electrolytes containing ruthenium only. The regularity does not depend on the concentration ratio of cobalt to ruthenium in the electrolyte.

Whereas, cobalt content in the electrolyte assessed based on intensity of a peak characteristic for the metal (Fig. 2c) in deposit obtained from electrolyte of concentrations ratio1:1 of the two metals in the solution increases to potential -0.8 V and reaches plateau. In case of applying 10-times higher concentration, a continuous increase of cobalt content is observed following the deposition potential change. It can be connected with too slow process of co-deposition of ruthenium with cobalt, which consequently produces a coating being a mixture containing a slight amount of a Co-Ru alloy and Co in a metallic form.

The tests applying X-ray diffractometer allowed to observe structure changes of the deposited ruthenium and Co-Ru alloy depending on the potential and composition of the electrolyte. Fig. 3a shows the structure of cathodic deposit obtained from an electrolyte containing ruthenium ions only. The presented diffraction patterns demonstrate occurrence of peaks at angle 38.67 and 44.15 coming from metallic ruthenium Ru(100) and Ru(101). The two peaks visible on the XRD patterns at $2\theta = 43.30$ and 50.43 originate from the copper substrate Cu(111) and Cu(200).

The diffraction patterns of coatings presented in Fig. 3b were obtained at potentials from -0.5 to -0.9 V from electrolytes containing cobalt with ruthenium in concentrations ratio 1:1. Fig. 3c shows XRD patterns of samples obtained in the same potential conditions from electrolytes containing cobalt with ruthenium in concentrations ratio 10:1. The analysis of curves indicates that application of more electro-negative potentials is accompanied by a change of the crystallographic structure of alloy coatings from hexagonal one of parameters close to the hcp structure of metallic ruthenium to deformed hexagonal structure characteristic for the Co-Ru alloy. The peak originating from metallic ruthenium at the angle values 38.39 and 44.01 is visible despite relatively low content of ruthenium in the alloy coating – approximately 20 % at. A decrease of the deposition potential causes gradual displacement of peaks taking place as a result of a fall of ruthenium content in the alloy through cobalt atoms building-in the cathodic deposit characterised by more than 50% difference in the elementary cell volume in relation to ruthenium.

Also, a significant lowering of intensity of peaks originating from the copper plate is observed. It results from the fact that thicknesses of the obtained coatings are higher and higher and textured copper does not provide so strong diffraction any longer. Peaks obtained on X-ray diffraction patterns are not as sharp as those coming from the substrate which is caused by a slight crystallites size.

On the basis of the Bragg law the distances between planes of a cobalt-ruthenium alloy of a hexagonal structure were calculated. The subsequently obtained results were used to determine grid parameters of the elementary cell. Taking into account increasing angle at which the peaks are observed in the function of cobalt concentration, the values of changes in

grid parameters of the obtained alloys were determined. They show that a gradual increase of cobalt content in crystalline structure of ruthenium causes a decrease of parameters of the elementary cell. Moreover, XRD patterns obtained for coatings of high cobalt content give reflexes from hexagonal structure of sizes characteristic for this element. A decrease of ruthenium amount in the deposit makes the alloy create bigger crystallites of sizes estimated at about 5.9 nm. Due to lower and lower fine graining, alloys containing 94% of cobalt are characterised by the parameter c, about 3.85 Å, which is close to the size typical for hcp cobalt.
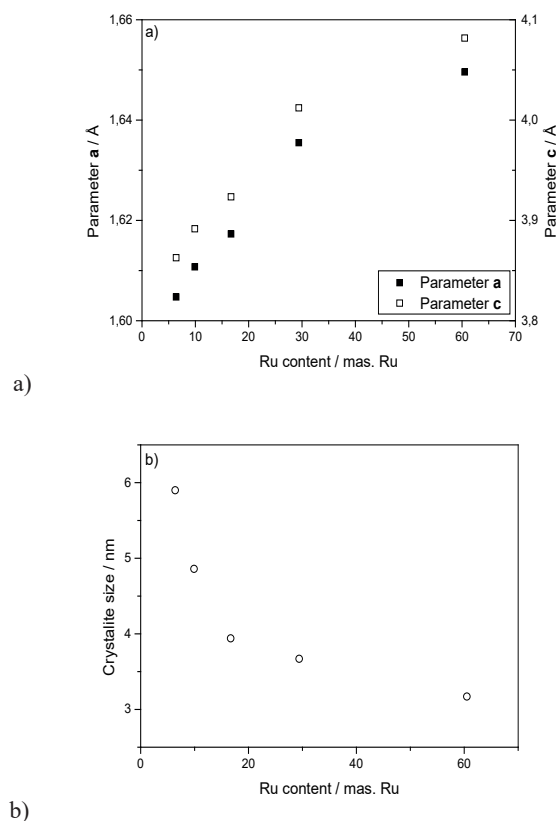

a)

b)

Fig. 4 Diagrams of dependencies: a) size of parameter a and c elementary cell, b) size of crystallites depending on percentage content of Ru in a coating for an alloy obtained from electrolyte composed of 10 mM $RuCl_3$ + 100 mM $CoCl_2$ and the deposition potentials range from -0.5 to -0.9 V vs SCE

Observations based on X-ray diffraction patterns were confirmed by tests of the surface morphology with the use of a scanning microscope. The deposit obtained at -0.5 V is homogeneous, of fine crystalline structure which could explain weak diffraction peaks coming from both cobalt and ruthenium. Applying more electro-negative potentials allows to observe gradual growth of crystallites and their irregular placement on the surface.

Regardless of the applied deposition potential and the content of cobalt and ruthenium in the coating, it can be noticed that the obtained deposit features a homogeneous composition which is shown in the mapping analysis. Mapping for potential -0.9 V, where ruthenium content in the coating decreases to 6.4%, enables to find some areas where its content is significantly lower. It can result from the change of the parameters in crystallographic
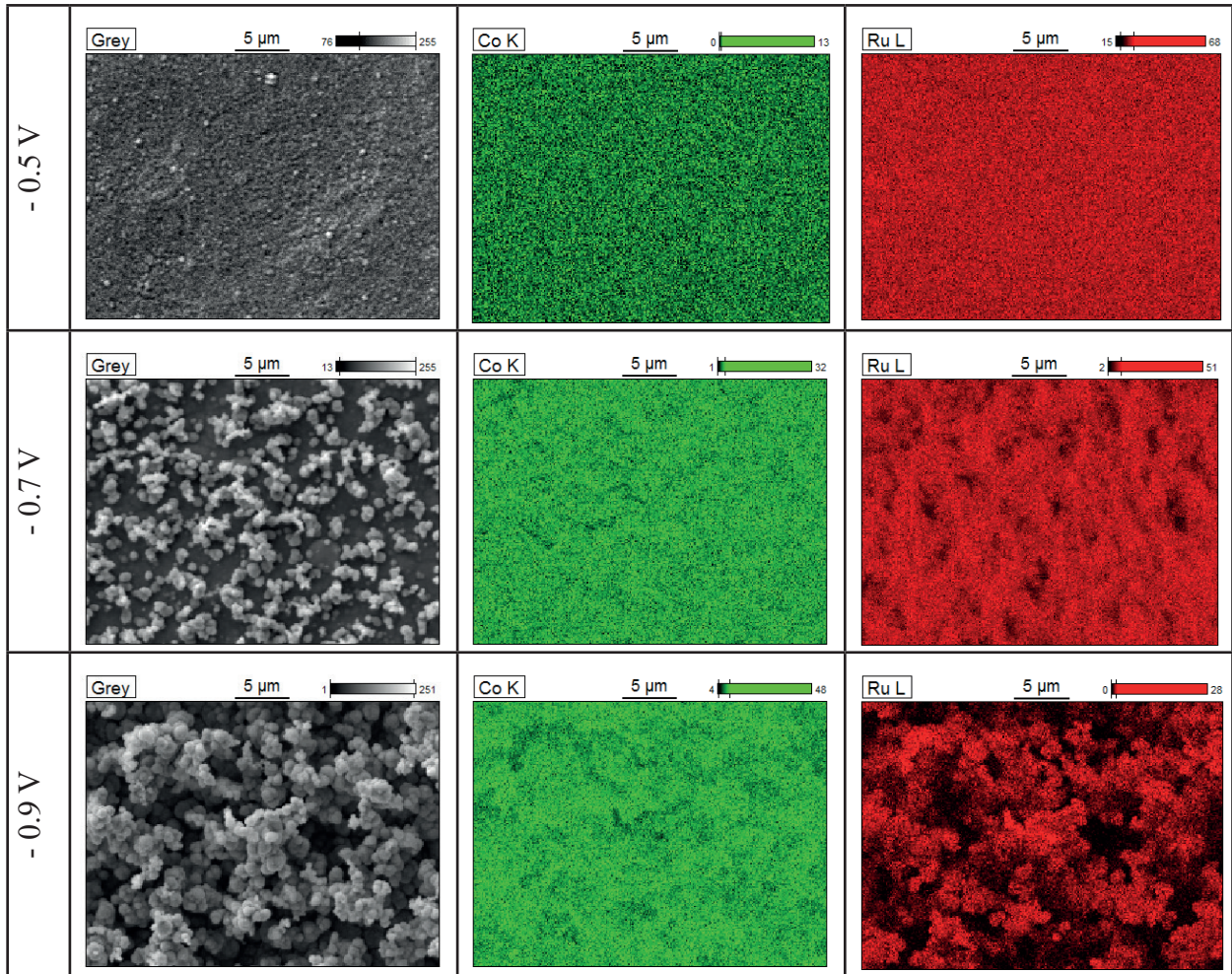
Fig. 5 SEM photograph presents a structure and elemental distribution of the obtained coatings quantified in 4000X, obtained from electrolyte containing 10 mM RuCl₃, 100 mM CoCl₂ at different deposition potentials

structure of the alloy which would cause occurrence of strong heterogeneousness of the surface, and consequently, potential places where cathodic deposit could build-in. The situation can be caused by the fact that velocity of cobalt deposition at so electro-negative potentials is much higher than at co-deposition of the Co-Ru phase.
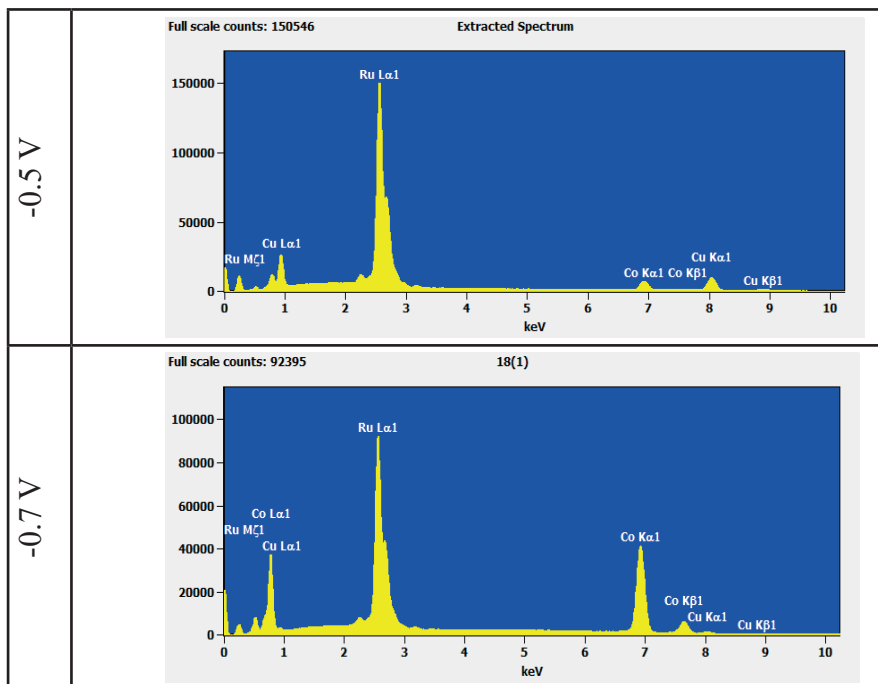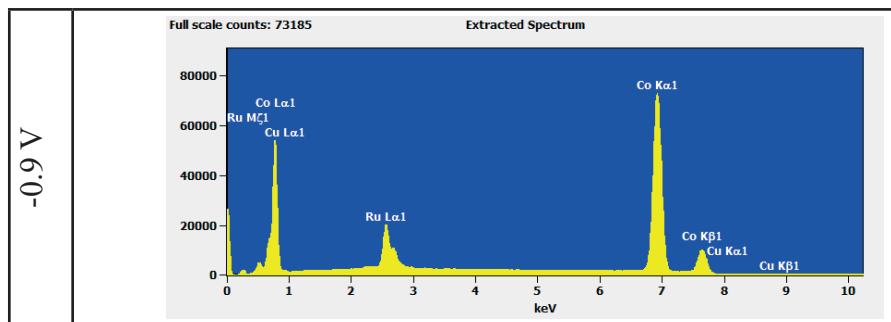
Fig. 6. Qualitative scanning analysis of elements in alloys obtained from electrolyte containing 10 mM RuCl$_3$, 100 mM CoCl$_2$ at different deposition potentials.

An additional analysis with the EDS device in the scanning microscope allowed clear confirmation of occurrence of both cobalt and ruthenium in the coatings. It is explicitly seen that intensity of ruthenium gradually lowers when more electro-negative potentials are applied. The analysis did not detect oxygen in the deposits which means that cobalt co-deposits with ruthenium in the form of the Co-Ru phase or in a metallic form.

4. Conclusions:

On the basis of voltammetric tests conducted at the preliminary phase of the tests, the potentials range at which it is possible to deposit Co-Ru alloy coatings from electrolytes containing ions of the metals was identified. Depending on the electrolysis potential and the composition of the electrolyte, the obtained coatings contained from 80 to 6.4% mas. Ru. It allows to obtain alloys of any different composition. There was observed a process of induced co-deposition of cobalt with ruthenium at potential -0.5 V which is much more electro-positive than the potential for which ions reduction of Co^{2+} to metallic form is observed in acid chloride solutions containing cobalt ions only. The X-ray analysis showed that applying lower and lower potentials made the obtained deposits feature smaller grid constants. A similar dependency was found for crystallites sizes, from 3.17 nm at alloys of 40% cobalt content to even 5.9 nm for 94% Co in the coating. The scanning analysis demonstrated very high homogeneity of the obtained coatings, however, for alloys richer in Co, occurrence of spongy cobalt crystallites is visible. The irregularity could be caused by a high catalytic activity of the obtained alloy and evolution of gaseous hydrogen on its surface during deposition. The scanning analysis excluded presence of cobalt and ruthenium oxides which could be created through an electrochemical reaction.

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