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## Electrodeposited Cobalt Alloys as Materials for Energy Technology

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### ABSTRACT

The influence of electrodeposition parameters on chemical composition, morphology and functional properties of such binary cobalt alloys as CoAg, CoW, and CoFe has been investigated. The alloys are shown to possess catalytic properties. Catalytic activity was preliminary estimated in the electrolytic hydrogen evolution reaction and tested by CO to CO<sub>2</sub> conversion during the catalytic benzene oxidation.

### INTRODUCTION

Metallic platinum and its alloys are known to be the most effective materials as catalysts, but their significantly high cost limits their usage. The focus of this study was to synthesize a replacement for the platinum based catalysts. Cobalt alloys were taken into consideration since they are highly effective in heterogeneous redox reactions [1-6].

The goal was to establish a relationship between the chemical composition and surface morphology and functional properties of binary cobalt alloys, namely CoAg, CoW, and CoFe.

### EXPERIMENTAL

CoFe and CoW alloys were deposited from citrate electrolytes and CoAg - from citrate-pyrophosphate. Electrodeposition was conducted in a standard three electrode glass cell at room temperature using a IPC-Pro M potentiostat in the pulse for CoAg and CoW and galvanostatic for CoFe mode. A platinum mesh was used as a counter electrode, and a saturated calomel electrode (SCE) was utilized as a reference electrode. The pH value was corrected by sodium hydroxide and boric acid and controlled by a pH-meter 150M. Thin films alloys were deposited onto copper, nichrome and steel substrates, respectively. The pre-experimental substrate preparation consisted of degreasing, washing and etching in the mixture of nitric and sulfuric acids (for copper and steel) and a saturated solution of ferric chloride (III) at 333 K (for nichrome). Weighing was performed before and after deposition to calculate current efficiency through Faraday's law.

Chemical composition of CoW, CoFe and CoAg alloys was determined by X-ray fluorescence analysis using a portable spectrometer “SPRUT”. Surface morphology was examined by scanning electron microscope ZEISS EVO 40XVP. The CoAg and CoW coatings surface roughness was investigated by scanning atomic force microscopy (AFM) NT-206.

Electrocatalytic and corrosion properties of CoW alloy thin films were determined from polarization dependencies in the solution of 0.001 M sulfuric acid and 1 M sodium sulfate. The cell was deoxygenated purging high purity argon for 15 min. The CoW alloy thin films were milled in strips of about 10×5 mm for catalytic property in a catalytic benzene oxidation reaction

experiment. The experiment was conducted by varying specific flow rate 20 000 and 40 000 h<sup>-1</sup>. The initial mixture of benzene and air was supplied to the reactor at different component ratio. Outlet gas composition was analyzed with chromatograph OXY 5M-5.

Catalytic properties of electrodeposited CoAg alloy coatings were tested in the carbon (II) oxide oxidation reaction using in-lab built equipment, representing a tubular flow reactor of quartz glass. Initial mixture of CO and air was supplied to the reactor inlet at a rate of 0.025 L/min at a concentration of 1 vol. %. Reactor temperature was increased within the range of 293 to 693 K. The CO gas content in the outlet mixture was analyzed using an indicator-analyzer "Dozor".

Electrocatalytic activity of CoFe alloys was tested in the hydrogen evolution reaction resulting from the aqueous alkali electrolysis.

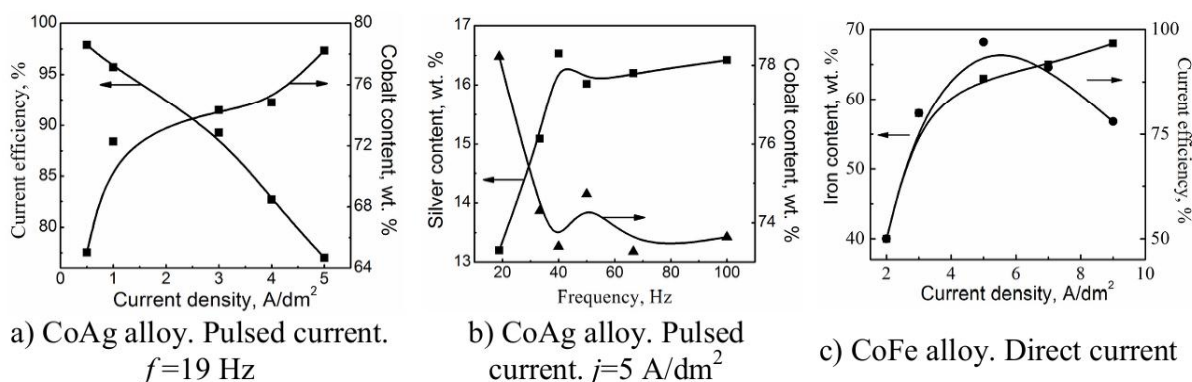
## DISCUSSION

### The effect of deposition conditions

The effect of deposition parameters on composition and current efficiency of CoAg alloy thin films is shown in figures 1 a) and b). In the range of pulsed current densities of 0.5 to 5.0 A/dm<sup>2</sup> cobalt content in the deposit nonlinearly increases from 65 to 78 wt. % while current efficiency value drops from 98 to 81 % due to intensification of hydrogen evolution side reaction (figure 1, a)). The change of pulsed current frequency  $f$  between 20 and 100 Hz allows for varying the cobalt content in the alloy from 78 to 73 wt. % with the higher frequency resulting in less of Co in the film (figure 1, b)).

The effect of direct current density on iron content in CoFe alloy and its current efficiency and is demonstrated in figure 1 c). The increase in current density in the range of 2 to 9 A/dm<sup>2</sup> leads to higher iron content – from 40 to 68 wt. %. Current efficiency increases from 50 % at 2 A/dm<sup>2</sup> to the highest value of 97 % at 5 A/dm<sup>2</sup> and then drops to 77 % at 9 A/dm<sup>2</sup>.

The influence of deposition parameters on CoW alloy composition and current efficiency was described earlier elsewhere [6]. It was possible to vary tungsten content from 5 to 55 wt. %.



**Figure 1.** The effect of electrodeposition parameters on cobalt alloys composition and current efficiency. a) and b) CoAg alloy, c) CoFe alloy. a) The influence of current density of pulsed current on cobalt content in CoAg alloy and its current efficiency at frequency of the current 19 Hz. b) The influence of frequency of pulsed current on silver and cobalt content in CoAg alloy. Current density 5 A/dm<sup>2</sup>. c) The influence of current density of direct current on iron content of CoFe alloy and its current efficiency.

## **Surface morphology**

The surface morphology (magnification  $\times 5000$ ) of CoAg coatings is shown in figure 2 a) and b). The coatings presented were deposited in pulse mode at duty cycle of 11 and current densities of 0.5 and 5.0 A/dm<sup>2</sup>. The fine-grained uniform surface was formed at 0.5 A/dm<sup>2</sup>. This is explained by the higher silver content in the coating - 35 wt. % in comparison with 18 wt. % for 5 A/dm<sup>2</sup>. Further current density increase promotes more cobalt into the film thus allowing for synthesis of developed surface.

The surface morphology (magnification  $\times 2000$ ) of CoW alloy coatings is presented in figure 2 c) and d). The coatings were deposited in pulse mode at duty cycle of 11 and current density of 12 A/dm<sup>2</sup> at different values of solution pH. The morphology of CoW deposit seem to depend strongly on pH and/or film composition. The coatings with tungsten content of 18 wt. % possess needle-like structure and are deposited at pH 5.3, while globular surface morphology is formed at pH 7.3 and is characteristic for the film with tungsten content of 50 wt. %.

The surface morphology (magnification  $\times 2000$ ) of CoFe alloy coatings is demonstrated in figure 2 e) and f). The deposits consist of large individual crystallites for the film deposited at direct current density of 2 A/dm<sup>2</sup> and containing 40 wt. % of iron. Fine-grained structure is formed as current density increases to 5 A/dm<sup>2</sup> and iron content goes up to 65 wt. %. Applying current density of 8 A/dm<sup>2</sup> leads to internally stressed deposit and causes cracking.

Atomic force microscopy of CoAg thin films allowed for concluding that the grain size was in the range of 80-100 nm. The CoW alloy surface consisted of bigger 1.5  $\mu$ m in diameter structures and smaller 600 nm agglomerates.

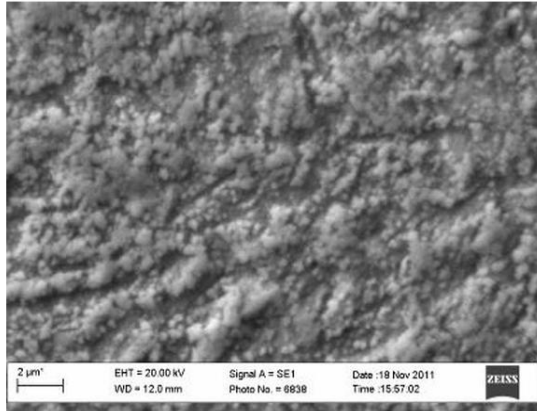
## **Functional properties**

Figure 3 a) represents the influence of tungsten content in CoW alloy on deposit corrosion resistance at pH 3.0 and its catalytic activity in a model reaction of electrolytic hydrogen evolution by means of log of hydrogen exchange current density. From the dependences, there is a plateau in the range of W content of 20 to 40 wt. % corresponding to the alloy composition possessing the highest activity towards the reaction of choice. Corrosion resistance of CoW film nonlinearly increases since the corrosion rate  $k$  decreases with the amount of W in the film in the acidic medium.

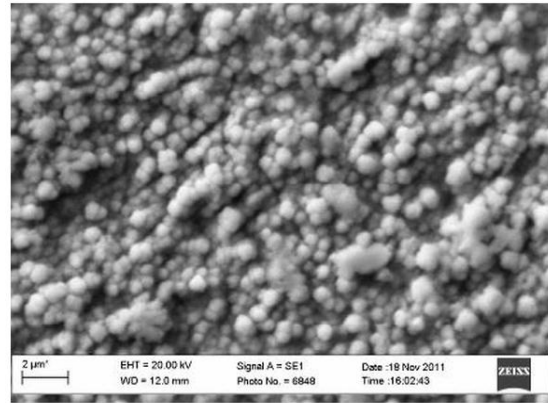
Figures 3 b) and c) are devoted to the catalytic activity of CoAg and CoW alloys in the reaction of flameless benzene oxidation. The catalytic activity was compared by measuring the content of CO<sub>2</sub> in the output gas and calculating the degree of CO to CO<sub>2</sub> conversion for different catalytic materials, including traditional Pt-containing catalyst. From figure 3 b), it is possible to conclude that the CO to CO<sub>2</sub> reaction on Pt-containing catalyst starts at temperatures around 180-200 °C while for CoAg alloy it is 240-250 °C, but for both materials at higher temperatures the CO conversion degree reaches 100 %.

Results of CoW alloy testing as a catalytically active material in the reaction of CO to CO<sub>2</sub> oxidation are in a good agreement with behavior predicted from the electrolytic hydrogen evolution reaction (figure 3 a)). Namely, dependences presented in figure 3 c) allow for concluding that the highest CO<sub>2</sub> volume content in the output gases was found when CoW with about 30 wt. % of W was utilized as an active material (line 1). Moreover, CO<sub>2</sub> volume was lower for CoW films with both higher (50 wt. %, line 2) and lower (10 wt. %, line 3) W content in the deposit, as well as for metallic cobalt (line 4). Benzene conversion degree reaches 86 %.

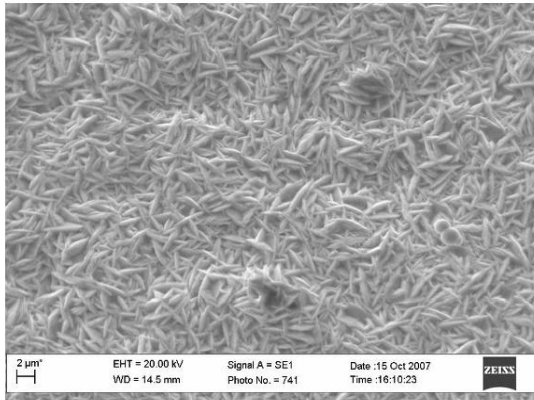




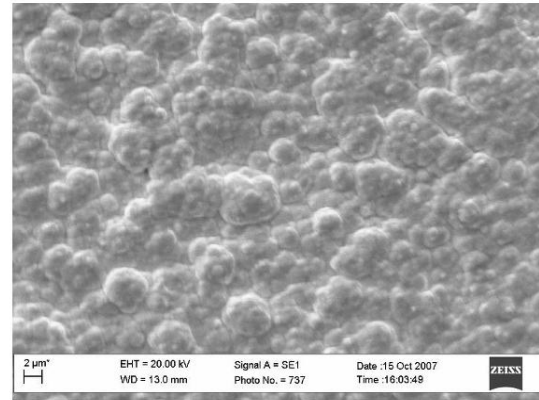
a) CoAg alloy x5000. Pulsed current 0.5 A/dm<sup>2</sup>.  
ω(Ag)=35 wt. %



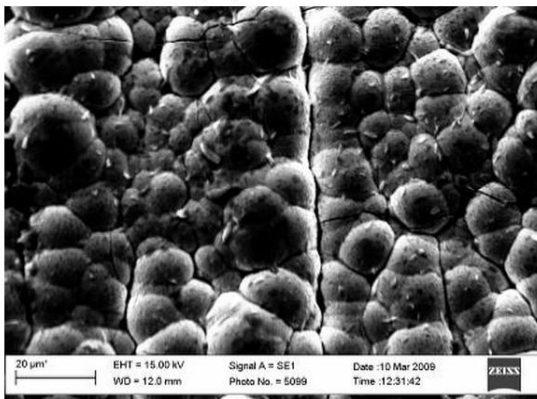
b) CoAg alloy x5000. Pulsed current 5 A/dm<sup>2</sup>.  
ω(Ag)=18 wt. %



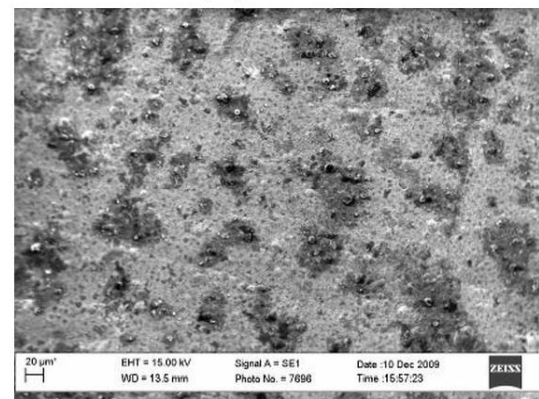
c) CoW alloy x2000. Solution pH 5.3.  
ω(W)=18 wt. %



d) CoW alloy x2000. Solution pH 7.3.  
ω(W)=50 wt. %

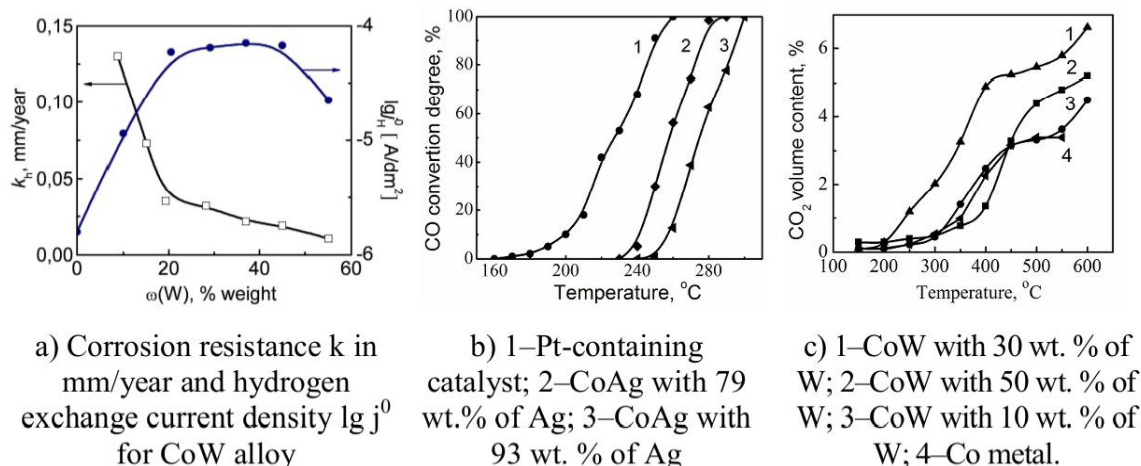


e) CoFe alloy x2000. Direct current 2 A/dm<sup>2</sup>.  
ω(Fe)=40 wt. %



f) CoFe alloy x2000. Direct current 5 A/dm<sup>2</sup>.  
ω(Fe)= 65 wt. %

**Figure 2.** Surface morphology of electrodeposited CoAg, CoW, and CoFe alloy thin films



**Figure 3.** Functional properties of CoAg, CoW, and CoFe alloys. a) Corrosion resistance and hydrogen exchange current density as a function of tungsten content in CoW alloy at pH 3.0. b) The degree of CO into CO<sub>2</sub> conversion as a function of temperature for different catalytic materials: 1–Pt-containing catalyst; 2–CoAg with 79 wt. % of Ag; 3–CoAg with 93 wt. % of Ag. c) The volume content of CO<sub>2</sub> as a function of temperature for different catalytic materials: 1–CoW with 30 wt. % of W; 2–CoW with 50 wt. % of W; 3–CoW with 10 wt. % of W; 4–Co metal.

Thus, the possibility of alloys catalytic activity preliminary estimation through the value of hydrogen exchange current density was proven to be valid by the CoW alloy example.

The catalytic properties of CoFe alloy thin films were tested in the electrolytic water splitting reaction. When deposits were utilized as electrode materials, it was possible to decrease the cell voltage by 15 % due to lowered overpotentials of both hydrogen and oxygen evolution.

## CONCLUSIONS

Electrochemical deposition is shown to provide a flexible control over the chemical composition and morphology and thus functional properties of CoAg, CoW and CoFe alloy thin films. The electrocatalytic activity of binary cobalt alloys was demonstrated for the model reaction of electrolytic hydrogen evolution and catalytic benzene oxidation. CoW alloy was determined to possess high corrosion resistance.

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