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Analysis of electrodeposition parameters influence on cobalt deposit roughness

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ABSTRACT

Over the last years an increased interest has been seen in the electrodeposition of cobalt and cobalt alloys. An essential challenge in the electrodeposition of cobalt is to control the structure and morphology which, in turn, depends on the preparation conditions. The work presents an assessment of the influence of parameters of cobalt deposition in potentiostatic conditions on the structure and morphology of the obtained deposits surface. The level of development of electrocatalytically deposited cobalt layers was examined through microscope methods with the use of the atomic force microscope. Additionally, the samples structure was analysed using X-radiation.

The conducted tests allow drawing the following conclusions. The level of surface development does not depend on the applied potential at which deposition of cobalt is carried out. Deposition at low potentials result in creating, on the surface the mixture of metallic cobalt and hydroxides with high level of surface development. High concentration of cobalt ions in the solution result in obtaining close values of the surface development level irrespective of the applied deposition potential.

1. Introduction

Over the last years an increased interest has been seen in the electrodeposition of cobalt and cobalt alloys. Materials obtained by this method have a wide range of applications (heterogenic catalysts [1], solid oxide fuel cells [2–8], energy storage systems [4–8], magnetic data carriers [9], constructing spin valve devices) mainly due to their magnetic properties. The properties as well as others like hardness, corrosion resistance and thermal stability of electrodeposited cobalt have encouraged scientists to conduct a deeper penetration into the kinetics and mechanism of the cobalt electrodeposition process [10–15]. The correlation between structure parameters and magnetic properties, i.e. coercivity, remanence and hysteresis is commonly known. Hence, an essential challenge in the electrodeposition of cobalt is to control the structure and morphology which, in turn, depends on the preparation conditions, i.e. electrolyte composition, temperature, pH of the solution, current density, substrate material, potential of the working electrode and the presence of additives [16–22].

One of the significant problems observed during the electrodeposition of cobalt is a parallel hydrogen evolution reaction (HER), which strictly affects the morphological and structural properties, locally increases the pH value and decreases the overall current efficiency [14–17]. The local increase of pH values at the cathode surface caused by hydrogen evolution results in creation of unwanted hydroxides. Therefore, in order to avoid changes of pH near the electrode many authors suggest application of boric acid (H_3BO_3) as a buffer agent to the electrolyte [18–22].

Totha et al. show [23] that tuning the Cu deposition potential drastically changes the surface roughness of the Ni–Co/Cu multilayers. This is critical for GMR (giant magnetoresistance) effect value. When the deposition potential is more negative than optimum potential, the roughness increases and for more positive potentials, the roughness decreases first and then remains constant. The different roughening behavior for the binary and ternary systems could be qualitatively explained with the help of the catalytic codeposition mechanism in the case of Ni–Co alloys which was suggested in the literature previously. This effect was investigated by several authors for different substrates and for various metallic deposits as well as multilayers and a short summary of these works has been given recently [24]. However there is still not sufficient data on cobalt layer roughness connected with deposition parameters in potentiostatic mode.

The work presents an assessment of the influence of parameters of electrocatalytic cobalt deposition in potentiostatic conditions (concentration of hydrated cobalt sulphate and potential) on the

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Table 1
Electrolyte composition.

Solutions composition	Concentration [g/l]			HCL
	$CoCl_2 \times 6H_2O$	$CoSO_4 \times 7H_2O$	H_3BO_3	
Co_I	23.8	–	–	18,8
Co_II	3.5	30	6.5	–
Co_III	3.5	20	6.5	–
Co_IV	3.5	10	6.5	–
Co_V	3.5	5	6.5	–

structure and morphology of the obtained cathodic deposits surface. The level of development of electrocatalytically deposited cobalt layers was examined through microscope methods with the use of the atomic force microscope. Additionally, the samples structure was analysed using X-radiation.

2. Experimental

The first electrolyte was prepared by dissolution of $CoCl_2 \cdot 6H_2O$ (analytical grade reagent) in deionised water. The concentration of Cl−ions in electrolyte was controlled by addition of HCl. The pH was adjusted by adding NaOH. The second to fifth solutions were prepared by dissolution of $CoCl_2 \cdot 6H_2O$, $CoSO_4 \cdot 7H_2O$ and H_3BO_3 (analytical grade reagent) in deionised water as shown in Table 1.

The tests were performed in a Teflon measurement cell. The working electrode (WE) was a copper disc of 2.8 cm^2 surface, reference electrode (RE) was Ag/AgCl (3 M KCl), and counter electrode (CE) was a platinum grid. The measurements were conducted at constant temperature 298 K. All electrochemical measurements were performed with the use of potentiostat/galvanostat Biologic SP-200. Cobalt coatings were deposited onto Cu sheet and were analysed with the use of atomic force microscope (AFM) Ntegra Aura (NT MDT) with tips NSG03, SEM microscopy Hitachi and Rigaku MiniFlex X-ray diffractometer.

3. Results

The course of the metallic coatings deposition process is determined by many parameters. One of the most important ones is composition of the electrolyte and concentration of ions of the deposited element. Additionally, in the electrolysis performed by the chronoamperometric method, a significant role is played by selection of proper potential. In order to assess the optimal potential the measurements were conducted with the use of the cyclic voltammetry method.

The location of the peak responsible for cathodic deposition of the metal was read from the curve registered in the solution containing cobalt ions. For the examined solutions these are potentials within the range: −900 to −700 mV. In these potentials the electrolyses are performed to obtain a cobalt coating.

A visual assessment of the deposited cobalt coatings allowed to state that the most metallic, taking into account colour, sheen and roughness of the surface, are coatings obtained at potential −800 mV. Additionally, in case of electrolysis in Co_I solution at potential −750 mV and in solution of Co_III at potential −800 mV, cobalt was deposited only at the edges of copper sheets. However, despite the ring-shaped deposition of the metal, the cathodic deposits are smooth and metallic.

Coatings obtained in the remaining conditions are characterised by darker colour and lower sheen and they also seem to be more rough. It is caused by a release of hydroxides in the electrodeposition process which is confirmed by an analysis of phase composition conducted with the use of X-radiation and presented in Fig. 1.

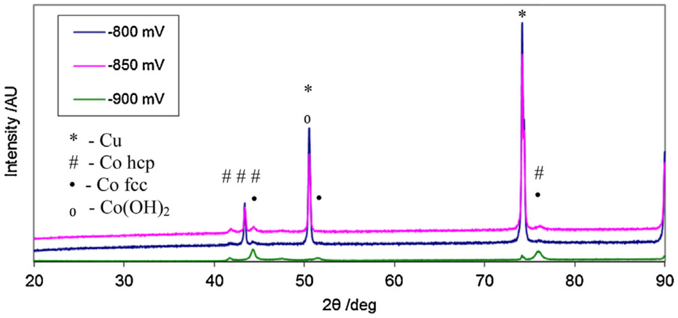

Fig. 1. The analysis of phase composition by X-radiation.

Table 2
Average roughness of cobalt coatings deposited electrocatalytically.

Solution	Average Roughness [nm]				
	−700 mV	−750 mV	−800 mV	−850 mV	−900 mV
Co_I	72	61	63	64	154
Co_II	71	68	53	–	–
Co_III	–	60	54	57	–
Co_IV	–	61	60	57	–
Co_V	–	82	86	63	–
Average Roughness [nm] of pure Cu substrate				47	

Electrodeposited cobalt crystalize in two systems: face centre cubic (fcc) and hexagonal close packed (hcp). The crystallization system is determined by deposition conditions. As can be seen from Fig. 1 cobalt has fcc structure for deposition at −900 mV. Changing the potential to −850 mV or more leads to change in crystallization system from fcc to hcp. The change in cobalt structure could be connected also with hydrogen evolution during electrolysis and cobalt hydroxide codeposition. This could lead to change of crystallization conditions at the surface and preferential build of deposit in one of the systems fcc or hcp.

The level of development of cobalt coatings created in the process of electrolytic deposition in potentiostatic conditions from solutions of different concentrations of cobalt ions and at different potentials can be determined with the use of an atomic force microscope (AFM). It is presented in Fig. 2.

The shape and size of grains in the examined cobalt layers are different depending on the composition of electrolyte and the value of potential at which the process was conducted. Generally deposited Co layers are smooth with only small difference in grains morphology. In case of electrodeposition of cobalt layer from Co_I solution at potential −800 mV the grains are small and rather regular (Fig. 2b). Whereas, for electrodeposition from Co_III solution at the same potential, the grains, presented in Fig. 2d, are considerably larger and irregular.

The observations done with AFM microscopy are confirmed by SEM microphotography.

Co layer deposited from electrolyte Co_I at potential −800 mV has grains rounded, small and rather regular shape (Fig. 3a). Similarly to AFM observations for deposit from Co_III solution at the same potential, the grains, presented in Fig. 3b are longer, larger and irregular non-rounded shape.

The degree of deposit surface development can be calculated from AFM images. AFM is essential for studying surface roughness at the nanoscale. Average roughness of the samples, calculated with the use of the NOVA AFM software shown in Table 2 indicates significant differences in surface development of the obtained cobalt coatings.

Fig. 4 presents dependency of average roughness of cathodic deposits from the potential value at which the electrolysis was conducted. For electrolysis from solutions Co_I and Co_III, an increase of the potential value is accompanied by an increase of the average roughness of the obtained deposits. For solution Co_II, at an increase

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