EFFECT OF THE ELECTRODEPOSITION CONDITIONS ON THE MORPHOLOGY AND CORROSION BEHAVIOR OF Ni-Co ALLOYS
PART 1: CHEMICAL COMPOSITION, CATHODIC CURRENT EFFICIENCY, AND MORPHOLOGY OF Ni-Co ALLOYS ELECTRODEPOSITED FROM CITRATE ELECTROLYTE
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ABSTRACT

Ni-Co alloys with varying cobalt content are electrodeposited in stationary potentiostatic mode employing citrate electrolyte, either with or without addition of saccharin (SHR) at different Ni/Co ratios and variable content of sodium citrate (Na3 citrate) in the electrolyte. The changes in the microstructure, chemical composition and cathodic current efficiency of deposition (CCE) of Ni-Co alloys are studied. Scanning electron microscope, energy dispersive X-Ray and atomic absorption analysis are used to characterize the alloy coating. The alloy deposition is proved to be of an anomalous type. It is found that with the increase of the value of ratio Ni/Co in the solution from 1 to 5, the percentage of Ni in the Ni-Co alloy grows to 48 mass % and the CCE decreases to about 70 % whereas more fine-crystalline Ni-Co coatings (size of crystallites less than 100 nm) are deposited. The addition of SHR results in a strong decrease of CCE (up to 50 %), but also in formation of smooth and shimmering coatings with average size of crystallites much less than 50 nm. The coatings obtained from electrolyte with higher content of sodium citrate contain more Ni but are more coarse-crystalline, as the effect of the complexing agent is generally less pronounced in comparison with the case with SHR addition.

Keywords: Ni-Co alloys, anomalous deposition, polarization studies, morphology, stationary potentiostatic mode.

INTRODUCTION

The nanostructured alloys and multilayer coatings, based on Ni and Co, have been highly topical recently in such areas as magnetoelectronics and medicine but also in oil, automotive and nuclear power industry [3] mainly due to the fact that the crystallites reach size of less than 100 nm, the microhardness, wear resistance, and corrosion resistance unevenly increase, unlike the conventional polycrystalline coatings [1 - 4]. The Ni-Co alloys are employed because of their specific magnetic and catalytic properties behavior combined with excellent mechanical and corrosion behavior [2, 3] in magnetic sensors, actuators and inductors, and in fuel elements [3, 5, 6].

The deposition of Ni and Co is of “anomalous” type in almost all studied electrolytes, i.e. such with predominant deposition of the more negative metal, which is Co in the current case [2, 3, 7 - 9]. This type of deposition is typical for the metals of iron group [2, 3] and shall be considered in the development of electrolytes and the selection of deposition methods.

The Ni-Co alloys are deposited from sulphate-electrolyte [8, 10 - 13] or typical Watts electrolyte [6, 10], chloride 10, 14], chloride-sulphate [15, 16], sulphamate [5, 7, 17, 18], glycinate [19], gluconate [20] and citrate
[21] electrolytes. The introduction of organic addition agents, most often saccharin (SHR) [4, 22, 23], or the application of ultrasound waves [20], or other impulse techniques [4, 7, 13, 14, 24, 25] are found to improve both the microstructure and the properties of the deposited Ni-Co alloys.

The aim of the present work is to study the effect of variation of Ni/Co ratio, the presence of saccharin, and the content of sodium citrate in weakly acidic citrate electrolyte on the chemical content, cathodic current efficiency and morphology of Ni-Co alloys electrodeposited in stationary potentiostatic mode.

EXPERIMENTAL

All electrochemical experiments were carried out in a thermostatic three-electrode cell without stirring. The cell with a total volume 150 dm3 includes a working electrode made of copper (Merck, 99.97 mass % Cu), a platinum counter electrode arranged concentrically around the working electrode, and as reference electrode - saturated calomel electrode in a special pan with Lugin’s capillary ($E_{SCE} = 0.241$ V). The kinetics of deposition is examined using copper electrodes shaped as discs with surface 1 cm².

For the purpose of electrodeposition of Ni-Co alloys coatings, copper cathode plates with dimensions 1.5x4 cm are prepared. Prior to each experiment the surfaces of the copper cathodes are fully cleaned from oxides by etching in an especially prepared solution (H₂SO₄ : HNO₃ = 1:1; 10% HCl). Then the cathodes are rinsed several times with distilled water and dried.

The Ni-Co alloys with thickness 8±2 µm, are dissolved in 30 % HNO₃ and the solution is subjected to Atomic Absorption Analysis (AAA). The data from AAA are used to determine the chemical composition of the coatings, which are the basis for calculating the current cathodic efficiency (CCE) upon Faraday’s law of electrolysis:

$$CCE = \frac{\Delta m_p}{q_{\text{Ni-Co}} \cdot Q} \cdot 100\%$$

where $\Delta m_p$ is the practical determined mass. $q_{\text{Ni-Co}}$ [geq C⁻¹] is the electrochemical equivalent of the alloy and it is also determined using the data for the chemical content of the alloy, and $q_{\text{Ni-Co}} \cdot Q = \Delta m_n$ is the theoretically determined mass of Ni-Co alloy.

The subject of investigation are 9 groups of coatings depending on the content of the electrolyte for each group (Table 1). The ratio Ni/Co in the solution varied from 1 to 5, and the content of Na₃citrate varied from 0.2 to 0.6 g dm⁻³, and the addition of saccharin varied from 0 to 2 g dm⁻³. The deposition kinetics of Ni-Co alloy was investigated using Wenking Electrochemical Analysis System (Germany) with linear speed of potential scanning 30 mV s⁻¹.

The content of the coatings is examined using atomic

<table>
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<tr>
<th>No</th>
<th>electrolyte</th>
<th>Ni, gmol dm⁻³</th>
<th>Co, gmol dm⁻³</th>
<th>(Ni/Co)ₑₓₜ</th>
<th>Na₃citrat, gmol dm⁻³</th>
<th>sacharin, gmol dm⁻³</th>
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</table>
absorption analysis (AAA) and is compared with the data from Energy Dispersive Spectral Analysis (EDSA). The morphology and the content of Ni-Co coatings (EDSA) are studied using equipment of Oxford Instruments, JSM-6390- Jeol by SEM though application of accelerating voltage of 20.0 kV.

**RESULTS AND DISCUSSION**

**Kinetics of electrodeposition of Ni-Co alloys**

The conditions for co-deposition of Ni and Co in Ni-Co alloy from solutions with different values of Ni/Co ratio with formulations corresponding to No 3, 4, and 5 from Table 1, were specified in our preliminary studies through the polarization dependencies obtained for each working solution. It is seen from the data shown in Fig. 1 and extensively discussed in [26] that the growth of the content of Co in the solution results in decrease of both the initial and the total polarization and in increase of the limiting current of co-deposition, as the maximum of the resultant peak is shifted to more negative values of the potential (Fig. 1).

It is shown that in presence of saccharin the polarization increases and the limiting diffusion current decreases due to adsorption of saccharin molecules (Fig. 1b).

The Ni-Co alloys are deposited in stationary potentiostatic mode at potentials close to the plateau of the limiting current in the summary polarization dependencies. These are potentials within the range from -1.1 V to -1.35 V (SCE) depending on the content of the working electrolyte (Table 1).

**Chemical composition and cathodic current efficiency of Ni-Co alloys**

The mass percent of cobalt content in the deposit was estimated by AAA and EDSA analysis. The effect of the component ratio in the solution on the cobalt content of Ni-Co alloys (in mass %) and on the cathodic current efficiency (CCE) is shown in Fig. 2. The analysis revealed that the amount of cobalt in the deposit was significantly higher as compared to that in the electrolyte. The data suggest that the increase of Ni/Co ratio in the solution from 1 to 5 results in decrease of the content of Co from about 95 mass % to 52 mass %. This observation proves that the co-deposition follows the so-called mechanism of “anomalous” deposition reported in a few subsequent studies [3 - 6], which indicates that electrochemical alloying leads to an increase in the reaction rate of cobalt at the expense of nickel reaction rate and this is in accordance with [5, 18]. Moreover, with the growth of Ni/Co ratio from 1 to 5, the CCE decreases from 92 % to 64 %. The increased content of Ni in the alloys may lead to an increase of the concurrent reactions, such as preliminary passivation of the electrode and evolution of hydrogen [3, 26] that significantly decrease the CCE.

The effect of presence of saccharin in the solution (Fig. 3) has also been studied, as well as the increase of the complexing agent Na₃citrat (Fig. 4) on the composition of Ni-Co alloys and on the CCE in potentiostatic mode at potentials close to the plateau of the limiting current in the summary polarization dependencies. These are potentials within the range from -1.1 V to -1.35 V (SCE) depending on the content of the working electrolyte (Table 1).

**Fig. 1.** Potentiodynamic polarization dependencies for co-deposition of Ni and Co: a) in solutions No 3 (curve 1); No 4 (curve 2); No 6 (curve 3) in absence of SHR; and b) in solution No 7, with presence of SHR.
deposition of Ni-Co alloys under comparable conditions (Ni/Co = 1). It was found that the presence of SHR in the solution increases the content of Co in the alloys with 5-6 mass % (Fig. 3, curve 1), as the CCE strongly decreases from 82 % (without SHR) to 43 % in presence of 2 g dm⁻³ SHR (Fig. 3, curve 2). This effect can be explained with the adsorption of the added agent and the strong reduction of the active cathodic surface due to its blocking effect.

The increase of the content of the complexing agent Na₃citrat leads to a slight reduction of about 4 – 5 mass % of Co content in the Ni-Co alloy (Fig. 4, curve 1) and to decrease of CCE (Fig. 4, curve 2) up to 72 %. The reason for such decrease shall be attributed, on one hand, to the reduced concentration of free metal ions due to their bonding in more stable citrate complexes, which increases the cathodic polarization, and hence the difficulties for electrodeposition of Ni and Co. On the other hand, the increased concentration of sodium citrate makes possible its independent adsorption onto the surface of the electrode. This process may, however, inhibit the process of formation of oxides or hydroxides on the surface, mainly with participation of Ni, thus facilitating the deposition of Ni, as it is seen from the data for the content of the alloy (Fig. 4, curve 1). The data obtained were compared with those about morphology (SEM images) and phase content (X-Ray diffractograms), and on a later stage, with the results for anodic behavior (potentiodynamic anodic dependencies) of Ni-Co alloys with different quantities of Co.

**Effect of Co content on the morphology of Ni-Co alloys**

Surface morphologies of Ni-Co alloys electrodeposited from citrate electrolyte, (magnification of 20000x) are illustrated in Fig. 5. The SEM images indicate that the content of Co, respectively Ni, in the alloys strongly affects both the size and the shape of the crystallites. The pure Ni (Fig. 5a) is characterized with round-shape particles, as the crystallization follows the original micro-roughness of the copper substrate. The average size of the crystallites is in the range 200 - 300 nm. With the increase of Co content in the alloys to 51 – 68 mass % (Fig. 5b,c), the coatings become more fine-crystalline and shiny, with average size of crystallites bellow 50
The further increase of Co content to 82 mass % (Fig. 5d) leads to more pronounced crystalline structure, as the smoothness decreases. The average size of the crystallites is below 100 nm. The alloys with 94 mass % Co (Fig. 5e) are very close to the pure cobalt coating in terms of morphology (Fig. 5f). A pronounced crystalline structure occurs with pyramidal crystallites with size within a wide range (from 50 nm to 400 nm).

The effect of addition of saccharin, (SHR) or sodium citrate (Na, citrate) on the morphology of Ni-Co alloy...
As it is seen, the higher content of sodium citrate (Fig. 6a) results in a quite different structure in comparison to the structures characteristic for all studied formulations of the electrolyte (Fig. 5 and Fig. 6b,c).

The crystals formed are larger, with rounded shape. Supposedly, the presence of larger quantities of sodium citrate affects the mechanism of deposition of the metals, as most probably the higher content of Ni is due to the facilitated formation of the citrate complexes of metal instead of the oxide or hydroxide compounds of nickel on the cathode, which passivate the surface. Thus deposition of Ni instead of nickel oxides/hydroxides occurs on the metal surface, which is also proved by the EDSA data.

**CONCLUSIONS**

Ni-Co alloys are deposited from weakly acidic citrate electrolyte with variable contents of saccharin and sodium citrate, and variable Ni/Co ratio. It is found that with the increase of Ni/Co ratio from 1 to 5, the content of Ni in the alloys increases to about 48 mass %, and the cathodic current efficiency decreases to about 70 %, thereby forming more fine-crystalline coatings with size of the crystallites less than 100 nm. It is shown that at all studied Ni/Co ratio in the solution the co-deposition of Ni and Co corresponds to the “anomalous” deposition, which is typical for the metals from the iron group. The addition of saccharin in the solution leads to deposition of smooth and shiny coatings, with average size of the crystallites less than 50 nm. The increase of the quantity of Na3citrate in the solution results in higher content of Ni in the alloy and deposition of more coarse-crystalline Ni-Co alloys.

**REFERENCES**

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