The Phase Structure and Morphology of Electrodeposited Nickel-Cobalt Alloy Powders

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Abstract:
Cobalt and nickel powders of three different compositions: Ni$_{0.8}$Co$_{0.2}$, Ni$_{0.55}$Co$_{0.45}$ and Ni$_{0.2}$Co$_{0.8}$ were obtained by electrodeposition from an ammonium chloride-sulphate solution. It was shown that the microstructure and morphology of the powders depended on the deposition current density as well as on the bath composition. Amorphous powder of Ni$_{0.8}$Co$_{0.2}$ was obtained at the current density higher than 200 mA cm$^{-2}$, but nanocrystalline powders having the same composition were obtained at current densities lower than 200 mA cm$^{-2}$. The nanocrystalline powders with lower Ni contents (0.55 and 0.2) obtained at a current density ranging from 40 mA cm$^{-2}$ to 450 mA cm$^{-2}$ were solid solutions of two phases, FCC ($β$-Ni) and HCP ($α$-Co) ones. The increase of the HCP phase in the powder was a result of both the Co content increase in the powder and decrease of the deposition current density.

Keywords: Ni-Co alloy, Nanostructures, Microstructure, X-ray diffraction

1. Introduction

The rapid progress in the development of new materials has now been facilitated to a great extent by fast development of novel technologies and modern scientific and technical progress. In recent years, a lot of new and technologically advanced materials have been obtained by sintering of powders, both amorphous and polycrystalline ones. Almost all metals can be obtained in powder form, but the method of obtaining such materials is dependent on desirable properties affected by their structure. In this sense, metallic amorphous and nanocrystalline alloys with magnetic properties have been especially widely applied. Alloys of the iron group of metals, Fe, Co and Ni have been considered as very good magnetic materials since 1921 [1-3]. These alloys are known to possess much better permanent magnetic properties compared to pure metals [1-3]. A special interest in this area has been focused on amorphous alloys having different composition as relatively new materials offering an excellent and specific combination of isotropic properties [4]. These materials are characterised by the absence of long-range order in the atom arrangement [5]. For multi-component alloys, this is a more universal way of their existence. Amorphous alloys can be considered as two- or multi-component solid solutions possessing typical properties of solids. However, the amorphous state is structurally and thermodynamically unstable and very susceptible to partial or complete crystallization, which requires very strict selection of the method and preparation conditions.

From the earliest papers on nanostructured material science [6] until nowadays,
scientists worldwide have focused on both the scientific and commercial aspect of these materials in their widespread research over the past couple of decades. Nanostructured materials not only provide us with an excellent opportunity to extend the understanding of the structure-property relationships in solid materials [7], they also serve as an attractive potential for technological applications [8].

The electrodeposition technique has significant advantages over other methods of synthesis of nanocrystalline materials [9]. This technique offers us excellent possibilities for obtaining such materials which have high purity, different structure and morphology. The chemical composition, phase structure, size and shape of the electrochemically obtained powders depend on the current density, bath composition, temperature and circulation rate of the solution, nature of the cathode and the ratio of the nucleation rate to the deposit growth rate [10-24]. The electrolytic powder production method usually yields products of desirable chemical composition, high purity, which can be pressed and sintered, as we have shown in our previous papers [11-14]. Therefore, by using different electrolysis regimes now it is possible to predict and obtain powders of desirable properties.

Electrodeposition of powders, nickel as well as cobalt ones, from solutions was established by the work of Calusaru [15]. However, only a few papers were devoted to Ni-Co powder electrodeposition as the method of obtaining alloy powders at constant concentration of metallic ions in the solution [16-21].

As shown in our previous papers [11-14], the thermal stability, electric and magnetic properties of the Co and Ni alloy powders electrochemically obtained from an ammonium bath, depend on the bath composition and deposition current density.

Electrodeposition is one of several laboratory-scale processing techniques currently available to produce nanocrystalline materials [15-25]. Electrodeposition (direct current and pulsed) has been used to produce sheets of nanostructured metals (such as Ni, Co, Cu) and binary alloys (such as Ni-Fe, Ni-W) [26-28].

Recently, several papers have been published on the effect of solution composition and deposition current density on the chemical composition, phase structure, electric and magnetic properties and corrosive stability of thin electrodeposited Co and Ni alloy films [29-33].

The purpose of this paper was to obtain the isotropic amorphous as well as nanocrystalline powder of the Ni-Co alloy by electrodeposition from ammonium chloride-sulphate solution using inert electrodes and to establish the relationship between the morphology and structure of the alloy powders and electrolysis parameters.

2. Experimental details

The powders were obtained in a 2.0 dm$^3$ open glass electrochemical cell. A titanium plate placed in the centre of the cell having a 6.0 cm$^2$ surface area and 0.2 cm thickness was used as a working electrode; RuO$_2$/TiO$_2$ with a 10 cm$^2$ surface area, placed close and parallel to the Ti-plate, were used as anodes. The cell was in a thermostat maintained at a working temperature of 293±1.0K. The solutions were made from analytical grade chemicals and triple distilled water. The alloy powders were electrodeposited from solutions containing different Ni$^{2+}$/Co$^{2+}$ concentration ratios [0.22 moldm$^{-3}$ (NiSO$_4$+CoSO$_4$); and 3.2 mol/dm$^3$ NH$_4$Cl, 2.3 mol dm$^{-3}$ NH$_2$OH] at pH=10. The electrodeposition of the powder was performed with a constant current regime ranging from 40.0 to 450.0 mA cm$^{-2}$ at room temperature [11, 12]. The deposition time was usually 2 h and the powder was removed by a soft brush after 30 minutes. All powder samples were washed several times with distilled water and 0.1% benzoic acid solution. After washing, the powders were dried at 378 K.
Polarisation diagrams were recorded with the three-compartment standard electrochemical cell at the temperature of 293±1.0K. The platinum foil counter electrode and the reference-calomel electrode (SCE) were placed at separate compartments, connected to the working electrode by Luggin capillary positioned 0.2 cm from the working electrode surface. The working electrode was a titanium electrode rod (d=0.4 cm). Before each experiment the working electrode surface was polished using 0.05 μm alumina impregnated polishing cloths.

Polarisation measurements were performed by computer controlled Electrochemical system (PAR M 273 A) using the corrosion software (PAR M352/252, version 2.01) with a sweep rate of 1 mVs⁻¹. For obtaining polarisation curves corrected for IR drop, the current interrupt technique was used with the time of current interruption being 0.5 s.

The current efficiency was determined at different current densities by measuring the volumes of hydrogen evolved on the titanium cathode as a working electrode. The working electrode was placed in the middle of the cell under the burette with the surface facing up so that the whole amount of the evolved hydrogen went into the burette. The burette was also kept at the same temperature. After each experiment where constant current was used, the electrode was taken from the solution, the remaining deposit was removed and its surface was again polished by the same procedure. At each applied current density hydrogen was collected starting from a clean electrode surface, as it was in the case of measuring the polarisation curves.

The current for hydrogen evolution was obtained using the equation for Faraday’s Law applied to the gas evolution process:

\[ j_{H_2} = \frac{nFV_o}{tV_n} \]

where \( V_o \) is the experimentally determined hydrogen volume at given pressure, \( P \) and temperature, \( T=298K \), \( t \) is the time of hydrogen evolution under constant current, \( V_n \) is the volume of the 1 mol of hydrogen at normal condition (22.4 dm³mol⁻¹), \( n \) is the number of exchanged electrons and \( F \) is the Faraday’s constant.

The current efficiency for the electrode position process was then obtained from the relation:

\[ \eta = \frac{j_{tot} - j_{H_2}}{j_{tot}} \cdot 100 \]

The chemical composition of the powder was determined by atomic absorption. The X-ray powder diffraction (XRD) analysis of Co and Ni alloy powders was carried out by Philips MPD diffractometer with CuKα radiation operated at a tube voltage of 40 kV and a tube current of 30 mA. A step scan mode was utilised with 0.03º 2θ per step. The step time was 1.15 s. The angular 2θ range investigated was 10-90º. The morphology of the electrodeposited powders was examined using scanning electron microscope SEM (JEOL-JSM 6460LV). In order to investigate the structural transformations the powders were annealed at 723 K and 973 K for 60 minutes in argon.

3. Results and Discussion

The cathodic polarisation curves significantly depended on the Ni (II)/Co (III) ratio in the solution (Fig. 1). With an increase in this ratio, nickel and cobalt codeposition took place at more negative potentials. At small current densities, the Tafel slope was 120 mV, indicating that the nickel and cobalt codeposition in this range was activationally controlled. Maximum current density up to which the 120 mV slope existed also depended on the Ni (II)/Co (III) ratio in the solution. When the Ni (II)/Co (III) ratio =4, the 120 mV slope existed
up to 10 mA cm$^{-2}$. When the ratio was 0.25, the slope existed up to 13 mA cm$^{-2}$.

In this current density range, the hydrogen evolution reaction was negligible. At current densities higher than the Tafel range, with the current density increase, there was an increase in the polarisation curve slope and a gradual rise in the current density share for the hydrogen evolution reaction. By using experimentally determined current efficiency values per alloy, partial currents of the nickel and cobalt codepositions were calculated for different Ni (II)/Co(III) ratios. At current densities higher than 10 mA cm$^{-2}$, with an increase in the current density, the slopes of the partial nickel and cobalt codeposition currents gradually increased until they reached limit current densities. These limit currents also depended on the Ni (II)/Co(III) ratio. With an increase in this ratio, the limit currents decreased. With the ratios of Ni (II)/Co (III)=4 and Ni (II)/Co (III)=0.25, the limit currents have values of 35 mA cm$^{-2}$ and 45 mA cm$^{-2}$, respectively.

In the current density range where the slope of the nickel and cobalt codeposition polarisation curves gradually increased with the current density increase, the deposition rate was determined by the homogeneous chemical reaction of partial complex dissociation. The limit current of the nickel and cobalt codeposition was determined by the limit complex dissociation rate.

Cobalt was deposited faster than nickel and its limit current was higher than the limit current of nickel deposition.

Despite having a less stable complex compared to cobalt, nickel was deposited slower and had lower limit current because the dissociation activation energy [Ni(NH$_3$)$_6$]$^{2+}$ was higher than the activation energy of the cobalt complex dissociation.

At current densities higher than about 200 mA cm$^{-2}$, there existed a 40 mV slope on the polarisation curves determined by simultaneous cobalt and nickel deposition and hydrogen evolution reactions. This slope was determined by the hydrogen evolution reaction on nickel and cobalt alloys.

At potentials more negative than this Tafel range, the hydrogen evolution reaction turned into an activation-free process, causing the emergence of the limit current [34].
At current densities lower than the limit current of nickel and cobalt codeposition on a titanium cathode a deposit in the form of a coating was formed, and at current densities higher than the limit current, a powder-like deposit was formed. At current densities higher than the current limit of nickel and cobalt codeposition, with an increase in the cathode overpotential, smaller powder particles and smaller crystal grains are formed. With an overpotential increase, there was an increase in the nucleation rate and the rate of nickel and cobalt atom supply for the crystal growth did not change causing the formation of smaller crystals.

The adequate choice of the Ni(II)/Co(III) ratio and current density resulted in the obtainment of nickel and cobalt alloys having different compositions. The phase structure and morphology of the Ni_{0.8}Co_{0.2}; Ni_{0.55}Co_{0.45} and Ni_{0.2}Co_{0.8} powders were examined in this paper.

The phase structure, particle shape and size of the electrochemically obtained cobalt and nickel alloy powders considerably depended on current density according to the analysis of X-ray diffraction patterns and SEM micrographs of the obtained powders, Figs 2-12. Thus, the alloy with the highest content of nickel, for higher deposition current densities, was amorphous but nanosized for the lower deposition current density.

**Amorphous and nano-sized Ni_{0.8}Co_{0.2} powder**

X-ray diffraction patterns of Ni_{0.8}Co_{0.2} powder sample electrodeposited at current density \( j = 220 \) mA cm\(^{-2}\) are shown in Fig. 2. The X-ray diffractogram (Fig. 2a) shows a broad peak in the range of smaller 2\( \theta \) values almost without sharp diffraction peaks indicating mainly amorphous structure of the powder. After annealing of the powder at 973 K for 60 minutes under argon, X-ray diffractogram was recorded (Fig. 2 b) again.

![Fig. 2. X-ray diffraction patterns of the Ni_{0.8}Co_{0.2} powder electrodeposited at j = 220 mA cm^{-2}, o- cubic phase of Ni_{0.8}Co_{0.2} alloy •, cubic phase of Ni_{0.8-x}Co_{0.2-y}O_{x+y} alloy: a) as-prepared powder, b) powder annealed for 60 minutes at 973 K.](image)

The diffractogram shows the emergence of a newly formed crystal phase according to the presence of the three well defined peaks of the FCC structure, for the planes (111), (200) and (220) of alloys [1997 JCPDS 04-0850]. During the process of annealing, owing to the presence of low oxygen concentration in the chamber, a partial oxidation of the powder occurred, too. Therefore, the diffractogram also shows three small peaks for different planes...
of the cubic phase of Ni_{0.8-x}Co_{0.2-y}O_{x+y}. [1997 JCPDS 47-1049]. The average crystallite size of the alloy was determined as 19 nm for the orientation (111) and 50 nm for the orientation (220).

Fig. 3. presents X-ray diffraction patterns of a) the as-prepared Ni_{0.8}Co_{0.2} alloy powder, b) the powder annealed at 723 K and c) the powder annealed at 973 K, electrodeposited at the current density of \( j = 150 \text{ mA cm}^{-2} \). As can be seen from the diffractograms, the obtained powder consisted of the FCC structure of the Ni_{0.8}Co_{0.2} solid solution of the orientation (111), (200) and (220) in addition to a small amount of amorphous phase observed at lower 2\( \theta \) value [1997 JCPDS 04-0850]. The average crystallite size was determined as 19 nm for the orientation (111), 23 nm for the orientation (200) and 63 nm for the orientation (220).

The samples annealed at \( T = 723 \text{ K} \) and \( T = 973 \text{ K} \) (Fig. 3) have more pronounced peaks and more enlarged grains in comparison with the non-annealed powder sample. After annealing of the as-prepared powders at 723 K, the average crystallite size increased to the values of 27 nm, 32 nm and 90 nm for the orientations (111), (200) and (220), respectively.

The further increase in the annealing temperature led to better crystallization of the powder into the FCC phase and to a reduction of the amorphous phase. The average crystallite size of the annealed alloy increased to the value of 38 nm for the orientation (111), 45 nm for the orientation (200) and 100 nm for the orientation (220). Weakly pronounced peaks of the cubic phase Ni_{0.8-x}Co_{0.2-y}O_{x+y} are observed in the diffractogram, too.

![Fig. 3. X-ray diffraction patterns of the Ni_{0.8}Co_{0.2} powder electrodeposited at \( j = 150 \text{ mA cm}^{-2} \), α-cubic phase of Ni_{0.8}Co_{0.2} alloy, a) as-prepared powder, b) powder annealed for 60 minutes at 723 K, c) powder annealed for 60 minutes at 973 K.](image)

SEM micrograph of typical Ni_{0.8}Co_{0.2} powder particles are shown in Fig. 4. The morphology of the powder content of Ni_{0.8}Co_{0.2} did not significantly depend on the current densities. For all the current densities from 65 mAm^{-2} to 400 mAm^{-2} typical cauliflower powder particles were obtained with the size of particles varying from 5 \( \mu \text{m} \) to about 200 \( \mu \text{m} \) composed of fine nanosized crystallites. On the deposits formed with higher current density the presence of craters formed by the hydrogen evolution could be easily observed. The number of craters increased with the increase of the current densities (see Fig. 4 b).
Fig. 4 SEM micrographs of electrodeposited Ni<sub>0.8</sub>Co<sub>0.2</sub> powders at: a) \( j = 220 \text{ mA cm}^{-2} \), and b) \( j = 400 \text{ mA cm}^{-2} \).

**Nano-sized Ni<sub>0.55</sub>Co<sub>0.45</sub> powder**

Three relatively well developed peaks coexist in the diffractogram, in a form of the Rietveld’s diagram, as presented in Fig. 5, for the as-prepared powder of the Ni<sub>0.55</sub>Co<sub>0.45</sub> alloy electrodeposited at current density \( j = 400 \text{ mA cm}^{-2} \).

An analysis of the Rietveld’s diagram revealed that Ni<sub>0.55</sub>Co<sub>0.45</sub> powder alloy consisted of a mixture of two crystal phases, a hexagonal close-packed HCP phase with lattice parameters of \( a = 0.2495(4) \text{ nm}, c = 4.08(2) \text{ nm} \) [1997 JCPDS 45-1027] and a cubic FCC phase with lattice parameters of \( a = 3.516(5) \text{ nm} \) [1997 JCPDS 04-0850]. The crystal part of the powder, as determined by the Rietveld’s [35] method of quantitative phase analysis contained 12(3)at.% of the HCP phase with the average crystallite size of 14.5 nm and 88(5)at.% of the FCC phase with the average crystallite size of 13.2 nm, Tab. I.

Fig. 5. Rietveld’s plot for the as-prepared Ni<sub>0.55</sub>Co<sub>0.45</sub> powder sample electrodeposited at \( j = 400 \text{ mA cm}^{-2} \). The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row represent positions of Bragg reflections for the HCP and FCC phase, respectively.
Tab.I. The crystallite size, lattice distortion and lattice parameters of the electrodeposited Ni$_{0.55}$Co$_{0.45}$ as-prepared powder for $j = 220$ mA cm$^{-2}$ and $j = 400$ mA cm$^{-2}$.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystal structure</th>
<th>Space group</th>
<th>Crystallite size (nm)</th>
<th>Lattice distortion</th>
<th>Lattice parameters (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
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</tr>
<tr>
<td>Ni$<em>{0.55}$Co$</em>{0.45}$</td>
<td>FCC</td>
<td>Fm3m</td>
<td>15.6</td>
<td>2.3 $10^{-3}$</td>
<td>0.35309(6)</td>
</tr>
<tr>
<td></td>
<td>HCP</td>
<td>P63/mmc</td>
<td>19.8</td>
<td>2.3 $10^{-3}$</td>
<td>0.2504(1)</td>
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<tr>
<td></td>
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<td></td>
<td></td>
</tr>
<tr>
<td>Ni$<em>{0.55}$Co$</em>{0.45}$</td>
<td>FCC</td>
<td>Fm3m</td>
<td>14.5</td>
<td>3.9 $10^{-3}$</td>
<td>0.35316(5)</td>
</tr>
<tr>
<td></td>
<td>HCP</td>
<td>P63/mmc</td>
<td>13.2</td>
<td>3.9 $10^{-3}$</td>
<td>0.2495(4)</td>
</tr>
</tbody>
</table>

The diffractogram of the Ni$_{0.55}$Co$_{0.45}$ alloy powder electrodeposited at $j = 220$ mA cm$^{-2}$ had more pronounced peaks compared to the diffractogram for the powder sample electrodeposited at a current density of $j = 400$ mA cm$^{-2}$ (Fig.6). This indicates that the decrease in the deposition current density resulted in the increase of the crystallite size and decrease of lattice distortion in both present phases, Tab. I.

Fig. 6. Rietveld’s plot for the as-prepared Ni$_{0.55}$Co$_{0.45}$ powder sample electrodeposited at $j = 200$ mA cm$^{-2}$. The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row represent positions of Bragg reflections for the HCP and FCC phase, respectively.

It was shown that the crystal part of the powder consisted of 27(5)at.% of the HCP phase and 73(7)at.% of the FCC phase. The average size of the crystallite of the FCC and HCP phases amounted to 15.6 nm and 19.8 nm, respectively, as can be seen from the results presented in the Table I. The lattice distortion for both phases was 2.3 $10^{-3}$.

A comparative analysis of diffractograms for Ni$_{0.55}$Co$_{0.45}$ powders electrodeposited at $j = 400$ mA cm$^{-2}$, $j = 220$ mA cm$^{-2}$ and $j = 65$ mA cm$^{-2}$ shows that the decrease of the current density resulted in better crystallisation, an increase of the crystallite size and higher HCP content. At lower current densities, a powder with a higher HCP phase content, larger crystal grains and lower lattice distortion was obtained (Fig.7).
Fig. 7. Rietveld’s plot for the as-prepared Ni$_{0.55}$Co$_{0.45}$ powder sample electrodeposited at $j = 65$ mA cm$^{-2}$. The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row represent positions of Bragg reflections for the HCP and FCC phase, respectively.

After the heat treatment of the Ni$_{0.55}$Co$_{0.45}$ alloy powder in an argon atmosphere, as shown by the diffractograms, the pronounced peaks existed only for the FCC phase (Fig. 8 and Fig. 9). The increase of the annealing temperature led to a significant crystallization indicated by the existence of a series of considerably higher and narrower X-ray peaks of the FCC phase. Also, a significant increase of the crystallite size up to 54.7 nm was observed. This shows the character of the structural change during the heat treatment involving transformation of the HCP phase into the FCC phase, crystal grains growth and decrease of lattice distortion in the FCC phase. Diffractograms also show three small peaks for different planes of the cubic phase of Ni$_{0.8-x}$Co$_{0.2-y}$O$_{x+y}$.

Fig. 8. Rietveld’s plot for the powder sample annealed for 60 minutes at 723K electrodeposited at $j = 65$ mA cm$^{-2}$. The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row mark the positions of Bragg reflections for the FCC phase of the Ni$_{0.55}$Co$_{0.45}$ and cubic phase Ni$_{0.8-x}$Co$_{0.2-y}$O$_{x+y}$, respectively.
Fig. 9. Rietveld’s plot for the powder sample annealed for 60 minutes at 973K electrodeposited at \( j = 65 \text{ mA cm}^{-2} \). The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row mark the positions of Bragg reflections for the FCC phase of the \( \text{Ni}_{0.55}\text{Co}_{0.45} \) and cubic phase \( \text{Ni}_{0.8-x}\text{Co}_{0.2-y}\text{O}_{x+y} \), respectively.

The morphology of the powder sample of the \( \text{Ni}_{0.55}\text{Co}_{0.45} \) alloy electrodeposited at different current densities shows a strong dependence on the applied current density as can be seen in Fig. 10.

Fig. 10. SEM micrographs of electrodeposited \( \text{Ni}_{0.55}\text{Co}_{0.45} \) powders at: a) \( j = 65 \text{ mA cm}^{-2} \) and b) \( j = 220 \text{ mA cm}^{-2} \).

The powders obtained at lower current densities had particles resembling the inlaid structure (see Fig. 10 a), while the powders deposited at current densities \( j > 220 \text{ mA cm}^{-2} \) had cauliflower-like particles, covered by small dendritic particles (Fig. 10 b).

**Nano-sized \( \text{Ni}_{0.2}\text{Co}_{0.8} \) powder**

The diffractogram for the as-prepared Co-rich powder sample of the \( \text{Ni}_{0.2}\text{Co}_{0.8} \) alloy electrodeposited at current density \( j = 400 \text{ mA cm}^{-2} \) shows the characteristic peaks for two crystal phases, the FCC and HCP structures Fig. 11. The crystal part of the sample contained 69(9)at.% HCP phase and 31(6)at.% FCC phase. Average crystallite sizes of the FCC and
HCP phases were identical, being 28 nm. The lattice distortion for both phases was $2.3 \times 10^{-3}$.

**Fig. 11.** Rietveld's plot for the as-prepared Ni$_{0.2}$Co$_{0.8}$ powder sample electrodeposited at $j = 400$ mA cm$^{-2}$. The values measured are presented by dots. The solid line a) represents values calculated for the given structural model and the solid line b) represents a difference between the measured and calculated values. Vertical lines in the upper and lower row represent positions of Bragg reflections for the HCP and FCC phases.

The sample of Ni$_{0.2}$Co$_{0.8}$ powder alloy electrodeposited at current densities lower than 220 mA cm$^{-2}$ consisted mostly of the crystalline phase having fine crystals. A decrease in the current density resulted in powders with larger crystal grains and a higher HCP phase content.

**Fig. 12.** SEM micrographs of electrodeposited Ni$_{0.2}$Co$_{0.8}$ powders at: a) $j = 65$ mA cm$^{-2}$ and b) $j = 220$ mA cm$^{-2}$.

The micrographs shown in Fig. 12 illustrate that the powders of the Ni$_{0.2}$Co$_{0.8}$ alloy obtained at lower current densities had particles of inlaid-like structure, while those obtained at the higher current densities had the cauliflower-like structure covered by needle-like dendritic particles. In addition, on the deposits of Ni$_{0.2}$Co$_{0.8}$ craters can be observed, and their number increased with the increase of the electrodeposited current densities.

**Fig. 13.** represents the dependence of the phase composition of the nickel-cobalt alloy powders obtained at current density of 220 and 400 mA cm$^{-2}$ on the chemical composition of
the alloys. The HCP phase was a dominant phase in powders with a higher cobalt content. The increase of the deposition current density led to a HCP phase decrease in the powders.

Fig. 13. The dependence of mol.% FCC and HCP phases of the electrodeposited powders in the crystal part of the samples on the chemical composition and current density: □ - FCC, j = 400 mA cm\(^{-2}\), ■ - FCC, j = 220 mA cm\(^{-2}\), △ - HCP, j = 400 mA cm\(^{-2}\), ▲ - HCP, j = 220 mA cm\(^{-2}\).

4. Conclusion

The microstructure as well as morphology of the Ni and Co alloy powders electrochemically obtained from an ammonium nickel and cobalt sulphate solution on Ti-cathode as a substrate, depended on the deposition current density and bath composition. The amount of the amorphous phase in the powder decreased with an increase in the Co content in the powder and with a decrease in the deposition current density. The FCC phase was a predominant phase in the crystal part of the alloy powders with more than 70 mol.% Ni. Decreases of Ni concentration in the alloy powders with less than 70 mol.% Ni, increased the content of the HCP phase in the crystal part of the powder. With a decrease in the deposition current density the amount of the HCP phase in the powder increased and the crystal grains growth of the FCC and HCP phases was observed, too. The crystalline phase increase and the amorphous phase decrease in the Ni and Co alloy powder samples occurred as a result of a rise in the annealing temperature, followed by the crystallisation of the amorphous phase into the FCC phase, the crystal grains growth of the FCC phase and the transformation of the HCP phase into the FCC phase.

Acknowledgements

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References

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Садржај: Прахови легуре кобалта и никла различитих састава: Ni₈₀Co₂, Ni₅₅Co₄₅ и Ni₆₂Co₃₈ добијени су електрохемијским таложењем из амонијачних раствора. Показано је да микроструктура и морфологија добијених талога зависи од густине струје таложења и од састава купатила. Аморфни прах Ni₈₀Co₂ је добијен на густинама струје вишим од 200 mA cm⁻², док се нанокристални прахови добијају на густинама нижим од 200 mA cm⁻².

Нанокристални прахови са мањим садржајем никла (0.55 и 0.2), добијени у интервалу густине струје од 40 mA cm⁻² до 450 mA cm⁻², су чврсти раствори две фазе FCC (β-Ni) и HCP (α-Co). Садржај HCP фазе у легури расте са повећањем садржаја кобалта у праху и са смањењем густине струје таложења.

Кључне речи: Ni-Co легура, наноструктура, микроструктура, дифракција X-зрака