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# STUDY ON SYNTHESIS AND MODIFICATION OF CONICAL Ni STRUCTURES BY ONE-STEP METHOD

In this work the conical Ni structures were obtained from an electrolyte containing $NH_4Cl$ as a crystal modifier. This process is called one-step method and allows to cover large areas with micro- and nanostructures during a single electrodeposition. Presence of $NH_4Cl$ promotes a vertical direction of structure growth in order to block a horizontal one. Additionally, this method does not require using chromic acid solution, which is dangerous for the environment. Due to the ferromagnetic properties of Ni, obtained coatings could be applied as magnetic devices. The influence of the parameters such as a preparation of copper substrate, a composition of electrolyte and electrodeposition conditions (time, the electrolyte temperature and current density) was investigated in this work.

*Keywords:* electrodeposition, one-step method, crystal modifier, nickel cones, free-standing structures

## 1. Introduction

The interest in the issue of renewable energy sources has been increasing these days. The production of hydrogen by water electrolysis is considered to be one of the best alternatives to hydrocarbon fuels [1]. This process is very energy-consuming, therefore catalysts should be used to reduce the energy needed. Most often they are platinum group precious metals, such as Pt and its alloys [2], which are very expensive and hardly available. They are also used in the methanol oxidation [3,4]. Nickel and its alloys show satisfactory electrocatalytic properties [5,6]. They can be successfully used in the industry [7,8]. Due to their ferromagnetic properties, they can be applied as magnetic devices as well [9]. The Ni cones can combine these properties. Moreover, the conical shape of structures can ensure the superhydrophobic properties of the material [10,11]. It also develops the active surface area for the same geometrical size of the sample, which is an important factor in the case of the electrocatalytic activity of the material. Furthermore, the conical shape of structures makes them more mechanically stable during intensive evolution of the hydrogen bubbles.

The most commonly used compounds of the bath for electrodeposition of the Ni conical structures are $NiCl_2$ and $H_3BO_3$, which is added as a buffer. To control the direction of structure growth, the presence of a crystal modifier is required. In the case of Ni cones, $NH_4Cl$ [12] or ethylenediamine dihydrochloride (EDA·2HCl) [13,14] are usually added to the solution to block the horizontal direction of growth and promote the vertical one. Other parameters of electrodeposition such as process duration, electrolyte temperature and pH should be investigated to synthesize conically-shaped structures [15]. To obtain nickel conical structures, the solution pH should be about 4. It ensures the stability of the solution. It means that all components of the electrolyte are fully dissolved.

M. Hashemzadeh and others [16] electrodeposited Ni cones from electrolytes containing different amounts of $NH_4Cl$ – 0, 150, 200, 250 and 300 g/l. The temperature of solutions was 60°C and the pH was adjusted to 4. Firstly, i = 2 $A/dm^2$ was applied for 10 min. It allowed obtaining micro cones. Later, the value of current density was immediately changed for 5 $A/dm^2$ for 3 min. In this way, Ni nano cones were synthesized on the surface of structures obtained previously. In this case, the amount of crystal modifier had almost no influence on the thickness of obtained coatings. In the case of [16], higher addition of $NH_4Cl$ caused a decrease in cones height. Addition of 1.5 mol/l of crystal modifier allowed to obtain cones height value equal to 600 nm [11]. The current density i = 2 $A/dm^2$ was applied for 8 minutes. These conditions allowed to synthesis of the superhydrophobic structures.

In this work, the Ni cones were successfully obtained. The influence of the electrodeposition parameters on the shape and

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quality of Ni deposits was investigated. The structures were analyzed using several methods, such as Scanning Electron Microscope (SEM), Energy-Dispersive X-ray Spectroscopy (EDS), X-Ray Diffraction (XRD) and Atomic Force Microscope (AFM) methods. The dependency between the pretreatment of Cu substrate and the obtained layers was checked as well. The novelty of this work is connected with the extensive analysis of many parameters, which influence the produced Ni deposits.

## 2. Materials and methods

Nickel cones were galvanostatically electrodeposited on the chemically polished copper substrates. The surface of the sample was equal to 2.8 cm$^2$. An electrolyte was composed of 200 g/l $NiCl_2$, 100 g/l $H_3BO_3$ and $NH_4Cl$ as a crystal modifier. The addition was equal to 10, 20 and 40 g/l. A nickel foil was used as an anode and Cu as a cathode. Coatings were electrodeposited at different current densities i = 10, 20 and 40 mA/cm$^2$. The influence of electrolyte temperature (50, 60 and 70°C) on morphologies was investigated. The electrodeposition time was equal to 10 min for these conditions. Then the influence of process duration was determined. All used reagents were analytical pure.

The sample surface was analyzed using SEM JEOL – 6000 Plus. In order to confirm obtaining nickel structures, its chemical composition and distribution of element on the surface was determined using EDS analysis. In order to check if there is any influence on crystal structure of material, samples were analyzed using XRD Rigaku MiniFlex II. The AFM Ntegra Aura microscope (NT MDT) with an NSG03 tip was used to analyze the sample surface.

## 3. Results and discussion

### 3.1. Influence of electrodeposition parameters

Firstly, the thickness of obtained coatings was determined using a mass change of electrodeposited coatings. The results are shown in Fig. 1.

It can be noticed that there is an increase of coatings thickness with an increase of applied current density. For sample synthesized at i = 10 mA/cm$^2$ 70°C and with 10 g/l $NH_4Cl$ the value of thickness was the greatest. In case of higher addition of crystal modifier obtained values are approximately equal. An increase of applied current density to 20 mA/cm$^2$

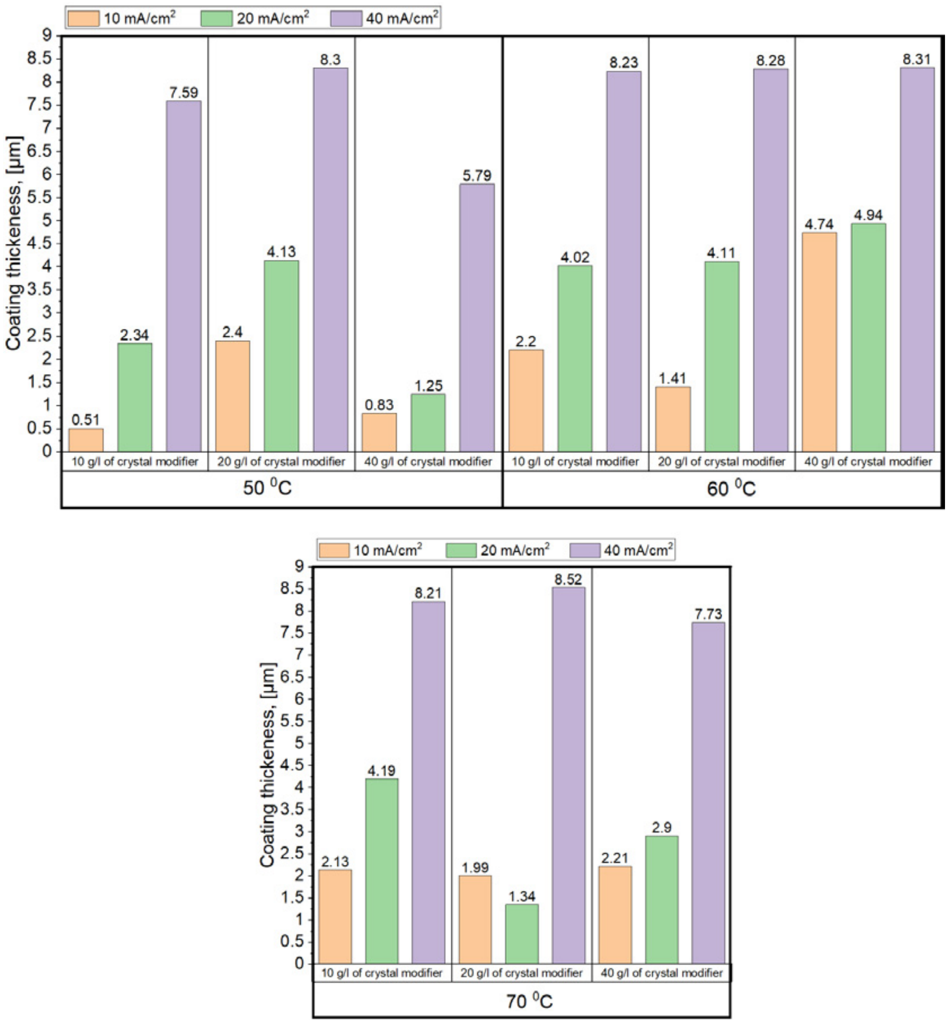


Fig. 1. Influence of electrodeposition conditions on coatings thickness

with the increases of amount of $NH_4Cl$ and temperature allowed to obtain thicker coatings. However, there is limited value. The highest decrease (about 3 μm) was observed for the sample obtained at 70°C from the electrolyte containing 40 g/l of crystal modifier. In the case of i = 40 mA/cm$^2$ the deposit thickness is equal to 8 μm. There is one exception (10 g/l $NH_4Cl$, T = 60°C), in this case, obtained value was lower in comparison to others and it is equal to about 2.5 μm. It can be summed up that the thickest coating (8.52 μm) was obtained at 70°C, i = 40 mA/cm$^2$ and with 40 g/l $NH_4Cl$. However, the thinnest one (0.50 μm) was synthesized at i = 10 mA/cm$^2$, 50°C and 10 g/l $NH_4Cl$.

In order to confirm the fabrication of Ni cones samples were analyzed using mapping analysis. Results are shown in Fig. 2. Based on the figure it can be noticed the metal was deposited uniformly.

Obtained results confirm the synthesis of conical Ni structures. The sample surface is well-order and the cones show the vertical direction of growth. The height of cones was determined using SEM photos as well. The example is shown in Fig. 3. Several cones have been selected randomly and marked in the figure, their height was determined and the average value was calculated.

It can be noticed that structures are sharp-ended. The average values of determined heights are shown in Fig. 4.

Obtained results show that by increasing the crystal modifier addition, the average height values decreased. However, there is a limited temperature –60°C. Subsequent heating of electrolytes caused the growth of cones. Determined values are approximate.

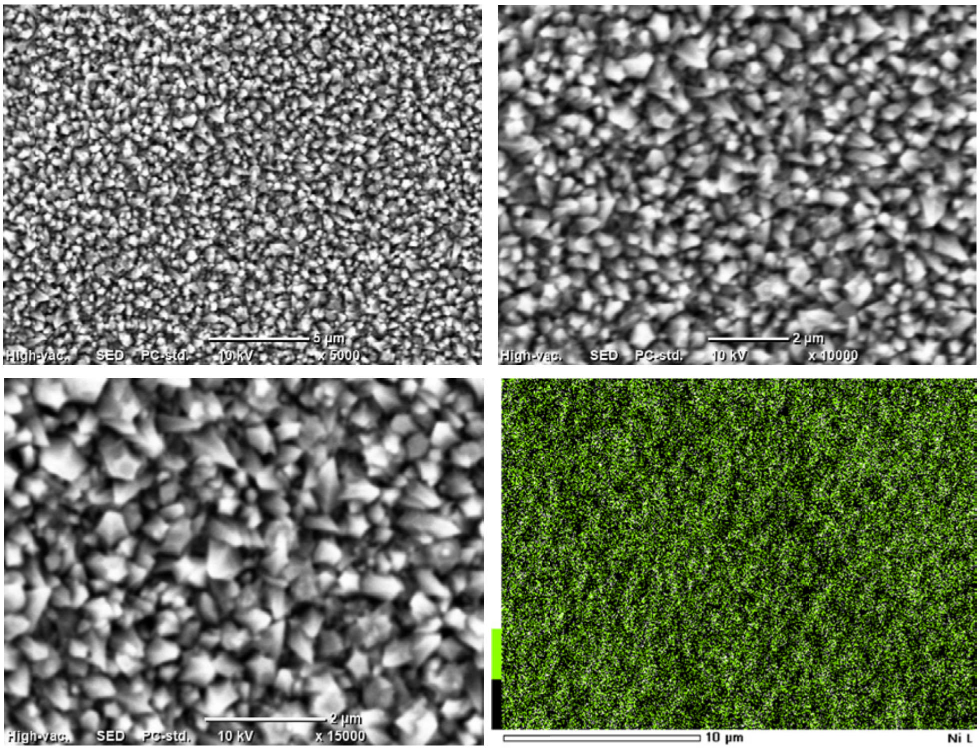


Fig. 2. SEM photos and mapping analysis of sample electrodeposited at 60°C, i = 10 mA/cm$^2$ with 20g/l $NH_4Cl$

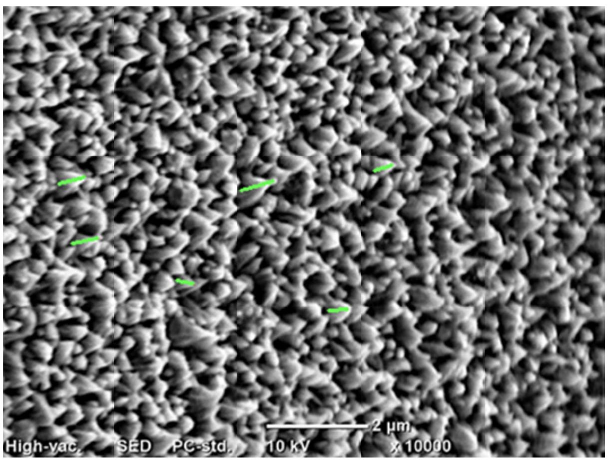


Fig. 3. Scheme of cones height determination. Electrodeposition parameters: 60°C, 10 mA/cm$^2$, 40g/l $NH_4Cl$

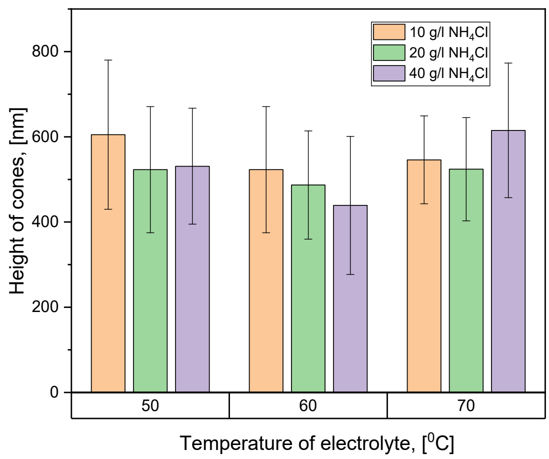


Fig. 4. The average values of cones height dependence on an amount of crystal modifier and electrolyte temperature

The number of synthesized conical structures was also checked using SEM photos. The square 2 µm × 2 µm was marked and the number of cones inside it was counted as is shown in Fig. 5.

A number of the conical structures per 1 µm$^2$ depending on the parameters of the electrodeposition process is shown in Table 1.

Based on determined numbers it can be noticed that at 70°C with an increase of current density, this value is lower for all amounts of crystal modifier. It is in agreement with previous results - the number of cones is lower due to their greater geometrical features. At 60°C the biggest number of structures appeared at i = 10 mA/cm$^2$. It is decreased with an increase of current density to 40 mA/cm$^2$. Then, it increased again. In the case of 50°C and 10 and 20 g/l $NH_4Cl$, the greatest number of cones appeared at i = 20 mA/cm$^2$.

The influence of applied current density on quality of coatings was investigated. SEM photos are shown in Fig. 6.

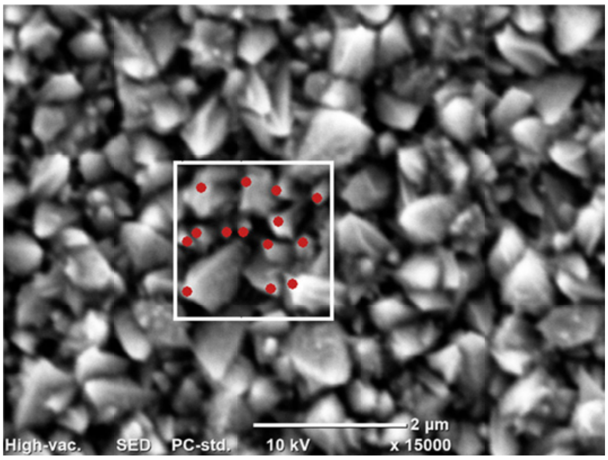


Fig. 5. Determination of cones number. Electrodeposition conditions: 60°C, 20 mA/cm$^2$, 40g/l $NH_4Cl$

TABLE 1

Number of the cones per 1 µm$^2$ in dependence of electrodeposition conditions

| Electrolyte temperature | Addition of $NH_4Cl$ | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|
| | 10 g/l | | | 20 g/l | | | 30 g/l | | |
| | Current density | | | | | | | | |
| | 10 mA/cm$^2$ | 20 mA/cm$^2$ | 40 mA/cm$^2$ | 10 mA/cm$^2$ | 20 mA/cm$^2$ | 40 mA/cm$^2$ | 10 mA/cm$^2$ | 20 mA/cm$^2$ | 40 mA/cm$^2$ |
| | Number of cones per 1 µm$^2$ | | | | | | | | |
| 50°C | 5 | 7 | 5 | 6 | 8 | 5 | 6 | 4 | 6 |
| 60°C | 6 | 4 | 5 | 8 | 4 | 6 | 7 | 3 | 5 |
| 70°C | 6 | 3 | 2 | 6 | 5 | 4 | 5 | 4 | 3 |

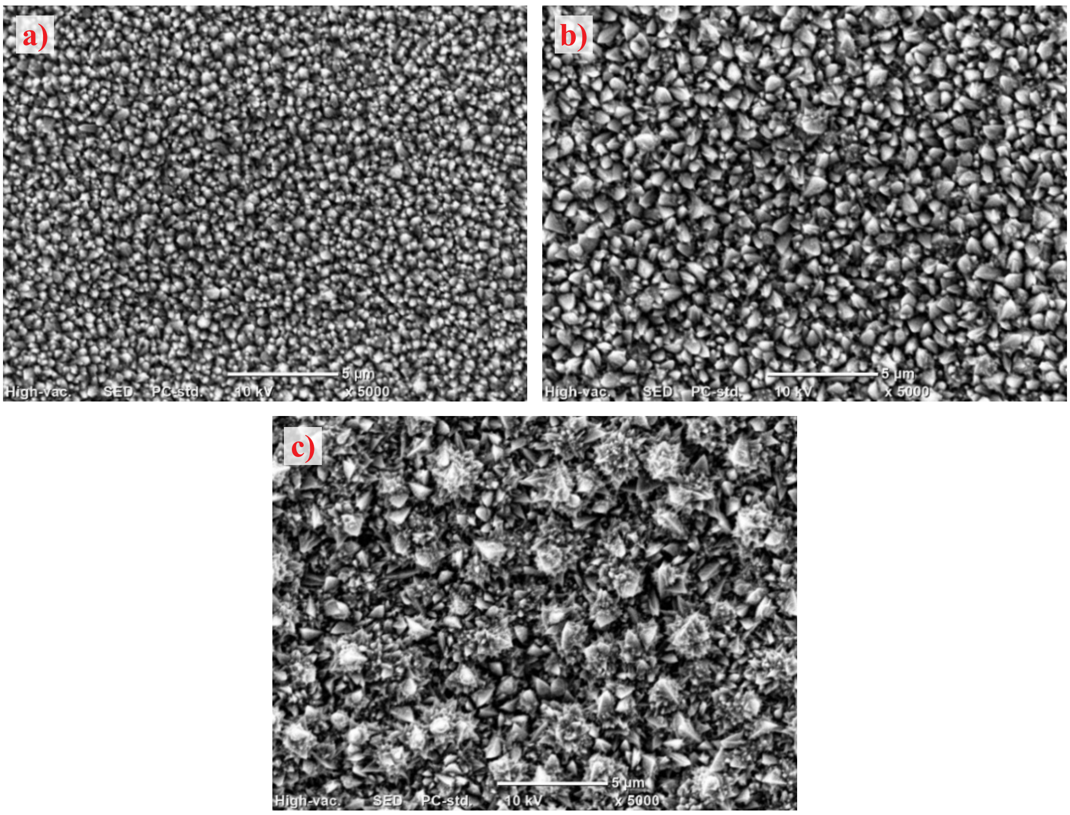


Fig. 6. Influence of applied current density on quality of synthesized coatings: a) 10 mA/cm$^2$, b) 20 mA/cm$^2$, c) 40 mA/cm$^2$. Electrodeposition parameters: 60°C, 40 g/l $NH_4Cl$. Magnification 5000×

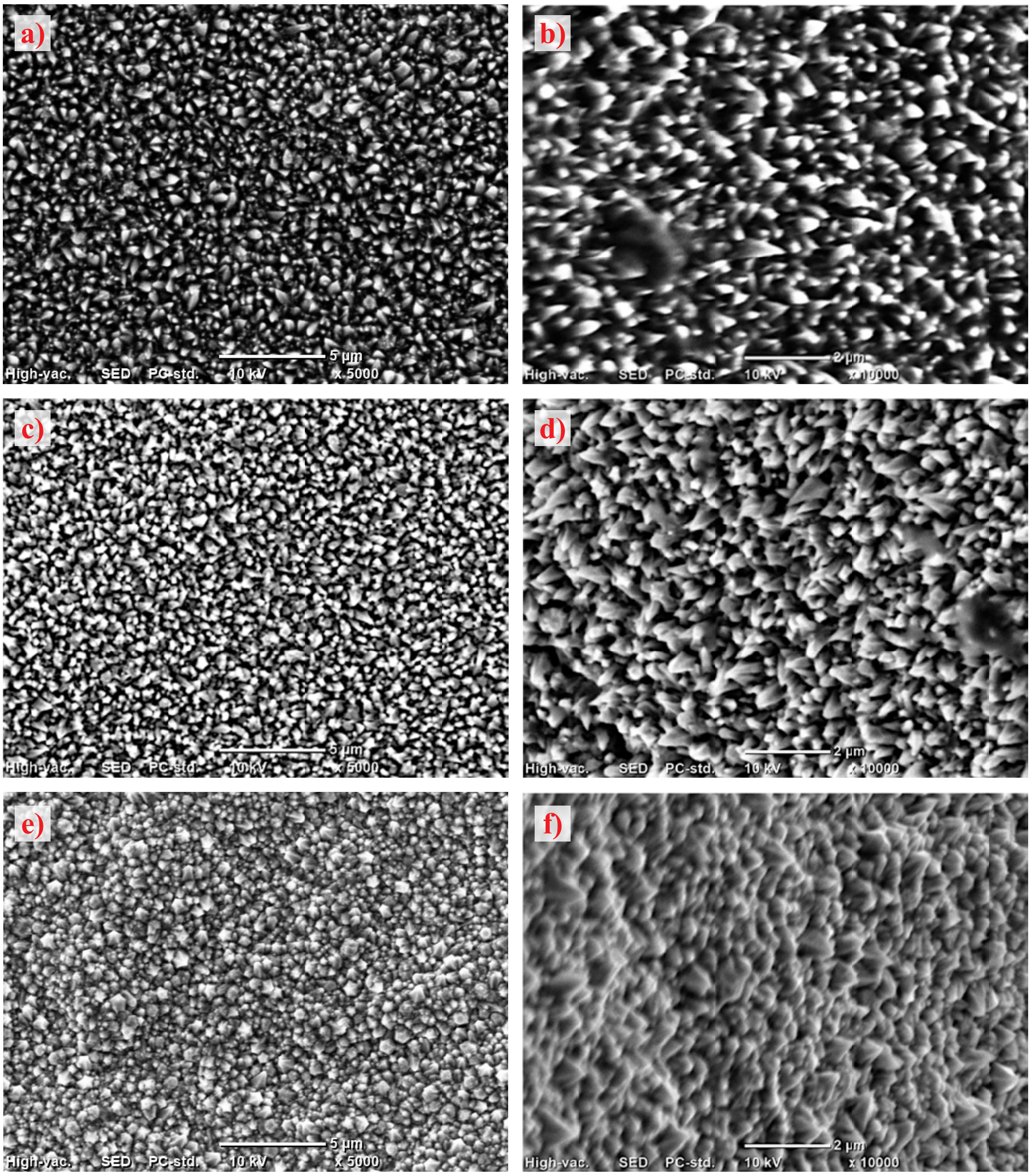


Fig. 7. Influence of temperature of electrolyte: a), b) 50°C, c), d) 60°C, e), f) 70°C. Electrodeposition parameters: 10 mA/cm$^2$, 20 g/l $NH_4Cl$

Results show that there is a strong influence of applied current density on the sample surface. For lower values of i, there are many small structures, well dispersed. With an increase of current density value to 40 mA/cm$^2$, they formed clusters and flower-like structures. Due to this phenomenon, the number of single cones decreased.

The dependence of electrolyte temperature on produced structures was also determined. The SEM pictures of obtained coatings morphology are shown in Fig. 7.

Based on SEM photos, it can be noticed that there are many small, sharp-ended structures at 50 and 60°C. However, the higher temperature of solutions caused the growth of cones in the horizontal direction as well.

The efficiency of the process was determined based on Faraday laws. The example of results for 10 g/l $NH_4Cl$ are shown in Fig. 8.

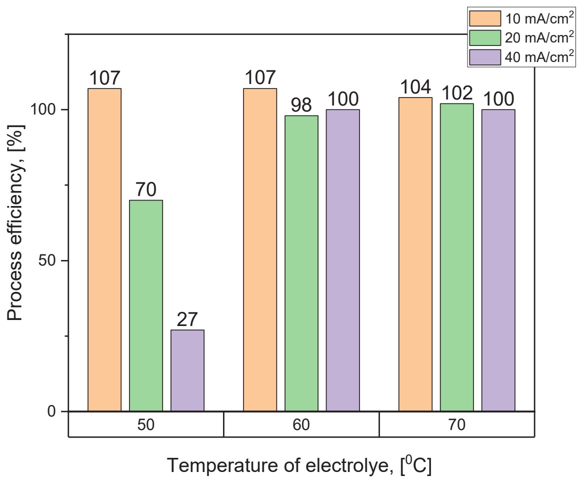


Fig. 8. Values of electrodeposition efficiency for samples obtained from the electrolyte containing 10 g/l $NH_4Cl$

Results show that the values of the process efficiency are about 100%. There are two exceptions for samples obtained at 50°C. In these cases, the deposition rates were the highest what resulted in the separation of coating from the substrate. The influence of temperature on the deposition rate as a function of the applied current density for 10 g/l $NH_4Cl$ is shown in Fig. 9. For higher additions of the crystal modifier, the efficiency was about 100%.

As it can be noticed, there is no strong influence of temperature on the deposition rate of coatings. The lowest values are obtained at 50°C at 20 and 40 mA/cm$^2$. In these cases, the efficiency of the process was also the lowest. As it had been mentioned before, the mechanical stability of these coatings was not sufficient.

The sample surface was analyzed using AFM method. The example of analysis is shown in Fig. 10.

The 3D image confirmed that the nickel cones were successfully synthesized. To check the structures crystal system, the XRD analysis was performed. The results are shown in Fig. 11.

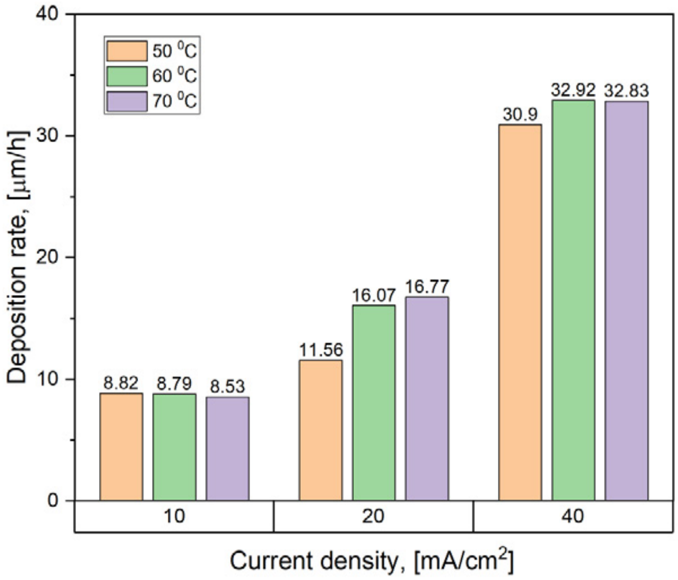


Fig. 9. Influence of temperature and applied current density on the deposition rate for samples obtained with 10 g/l $NH_4Cl$

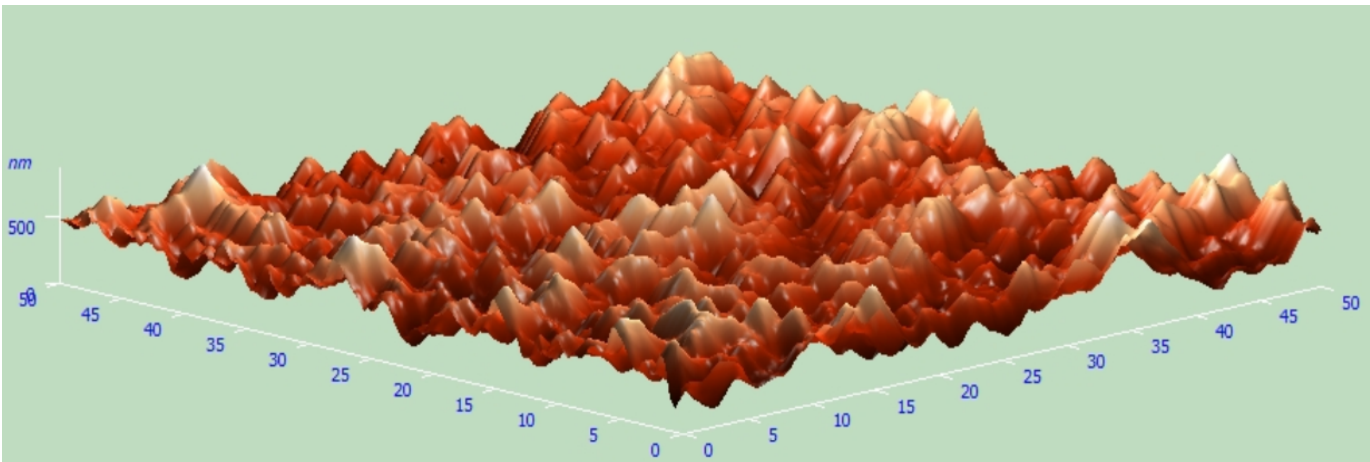


Fig. 10. The 3D image of the obtained structure. Electrodeposition parameters: T = 60°C, i = 20 mA/cm$^2$ and 20 g/l $NH_4Cl$

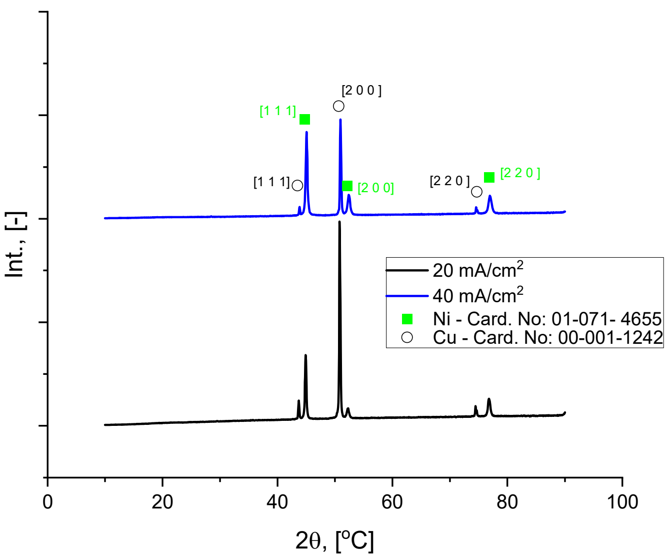


Fig. 11. Examples of diffractograms of samples electrodeposited at T = 60°C, 20 g/l $NH_4Cl$ at different current densities

Obtained results confirmed that there is the presence of Ni in the synthesized layers. There are also peaks connected with the Cu substrate. The coatings are characterized by face centered cubic (fcc) structure.

### 3.2. Preparation of copper substrate

To check if there is any influence of preparing copper substrates, the samples were also polished in two steps using 600 and then 1000 grit of the emery papers. SEM photos before and after this process are shown in Fig. 12.

It can be noticed that polishing with the emery papers caused appearing of scratches on the sample surface. However, chemical polishing of samples in a mixed solution of $H_3PO_4$, $CH_3COOH$ and $HNO_3$ at 70°C for 10 sec. etched copper substrate.

The influence of mechanical polishing on the morphology of the coatings is shown in Fig. 13.

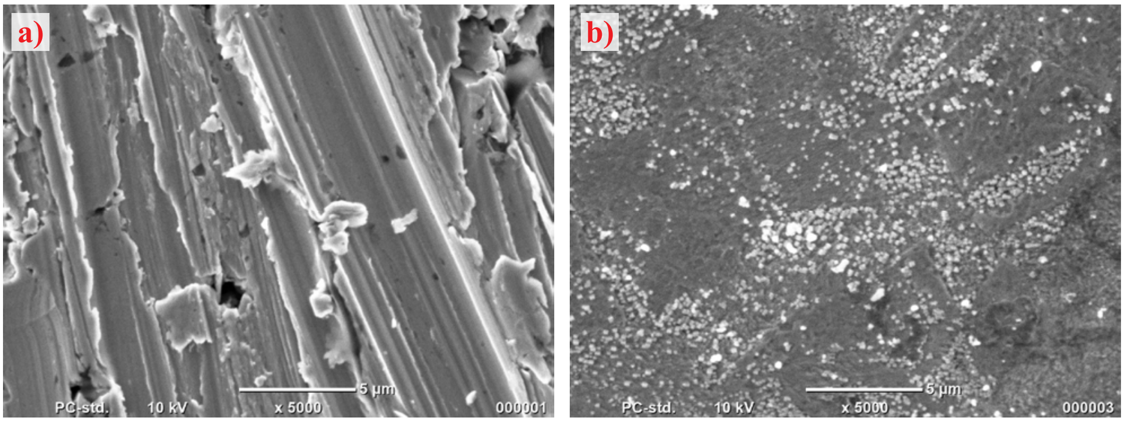


Fig. 12. SEM photos of the surface of copper substrate: a) with and b) without polishing

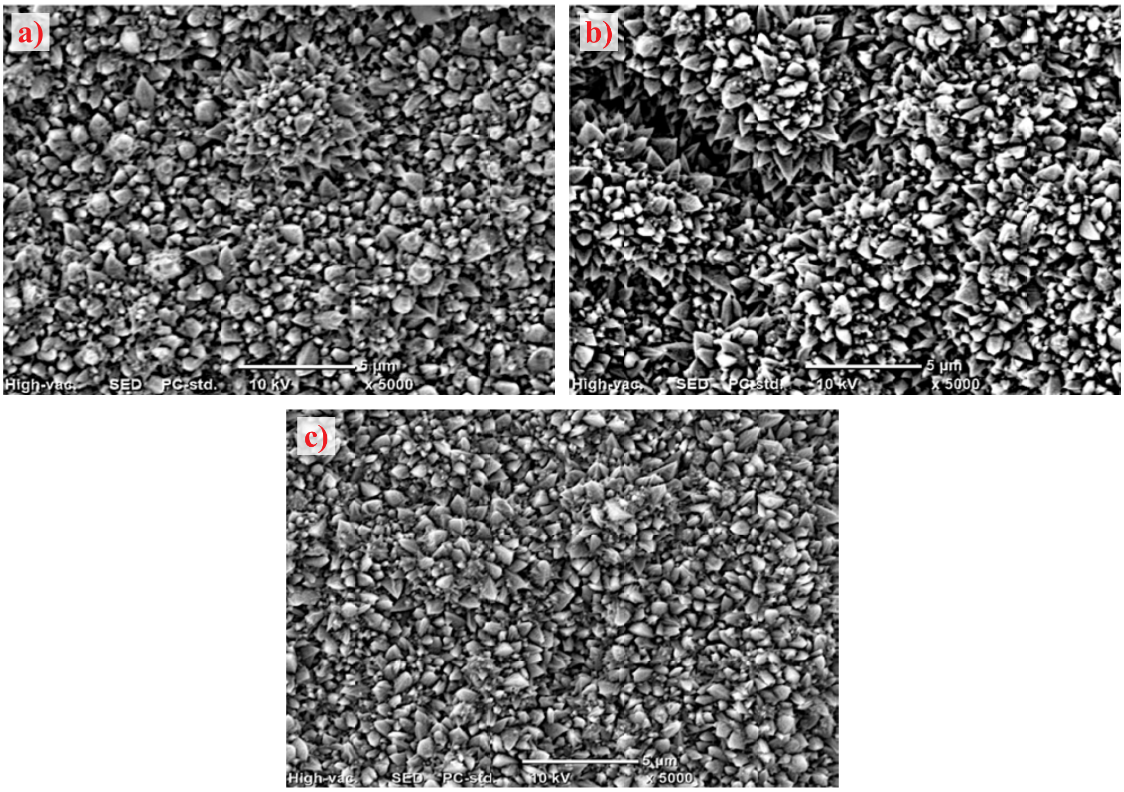


Fig. 13. Influence of the concentration of crystal modifier on the quality of the obtained structures at i = 20 mA/cm$^2$ and T = 60°C: a) 10 g/l, b) 20 g/l, c) 40 g/l. Polishing of the sample surfaces before the electrodeposition using 600 and 1000 grit of the emery papers

Results show that mechanical polishing before electrodeposition promoted appearing of flower-like structures. The number of cones per 1 µm$^2$ was determined as previously. Results are shown in Table 2.

The number of structures fell by half in comparison for samples where only etching was used before the deposition process.

### 3.3. Reduction of electrodeposition time

The influence of shorter electrodeposition time on the sample surface morphology was checked. The process was carried out for 5 min. The SEM photos are shown in Fig. 14.

TABLE 2

Number of the cones per 1 µm$^2$ in dependence of pre-preparation of Cu surface

| Addition of crystal modifier | Number of the cones per 1 µm$^2$ on the polished surface | | Number of the cones per 1 µm$^2$ on the non-polished surface | |
|---|---|---|---|---|
| | 60°C | 70°C | 60°C | 70°C |
| 10 g/l | 2 | 1 | 3 | 3 |
| 20 g/l | 3 | 3 | 4 | 5 |
| 40 g/l | 2 | 2 | 3 | 4 |

With a decrease in the process duration, the structures showed worse quality at i = 10 and 20 mA/cm$^2$. Many small

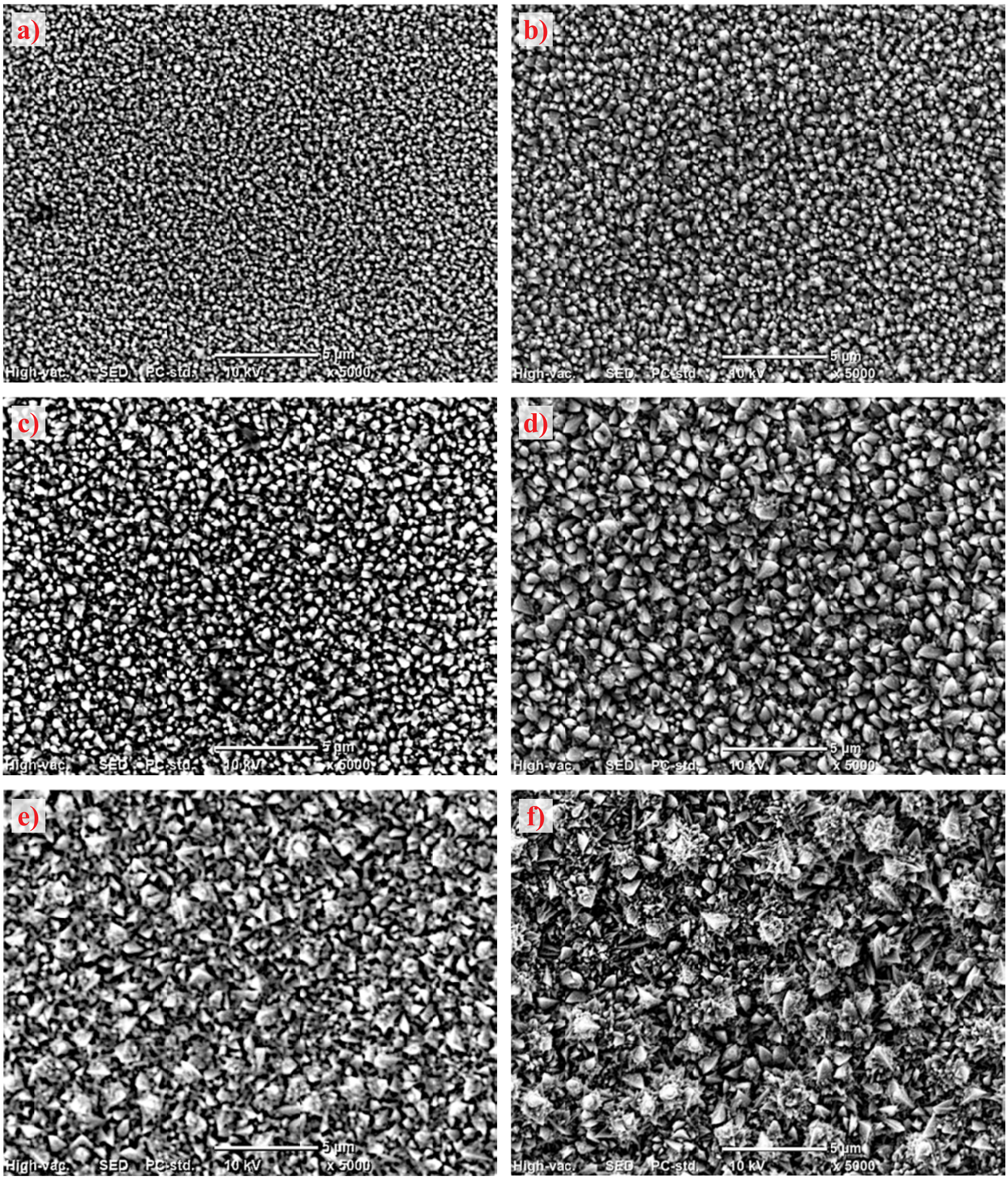


Fig. 14. Influence of the current density value on the quality of the deposited structures. Electrodeposition parameters: 40 g/l $NH_4Cl$, T = 60°C for 5 min (a, c, e) and 10 min (b, d, f): a), b) 10 mA/cm$^2$, c), d) 20 mA/cm$^2$, e), f) 40 mA/cm$^2$

deposits were fabricated. However, their quality was worse than the ones obtained for 10 min. In the case of samples obtained at i = 40 mA/cm$^2$, the reduction of time to 5 min allowed producing more cones with sharp tips instead of flower-like structures.

In this case, the number of cones per 1 um$^2$ were determined as well. The results are shown in Table 3.

At a lower value of current density, the number of cones per 1 um$^2$ was equal to 15 for the sample electrodeposited for 5 min. With an increase of current density, the number of deposits decreased.

TABLE 3

Number of the cones per 1 µm$^2$ in dependence of pre-preparing of Cu surface

| **Temperature** | **Number of the cones per 1, t = 5 min** | | | **Number of the cones per 1 µm$^2$, t = 10 min** | | |
|---|---|---|---|---|---|---|
| | **10 mA/cm$^2$** | **20 mA/cm$^2$** | **40 mA/cm$^2$** | **10 mA/cm$^2$** | **20 mA/cm$^2$** | **40 mA/cm$^2$** |
| 60°C | 15 | 10 | 7 | 13 | 7 | 10 |

## 4. Conclusions

Based on the obtained results, it was found that it is possible to obtain Ni cones by electrodeposition with a crystal modifier. With the increase of $NH_4Cl$ concentration, the height of the obtained cones and the number of cones per 1 $\mu m^2$ decreased. The limit temperature T = 60°C was found, beyond which the nickel cones grow again on previously synthesized conical structures. Surface polishing before the electrodeposition process caused the increase of the cone's height and the decrease of the number of cones. In addition, there was a tendency to form clusters of cones in the form of the so-called flowers. Reduction of process time allowed to enhance the surface quality for electrodeposition at 40 $mA/cm^2$. To obtain a multitude of sharp-ended cones following electrodeposition parameters have to be applied: 40 g/l $NH_4Cl$, 60°C and 20 $mA/cm^2$.

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