

Features of thermoreactivity of electrolytic nickel coatings with different surface morphologies

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Abstract: Nickel coatings consisting of oriented structures have unique catalytic properties. However, the temperature range for the use of such coatings is not determined, and a comprehensive study of their thermal properties in aggressive environments is required. This work studied the influence of the characteristics of the habit of nickel crystals on their reactivity with increasing temperature (thermoreactivity). The authors studied nickel coatings produced by electrodeposition with the addition of inhibitory additives, in the form of alkali metal chlorides to the electrolyte. Differential thermal analysis was used to study the reactivity of coatings in temperature fields. Oxygen was used as an aggressive medium. The phase composition of the samples after heating was determined, using a powder X-ray diffractometer. The introduced additives in the form of alkali metal chlorides allowed forming coatings consisting of crystals of a cone-shaped habit. It was found that the introduction of additives, in the form of alkali metal salts into the electrolyte, makes it possible to change the habit of nickel crystals, and increase the surface area of the coating by approximately 10–15 %. The study showed that electrodeposited nickel coatings, consisting of crystals in the form of micro- and nanocones, have (compared to the control coating) a reduced thermoreactivity. Experimental data allowed concluding that a decrease in the intensity of oxidation on the coatings under study, may be associated with the presence of a preferential development of certain crystallographic faces of the crystals, which causes a change in the nature of the nickel-oxygen interaction, and as a consequence, a change in the oxidation intensity.

Keywords: nickel coatings; nickel electrodeposition; cone-shaped crystals; thermoreactivity.

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INTRODUCTION

The development of modern technologies raises the requirements for electrodeposited metal coatings. Traditionally, nickel plating is used to protect against corrosion, increase the wear resistance and strength of parts, decorative surface finishing, etc. However, recently, the technology for producing nickel coatings or films, consisting of arrays of oriented structures has been actively developed. Among the large volume of scientific information, a significant number of publications covers, specifically the methods of forming nickel coatings with a developed surface, consisting of arrays of oriented structures [1–3]. In particular, in [1], magnetron sputtering of a nickel target was used to produce films from nickel nanocolumns. In [2–4], the electrodeposition method was used to create oriented structures on surfaces of various natures. In works [2; 5; 6], nickel coatings consisting of columnar structures were produced by modifying the electrolyte. The authors of [2] proposed to introduce a modifying agent, in the form of hydrochloric ethylenediamine into the electrolyte to obtain arrays of nickel nanocones. In works [6–8], calcium, sodium and potassium chlorides played the role of modifying agents. The authors of [9] produced vertical-

ly arranged arrays of nickel micro- and nanorods by galvanostatic electrolysis onto a titanium substrate, without any solid templates or surfactants.

Analysis of publications, allowed identifying works covering the study of the properties of coatings, made from arrays of oriented structures. In [10; 11], the corrosion properties of highly hydrophobic hierarchical nickel coatings were studied. Research showed that the corrosion resistance of coatings increases when using a chloride electrolyte, and nanostructured nickel as a matrix. In [12], it was proposed to use a nickel-cobalt developed surface, as a metal frame to create highly efficient supercapacitors. Studies [2] of the magnetic properties of arrays of nickel structures have demonstrated the existence of strong anisotropy. It was proposed to apply a silicon composite to nickel substrates, with a developed surface to increase the capacity of lithium-ion batteries [2; 13].

Nickel coatings with a developed surface, consisting of oriented structures or cone-shaped crystals, have high potential for practical application. In semiconductor technology, they are supposed to be used to create sensor devices and magnetic information storage devices [14]. Nickel coatings are used as ultrahydrophobic layers [10; 11], supercapacitors [12], and catalysts [15–17]. In [13], it was proposed to use electrodeposited nickel micro- and nano-

cones, to create a hierarchically structured current collector for lithium batteries.

In the above works, the magnetic, hydrophobic, corrosion, and catalytic properties of nickel coatings with a developed surface were studied, but there are no publications related to studies of their thermal properties in aggressive environments.

In this work, thermoreactivity will be understood to be the intensity of nickel oxidation in oxygen, under the influence of elevated temperatures. It is known [18] that reactivity can depend on the crystal structure, defect concentration, and the metal surface morphology.

The purpose of the research is to study the influence of the habit characteristics of nickel crystals in electrodeposited coatings on their reactivity when increasing temperature.

METHODS

Nickel coatings, consisting of cone-shaped crystals, were produced by electrodeposition from a nickel electrolyte based on grade Ch $\text{NiSO}_4 \cdot 7\text{H}_2\text{O}$ in a concentration of 3 mol/l. To produce coatings with different surface morphologies, alkali metal salts (sodium chloride and potassium chloride) taken in the same molar amount (3 mol/l of electrolyte), were introduced into the initial electrolyte.

Electrodeposition was carried out on substrates – stainless steel microgrids. The substrates were pre-prepared for electrodeposition: cleaned, degreased, washed, and dried. Nickel NPAN (semi-finished anode non-passivated nickel) was used as an anode. Electrodeposition was carried out at temperature of $t=60\text{ }^\circ\text{C}$ and current density of $j=1.5\text{ A/dm}^2$. Electrodeposition time was $\tau=600\text{ s}$.

To assess the surface morphology of the resulting nickel coatings, a Carl Zeiss Sigma scanning electron microscope, and an Olympus LEXT OLS4000 laser scanning microscope were used. To identify the influence of crystal habit, and surface morphology of electrodeposited nickel coatings on their reactivity (nickel behaviour in an aggressive environment with increasing temperature), differential thermal analysis (DTA) was used, which was carried out on a DTG60/60H device. Oxygen was used as an aggressive medium. Heating was carried out from room temperature to $1100\text{ }^\circ\text{C}$ at a rate of 10 deg/min , with a gas supply rate of 35 ml/min . To carry out differential thermal analysis of nickel coatings of different morphologies, disks with a diameter equal to the internal diameter of ceramic crucibles for direct annealing in the device were cut out. The weight of the samples was the same, and amounted to $m=(7.0\pm 0.5)\text{ mg}$. For each type of coating, at least 10 calorimetric studies were carried out.

The phase and approximate quantitative composition of the samples was determined, using a Shimadzu XRD-7000 powder X-ray diffractometer. Phase identification was performed using the JCPDS powder diffraction reference standard database, by comparing peak intensities and interplanar distances. The oxidation intensity was assessed using an X-ray diffractometer, based on changes in the quantitative composition of the phases of the samples after heating.

RESULTS

Fig. 1 presents microphotographs of the samples under study. Fig. 1 a shows the surface morphology of a sample produced from a pure electrolyte, without the addition of chlorides – a control sample. Scanning electron microscopy images showed that in this case, the nickel coating has a morphology without a pronounced surface microrelief (Fig. 1 a). When introducing the additives under study into the electrolyte, the surface relief changes significantly (Fig. 1 b–d), due to the formation of coatings consisting of cone-shaped habit crystals. In the coating with sodium chloride (Fig. 1 b), crystals with pentagonal symmetry are found in significant quantities (Fig. 1 c). At the same time, a more uniform surface morphology is observed in coatings, produced with the potassium chloride introduction into the electrolyte (Fig. 1 d).

Detailed microscopic studies showed that the potassium chloride introduction into the initial electrolyte, allows producing a coating, consisting of almost 100 % cone-shaped crystals (Fig. 1 d, 2 a). Of these, about 40 % of the crystals at the base in the transverse direction are nanosized ("a" parameter in Fig. 2 b). Determining the surface area of nickel coatings, using a laser scanning microscope, showed that the introduction of additives in the form of alkali metal salts into the electrolyte allows both changing the habit of nickel crystals in the coating, and increasing its surface area. Thus, if we take the control sample surface area (nickel coating produced from a pure electrolyte (Fig. 1 a)) as 100 %, then the surface area of coatings produced from electrolytes with NaCl and KCl additives increased by 10 and 15 %, respectively.

Using electron scanning microscopy, the average size of nickel cones in the coatings under study was assessed. Fig. 2 c presents a diagram of the dependence of the average size of cone-shaped crystals in the coating on the type of additive in the electrolyte. In Fig. 2 d, the ratio of the cone height to its base is estimated. The results obtained indicate that the potassium chloride addition to the electrolyte allows increasing the coating surface area, due to the pronounced anisotropy of crystal growth. Thus, the use of potassium chloride makes it possible to produce finer-crystalline coatings, consisting of cone-shaped habit crystals with an average size of 300–400 nm.

The results of DTA studies are presented in Fig. 3–5. In the graph (Fig. 3) of the control sample, no peaks of heat absorption and heat release are observed throughout the entire temperature range. The sodium chloride electrolyte sample exhibits two peaks. In the temperature range from 600 to $710\text{ }^\circ\text{C}$, there is an endothermic peak; in the temperature range from approximately 810 to $870\text{ }^\circ\text{C}$, there is an exothermic peak (Fig. 4). For another sample (from an electrolyte with potassium chloride), two similar peaks can also be observed, but shifted to a higher temperature range. Endothermic peak is from 630 to $740\text{ }^\circ\text{C}$, exothermic peak is from 830 to $880\text{ }^\circ\text{C}$ (Fig. 5).

Fig. 6 shows diffraction patterns with marked phase lines for all three types of coatings. Due to the fact that the coating is applied to stainless steel microgrids, in addition to the nickel and nickel oxide phases, phases of other compounds can be observed. The noise present in the diffraction patterns is determined by the presence of fluorescent iron in the microgrid itself.

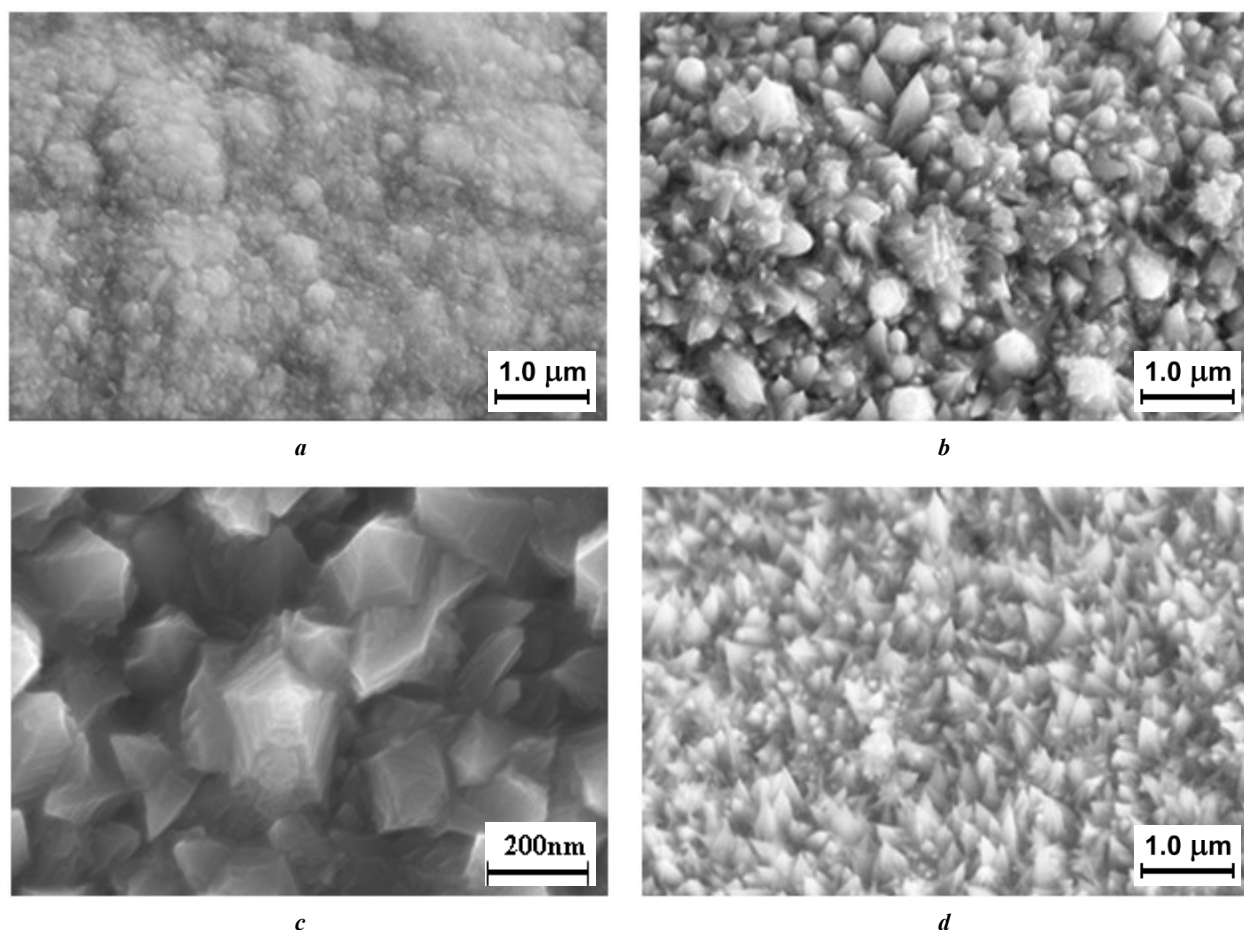


Fig. 1. Electron micrographs of a nickel coating on a stainless steel microgrid:

a – sample of pure electrolyte; **b, c** – sample with added sodium chloride; **d** – sample with added potassium chloride

Рис. 1. Электронно-микроскопические снимки никелевого покрытия на микросетке из нержавеющей стали:

a – образец из чистого электролита; **b, c** – образец с добавлением хлорида натрия; **d** – образец с добавлением хлорида калия

The approximate quantitative phase composition suggests that the control coating undergoes significant oxidation (approximately 53 % of nickel was oxidised), the oxidation intensity of coatings made of electrolytes with additives is lower (for coatings from an electrolyte with NaCl, it was approximately 17 %, for coatings from an electrolyte with KCl – approximately 39 %).

DISCUSSION

We associate the first peaks in the samples with the annealing of defects of growth origin and with the nickel recrystallisation processes within this temperature range. According to the Bochvar's formula ($T_r = a \times T_{\text{melt}}$, where T_r is the recrystallisation temperature, a is a coefficient depending on the metal purity, T_{melt} is the melting temperature), the recrystallisation of nickel can begin already at a temperature of $T_r = 0.4T_{\text{melt}}$. For nickel, this is (according to various sources) approximately 580–600 °C. In the nickel coating of the control sample, the recrystallisation process is not as pronounced as for the samples under study. In our opinion, this is associated with the fact that during the formation of coatings on the samples under study, selective inhibition of crystal growth occurs. Due to the inhibition of some crystallographic faces, others received preferential

development. The work [13] presents the results of X-ray diffraction analysis of such coatings. They showed that when adding sodium chloride or potassium chloride to the electrolyte, the crystals formed in the coating exhibit preferential development of (111) faces and inhibition of the development of (200) faces.

Coatings with the addition of sodium chloride contain cone-shaped crystals with pentagonal symmetry [19; 20], which have large stored internal energy [21]. Therefore, in coatings made of electrolyte with NaCl, an intensive recrystallisation process begins at lower temperatures.

According to thermal analysis, the change in enthalpy (ΔH) at the occurrence of the first peaks for the coating with KCl is approximately 20 % greater than for the coating with NaCl. This may indicate that structural changes in these samples occur more actively, which may be associated with the dimensional characteristics of the crystals (Fig. 2).

We associate the further peaks (Fig. 3, 4) with phase transformations that occurred during the oxidation of nickel in oxygen. According to reference data, visible oxidation of nickel in an oxygen-containing environment is observed at temperatures above 700–800 °C. The occurrence of exothermic peaks in the thermograms of the samples is observed in a similar temperature range.

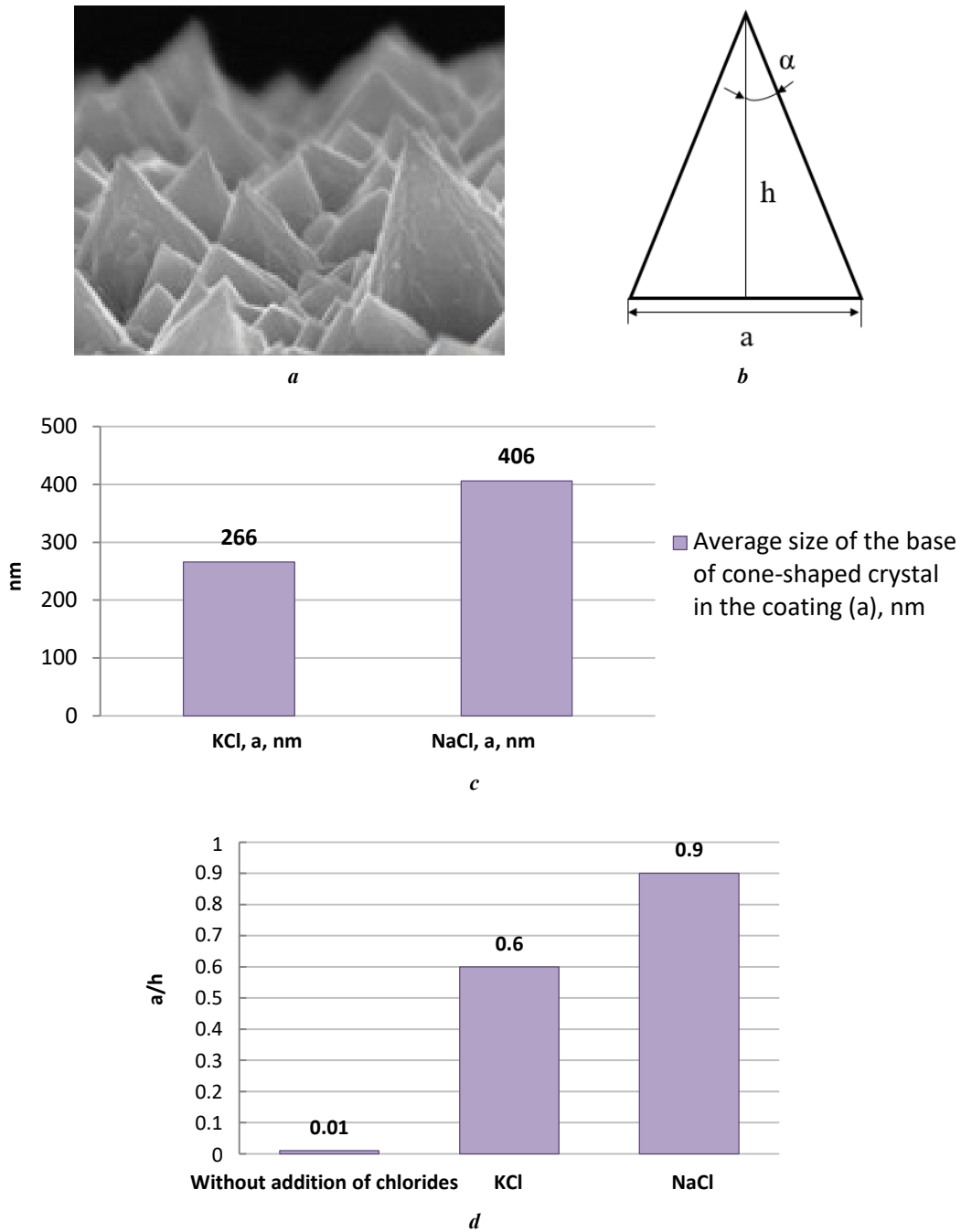


Fig. 2. A view of cones in the coating, where a is the base, h is the cone height, α is the angle at the apex (a); schematic representation of a cone-shaped nickel crystal and its geometric parameters (b); diagram of the average size of nickel crystals in the coating with different additions to the electrolyte (c); diagram of the ratio of the linear dimensions of cones in coatings of different morphologies (d)

Рис. 2. Вид конусов в покрытии, где a – основание, h – высота конуса, α – угол при вершине (a); схематичное изображение конусообразного кристалла никеля и его геометрических параметров (b); диаграмма среднего размера кристаллов никеля в покрытии при разных добавках в электролит (c); диаграмма отношения линейных размеров конусов в покрытиях разной морфологии (d)

X-ray phase studies of samples, showed that when heating nickel in oxygen, its surface oxidises. However, for the control coating, oxidation occurs gradually and more actively within the entire temperature range.

As late as in the middle of the 20th century, the oxygen adsorption on films of nickel, and other metals was studied. It was discovered that chemisorption on different crystallographic surfaces occurs with varying intensity

degrees [22]. Later works [23] confirmed this specificity in terms of reaction rate. All this suggests that the decrease in the intensity of oxidation on the coatings, under study, may be associated exactly with the presence of preferential development of certain crystallographic facets in the crystals. This causes a change in the nature of the nickel-oxygen interaction and, as a consequence, a change in the oxidation reaction rate.

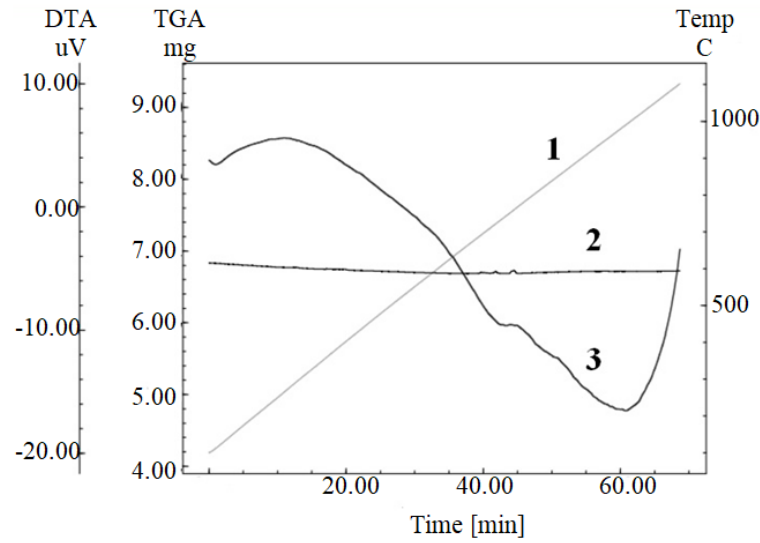


Fig. 3. Thermogram after annealing of microgrids with a nickel coating produced from the pure electrolyte in oxygen.

1 – graph of temperature changes in the device chamber;

2 – graph of changes in the mass of the studied samples during the heating process; 3 – DTA curve

Рис. 3. Термограмма после отжига микросеток с никелевым покрытием, полученным из чистого электролита, в кислороде.

1 – график изменения температуры в камере прибора;

2 – график изменения массы исследуемых образцов в процессе нагревания; 3 – кривая ДТА

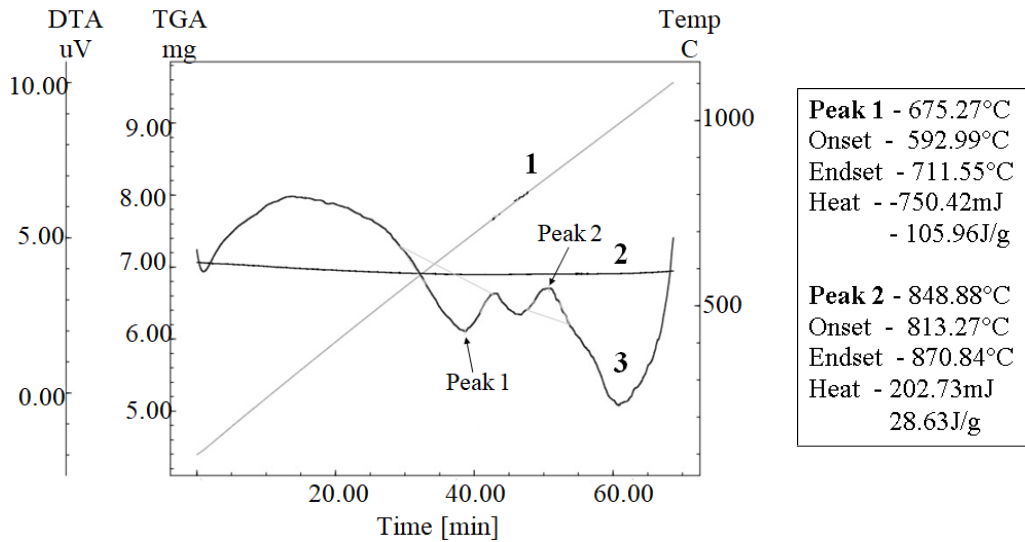


Fig. 4. Thermogram after annealing of microgrids with a nickel coating produced with the addition of sodium chloride in oxygen.

1 – graph of temperature changes in the device chamber;

2 – graph of changes in the mass of the studied samples during the heating process; 3 – DTA curve

Рис. 4. Термограмма после отжига микросеток с никелевым покрытием, полученным с добавлением хлорида натрия, в кислороде.

1 – график изменения температуры в камере прибора;

2 – график изменения массы исследуемых образцов в процессе нагревания; 3 – кривая ДТА

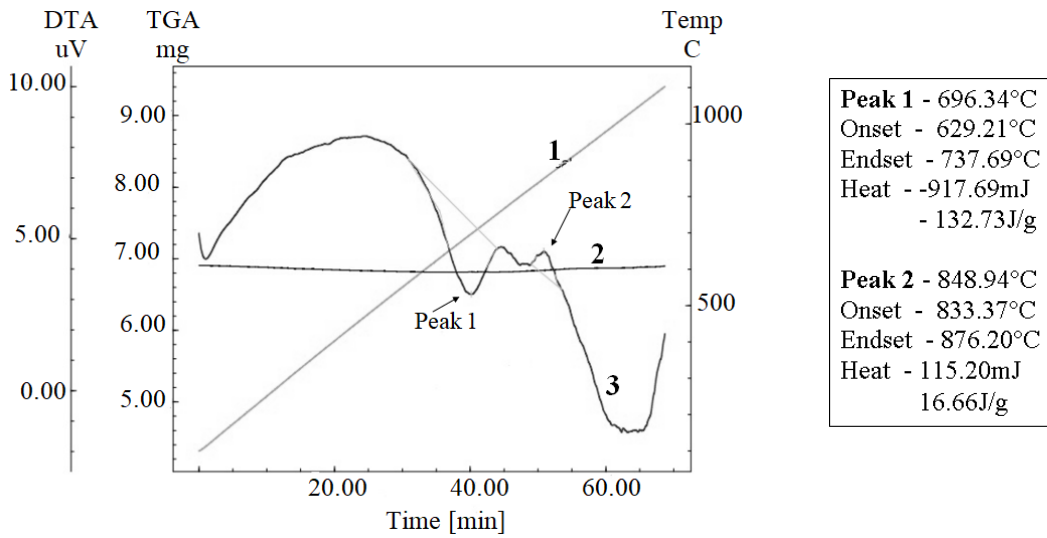


Fig. 5. Thermogram after annealing of microgrids with a nickel coating produced with the addition of potassium chloride in oxygen.

1 – graph of temperature changes in the device chamber;

2 – graph of changes in the mass of the studied samples during the heating process; 3 – DTA curve

Рис. 5. Термограмма после отжига микросеток с никелевым покрытием, полученным с добавлением хлорида калия, в кислороде.

1 – график изменения температуры в камере прибора;

2 – график изменения массы исследуемых образцов в процессе нагревания; 3 – кривая ДТА

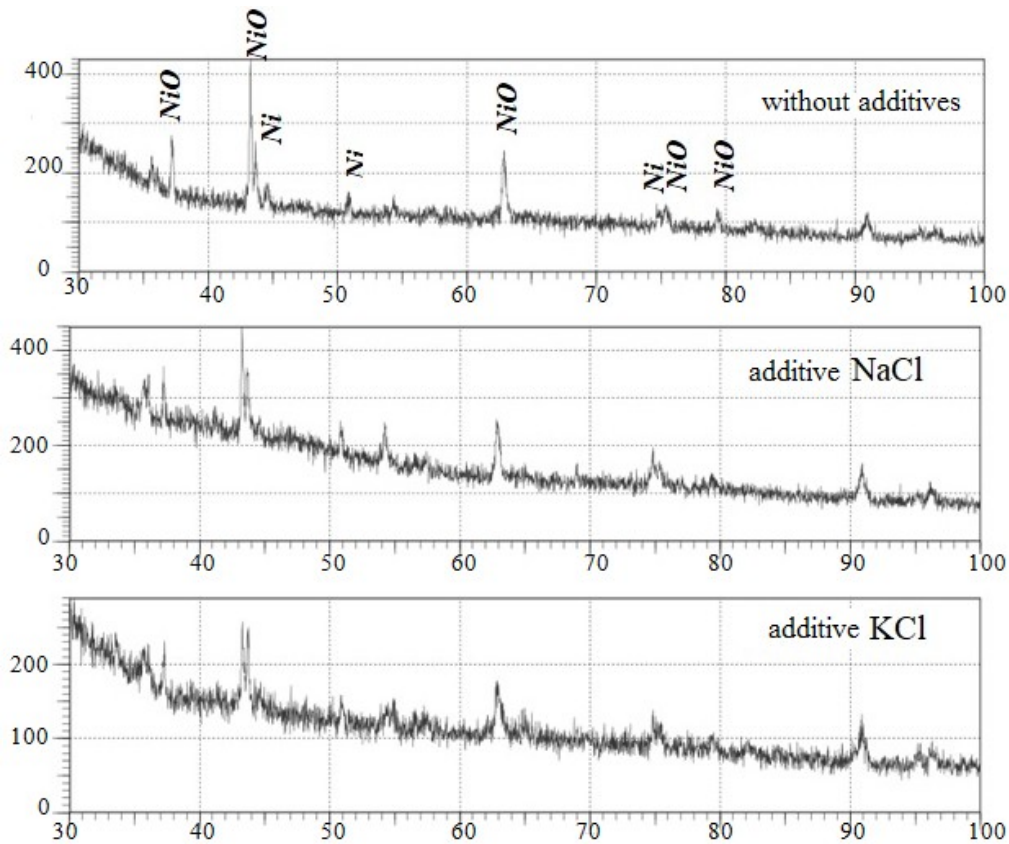


Fig. 6. X-ray patterns of nickel coatings after differential thermal analysis

Рис. 6. Рентгенограммы никелевых покрытий после дифференциально-термического анализа

CONCLUSIONS

It is possible to change the habit of growing crystals in the coating, and control their sizes, both by selecting the electrodeposition mode and by introducing various inhibitory additives into the electrolyte.

Differential thermal analysis of the behaviour of samples with additives in oxygen, showed the presence of two pronounced peaks. We associate the first of them with the recrystallisation of nickel, and the relaxation of large elastic stresses, caused by a high concentration of growth defects in the coating. We associate the second peak with selective chemisorption, with the result that the nickel oxidation (within a very narrow temperature range), first occurred at a high speed (a sharp change in enthalpy occurred), then slowed down significantly. This led to the fact that the intensity of nickel oxidation on the samples under study, was significantly lower.

Analysis of experimental data, allowed concluding that electrodeposited nickel coatings consisting of crystals, in the form of micro- and nanocones have (compared to the control coating) a reduced thermoreactivity even when heated to 1100 °C, which ensures additional possibilities for the use of such coatings, for example, as catalysts operating at high temperatures.

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Особенности терморреакционной способности электролитических никелевых покрытий с различной морфологией поверхности

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Аннотация: Никелевые покрытия, состоящие из ориентированных структур, обладают уникальными каталитическими свойствами. Однако температурный интервал применения таких покрытий не определен, и требуется всестороннее изучение их термических свойств в агрессивных средах. В работе изучалось влияние особенностей габитуса кристаллов никеля на их реакционную способность с повышением температуры (терморреакционную способность). Исследовались никелевые покрытия, полученные методом электроосаждения с добавлением в электролит ингибирующих добавок в виде хлоридов щелочных металлов. Для исследования реакционной способности покрытий в температурных полях применялся дифференциальный термический анализ. В качестве агрессивной среды использовался кислород. Фазовый состав образцов после нагрева определялся при помощи порошкового рентгеновского дифрактометра. Введенные добавки в виде хлоридов щелочных металлов позволили сформировать покрытия, состоящие из кристаллов конусообразного габитуса. Обнаружено, что введение в электролит добавок в виде солей щелочных металлов позволяет изменить габитус кристаллов никеля и увеличить площадь поверхности покрытия примерно на 10–15 %. Показано, что электроосажденные никелевые покрытия, состоящие из кристаллов в виде микро- и наноконусов, обладают (по сравнению с контрольным покрытием) пониженной терморреакционной способностью. Экспериментальные данные позволили сделать вывод, что уменьшение интенсивности окисления на исследуемых покрытиях может быть связано с наличием преимущественного развития определенных кристаллографических граней у кристаллов, что обуславливает изменение характера взаимодействия никеля с кислородом и, как следствие, изменение интенсивности окисления.

Ключевые слова: никелевые покрытия; электроосаждение никеля; конусообразные кристаллы; терморреакционная способность.

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