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ELECTROCHEMICAL EXTRACTION OF NICKEL FROM METHANESULFONATE SOLUTION IN THE PRESENCE OF SODIUM CUMENESULFONATE

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Abstract

The work is devoted to solving an urgent scientific and practical problem involving the processing of nickel-containing heat-resistant alloys, with the extraction of nickel via electroextraction from leaching solutions. Nickel is one of the strategically important metals that are widely used in the defense-industrial complex, and its secondary use is of priority importance due to the limited natural resources and the high cost of primary production. The high purity of the nickel obtained from the processing of heat-resistant alloy waste is achieved through the use of electrochemical methods to extract the metal from leaching solutions. In the work, a new methanesulfonate solution was used as the leaching medium. Electrochemically deposited nickel is characterized by significant internal tensile stresses, which can cause its delamination from the cathode surface. The work established that the formation of nickel deposits with a reduced level of internal stresses requires the use of sulfur-containing organic modifiers. During their electrochemical decomposition on the surface of the nickel electrode, sulfur is incorporated into the deposit in concentrations close to the maximum permissible, which ensures an effective reduction in internal stresses due to the formation of a solid solution of sulfur in nickel. At the same time, the content of hydrocarbon decomposition products of additives in the coating should be minimized. It has been shown that the addition of sodium cumenesulfonate to a methanesulfonate solution in an amount of 10 mmol/l reduces the internal stresses of nickel to almost zero. It was found that in the methanesulfonate solution there is a wider range of current densities in which nickel can be deposited with constant internal stress values compared to the sulfate solution.

Keywords: electroextraction; nickel; sodium cumenesulfonate; structure; internal stresses.

ЕЛЕКТРОХІМІЧНЕ ВИДІЛЕННЯ НІКЕЛЮ З МЕТАНСУЛЬФОНАТНОГО РОЗЧИНУ ЗА ПРИСУТНОСТІ НАТРІЙ КУМОЛСУЛЬФОНАТУ

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Анотація

Робота присвячена вирішенню актуальної науково-практичної проблеми переробки нікельвмісних жаростійких сплавів із одержанням нікелю методом електроекстракції з розчинів вилуговування. Нікель належить до стратегічно значущих металів, які широко використовуються в оборонно-промисловому комплексі, а його вторинне використання набуває пріоритетного значення з огляду на обмеженість природних ресурсів і високу вартість первинного виробництва. Забезпечення високого ступеня чистоти нікелю, отриманого в процесі переробки відходів жаростійких сплавів, досягається завдяки застосуванню електрохімічних методів вилучення металу з розчинів вилуговування. У роботі як середовище вилуговування використано новий метансульфонатний розчин. Електрохімічно осаджений нікель характеризується значними внутрішніми напругами розтягнення, що може зумовлювати його деламінацію від поверхні катода. У роботі встановлено, що формування нікелевих осадів із пониженим рівнем внутрішніх напруг потребує застосування сульфурвмісних органічних модифікаторів. Під час їх електрохімічного розкладу на поверхні нікелевого електрода відбувається інкорпорація сульфуру в осад у концентраціях, близьких до гранично допустимих, що забезпечують ефективне зниження внутрішніх напруг за рахунок утворення твердого розчину сірки в нікелі. Водночас вміст вуглеводневих продуктів розкладу добавок у покритті має бути мінімізований. Показано, що додавання натрій кумолсульфонату до метансульфонатного розчину в кількості 10 ммоль/л знижує внутрішні напруги нікелю практично до нуля. Встановлегно, що в метансульфонатному розчині спостерігається ширший діапазон густин струму, в якому можна осадити нікель із постійними значеннями внутрішніх напруг порівняно з сульфатним розчином.

Ключові слова: електроекстракція; нікель; натрій кумолсульфонат; структура; внутрішні напруги.

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Introduction

Nickel is widely used in industry due to its good corrosion resistance, excellent electrical conductivity, and thermal conductivity. Due to its mechanical properties, nickel has become an indispensable strategic metal in the field of new materials, renewable energy, information technology, aerospace, defense, and other industries [1–4]. Nickel is used, in particular, for the production of superalloys. These materials are characterized by high heat resistance and the ability to maintain stiffness, strength, toughness and geometric stability at temperatures significantly higher than other structural materials used in aerospace engineering. In addition, superalloys are characterized by good resistance to corrosion and oxidation under high-temperature operating conditions of jet engines. Nickel superalloys are capable of operating for a long time in the temperature range of 800–1000 °C, which makes them suitable for use in the most thermally loaded components of gas turbine engines. Such materials are used for the manufacture of high-pressure turbine blades and disks, combustion chamber elements, afterburners and thrust reverser systems [5–9]. The growing demand for critical materials inevitably leads to an increased burden on the primary processes of their extraction and processing. In the absence of effective recycling systems, meeting future needs can lead to excessive depletion of natural resources, increased production costs and increased negative environmental impacts. At the same time, the processing and use of nickel-based superalloys produces a large amount of scrap. This waste has high value due to the content of over 50% nickel and rare and precious metals such as rhenium, tungsten, tantalum, etc. [10]. In this context, the recycling of spent superalloys takes on special importance and actually becomes a necessary component of resource-saving industrial policy [11–15]. Therefore, there is an obvious demand for scientific research into the regularities of the processes that occur during the processing of superalloy waste and the creation of new technologies for the regeneration of valuable metals from scrap. An important aspect of the processing of spent superalloys or waste from their mechanical processing is the isolation of pure individual metals. In particular, metallic nickel, which is separated by the hydrometallurgical method, is obtained by electroextraction [5,16-19].

During nickel electrodeposition, as a rule, a hydrogen evolution reaction occurs simultaneously, which causes an increase in pH in the cathode layer and promotes the formation of poorly soluble basic nickel compounds [20]. Particles of these compounds, adsorbed on the cathode surface, can be incorporated into the deposit, which results in changes in the kinetic patterns of the nickel release process, as well as the structure and physicochemical properties of the formed deposit. For nickel obtained from solutions without organic additives, internal tensile stresses are typical [21], which negatively affect the mechanical characteristics of the metal and complicate the formation of thick nickel layers under electroextraction conditions. The most effective and inexpensive way to reduce such stresses is to introduce sulfur-containing compounds into the electroextraction solution, the use of which helps to improve the nickel structure [22–26].

In [27] it was found that the new methanesulfonate solution is a very promising alternative to traditional sulfate, nitrate or chloride leaching solutions. It turned out that the use of methanesulfonic acid with sodium chloride is effective for the initial stage of processing of heat-resistant superalloys, since it combines higher mass efficiency of the process with the possibility of uniform extraction of strategically important metals. In such a solution, anodic dissolution of the superalloy occurs more effectively than in a sulfuric acid solution containing sodium chloride. Despite the lower electrical conductivity, the methanesulfonate solution provides greater solubility of the formed salts and, accordingly, a lower susceptibility of the surface to salt passivation. Therefore, the current scientific and technical task is to establish the regularities of nickel extraction by electroextraction from methanesulfonate leaching solution in the presence of sulfur-containing organic modifiers of the nickel structure.

Materials and methods

Electrochemical extraction of nickel was carried out in galvanostatic mode using a BVP Electronics current source from methanesulfonate and sulfate solutions with pH3. The composition of the methanesulfonate solution: 1M $Ni(CH_3SO_3)_2$ + 0.5M NaCl + 0.7M H_3BO_3. The composition of the sulfate solution: 1M $NiSO_4$ + 0.5M NaCl + 0.7M H_3BO_3. The sulfur-containing organic compound sodium cumenesulfonate was used as a nickel structure modifier. Electrodeposition was carried out in a two-electrode cell, which was thermostated using a WB-4 water bath with an accuracy of ±0.5 K. The electrolysis temperature was 333 K.

The internal stresses of nickel were determined by the flexible cathode method. Copper foil was used as a substrate, which was insulated on one side. The upper end of the cathode was fixed, the lower end was free. During the electrodeposition process, internal stresses arise in nickel. The cathode bends. The equation for calculating internal stresses σ_{is} has the form [28]:

$$\sigma_{is} = \frac{E_c \cdot d_c \cdot (d_c + d_{dep}) \cdot z}{3 \cdot l^2 \cdot d_{dep}}, \quad (1)$$

where E_c – the modulus of elasticity of the cathode foil; d_c – the thickness of the cathode; d_{dep} – the thickness of the deposit; l – the length of the working part of the cathode; z – the deviation of the cathode end from the initial position.

When determining the internal stresses, nickel was deposited on a copper plate with a thickness of 25 μm. The reproducibility of the experimental results was checked by repeating each study five times. The confidence interval limits for the values of the internal stresses of nickel deposits were found using the Student's test for a confidence probability of 95 %.

The structure of nickel was studied using a DRON-3 X-ray diffractometer in monochromatized CuKα-radiation. The calculation of crystallite sizes was carried out according to the Scherrer formula:

$$L = \frac{k \cdot \lambda}{\beta \cdot \cos\theta} \quad (2)$$

where λ – the wavelength of the radiation;

β – the half-width of the diffraction line of the sample; k – the shape factor (k = 0.940); θ – the diffraction angle.

To calculate the dislocation density, the equation was used:

$$D = A \cdot \beta^2, \quad (3)$$

where A – a coefficient that depends on the elastic properties of the material. In the case of metals with a cubic crystal lattice type $A = 2 \cdot 10^{-16}$ cm^{-2}.

Microphotographs of the nickel surface morphology were obtained using a scanning electron microscope PEM-106-I.

The sulfur and carbon content in nickel was determined using an X-ray spectrometer "Sprut" X100 equipped with a Si(Li) detector [29].

Results and discussion

Electrodeposition of nickel from solutions that do not contain organic additives leads to the formation of microcrystalline precipitates (Fig. 1). Moreover, the grain size of nickel obtained from methanesulfonate solution turned out to be smaller compared to the grain size of the deposit deposited from sulfate solution. The explanation for this fact should be sought in the conditions of electrocrystallization of nickel in the studied solutions, in particular, the adsorption on the electrode surface of various particles, which, in the absence of organic additives, can be $Ni(OH)_2$, H_{ads}, H_2 [30].

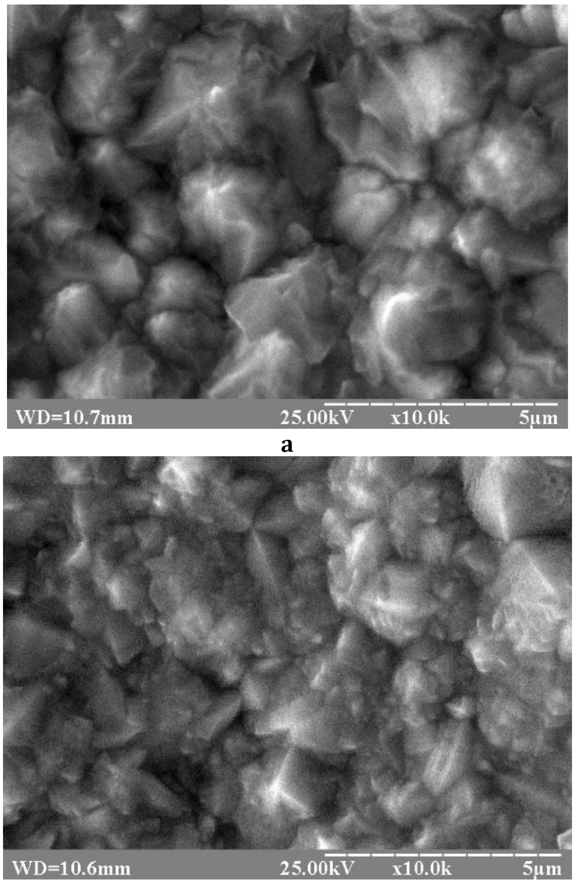

Fig. 1. Surface morphology of nickel electrodeposited from sulfate (a) and methanesulfonate (b) solutions

During the electrolysis of nickel, the percentage of hydrogen released for sulfate and methanesulfonate solutions is approximately the same and is about 3 %. At the same time, the buffer properties of the methanesulfonate solution are lower than those of the sulfate solution [20]. Since boric acid in nickel extraction solutions does not ensure complete equalization of pH values in the bulk and in the near-electrode layer, in the case of a methanesulfonate solution, the formation of nickel(II) hydroxide near the electrode surface is more intense. The latter, in turn, contributes to greater inhibition of crystal growth due to the adsorption of nickel(II) hydroxide on the active growth centers of the nickel deposit.

X-ray structural studies of nickel obtained from methanesulfonate solution showed that nickel in all cases is in the β-modification with the value of the lattice parameter a in the range from 0.35212 nm to 0.35285 nm, which corresponds to a face-centered cubic structure that has defects. Similar values of the lattice parameter were obtained for nickel isolated from sulfate solution.

The introduction of the organic structure modifier sodium cumenesulfonate into the methanesulfonate solution leads to a decrease in the size of the crystallites (Fig. 2). When the concentration of sodium cumenesulfonate is increased to 15 mmol/l, the size of the crystallites decreases by more than one and a half times. Further increase in the concentration of the structure modifier does not lead to a significant decrease in the size of the crystallites. Nickel obtained from the methanesulfonate solution in the presence of sodium cumenesulfonate is characterized by smaller crystallite size values compared to nickel deposited under similar conditions from the sulfate solution.

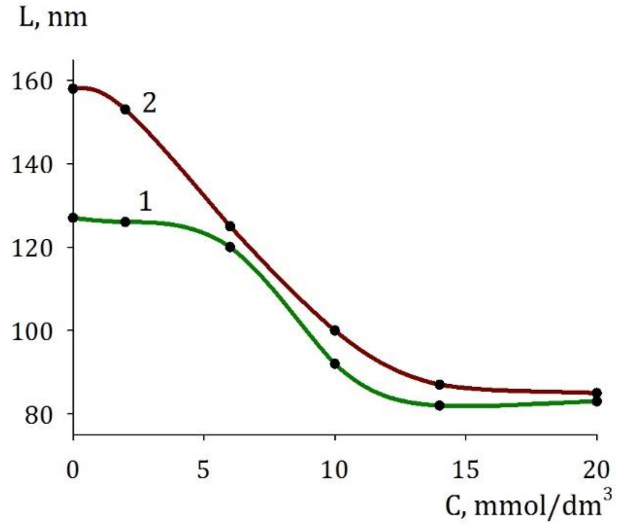

Fig. 2. Effect of sodium cumenesulfonate concentration on the size of nickel crystallites precipitated from methanesulfonate (1) and sulfate (2) solutions

Along with reducing the size of crystallites, the introduction of sodium cumenesulfonate into the methyl sulfonate solution contributes to an increase in the density of dislocations in nickel deposits (Fig. 3). A comparison of data on the effect of the structure modifier on the crystallite size and dislocation density of nickel precipitates for methanesulfonate and sulfate solutions shows that the changes in the structure of nickel obtained from methanesulfonate solution are more pronounced.

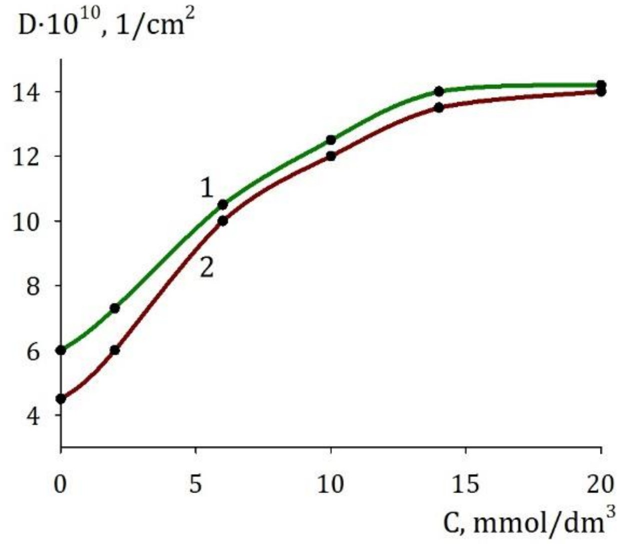

Fig. 3. Effect of sodium cumenesulfonate concentration on the dislocation density in nickel precipitates obtained from methanesulfonate (1) and sulfate (2) solutions

Based on the above data, it can be concluded that sodium cumenesulfonate has a greater effect on the structure of nickel deposit electrodeposited from methanesulfonate solution compared to sulfate solution. This, in turn, should be reflected in the physical and mechanical properties of the resulting deposits, in particular the internal stresses of nickel.

Nickel deposits electrodeposited from methyl sulfonate solution are characterized by rather high values of internal tensile stresses (Fig. 4). Introduction of 5 mmol/l sodium cumenesulfonate into methanesulfonate solution causes reduction of internal tensile stresses of nickel by more than four times. When the modifier concentration increases to 10 mmol/l, the internal tensile stresses reverse to compressive stresses. It should be noted that in the presence of sodium cumenesulfonate, the internal stresses of nickel deposits increase with increasing current density. Obviously, with increasing current density, the renewal of the cathode surface is accelerated and the adsorption of the organic modifier on nickel decreases. This leads to a decrease in the efficiency of the modifier in its effect on the structure, and therefore on the internal stresses of nickel.

To establish the specifics of the effect of sodium cumenesulfonate on the internal stresses of nickel obtained from methanesulfonate solution, a comparison of the internal stresses of nickel deposits obtained from methanesulfonate and sulfate solutions was carried out. From Fig. 5 it is seen that in the range of current densities from 2 to 7 A/dm^2, the tensile stresses of nickel obtained in sulfate solution in the absence of an organic modifier are in the range from 130 to 160 MPa, which is less than the internal stresses arising in nickel isolated from pure methanesulfonate solution. The introduction of sodium cumenesulfonate into the sulfate solution, as well as in the methanesulfonate solution, contributes to a decrease in the internal tensile stresses of nickel. However, the greater dependence of the internal stresses of nickel on the current density attracts attention. Thus, a comparison of experimental data obtained in methanesulfonate and sulfate solutions in the presence of sodium cumenesulfonate indicates that in the methanesulfonate solution there is a wider range of current densities in which nickel can be deposited with constant values of internal stresses.

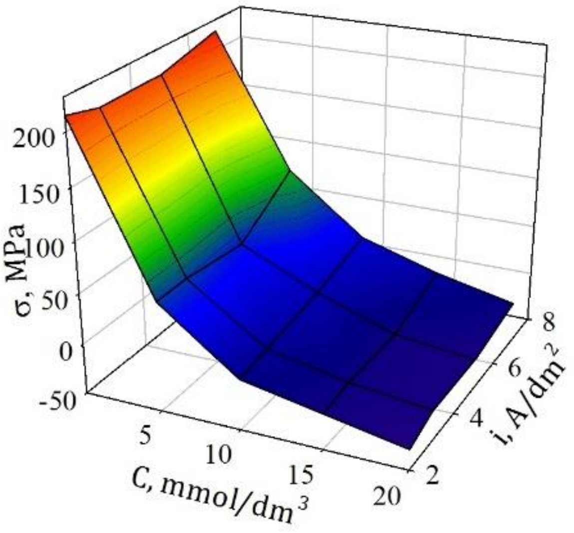

Fig. 4. Effect of deposition current density and sodium cumenesulfonate concentration on the internal stresses of nickel obtained from methanesulfonate solution

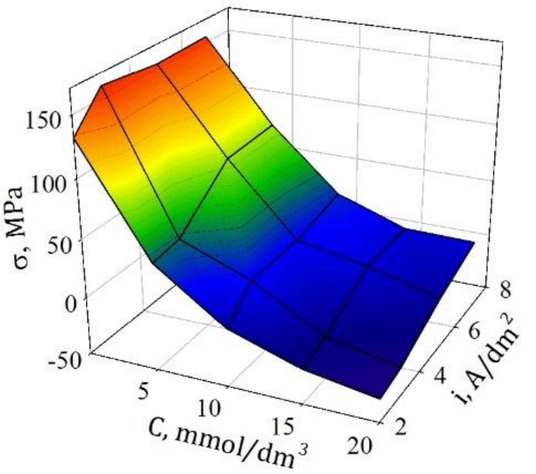

Fig. 5. Effect of deposition current density and sodium cumenesulfonate concentration on the internal stresses of nickel obtained from sulfate solution

The established patterns of the influence of sodium cumenesulfonate on the internal stresses of nickel are obviously due to the influence on electrocrystallization, the structure and composition of the resulting deposits.

As is known, the internal tensile stresses characteristic of nickel are caused by compression of the deposit during electrolysis. The introduction of sulfur-containing organic modifiers into the solution reduces this effect. Based on this, the influence of sodium cumenesulfonate on the internal stresses of nickel and the distinctive features that appear in the methanesulfonate solution can be due to transformations at the cathode of the studied substance and an increase in the content of alloying elements in the nickel deposit.

According to [31], simultaneously with the electrodeposition of nickel, the following transformations occur at the cathode with the participation of a sulfur-containing modifier:

$$RSO_3^- \rightarrow RSO_3^-{}_{ads}, \qquad (4)$$

$$RSO_3^-{}_{ads} + 2H^+ + 2e \rightarrow RH + HSO_3^-{}_{ads}, \qquad (5)$$

$$HSO_3^-{}_{ads} + ne \rightarrow S_{included}, \qquad (6)$$

where R – a hydrocarbon radical.

As can be seen from Table 1, the amount of sulfur incorporated into nickel in the presence of sodium cumenesulfonate in the methanesulfonate solution increases with increasing modifier concentration up to 15 mmol/l. Further concentration of the solution by sodium cumenesulfonate does not lead to a significant increase in sulfur in the deposits. A similar pattern is observed in the sulfate solution. The amount of sulfur detected in nickel electrodeposited in the presence of sodium cumenesulfonate from the sulfate solution was approximately 20% less than the values obtained in the methanesulfonate solution.

Nickel electrodeposition occurs in the region of potentials more negative with respect to the zero charge potential of nickel and the electrode surface is negatively charged. The negative charge of the electrode in the methanesulfonate solution is smaller than in the sulfate solution, which is due to the lower values of the overvoltage of nickel release [32]. In this case, the anionic modifier used in this work should be adsorbed more easily. The latter is probably the reason for the higher surface concentration of the sulfur-containing organic modifier in the methanesulfonate solution. This, other things being equal, leads to an increase in the rate of decomposition of organic matter with the introduction of sulfur into the nickel deposits;

and as a result, the sulfur content in the nickel obtained from the methanesulfonate solution exceeds the values corresponding to the sulfate solution.

Table 1

Sulfur content in nickel (% wt.) obtained from methanesulfonate (I) and sulfate (II) solutions in the presence of sodium cumenesulfonate

Concentration of sodium cumenesulfonate, mmol/l	Sulfur content in nickel, % wt.			
	I		II	
	Current density, A/dm^2			
	2	5	2	5
0	0.000	0.000	0.000	0.000
5.00	0.022	0.021	0.015	0.011
10.0	0.037	0.036	0.030	0.025
15.00	0.049	0.048	0.042	0.038
20.00	0.050	0.049	0.043	0.039

To explain the effect of sodium cumenesulfonate on the internal stresses of nickel, we will use the dislocation-sorption model of internal stresses, according to which the observed internal stresses of galvanic deposits consist of oppositely acting internal tensile stresses and internal compressive stresses. The resulting values of internal stresses depend on the conditions of obtaining the deposits.

One of the causes of internal tensile stresses is the spontaneous movement of dislocations in newly formed crystals to the periphery and their annihilation at grain boundaries. Since dislocations of the same sign predominate in crystals of electrochemically deposited metal, and dislocation lines have a largely similar orientation, mutual repulsion of dislocations occurs. The consequence is the predominant movement of dislocations to the periphery and their partial exit to the surface of the crystals. This process is facilitated by the attraction of dislocations to free surfaces. As dislocations exit, the density decreases, and the repulsion forces weaken. When the driving forces are equal to the braking forces, the exit of dislocations stops. The decrease in the density of dislocations requires a decrease in the volume of the crystal, which is prevented by adhesive bonds with the substrate. In such a situation, it is customary to speak of the occurrence of internal tensile stresses in electrolytic deposits.

Internal compressive stresses in electroplated deposits are associated with the introduction of foreign particles into the metal, which exert pressure on the metal crystals, causing their plastic deformation. The desire of the intergranular substance to increase the volume of the intercrystalline layers is resisted by the adhesive bonds between the metal and the substrate. As a result, internal compressive stresses arise in electroplated deposits.

The change in the internal tensile stresses of electroplated deposits, which is provided by the use of sulfur-containing organic substances, is probably associated with the introduction of sulfur into the deposit, which is formed during the reduction of the modifier. The latter contributes to the inhibition of the movement of dislocations and the return processes that occur in nickel deposits in the case of the dissolution of sulfur in the nickel lattice. Compressive stresses can arise as a result of an increase in the volume of intercrystalline gaps due to the capture of foreign particles by the deposit, such as nickel sulfide adsorbed on grain boundaries and hydrocarbon compounds from the decomposition of the modifier.

Sulfur is included in electrolytic nickel in the form of a solid solution in an amount of up to 0.057 % by weight. As can be seen from Table 1, the sulfur content in almost all studied sediments does not exceed this value. Thus, provided that there is no introduction of undecomposed sulfur-containing compounds into the sediment, in the considered samples sulfur is mainly incorporated into the metal lattice.

The introduction of sodium cumenesulfonate into the methanesulfonate solution in an amount of 10 mmol/l leads to an increase in the dislocation density from $6 \cdot 10^{10}$ 1/cm^2 to $12.5 \cdot 10^{10}$ 1/cm^2 (Fig. 3). The size of the crystallites decreases accordingly from 128 nm to 92 nm (Fig. 2). At the same time, the internal stresses changed from 214 MPa to 0 MPa of tensile stresses. The obtained values of the nickel dislocation density depend on the content of sulfur incorporated into the crystal lattice. Indeed, an increase in the concentration of sodium cumenesulfonate leads to an increase in the sulfur content in nickel deposits, an increase in the degree of dislocations and a decrease in internal tensile stresses. It should be emphasized that a further increase in the content of this modifier in the solution causes compressive stresses in the deposits. This is due to the introduction of hydrocarbon decomposition products of this organic substance into nickel. As can be seen from Table 2, the carbon content, which indicates the inclusion of hydrocarbon fragments of the modifier in nickel, increases with increasing sodium cumenesulfonate concentration. Probably, the amount of hydrocarbon decomposition products of the modifier, which are adsorbed on grain boundaries and contribute to the occurrence of internal compressive stresses, when using sodium cumenesulfonate above 10 mmol/l is large enough to cause compressive stresses.

Table 2

Carbon content in nickel (% wt.) obtained from methanesulfonate (I) and sulfate (II) solutions in the presence of sodium cumenesulfonate

Concentration of sodium cumenesulfonate, mmol/l	Carbon content in nickel, % wt.			
	I		II	
	Current density, A/dm^2			
	2	5	2	5
0	0.00	0.00	0.00	0.00
5.0	0.20	0.18	0.16	0.11
10.0	0.33	0.30	0.28	0.22
15.0	0.42	0.40	0.38	0.32
20.0	0.43	0.41	0.39	0.33

The introduction of sulfur and carbon into nickel deposits obtained from sulfate solution occurs to a somewhat lesser extent than during electrodeposition of nickel from methanesulfonate solution. In this case, nickel with lower dislocation density is deposited in sulfate solution.

It should be noted that the influence of carbon on the internal stresses of nickel deposits is probably significantly lower compared to the influence of sulfur. As can be seen from Table 1 and Table 2, the content of carbon in nickel is an order of magnitude higher than that of sulfur, however, the decrease in internal tensile stresses associated with the incorporation of sulfur into nickel is more pronounced than the change in internal compressive stresses arising from the inclusion of carbon in the deposits. Obviously, the different order in the observed effects is associated with the different degrees of influence of sulfur and carbon on the metal structure. The incorporation of sulfur, unlike carbon, causes significant distortions of the crystal lattice, which leads to noticeable changes in the physical and mechanical properties of nickel. Therefore, in a first approximation, the influence of carbon on the internal stresses of nickel can be neglected and the change in internal tensile stresses associated with changes in the nickel structure under the influence of sulfur can be analyzed in detail.

The quantitative dependence of internal tensile stresses on the dislocation density of the electrodeposit and crystallite size can be represented as follows:

$$\sigma = \sqrt{\frac{\omega nez\eta_1\gamma\lambda\nu}{L(1-\mu)}}, \qquad (7)$$

where σ – the internal tensile stress, Pa; ω – the relative fraction of the “excess” energy that is converted into dislocation energy; n – the number of atoms per unit volume of the deposit; e – the elementary charge, C; z – the valence of the metal; η_1 – the overvoltage during electrodeposition of the metal, V; γ – a coefficient that depends on the grain shape; λ – the average “mileage” of the dislocation towards the periphery during the time period before the dislocation movement stops, m; ν – the modulus of elasticity, Pa; L – the average crystallite size, m; μ – the Poisson’s ratio of the metal being deposited.

The average “mileage” of the dislocation is:

$$\lambda=\lambda^0\cdot(D^0 - D), \qquad (8)$$

where the proportionality coefficient λ^0 is numerically equal to the value of the “mileage” of dislocations in the case when the excess of the initial dislocation density D^0 over the defined “equilibrium” D is unity. After transforming equation (7) taking into account (8), we can obtain:

$$\sigma = \sqrt{\frac{\omega nez\eta_1\gamma\nu\lambda^0}{(1-\mu)}}\sqrt{\frac{D^0-D}{L}} \qquad (9)$$

As can be seen from expression (9), the internal stresses are a function of the variables D and L. Neglecting changes in the other terms of the equation, we write expression (9) in the form:

$$\sigma = B\sqrt{\frac{D^0 - D}{L}}, \qquad (10)$$

where B = const.

Analysis of equation (10) allows us to assess the influence of organic sulfur-containing modifiers on the magnitude of internal tensile stresses of electroplated deposits, which is associated with a change in the nickel structure. Obviously, an increase in the dislocation density should be accompanied by a decrease in internal tensile stresses, and a decrease in the crystallite size should lead to the opposite effect.

The introduction of sodium cumenesulfonate into the methanesulfonate solution leads to an increase in the dislocation density and a decrease in the size of the crystallites. At the same time, the internal tensile stresses decrease. This indicates that the magnitude of the dislocation density affects the internal tensile stresses to a greater extent than the size of the crystallites. The value of the dislocation density of nickel depends on the sulfur content incorporated into the crystal lattice. Indeed, increasing the concentration of sodium cumenesulfonate leads to an increase in the sulfur content in nickel deposits, an increase in the degree of dislocations, and a decrease in internal tensile stresses.

The incorporation of sulfur into nickel deposits obtained from sulfate solution occurs to a lesser extent than during electrodeposition of nickel from methanesulfonate solution. In this case, nickel with lower dislocation density values is deposited in the sulfate solution. At the same time, at a concentration of sodium cumenesulfonate of 10 mmol/l, both in methanesulfonate and sulfate solutions, the internal tensile stresses decrease to zero. Obviously, this effect occurs due to the fact that nickel precipitates obtained from sulfate solution without modifier have lower tensile stresses compared to nickel isolated from pure methanesulfonate solution. Thus, less sulfur is required to reduce these stresses, which enters nickel during the decomposition of sulfur-containing organic modifiers.

Conclusions

1. The work shows that for the isolation of nickel with low internal stresses it is advisable to use sodium cumenesulfonate as an organic modifier containing sulfur. When this modifier decomposes on a nickel electrode, sulfur is incorporated into the precipitate in an amount sufficient to reduce internal stresses due to the formation of a solid solution of sulfur in nickel. At the same time, the amount of hydrocarbon decomposition products from the additive that ends up in the nickel does not lead to a significant increase in internal compressive stresses. The use of 10 mmol/l sodium cumenesulfonate as a structure modifier made it possible to eliminate internal stresses in nickel obtained from a methanesulfonate solution. The amount of incorporated sulfur did not exceed 0.037 wt.%. The carbon content was 0.33 wt.%.

2. It is shown that the methanesulfonate solution differs from the sulfate solution in a wider range of current densities, in which, in the presence of sodium cumenesulfonate, nickel with low internal stresses can be obtained. This feature may be due to the fact that this organic additive is more strongly adsorbed onto the surface of the forming nickel deposit, and its decomposition proceeds more rapidly when sulfur enters the precipitate. Inhibition of dislocation motion and return processes occurring in nickel deposits during the dissolution of sulfur in the nickel lattice leads to a decrease in internal tensile stresses. The higher sulfur content in nickel obtained from the methanesulfonate solution allows the use of a wider range of current densities for the electrodeposition of nickel with low internal stresses.

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