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ELECTROCHEMICAL DISCHARGE OF NICKEL WITH LOW INTERNAL STRESSES

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Abstract

The work is devoted to the current topic of electrochemical separation of nickel with low voltages from sulfate electrolytes of electroextraction. Scrap processing of strategic nickel-containing superalloys with electroextraction of nickel is an urgent task today. Electrochemically deposited nickel is characterized by high internal tensile stresses, which leads to its delamination from the cathode surface. To reduce the internal stresses of nickel deposits obtained in such systems, it is proposed to use sulfur-containing organic compounds of sodium allylsulfonate, sodium orthoarylsulfonate, and sodium propynylsulfonate. It was established that allylsulfonate and orthoarylsulfonate practically do not affect the kinetics of nickel release. Propynyl sulfonate with a concentration of more than 5 mmol/l significantly inhibits the process of electrodeposition of nickel, which is related to the adsorption capacity of this compound with the triple bond present in the molecule. It is shown that due to the presence of a sulfo group in the composition of the molecules, the used organic additives contribute to the reduction of the internal stresses of nickel deposits. It was established that allyl sulfonate and orthoaryl sulfonate are the most promising reagents that contribute to reducing the internal stresses of electrodeposited nickel. Low-stress nickel deposits can be obtained in the range of current densities from 2 to 7 A/dm2 at a concentration of these additives from 15 to 30 mmol/l.

Key words: electrodeposition; nickel; sulfur-containing organic substances; kinetics; internal stresses.

ЕЛЕКТРОХІМІЧНЕ ВИДІЛЕННЯ НІКЕЛЮ З НИЗЬКИМИ ВНУТРІШНІМИ НАПРУГАМИ

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Анотація

Робота присвячена актуальній темі електрохімічного виділення нікелю з низькими напруженнями із сульфатних електролітів електроекстракції. Переробка лому стратегічних нікельвмісних суперсплавів з електроекстракцією нікелю є нагальною задачею сьогодення. Електрохімічно осаджений нікель характеризується високими внутрішніми напругами розтягнення, що призводить до його відшаровування від катодної поверхні. Для зниження внутрішніх напруг нікелевих осадів, отримуваних в таких системах запропоновано використовувати сульфурвмісні органічні сполуки аллілсульфонату натрію, ортоарилсульфонату натрію та пропінілсульфонату натрію. Встановлено, що аллілсульфонат та ортоарилсульфонат практично не впливають на кінетику виділення нікелю. Пропінілсульфонат з концентрацією понад 5 ммоль/л суттєво загальмовує процес електроосадження нікелю, що пов'язано з адсорбційною здатністю цієї сполуки з наявним в молекулі потрійним зв'язком. Показано, що внаслідок наявності сульфогрупи в складі молекул використовувані органічні добавки сприяють зниженню внутрішніх напруг нікелевих осадів. Встановлено, що аллілсульфонат та ортоарилсульфонат є найбільш перспективними реагентами, що сприяють зменшенню внутрішніх напруг електроосадженого нікелю. Малонапружені нікелеві осади можна отримати в діапазоні густин струму від 2 до 7 А/дм^2 при концентрації цих добавок від 15 до 30 ммоль/л.

Ключові слова: електроосадження; нікель; сульфуровмісні органічні речовини; кінетика; внутрішні напруги.

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Introduction

Nickel is one of the strategic metals, which is mainly used for the production of stainless steel and superalloys [1–3]. Superalloys refer to alloys with extraordinary strength, heat resistance, and oxidation resistance and can be used in environments with a temperature of over 1000 °C. Due to their high melting point, creep resistance, and corrosion resistance, they are mainly used in gas turbines of aircraft engines and power plants [4–6]. A large amount of alloy scrap is produced during the processing and use of nickel-based superalloys. Nickel-based superalloy waste has high value due to the content of more than 50 % nickel and rare and precious metals such as rhenium, tungsten, tantalum, etc. [7]. In view of this, scrap superalloys are subject to recycling processing with the separation of alloy components [8–11]. Therefore, there is an urgent need for a scientific study of the regularities of the processes that occur during the processing of such waste and the creation of new technologies for the regeneration of valuable metals from scrap superalloys. Special attention is paid to obtaining high-purity metals when processing spent superalloys or their mechanical processing waste. In particular, the extraction of nickel in metallic form extracted during their hydrometallurgical processing is carried out by electroextraction [4; 12–15].

Electrodeposition of nickel, as a rule, is accompanied by the release of hydrogen, as a result of which the pH of the near-cathode layer increases and the formation of poorly soluble basic compounds of nickel occurs [16], the particles of which, adsorbed on the surface, are included in the cathode deposit and change the kinetics of the nickel plating process, its structure and physicochemical properties sediment Nickel electrodeposited from electrolytes that do not contain organic additives is characterized by internal tensile stresses [17], which worsens the mechanical properties of the deposit and makes it difficult to apply thick layers of nickel during electroextraction. It is possible to reduce the internal tension of nickel by introducing sulfur-containing compounds into the electrolyte [18–20].

In [21], a study of the influence of saccharin on the patterns of nickel electrodeposition from a sulfate electrolyte at pH 4.2 and a temperature of 50 °C and the properties of the obtained precipitates was carried out. It is shown that for sediments obtained at a current density of 4 A/dm^2 in the presence of 0.1 to 1.2 g/l of saccharin, a change in internal stresses from tensile stresses to compressive stresses is observed. The authors [22] studied the dependence of the structure and properties of nickel on the composition of the electrolyte containing saccharin and sodium citrate. In [23], the change in the structure and physicochemical properties of nickel electrodeposited from a sulfate electrolyte in the presence of organic additives of coumarin and the trisodium salt of 1,3,6-naphthalene trisulfonic acid was investigated. It is shown that coumarin contributes to the incorporation of hydrogen into the precipitate and the increase of internal tensile stresses. In contrast, the trisodium salt of 1,3,6-naphthalene trisulfonic acid affects the structure of nickel in such a way that internal compressive stresses occur in it. The latter is caused by the incorporation of sulfur into the crystal lattice of nickel, the source of which is the trisodium salt of 1,3,6-naphthalene trisulfonic acid.

In modern nickel plating electrolytes, in addition to the above, sulfur-containing substances such as sodium allylsulfonate, sodium propynylsulfonate and sodium orthoarylsulfonate are usually used. However, there are no data on their influence on the physical and mechanical properties and kinetics of nickel electrodeposition. Taking into account the relevance of the problem of obtaining nickel deposits with low internal voltages, in this work, the regularities of nickel electrodeposition from sulfate electrolytes in the presence of the indicated salts of sulfonic acids were studied.

Materials and methods

The voltammograms were obtained using the IPC – Pro potentiostat with the IPC – 2000 software. A platinum electrode was used as the working electrode, on which a nickel coating was applied immediately before the measurements with an electrolyte of the following composition: 1M NiSO4 + 0.5M NaCI + 0.7M. A nickel plate served as an auxiliary electrode, and a silver chloride electrode of the EVL – 1M1 brand, immersed in a saturated solution of potassium chloride, was used as a reference electrode. The experiments were conducted in an electrochemical cell made of heat-resistant glass with a volume of 50 cm^3. The temperature of the solutions was maintained using a UT-15 thermostat with an accuracy of 0.5 °C.

The internal stresses of nickel deposits were determined by the flexible cathode method. The upper end of the copper plate isolated on one side was fixed immovable, the lower end was free. In the process of electrolysis, the cathode bends under the influence of internal stresses arising in the sediment. The equation for calculating internal stresses σvn has the form [24]:

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

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

When determining the internal stresses, a nickel deposit with a thickness of 25 μm was applied to the copper plate. Each experiment was repeated at least 5 times. The limits of the confidence interval for the values of internal stresses of nickel deposits were found using the Student's test for a confidence probability of 95 %.

The reagents used in the experiments had a qualification not lower than (p.f.a.), distilled water. All experiments were carried out at an electrolysis temperature of 333 K and pH 3.

Results and discussion

It is known that additives to the nickel electrolyte of the first class slightly inhibit the cathodic process, and the polarization dependences of nickel electrodeposition from sulfate electrolyte in the presence of orthoaryl sulfonate (Fig. 1, curve 2) and allyl sulfonate (Fig. 1, curve 3) confirm this.

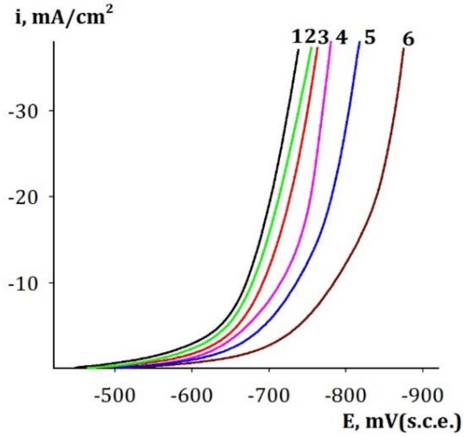

Fig. 1. The voltammograms of nickel electrodeposition from an electrolyte of 1M $NiSO_4$ + 0.5M NaCI + 0.7M H_3BO_3 (1) and in the presence of: 2 – 5 mmol/l orthoarylsulfonate (ARS); 3 – 5 mmol/l allyl sulfonate (AS); 4 – 1 mmol/l propynylsulfonate (PS); 5 – 5 mmol/l PS; 6 – 10 mmol/l PS.

Moreover, at equal concentrations, orthoarylsulfonate affects the process to a lesser extent than allylsulfonate. Note that increasing the concentration of either one or the other additive from 5 to 30 mmol/l does not lead to a noticeable increase in polarization. The course of the current-voltage curve obtained in the presence of propynyl sulfonate (Fig. 1, curve 4) is excellent. Here we see a significant inhibition of nickel electrodeposition, which increases with increasing propynyl sulfonate concentration (Fig. 1, curves 4, 5, 6).

On the basis of the obtained data, it is possible to judge the ability of the investigated substances to adsorb on the cathode and influence the kinetics of nickel electrolysis. Considering the small size of the hydrophobic radicals of the adsorbate molecules, the adsorption of additives on nickel occurs mainly as a result of the interaction of their excess electron density and the unfilled d-orbital of the metal. Obviously, propynylsulfonate, characterized by the presence of a triple bond, has the highest adsorption capacity compared to allylsulfonate, which contains a double bond, and orthoarylsulfonate, which includes an aryl ring. In the investigated concentration range, allylsulfonate and orthoarylsulfonate are practically not adsorbed on the electrode surface, and the degree of filling of the surface with their molecules, which determines the inhibition effect [25], is apparently insignificant.

The study of changes in the internal stresses of nickel deposits at different current densities showed that in the range of current densities from 2 to 7 A/dm2, tensile stresses vary from 115 to 145 MPa (Fig. 2, curve 1) and are characterized by a maximum at 3 A/dm² (180 MPa).

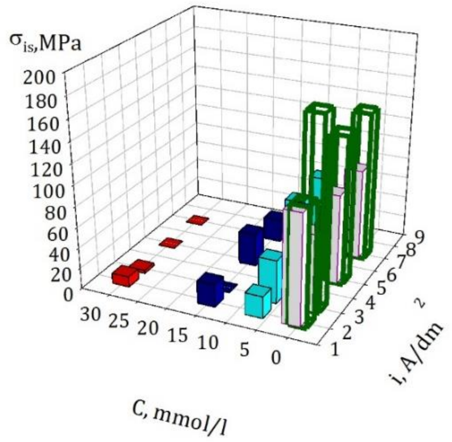

Fig. 2. Dependence of the internal stresses of the nickel deposit on the density of the deposition current in the electrolyte 1M NiSO4 + 0.5M NaCI + 0.7M H3BO3 (1) in the presence of allyl sulfonate, mmol/l: 2 – 1; 3 – 7; 4 – 15; 5 – 30.

The introduction of allyl sulfonate into the electrolyte helps to reduce the internal tensile stresses of sediments obtained at different current densities (Fig. 2).

In the presence of less than 15 mmol/l allyl sulfonate in the electrolyte, the change in the values of internal stresses corresponding to different current densities is not the same. It is characteristic that the reduction of internal stresses in the region of low current densities is more intense than in the region of high current densities (Fig. 2, curves 2, 3). Constant values of internal tensile stresses in nickel precipitates, obtained in the range of 2–7 A/dm^2, can be achieved by increasing the concentration of allyl sulfonate above 15 mmol/l.

The dependences corresponding to electrolytes with orthoarylsulfonate show a similar tendency to lower internal stresses with increasing concentration of the additive (Fig. 3). However, it should be noted that an increase in the current density of nickel electrodeposition has a smaller effect on the change in the internal stresses of deposits obtained in the presence of orthoaryl sulfonate (Fig. 3, curve 3) compared to coatings deposited from electrolytes containing allyl sulfonate (Fig. 2, curve 3).

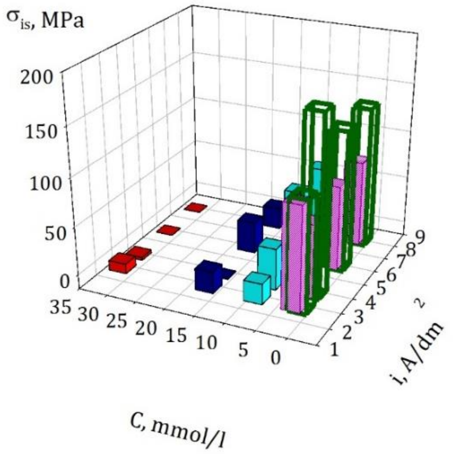

Fig. 3. Dependence of the internal stresses of the nickel deposit on the density of the deposition current in the electrolyte 1M $NiSO_4$ + 0.5M NaCI + 0.7M H_3BO_3 (1) in the presence of orthoaryl sulfonate, mmol/l: 2 – 1; 3 – 7; 4 – 15; 5 – 30

The analysis of the dependence of the internal stresses of nickel on the current density at different concentrations of propynylsulfonate demonstrates that an increase in the concentration of propynylsulfonate to 7 mmol/l contributes to a decrease in internal voltages (Fig. 4, curves 2, 3), and a further increase in the concentration of the additive leads to the deposition of more intense precipitates. than those obtained from pure electrolyte (Fig. 4, curve 5).

A similar effect of propynylsulfonate is due to the fact that, on the one hand, as a result of the inclusion of sulfur in the coating, internal stresses decrease, and on the other hand, the strong adsorption of this compound, due to the presence of a triple bond in the molecule, on the surface of the metal in the electrolysis process causes a change in the structure of the deposit , which causes an increase in internal tensile stresses.

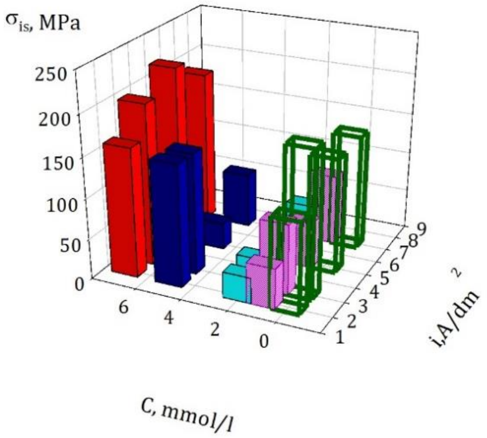

Fig. 4. Dependence of the internal stresses of the nickel deposit on the density of the deposition current in the electrolyte 1M $NiSO_4$ + 0.5M NaCI + 0.7M H_3BO_3 (1) in the presence of propynyl sulfonate, mmol/l: 2 – 1; 3 – 2; 4 – 5; 5 – 7

In the presence of small concentrations of the additive, the effect of reducing the internal tension exceeds the reverse effect. When the concentration of propynylsulfonate reaches 7 mmol/l, the decrease in internal voltages associated with the ingress of sulfur into the metal becomes insufficient to compensate for the opposite effect characteristic of acetylene derivatives.

As can be seen from the above data, sulfonic acids of unsaturated and aromatic compounds do not have the same effect on the kinetics of electroreduction of nickel and its physical and mechanical properties. The inhibitory effect of propynylsulfonate, which contains a triple bond, is superior to the inhibition effects of nickel deposition observed for orthoarylsulfonate and allylsulfonate. The precipitates obtained in the presence of these substances have different internal stresses. Thus, when choosing a composition for obtaining unstressed nickel deposits, the structure of sulfur-containing compounds should be taken into account and their concentration should be selected taking into account the technological parameters of the process and the effect on physical and mechanical properties.

Conclusions

1. It was established that allyl sulfonate and orthoallyl sulfonate in the concentration range of 1–30 mmol/l have little effect on the rate of nickel release. The inhibitory effect of propynyl sulfonate on electrodeposition of nickel turned out to be quite significant already at a concentration of 5 mmol/l. This is due to the high adsorption capacity of this substance due to the triple bond present in the molecule.

2. It is shown that allyl sulfonate and orthoallyl sulfonate reduce the internal tensile stresses of nickel when the concentration of additives increases above 7 mmol/l. A uniform reduction of internal stresses at the level of 10–20 MPa, depending on the density of the electrodeposition current, is achieved at an additive concentration of more than 15 mmol/l. It was established that the use of propynyl sulfonate as an additive that reduces the internal tensile stress of nickel deposits is limited to a concentration of 2 mmol/l. Further concentration of the sulfate electrolyte, the release of nickel from this component leads to an increase in internal tensile stresses.

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