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PROPOSED COMPOSITION OF COMPLEXES AND ION ASSOCIATES IN CITRIC ACID SOLUTIONS CONTAINING NICKEL SULFAMATE AND POTASSIUM PERRHENATE.

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The article presents an analysis of the experimental data available in the scientific literature on the conditions for obtaining nickel-rhenium alloys, promising as cathodes for electrolytic hydrogen production. The problem of searching for additional evidence of the mutual influence and interaction of nickel (II), citrate and perrhenate ions in the deposition electrolyte is formulated. For this purpose pH-metric titration of solutions containing (1) citrate ions only; (2) citrate and nickel(II) ions; (3) citrate, nickel(II) and potassium perrhenate ions – was carried out in the pH range from 1.5 to 2.0. Simultaneous release of protons associated with both the reaction of nickel with citrate to form the corresponding $NiHCit^-$ complexes and the reaction of citrate with perrhenate to form the $(ReO_4 \cdot H_2Cit)^{2-}$ complexes was shown. Since the total concentration of reacted protons in the solution with nickel (II) and perrhenate corresponds to the sum of the concentrations of nickel and perrhenate ions, this confirms that reaction of complexes of citrate/perrenate formation occurs simultaneously (in parallel) with the reaction of the formation of the nickel-citrate complexes. And further pH arising should lead to well-known formation of $NiCit_2^{4-}$ complexes, which can be associated with two ions of perrenate. Based on the analysis of date concerning the influence of the components of nickel-rhenium alloy deposition electrolytes on electrodeposition results, it was concluded that the predominant form providing the observed results concern both high current yield and high rhenium content in the alloy is an electrochemically inactive ion associate consisting of the $NiCit_2^{4-}$ complex and two perrhenate ions. Destroying in the near-cathode solution layer, it provides a periodic predominance of perrhenate ions, which can be restored without kinetic difficulties. The composition of complexes and ionic associates is proposed for a wide range of experimental data on the induced deposition of nickel-rhenium alloy coatings from citrate electrolytes, based on the quantitative ratios of the complex components in the electrolyte and the pH value.

Key words: nickel-rhenium alloys, citrate complexes, ion interaction, pH-titration, electrolyte composition, calculations.

INTRUDUCTION. Many research groups have shown a significant decrease in the overpotential of the hydrogen evolution reaction (HER) in an alkaline medium in comparison with individual alloy components on iron-rhenium subgroup metal alloys, and have confirmed the acceptable stability of the alloy properties and their high corrosion resistance. In 2008, the authors of [1] reviewed the works on the electrodeposition of rhenium and its alloys, in which, among other things, it was noted that the deposition mechanism of rhenium alloys is a subject of discussion. A number of studies since 2009 [2–7] have been aimed at studying the electrodeposition and properties of nickel-rhenium alloy coatings from citrate-containing electrolytes, as well as the proposed mechanisms of metal co-deposition in the alloy. Most of the electrolytes contained nickel sulfamate, boric acid, citrate and perrhenate ions. Addition of sulfamate to galvanic baths results in higher deposition rates, superior scattering ability, and reduced porosity and residual stresses in the coating [8]. Citrate forms stable complexes with Ni, Co, and Fe, which has a positive effect on the deposition of alloys of these elements [9]. It was found that the alloy composition is influenced by such key factors as the ratio of concentrations of the three components of the electrolyte (nickel, citrate, perrhenate ions), pH of the solution, temperature and the applied value of the deposition current density. It should be noted that with a ratio of citrate and nickel ions of 1:1 (34 mmol/l), the maximum achieved concentration of rhenium in the alloy was 54.9 at. %, with a current efficiency of no more than 60% [7]. At the same time, a detailed study of the effect of the ratio of the concentrations of the iron group metal and citrate ions showed [4] that it is in this case that the ratio of partial deposition currents Ni/Re is maximum, and to increase the concentration of rhenium in the alloy, it is necessary to increase the concentration of citrate ions in the electrolyte. The question of the existence of complexes of the putative composition ReO_4^-/$(NiCit)^-$ or ReO_4^-/$(NiCit)_2^{4-}$ in such solutions arose on the basis of data on the mutual influence of both the presence and the change in the concentration of each of the deposited components on the current efficiency and the composition of the resulting alloy. Based on the results of these studies and some earlier ones, it could be assumed that the simultaneous electrodeposition of nickel and rhenium is due to the interaction of ions of all three components in the electrolyte: perrhenate, nickel and citrate. The mechanism proposed in [2] was based on a special type of chemical precipitation in which the reducing agent is metallic Ni, formed in situ. In [3], the probable mechanism by which the addition of Ni, Fe or Co to the solution increases the deposition rate of Re is a unique type of chemical precipitation in which the reducing agent is Me0, formed *in situ*. The authors of the study [4] indicate that, based on all the signs discovered, the electrodeposition of the nickel-rhenium alloy should be recognized as induced, by analogy with the deposition of alloys of iron subgroup metals with molybdenum and tungsten. Induced co-deposition of rhenium from such rhenium-containing electrolytes proceeds without kinetic difficulties. Coatings up to 25 microns thick were obtained in 60 minutes of deposition with a current efficiency of up to 95%, and the concentration of rhenium in the alloy can reach a value greater than 90%. The assumption about the interaction of perrhenate and citrate ions with the formation of a reversible electroactive

complex citrate/perrhenate $(H_2CitReO_4)^{2-}$ was previously put forward to explain the catalytic effect of citrate ions on the reduction of ReO_4^- ions in electrolytes with medium acidity (pH = 2–5), which was demonstrated by polarography [10]. However, the authors failed to confirm the formation of such complexes by spectrophotometry either in the visible or UV spectrum. In later studies of the ternary system «nickel-citrate-perrhenate», nickel complexes with perrhenate ions were also not detected [11]. At the same time, the alloy deposition indices indicate the interaction of all three components in the electrolyte. The authors of [11] particularly emphasize the fact that the manifestation of the above phenomena requires the simultaneous presence of the three components in the electrolyte. And this fact leads to the conclusion about the existence of a precursor similar to that detected in the case of induced co-precipitation of alloys with tungsten [12–14]. But since in the case of a direct analogy it is necessary to assume the formation in solution of a complex containing 9 perrhenate molecules, which is impossible, on the basis of the fundamental role of freshly deposited nickel in the electroreduction of rhenium, discovered in works [2–6], a catalytic mechanism of alloy deposition was proposed according to which Ni^{2+} ions are reduced and deposited first and, as a strong reducing agent, promote the reduction of 7-valent rhenium in perrhenate ions to the 5-valent form in ReO^{3-} ions. Thus, the electrodeposition of the alloy is interpreted as a catalytic process in which nickel plays the role of a catalyst for the reduction of rhenium. Its concentration should not change as a result of the overall reaction. But since some amount of nickel was detected in the part of the coating consisting mainly of rhenium, it had to be stated that the process is unique and the catalyst is formed in situ as part of the reduction process.

In contrast to earlier studies [2–7], in which the deposition time of alloy coatings was minutes and hours, the initial stages of alloy deposition were studied in [9] in order to better understand and confirm the catalytic mechanism of deposition. In this work, the electrodeposition of Re-Ni alloys was studied at a deposition time of 0.05–60 s, and the authors found rhenium current efficiency values significantly exceeding 100%. The alloy current efficiency and the rhenium content in the coating decreased with increasing alloy deposition time. According to the authors, this nature of the dependence of rhenium deposition on deposition time indicates the occurrence of a parallel chemical reaction at the early stages of alloy deposition, catalyzing the deposition of rhenium into the alloy. A sharp decrease in the rate of this chemical reaction, leading to a decrease in the current efficiency and the rhenium content in the alloy, was previously interpreted by the authors as a change in the catalytic properties of the surface as the alloy is deposited. Despite the convincingness of the catalytic mechanism of alloy electrodeposition, subsequent works by these authors are aimed at clarifying the possibility of interaction between the components of the electrolyte, which determines the previously discovered interdependencies of the current yields and metal concentrations in the alloy on the ratio of component concentrations in the solution. In the study [15], the concept of weak ionic interaction in electrolytes was proposed, which was verified based on conductometry, UV-visible and Raman spectroscopy data. The dependences of the intensity ratios in the spectra related to different vibrations in perrhenate ions indicate some deformation of

these ions, and, as a consequence, the nickel-citrate complex, due to their interaction in the electrolyte. However, the formation of the ternary complex «nickel-citrate-perrhenate» was not confirmed. No evidence of perrhenate complexes with the other two components of the electrolyte was also found. However, the increasing deformation of the perrhenate ions with increasing molar ratio $[NiCit]^-/ReO_4^-$ was clearly demonstrated by Raman spectroscopy. Therefore, the weak interaction of these ions in solution is definitely observed and is strong enough both to change the shape of ReO_4^- and $[NiCit]^-$ or [NiHCit] particles in solution and to increase the alloy deposition rate. In this case, it seems to the authors that the induced interaction is a catalytic process involving the stage of simultaneous reduction of ReO_4^- and $[NiCit]^-$ or [NiHCit] particles, which mutually influence each other due to the weak interaction in solution. In [16], rhenium-nickel-citrate electrolytes of different compositions were studied by Raman spectroscopy. The peaks of two main bonds in ReO_4^-, at 972 cm^{-1} and 331 cm^{-1}, were attributed to the symmetric Re=O stretching and O-Re-O deformation, respectively. It was shown that the ratio of these intensity peaks decreases with increasing Ni ion concentration and Ni/Re ion ratio in the electrolyte. The effect of Ni-Cit ions on the vibrations of the atom in ReO_4^- denotes the deformation of ReO_4^- ions. Based on these results, the authors suggested some interaction of Ni-Cit ions with ReO_4^-, leading to their deformation. It was assumed that the interaction was weak, since no shift in fundamental positions was observed. In addition, no complexes of ReO_4^- and Ni ions were observed in citrate electrolytes using UV-V spectroscopy and conductometry methods for identifying such complexes. Recently, the authors further confirmed the proposed mechanism experimentally using aberration-corrected spherical scanning transmission electron microscopy (STEM) and atom probe tomography to characterize the structures at the atomic scale and the part-per-million atomic level 3D chemistry. A unique combination of multilayered and columnar Re-Ni structure consisting of thicker Re and thinner Ni-rich alternating layers was observed. In this work, the coatings formed during the initial stage of electrodeposition of alloy coatings were investigated by the such methods: Time-of-Flight Secondary-Ion Mass Spectrometry (TOF-SIMS) and High-Resolution X-Ray Photoelectron Spectroscopy (HR-XPS)). The observed results support the concept of a chemical reaction that decays with increasing deposition time and are consistent with the changes in the composition of the catalytic electrode surface during the deposition process. In all deposited coatings studied, both bound Re-Ni ions and individual Ni and Re ions were detected. The intensity associated with nickel increased significantly in the direction from the substrate-coating interface to the outer side of the Re-Ni alloy coating. This trend corresponds to the decrease in rhenium concentration with increasing deposition time, and small periodic increases and decreases in the intensity related to Ni ions were also observed as well as a periodic changes in the intensities related to Re and Re-Ni ion with sputtering time. The increase of the Re and Re-Ni intensities was accompanied by a decrease of Ni intensity, and vice versa. According to the SIMS and XPS results, Re-Ni, Re-NiO_x (Re-Ni-O, Re-Ni-O_2) and C_2H_4-O-Re-Ni are present on the surface, while Re-Ni is present in the bulk, indicating a significant interaction between Ni

and Re in the Re-Ni coatings. Although such interaction cannot be considered as a definitive proof of simultaneous deposition from a precursor containing ReO_4^- and complexes of the composition $(NiCit)^-$ or $(NiCit)_2^{4-}$, it is indirect evidence for this idea. In [17], the dependences of the amount of formed citrate-perrhenate complexes $(ReO_4 \cdot H_2Cit)^{2-}$ on the pH of the solution are presented. Based on the acid-base equilibria described in [17], one can assume different behavior of solutions of citric acid, citric acid with the addition of nickel sulfamate, and citric acid with the addition of nickel sulfamate and potassium perrhenate with the sequential addition of alkali, similar to the process of potentiometric titration. A quantitative assessment of the change in the pH of solutions upon the addition of 1 M KOH, according to our assumptions, could provide additional information on the processes occurring in citrate electrolytes for the deposition of coatings with the NiRe alloy.

EXPERIMENT AND DISCUSSION OF THE RESULTS. A solution of citric acid (*Cit*) containing 0.32 mol·dm^{-3} of citric acid was prepared, as well as solutions of (*Cit-Ni(II)*) and (*Cit-Ni(II)-ReO_4^-*), containing the same concentrations of citric acid (0.32 mol·dm^{-3}) and nickel sulfamate (0.1 mol·dm^{-3}) and differing in the presence of perrhenate ions in the composition. The concentration of potassium perrhenate in the *Cit-Ni(II)-ReO_4^-* solution was 0.03 mol·dm^{-3}. The composition of the solutions for potentiometric titration is given in Table 1.

Table 1.

Composition of solutions for pH-metric titration.

Solution	*C*, mol·dm^{-3}		
	$C_6H_8O_7 \cdot H_2O$	$Ni(SO_3NH_2)_2 \cdot 4H_2O$	$KReO_4^-$
Cit	0.32	–	–
Cit-Ni(II)	0.32	0.1	–
Cit-Ni(II)-ReO_4^-	0.32		0.03

The initial pH values of the *Cit-Ni(II)* and *Cit-Ni(II)-ReO_4^-* solutions were the same: 1.56 pH units, and 1.81 pH units for the *Cit* solution (16 °C). Precisely measured volumes of 1 M KOH solution were added to the solutions, mixed for 30–40 min, and the equilibrium pH values were measured. Figure 1(a) shows the dependences of the equilibrium pH values of *Cit*, *Cit-Ni(II)* and *Cit-Ni(II)-ReO_4^-* solutions after adding a 1 M KOH solution. From the obtained dependences, the pH values of all three solutions were extracted to calculate the change in the proton concentration in the *Cit-Ni(II)* and *Cit-Ni(II)-ReO_4^-* solutions in relation to the proton concentration in the *Cit* solution during titration with 1 M KOH:

$$\Delta C_{H+} = 10^{-pH(1)} - 10^{-pH(2)} \quad (1),$$

where pH(1) and pH(2) are the equilibrium values in *Cit-Ni(II)* (or *Cit-Ni(II)-ReO_4^-*) and *Cit* solutions after addition of 1 M KOH. The calculations results are shown in Fig. 1(b), changing of additional OH^- and H^+ concentration ΔC_{H+}, ΔC_{OH-} are summarized.

The release of protons into a *Cit* solution upon addition of alkali can be described by the equation:

$$H_3Cit + OH^- => H_2Cit^- + H_2O \quad (2)$$

(curve 1 in Fig. 1(a))

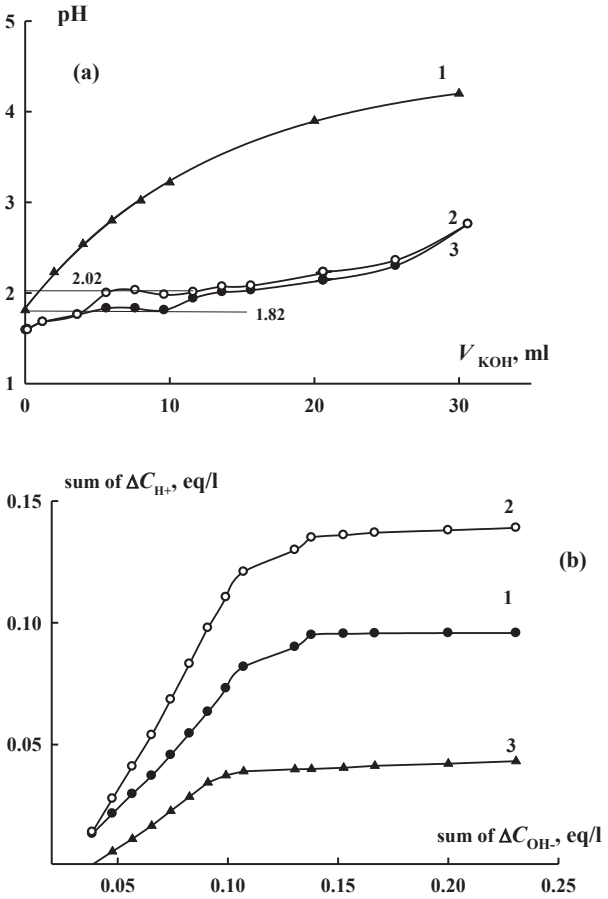

Fig. 1 – Results of pH-metric titration of solutions: *Cit* (1), *Cit-Ni(II)* (2), *Cit-Ni(II)-ReO_4^-* (3) (a) and the total change in proton concentration in solutions of *Cit-Ni(II)* (1), *Cit-Ni(II)-ReO_4^-* (2) in relation to *Cit* after addition of KOH solution; (3) – the difference between curves (2) and (1).

The release of protons into the Cit-Ni(II) solution occurs according to the well-known reaction of the formation of a protonated nickel complex.

As follows from the results presented in Fig. 1, in the presence of perrhenate ions in a solution containing citrate and nickel, another reaction occurs, accompanied by the release of a certain amount of protons.

This reaction could be represented as the addition of perrhenate ions to the NiCitH complex already present in the solution, and "weak ionic interaction" occur in the solution in accordance with the assumptions set out in [15]):

$$X\text{NiCitH} + Y\text{ReO}_4^- => Y\text{NiCitReO}_4^- + (X\text{-}Y)\text{NiCitH} + YH^+ \quad (3)$$

$$0.1\ \text{NiCitH} + 0.032\text{ReO}_4^- => 0.032\text{NiCitReO}_4^- + 0.068\text{NiCitH} + 0.032H^+ \quad (4),$$

or it can be related to the occurrence of a reaction between citrate ions and perrhenate ions that is independent of the presence of nickel ions (reactions 4, 5 [18]):

$$\text{ReO}_4^- + H_3Cit => (\text{ReO}_4\cdot H_2Cit)^{2-} + H^+ \quad (5)$$

$$\text{ReO}_4^- + H_2Cit^- => (\text{ReO}_4\cdot H_2Cit)^{2-}. \quad (6)$$

Reaction (5) can occur simultaneously with reaction (4), affecting the total number of protons released into solution and reducing the stoichiometric number of protons in accordance with reaction (4).

But, based on the parallel release of protons in these two solutions upon addition of alkali, reactions accompanied by the release of protons, as can be assumed, occur with the same citric acid ions, i.e. the formation of the corresponding amount of NiCit-ReO_4^- occurs according to reaction (3), (4). In more detail, this complex can be written as $HO\text{-}C_3\text{-}(COO\text{-})_3NiReO_4^-$ in which nickel can be bound, as an assumption, to one of the car-

boxyl groups, and the perrhenate ion – to two. It is also likely that the acidic residue of perrhenate can be bound to the alcohol group of citrate («weak ionic interaction», [15]):

$$ReO_4^- + HO\text{-}C_3\text{-}(COO^-)_3HNi + OH^- \Rightarrow$$
$$\Rightarrow ReO_4^- C_3\text{-}(COO^-)_3HNi + H_2O. \quad (7)$$

In both cases, the formation of a complex or, rather, an ionic associate in solution takes place, binding rhenium and nickel in a 1:1 ratio, as was first suggested back in 1985 by the H. Fukushima.

What conclusions can be drawn from the results presented in Fig. 1(b)? Firstly, the total concentration of protons released into the solution in both cases – for the *Cit-Ni(II)* solution and for the *Cit-Ni(II)-*ReO_4^- solution, in the first approximation, corresponds to the total concentration of the components of the solutions. This gives grounds for assuming that the corresponding reactions occur – the formation of the citrate complex and reactions (5) and/or (6). Almost all nickel ions in the solution are converted into the citrate complex, since the total concentration of reacted protons is close to 0.1 mol·dm^{-3}. Secondly, since the total concentration of reacted protons in the solution with perrhenate corresponds to the sum of the concentrations of nickel and perrhenate, this confirms that reaction (5), (6) occurs simultaneously (in parallel) with the reaction of the formation of the nickel-citrate complex. When converting the pH value of the solution containing all components to the alkaline region, the predominant citrate complex of nickel will be the $NiCit_2^{4-}$ form [1]. Thus, under the conditions of NiRe alloy precipitation (pH not lower than 5 and nickel concentration of 0.1 mol·dm^{-3}), the $NiCit_2^{4-}$ form is present in the solution in a significant amount, increasing to a maximum value with an increase in the concentration of citrate ions. At an elevated temperature, at which the alloy is precipitated, the addition of perrhenate ions with the formation of an ionic associate of the $NiCit_2^{4-}$ form and 2 ReO_4^- ions becomes more likely.

To establish the type of influence of citrate concentration and the ratio of electrolyte components on the alloy composition, the data from [2, 7, 4] were analyzed. Fig. 2 shows the dependences of the ratio of alloy component concentrations (Ni, Re) on the ratio of the concentrations of the components of the ionic components of the solution (Ni, Re, Cit). The alloys were deposited at a current of 25 [7] – 50 [2] mA·cm^{-2}.

The dependences in Fig. 2 show that the concentration of citrate ions significantly affects the ratio of components in the alloy and partial currents. It should be taken into account that an increase in the concentration of citrate ions in the nickel-citrate system leads to an increase in the proportion of the $NiCit_2^{4-}$ complex [1]. Similarly, an increase in the concentration of iron subgroup metal ions in the solution leads to an increase in the concentration of this complex. In [1] on Fig 1(b) the concentration distribution of Ni^{2+}-Cit^{3-} complexes as a function of the overall citrate concentration (0.1 M $NiSO_4$, pH = 8.0) is shown. From the data it can be concluded that sharp arising of $NiCit_2^{4-}$ concentration occurs along concentration of citrate in solution. Therefore, it is this complex, capable of adding two perrhenate ions to form the corresponding ionic associate $NiCit_2(ReO_4)_2$, that can play a significant role in the process of electrodeposition of NiRe alloys. The concentration of $NiCit_2(ReO_4)_2$ should be very high, respectively, under conventional conditions of the alloys electrodeposition.

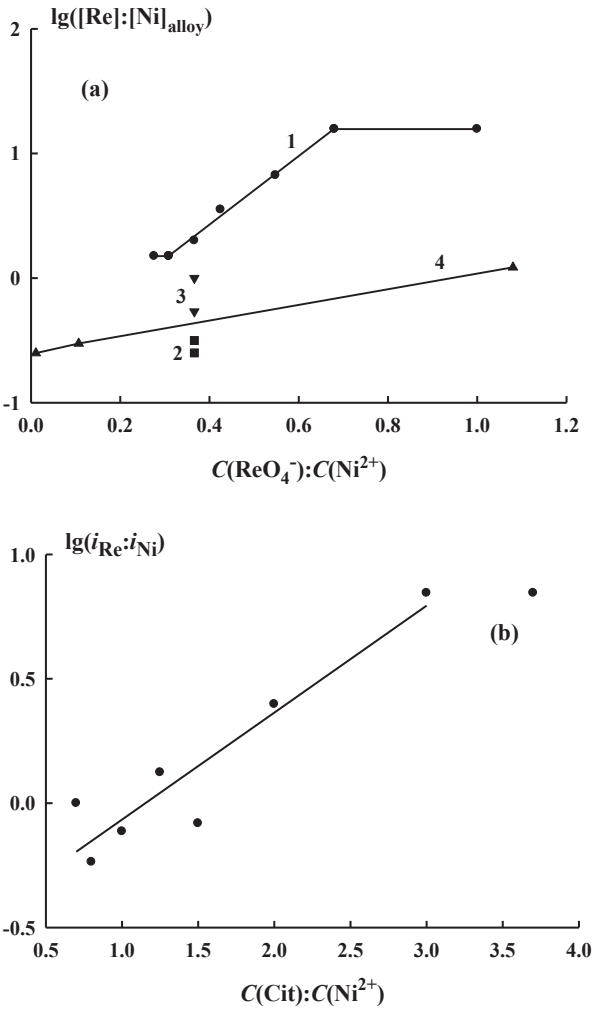

Fig. 2 – The ratio of Re to Ni concentrations in the NiRe alloy on the ratio of their ion concentrations in the solution: 1, 2, 3 [2], 4 [7]; the ratio of the concentrations of citrate ions and nickel ions: 3:1 (1), 2:1 (3), 1:1 (2, 4) (a) and the ratio of rhenium to nickel partial currents of deposition on the ratio of the concentrations of citrate ions and nickel ions [4].

Based on the concentrations of nickel and rhenium in the alloy, in accordance with the results of the study [4], the estimated concentrations of complexes and ionic associates in the electrolyte were calculated.

Figure 3 is constructed based on the data of work [4] (Fig. 3(a), averaged data) and the estimated calculation of the ratio of various complexes ($NiCitReO_4^-$; NiHCit; $NiCit^-$; $NiCit_2H_2$; $NiCit_2(ReO_4^-)_2$) in the electrolyte of the composition, mmol: ReO_4^- – 34; Ni^{2+} – 93; Cit – (93-340). Experimental results and calculation are represented for the given deposition current density of 50 mA·cm^{-2}.

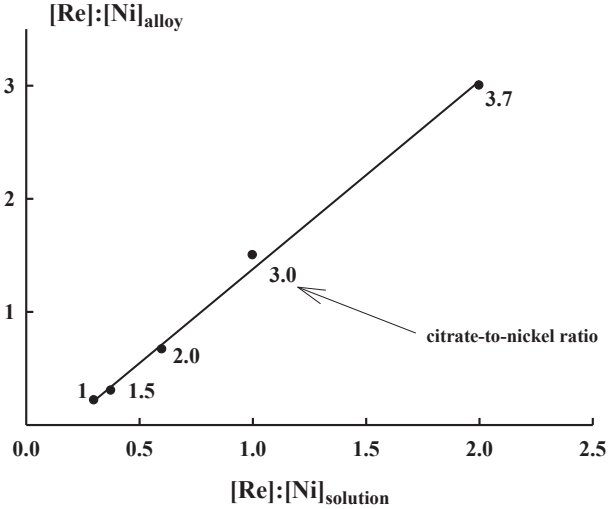

Fig. 3 – The ratio of the concentrations of the alloy components depending on their ratio in the composition of the supposed complexes contained in the electrolyte.

Examples of calculation:

1. C(Cit):C(Ni^{2+}) = 1:1 and [Re]:[Ni]$_{alloy}$ = 18:82 (point 0.22 on the Y coordinate axis).

By analogy with the equation (3) we can write:

0.034$NiCitReO_4^-$ + 0.066$NiCit^-$, and point on the X coordinate axis will be 0.034/0.066 = 0.34

2. C(Cit):C(Ni^{2+}) = 2:1 and [Re]:[Ni]$_{alloy}$ = 40:60 (point 0.67 on Y coordinate axis).

By analogy with the equation (3) we can write:

$0.034NiCitReO_4^- + 0.066NiCit^- + 0.1Cit^{3-} =>$
$=> 0.034NiCitReO_4^- + 0.023NiCit^- +$
$+ 0.043NiCit_2^{4-} + 0.057Cit^{3-}$
and point on the X coordinate axis will be 0.034/0.057 = 0.6, because of $NiCit_2^{4-}$ is electrochemically inactive form, and shouldn't be calculated.

3. $C(Cit):C(Ni^{2+})$ = 3.7:1 and $[Re]:[Ni]_{alloy}$ = 75:25 (point 3 on Y coordinate axis).

By analogy with the equation (3) we can write:
$0.034NiCitReO_4^- + 0.066NiCit^- + 0.2\ Cit^{3-} =>$
$=> 0.034NiCitReO_4^- + 0NiCit^- + 0.07\ NiCit_2^{4-} +$
$+ 0.13Cit => 0.025NiCit_2(ReO_4)_2 +$
$+ 0.005NiCitReO_4^-$
and point on the X coordinate axis will be 0.034/0.057 = 2.2.

CONCLUSIONS. The article presents an analysis of the experimental data available in the scientific literature on the conditions for obtaining nickel-rhenium alloys, promising as cathodes for electrolytic hydrogen production. The problem of searching for additional evidence of the mutual influence and interaction of nickel(II), citrate and perrhenate ions in the deposition electrolyte is formulated. For this purpose pH-metric titration of solutions containing (1) only citrate; (2)citrate and nickel(II); (3)citrate, nickel(II) and potassium perrhenate in the pH range from 1.5 to 2.0 was carried out. Simultaneous release of protons associated with both the reaction of nickel with citrate to form the corresponding NiHCit complex and the reaction of citrate with perrhenate was shown.

Based on the analysis of experimental results concerning the influence of the components of nickel-rhenium alloy deposition electrolytes on electrodeposition results, it was concluded that the predominant form providing the observed results in high current yield and rhenium content in the alloy is an electrochemically inactive ion associate consisting of the $NiCit_2^{4-}$ complex and two perrhenate ions. Destroying in the near-electrode layer, it provides a periodic predominance of perrhenate ions, which can be restored without kinetic difficulties. The composition of complexes and ionic associates is proposed for a wide range of experimental data on the induced deposition of nickel-rhenium alloy coatings from citrate electrolytes, based on the quantitative ratios of the components in the electrolyte and the pH value.

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ВІРОГІДНИЙ СКЛАД КОМПЛЕКСІВ ТА ІОННИХ АСОЦІАТІВ У РОЗЧИНАХ ЛИМОННОЇ КИСЛОТИ, ЩО МІСТЯТЬ СУЛЬФАМАТ НІКЕЛЮ І ПЕРРЕНАТ КАЛІЯ

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У статті представлено аналіз наявних у науковій літературі експериментальних даних про умови отримання нікель-ренієвих

сплавів, перспективних як катоди для електролітичного отримання водню. Сформульовано завдання пошуку додаткових доказів взаємного впливу та взаємодії іонів нікелю(II), цитрату та перренату в електроліті осадження. Проведено pH-метричне титрування розчинів, що містять (1) тільки цитрат; (2) цитрат та нікель (II); (3) цитрат, нікель (II) та перренат калію в діапазоні pH від 1.5 до 2.0. Показано одночасне виділення протонів, пов'язане як із реакцією нікелю з цитратом з утворенням відповідного комплексу $NiHCit^-$, так і з реакцією цитрату з перренатом з утворенням комплексу $(ReO_4 \cdot H_2Cit)^{2-}$. На підставі аналізу даних щодо впливу компонентів електролітів осадження нікель-ренієвих сплавів на результати електроосадження зроблено висновок про те, що переважною формою, що забезпечує результати з високим виходом за струмом і вмісту ренію в сплаві, є іонний асоціат, що складається з комплексу $NiCit_2^{4-}$ та двох перренат-іонів. Руйнування цієї електрохімічно неактивної форми в прилектродному шарі призводить до періодичного суттєвого збільшення концентрації перренат-іонів, які можуть відновлюватися без кінетичних труднощів. На підставі літературних експериментальних даних щодо індукованого осадження покриттів сплавом нікель – реній з цитратних електролітів запропоновано варіанти співвідношення комплексів та іонних асоціатів залежно від складу електроліту та значення pH.

Ключові слова: сплави нікель – реній, цитратні комплекси, іонна взаємодія, pH-титрування, склад електроліту, розрахунки.

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