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Қ. И. Сәтпаев атындағы Қазақ ұлттық техникалық зерттеу университеті

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ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК
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NEWS

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OF THE REPUBLIC OF KAZAKHSTAN
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Қазақстан Республикасы Ұлттық ғылым академиясы "ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы" ғылыми журналының Web of Science-тің жаңаланған нұсқасы Emerging Sources Citation Index-те индекстелуге қабылданғанын хабарлайды. Бұл индекстелу барысында Clarivate Analytics компаниясы журналды одан әрі the Science Citation Index Expanded, the Social Sciences Citation Index және the Arts & Humanities Citation Index-ке қабылдау мәселесін қарастыруда. Web of Science зерттеушілер, авторлар, баспашылар мен мекемелерге контент тереңдігі мен сапасын ұсынады. ҚР ҰҒА Хабарлары. Геология және техникалық ғылымдар сериясы Emerging Sources Citation Index-ке енуі біздің қоғамдастық үшін ең өзекті және беделді геология және техникалық ғылымдар бойынша контентке адалдығымызды білдіреді.

НАН РК сообщает, что научный журнал «Известия НАН РК. Серия геологии и технических наук» был принят для индексирования в Emerging Sources Citation Index, обновленной версии Web of Science. Содержание в этом индексировании находится в стадии рассмотрения компанией Clarivate Analytics для дальнейшего принятия журнала в the Science Citation Index Expanded, the Social Sciences Citation Index и the Arts & Humanities Citation Index. Web of Science предлагает качество и глубину контента для исследователей, авторов, издателей и учреждений. Включение Известия НАН РК. Серия геологии и технических наук в Emerging Sources Citation Index демонстрирует нашу приверженность к наиболее актуальному и влиятельному контенту по геологии и техническим наукам для нашего сообщества.

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STUDY OF A MICROELECTRODE MANUFACTURED OF A NEW MATERIAL – KOVAR, AND A MERCURY-FILM ELECTRODE ON THE BASIS OF THIS MATERIAL

Abstract. Studies of the processes, proceeding on the surface of the 29 NK alloy in various media (H₂SO₄, HNO₃, HCl, NaOH, NH₄Cl) have been carried out. It has been found that kovar is characterized by a more negative potential than pure nickel. This is due to the fact that in the 29 NK alloy, iron is potential-determining, the normal potential of which is much more negative than that of nickel ($E_{\text{Fe/Fe}^{2+}}^0 = -0.441\text{V}$; $E_{\text{Ni/Ni}^{2+}}^0 = -0.250\text{V}$, respectively). The course of the potentiometric curves makes it possible to conclude that in all studied acidic solutions, corrosion proceeds according to an electrochemical mechanism, which is observed for pure nickel only in the sulfuric acid solutions.

These studies have been the basis for the creation and introduction into the analytical practice of a mercury-film microelectrode based on the 29 NK alloy. In this connection, the peculiarities of the redox processes of some electrodepositive metals, in particular, mercury, on this indicator microelectrode have been studied.

Upon the reduction of mercury two sharp waves have been detected: the first one - at the potential of 0.25 V (a pre-wave), the second one - at 0.40 V. The character of the reactions proceeding upon the cathode polarization has been determined with the help of the potentiometric studies.

It has been established that the high power yields in the initial potential region are explained by the proceeding of a mercury cementation reaction due to the dissolution of the cathode material, alongside with the electrolytic reduction process.

The conducted studies allow us to come to the conclusion of expediency of using the 29 NK alloy with a mercury-film coating as an indicator electrode for the electrochemical determination of metals within the potential range of 0.2 – 0.6 V in the sulfuric acid electrolyte.

Key words: mercury–film, microelectrode, Alloy Kovar, corrosion, electrochemical determination.

Introduction. Kovar, an alloy based on the ferrous metals (29 NK), contains (mas.%): Ni - 29, Co - 18, Fe - 53, i.e. the basis of such an alloy is iron, and, therefore, one can expect that the regularities of the corrosion process will not differ significantly from those of pure iron. In most cases, iron passes into the solution in the form of iron ions Fe²⁺, which are then oxidized to Fe³⁺ in the presence of oxygen or other oxidizing agents. The corrosion rate of iron is very dependent on pH of the medium [1].

Corrosion can be caused by both chemical and electrochemical processes. The chemical corrosion is stipulated by an interaction of metals with dry gases and liquid non-electrolytes under the conditions, when moisture is absent on the metal surface and no electrode processes occur at the phase boundary. Upon the chemical corrosion of iron, metal is oxidized without the formation of an electric current circuit:



the oxide film formed on the iron surface is very loose, it does not adhere tightly to the metal surface, that is why corrosion proceeds until the complete destruction of the object.

The cause of the electrochemical corrosion is the formation of a large number of micro-galvanic pairs on the metal surface, as a result of the conjugated electrode processes, and it occurs when metals come into contact with electrolytes. The electrochemical corrosion can occur both during a contact of two metals, and in the absence of a contact with other metals. Since we are interested in the effect of acid cations and pH of the medium upon the corrosion of iron, let us consider the mechanism of electrochemical corrosion initiation, accounting for the nature of the medium. The pH index is a quantitative characteristic of acidity of the solutions. It shows the measure of activity of hydrogen ions, and is calculated as a negative decimal logarithm.

The electrochemical corrosion of metals is the result of the two simultaneous processes:

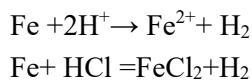
- an anodic process of metal ionization (metal oxidation);
- a cathode process of reduction of the oxidizing component of the corrosive medium (reduction of hydrogen ions or dissolved oxygen in water).

Corrosion with the release of hydrogen is possible if the potential of a hydrogen electrode is more positive than that of the metal. Corrosion with oxygen absorption is possible if the potential of an oxygen electrode is more positive than that of the metal [2]. All metals, whose equilibrium potentials are more negative than the potentials of the hydrogen or oxygen electrodes, corresponding to these conditions, can be dissolved, and the metals, whose equilibrium potentials are more positive than the latter, are not subject to corrosion.

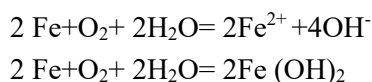
If the medium is acidic, then the depolarizers of the cathode process are hydrogen ions; in the neutral, alkaline media and in the atmospheric conditions the depolarizers of the cathode process are the molecules of oxygen, dissolved in the electrolyte [3].

Since the standard electrode potential of iron is $E^0 = -0.44$ V, iron can be subject to corrosion both with hydrogen and oxygen depolarization, depending on pH of the medium.

The process of iron corrosion in the acidic medium of the electrolyte solution proceeds with hydrogen depolarization and is represented by the equation:



The process of iron corrosion in the neutral medium proceeds with oxygen depolarization and is represented by the equation:



As a result of an analysis of the literature on the effect of various media upon the rate of iron corrosion, it has been shown that the pH range of the medium, within the limits of which the pH value influences changing the rate of the corrosion process, as well as the effect of the nature of an acidic anion upon the iron corrosion process with different pH values are not always unambiguous and it requires an additional research [3].

Besides, it is interesting to reveal the effect of the nature of acidic anions in a weakly acidic medium, most frequently occurring in the environment.

Experimental method. Voltammetric measurements were carried out on a PI-50.1.1 potentiostat, which made it possible to operate in the mode of cyclic and inversion voltammetry with different potential sweep rates. The analysis was carried out in a three-electrode cell, while stirring the solution ($V = 25$ ml) due to the electrode rotation at the rate of 900–960 rpm.

A mercury-film electrode of the 29 NK alloy served as a working electrode with an apparent surface area of 0.013 cm^2 . The voltammograms were recorded on a two-coordinate self-recording potentiometer UI-2 with the scanning rate of 100–200 mV/s. The reference electrode was the silver-chloride electrode EVL-1MZ.1, the potential of which in relation to normal hydrogen equivalent in a saturated KCl solution at 20°C is equal to 0.237 V. Pt wire was used as an auxiliary electrode. Removal of oxygen from the solution was achieved by purging it with argon for 15 minutes. The initial solutions of the studied metals were prepared from salts of chemically pure and extra-pure grades. The solutions of lower concentrations were

obtained by diluting the initial electrolytes with the background electrolytes. The background electrolytes were prepared by dissolving the corresponding salts of extra-pure grade in distilled water.

A mercury-film coating on the surface of the electrodes was applied by way of electrolysis of 0.05-0.06 M HgSO_4 solution for 3-5 minutes according to the method developed by us [4].

Experimental. Only the data, related to the manufacture of ignition electrodes of the 29 NK alloy, which can be used in metallurgy, space technology, instrument making and power engineering with sequential spraying of alumina and titanium nitride on the nickel-aluminum intermetallic sublayer, are known [5]. Unfortunately, the authors were interested in the other branches of science.

For studying the corrosion process of the 29 NK alloy, studies of the electrochemical processes, proceeding on the surface of the 29 NK alloy in various media have been carried out. The potentiometric curves for the 29 NK alloy in the studied solutions (H_2SO_4 , HNO_3 , HCl , NaOH , NH_4Cl) are presented in figure 1 a,b.

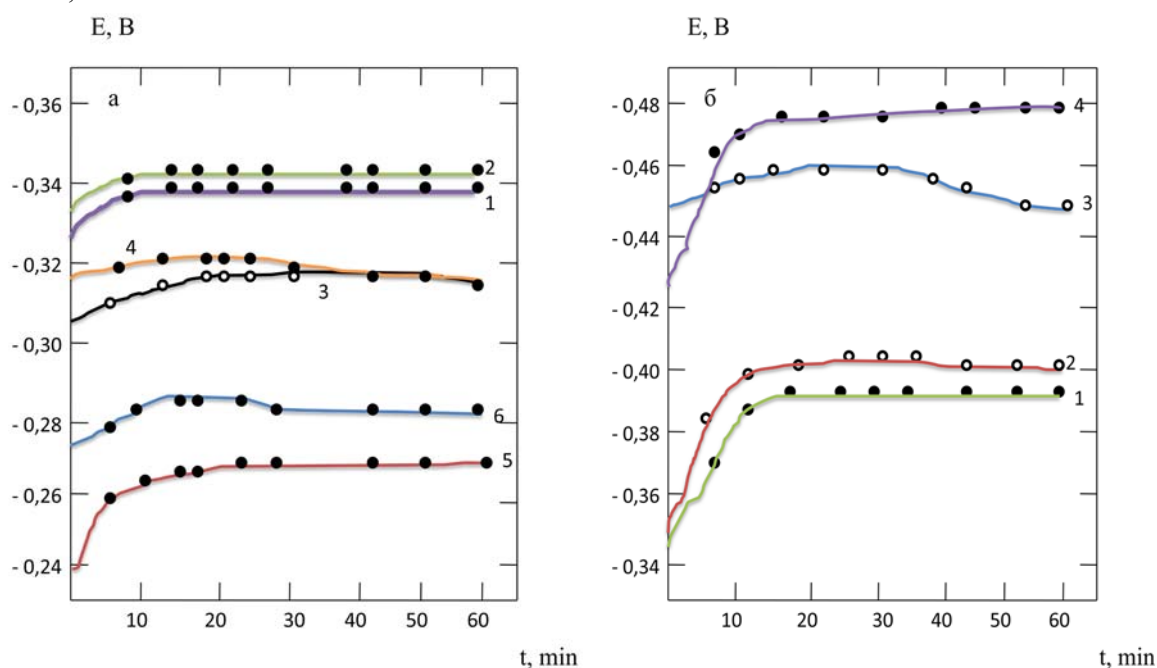


Figure 1 – Corrosion resistance of a kovar electrode in various media:

a) 1.2 - H_2SO_4 ; 3.4 - HCl ; 5.6 - HNO_3 ; б) 1.2 - NH_4Cl ; 3.4 - NaOH ; C, mol/l: 1, 3, 5 - 0.1; 2, 4, 6 - 0.5

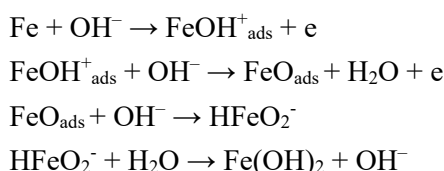
As is seen from the presented data, kovar is characterized by a more negative potential than pure nickel, which is connected with the fact that in the 29 NK alloy iron is potential-determining, the normal potential of which is much more negative than that of nickel ($E_{\text{Fe}/\text{Fe}}^0 = -0.441$ V; $E_{\text{Ni}/\text{Ni}}^0 = -0.250$ V, respectively).

In this connection it follows, that the corrosion process in the alloy will proceed due to iron dissolution. In our opinion, the course of the potentiometric curves allows us to conclude that in all studied acidic solutions, corrosion proceeds according to the electrochemical mechanism, which for pure nickel is observed only in the sulfuric acid solutions. This difference in the behavior of kovar and pure nickel, for which the mixed (HCl) and chemical (HNO_3) mechanisms of corrosion are marked, is explained by the electrochemical mechanism, because it is facilitated due to the local corrosion. In the latter case, the release of hydrogen occurs on a metal with a lower overvoltage value – nickel; and iron, being a more electronegative metal, dissolves and supplies its ions to the solution [6].

The mixed mechanism of the corrosion process of a kovar electrode is also preserved in a weakly acidic medium, as indicated by the course of the E, τ curves (figure 1b, curves 4, 5). The two characteristic sections are distinguished on the potentiometric curves. Herewith, on the first of them corrosion proceeds according to the mixed mechanism, and on the second one, where a stable state with a slight shift of potential to the positive direction is marked, corrosion proceeds according to the electrochemical mechanism.

The course of the potentiometric curves of kovar in the alkaline solutions is somewhat different, with an increase in the concentration of alkali a shift of the potential to the electronegative direction is observed. In this case, the electrode potential reaches a certain stable value only after 20 minutes of contact with the electrolyte. Herewith, the transition of the kovar electrode to the passive state is possible.

Our results and their explanation comply with the data of Frumkin et al. [7, 8], who have found that the dissolution rate of iron in the alkaline solution is higher than that in the acidic one, and it increases in proportion to an increase in the concentration of hydroxyl ions $[\text{OH}^-]^2$ [9]. The authors have developed an idea of a multi-stage electrochemical corrosion process, and for the case of dissolving Fe in NaOH, the following process scheme has been proposed:



The second stage of the process is limiting, therefore, the corrosion rate of anodic iron dissolution is described by a kinetic equation [9]:

$$I_c = k_2[\text{FeOH}_{\text{ads}}^+][\text{OH}^-]\exp[(1-\alpha)FE/RT] = k[\text{OH}^-]^2\exp[(1-\alpha)FE/RT]$$

(α – an electron transfer coefficient in the cathode process).

The second order of the reaction for OH – ions has been confirmed in their further works. According to the above scheme, the aqua-hydrocomplex of iron $\text{FeOH}_{\text{ads}}^+$, adsorbed on the surface of an iron electrode, acts as a corrosion catalyst, and in the slow stage a simultaneous transfer of the two electrons takes place. The considered regularities of the corrosion process of pure iron in the alkaline medium, in our opinion, hold also true for its alloy, in which it is the base metal with the most electronegative potential.

Thus, based on the obtained data, a conclusion may be drawn that the acidic solutions (H_2SO_4 , HNO_3) and weakly acidic solutions (NH_4Cl) solutions are most suitable as the background electrolytes upon using an indicator kovar electrode in the method of inversion voltammetry (IVA).

Our work presents the studies of a new material as an indicator electrode and the development of methods for determining the ultramicrogram quantities of heavy metals by the method of inversion voltammetry. Voltammetry, on the whole, has shown remarkable capabilities, for example, for highly sensitive ($10^{-8} - 10^{-9}$ mas.%) determination of impurities. In all sectors of the national economy and various environmental services there is a high need for analytical control of substances in very small doses. In this connection, one of the most urgent tasks is the development of highly sensitive methods for determining a wide range of elements in ultra-small quantities.

In recent years the number of publications, devoted to the inversion methods, has been steadily increasing. This is due to the emergence of new devices, as well as the transition to the application of mercury-film and solid electrodes. In the review papers and books on the electrochemical inversion analysis, published so far, the emphasis has been made on the works, dedicated to a classical mercury electrode.

Over the last years, the mercury-film electrodes (MFE) are most commonly used. These include the electrodes, obtained by applying a uniform mercury film on an inert electrically conductive substrate [10]. The advantages of MFE are as follows: stability, simplicity and low cost, as well as a possibility of use them in the flow systems. An important advantage of a film electrode is a possibility of electrochemical cleaning, which allows it to be used repeatedly. For studying the processes of electro-oxidation and electro-reduction of substances, reducing the detection limit, improving the accuracy and reproducibility of the method, it is important to forecast the analytical properties of indicator electrodes and to select the most promising ones of them. The creation and introduction into the analytical practice of the mercury-film microelectrodes, wherein metals and alloys, weakly interacting with mercury, are also used as the base material, have necessitated studying the peculiarities of the redox processes, using the example of some electropositive metals, in particular, that of mercury.

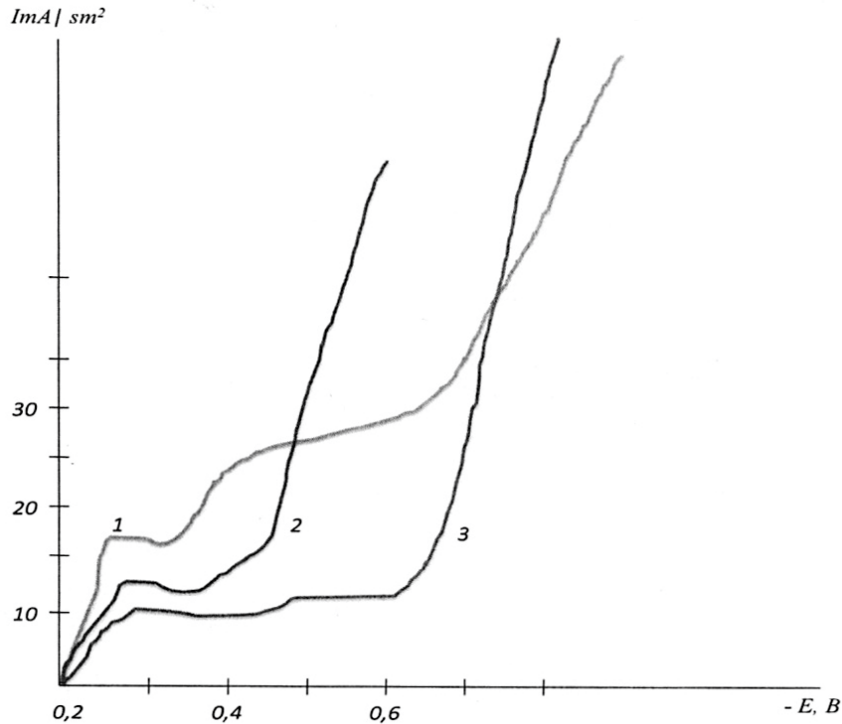
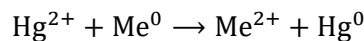


Figure 2 – Polarization curves of double-charged mercury reduction in the sulfuric acid electrolyte on a mercury-film electrode, based on the 29 NK alloy: 1 – 10⁻⁴ mol/l; 2 – 10⁻⁵ mol/l; 3 – 10⁻⁶ mol/l

The 29 NK alloy (kovar), proposed by us for the first time as a promising material for manufacturing an indicator microelectrode with a mercury-film coating, has been chosen as a study object.

The cathode polarization curves, recorded on the 29 NK, are shown in figure 2.

As a result, it has been found that in the pre-wave potential region on the 29 NK alloy the power yield (VT) of the process of mercury reduction exceeds 100%. With the potentials, corresponding to the limiting current of the main wave, VT approaches 100%. A further increase in the current leads to a decrease in VT, related to the release of hydrogen, which is well seen on the basis of the comparison with the background electrolyte curve. The high power yields in the initial potential region are explained by a reaction of mercury cementation due to the dissolution of the cathode material, alongside with the electrolytic reduction process:



This is evidenced by the results of the specially conducted experiments. A sample of the material has been kept in the working electrolyte without the current for 60 minutes, after which the quantity of the recovered mercury has been determined, and the values of the corresponding cementation currents have been calculated: $i_{cem} = i_{ox}$, where i_{cem} and i_{ox} , are the currents of mercury cementation and substrate oxidation, respectively.

The cementation current, which determines namely the corrosive current, largely depends upon the ion concentration of double-charged mercury throughout the polarization curve. It becomes clear when considering the partial curves of ions and oxidation of the material - the substrate. For the 29 NK alloy, it corresponds to the value of $2.6 \cdot 10^{-3}$, mA/cm² and satisfactorily agrees with the experimentally found values of the limiting currents of the main cathode wave (i).

Reduction of double-charged mercury on the surface of the 29 NK alloy by way of cementation

Material	E_{st}, V	mHg, mg	$i_{cem} 10^{-3}, mA/cm^3$
29 NK (kovar)	- 0.12	5.12	2.32
	-0.20	4.57	2.65

For the period of the alloy polarization, upon recording the cathode curves, the electrode surface does not have time to be covered completely with a mercury film. Due to this, the potentials of the beginning of hydrogen release in the working and background electrolytes are the same and depend on the nature of the substrate (figurer 3).

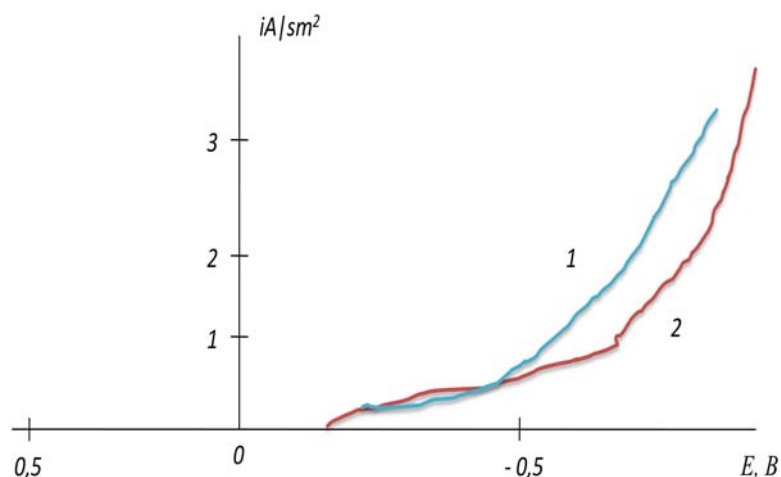


Figure 3 – Curves in the background (1) and working (2) electrolytes on the 29 NK alloy

Conclusions. Thus, the conducted studies allow us to draw a conclusion of expediency of using the 29 NK alloy with a mercury-film coating as an indicator electrode for the electrochemical determination of metals within the potential range of 0.2 – 0.6 V in the sulfuric acid electrolyte. The essential difference of the proposed electrode material from the indicator mercury-film electrode on a nickel substrate consists in the fact that the content of the alloy component Ni, relatively well-soluble in mercury, makes up only 29%. This property of the alloy makes it possible to practically exclude the formation of an intermetallic compound NiHg₄ and other chemical processes, related to the cementation reaction, proceeding in the systems under consideration.

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ЕРІТІНДІ КОВАР ЖӘНЕ СЫНАП-ПЛЕНКАЛЫ МИКРОЭЛЕКТРОДТЫ ЖАҢА МАТЕРИАЛДАН ӨНДЕЛГЕН ЗАТТАР НЕГІЗІНДЕ ЗЕРТТЕУ

Аннотация. 29НК қорытпасының бетінде әр түрлі ортада (H₂SO₄, HNO₃.HCl, NaOH, NH₄Cl) өткен процестерді зерттеу жұмыстары жүргізілді. Таза никелге қарағанда коварға теріс потенциал тән екендігі анықталды. Бұл 29НК қорытпасында потенциал анықтаушы темір болып табылады, оның қалыпты потенциалы никельге қарағанда терістеу (сәйкесінше E⁰_{Fe/Fe} = -0.441В; E⁰_{Ni/Ni} = -0,250 В) болуына байланысты. Потенциалөлшеуші қисықтардың жолы, барлық зерттеулер бойынша тотбасу процесі электрохимиялық механизммен өтетіндігі ал, никель үшін тек күкірт қышқылы ерітіндісінде жүретіндігін көрсетті.

Бұл зерттеулер 29НК ковар ерітіндісі негізіндегі сынап-пленкалы электродтардың аналитикалық практикасын ендірумен қалыптастыруға негіз болды. Осыған байланысты кейбір оң электрлі металлдардың, сынап мысалында осы индикаторлы электродтарында тотығу-тотықсыздану процесстерінің ерекшеліктері анықталды.

Сынапты қалпына келтіруде анық екі толқын көрінді: 1 – 0,25 В (алдыңғы толқын) потенциалында, 2 – -0,40 В. Реакциялардың қасиеті, катодты поляризациядан өту жолы потенциметриялық зерттеулер көмегімен анықталды.

Катод материалдарының еруі есебінен сынаптың цементтелуі реакциясы электрлі қайта қалпына келу процесі потенциалдың алғашқы аумағында жоғары ток шығуы қатары арқылы жүретіндігімен түсіндірілетіні айқындалды.

Жүргізілген зерттеулер 29НК ерітіндісі сынап-пленкалы жабынды индикатор электрод ретінде металдарды электрохимиялық анықтауда – 0,2–0,6 В интервал аралығында күкіртті қышқыл электролитінде пайдалану ұсынылады.

Түйін сөздер: сынап-пленкасы, микроэлектрод, ковар ерітіндісі, тотықтану, электрохимиялық анықтау.

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ИССЛЕДОВАНИЕ МИКРОЭЛЕКТРОДА ИЗ НОВОГО ВЕЩЕСТВА – СПЛАВА КОВАР И РТУТНО-ПЛЕНОЧНОГО ЭЛЕКТРОДА НА ОСНОВЕ ЭТОГО МАТЕРИАЛА

Аннотация. Были проведены исследования процессов, проходящих на поверхности сплава 29НК в различных средах (H₂SO₄, HNO₃.HCl, NaOH, NH₄Cl). Установлено, что для ковара характерен более отрицательный потенциал, чем для чистого никеля. Это связано с тем, что в сплаве 29НК потенциалопределяющим является железо, нормальный потенциал которого значительно отрицательнее никелевого (соответственно E⁰_{Fe/Fe} = -0,441В; E⁰_{Ni/Ni} = -0,250 В). Ход потенциметрических кривых позволяет сделать заключение, что во всех изученных кислых растворах коррозия протекает по электрохимическому механизму, который для чистого никеля наблюдается только в растворах серной кислоты.

Эти исследования явились основой для создания и внедрения в аналитическую практику ртутно-пленочного микроэлектрода на основе сплава ковар 29НК. В связи с этим были изучены особенности окислительно-восстановительных процессов на этом индикаторном микроэлектроде некоторых электроположительных металлов, в частности ртути.

При восстановлении ртути выявлены две четкие волны: 1-ая – при потенциале – 0,25 В (предволна), 2-ая при – 0,40 В. Характер реакций, протекающих при катодной поляризации выяснен с помощью потенциметрических исследований.

Установлено, что высокие выходы по току в начальной области потенциалов объясняются протеканием наряду с процессом электролитического восстановления реакции цементации ртути за счет растворения материала катода.

Проведенные исследования позволяют сделать вывод о целесообразности использования сплава 29НК с ртутно-пленочным покрытием в качестве индикаторного электрода при электрохимическом определении металлов в интервале потенциалов – 0,2–0,6 В в серноокислом электролите.

Ключевые слова: ртутная – пленка, микроэлектрод, сплав ковар, коррозия, электрохимическое определение.

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