ҚАЗАҚСТАН РЕСПУБЛИКАСЫ ҰЛТТЫҚ ҒЫЛЫМ АКАДЕМИЯСЫНЫҢ

Д.В. Сокольский атындағы «Жанармай, катализ және электрохимия институты» АҚ

ХАБАРЛАРЫ

ИЗВЕСТИЯ

НАЦИОНАЛЬНОЙ АКАДЕМИИ НАУК РЕСПУБЛИКИ КАЗАХСТАН АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского»

NEWS

OF THE ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry»

SERIES CHEMISTRY AND TECHNOLOGY

1 (445)

JANUARY - FEBRUARY 2021

PUBLISHED SINCE JANUARY 1947

PUBLISHED 6 TIMES A YEAR



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«ҚР ҰҒА Хабарлары. Химия және технология сериясы».

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Меншіктенуші: «Қазақстан Республикасының Ұлттық ғылым академиясы» Республикалық қоғамдық бірлестігі (Алматы қ.).

Қазақстан Республикасының Ақпарат және қоғамдық даму министрлігінің Ақпарат комитетінде 29.07.2020 ж. берілген № KZ66VPY00025419 мерзімдік басылым тіркеуіне қойылу туралы куәлік.

Тақырыптық бағыты: химия және жаңа материалдар технологиясы саласындағы басым ғылыми зерттеулерді жариялау.

Мерзімділігі: жылына 6 рет.

Тиражы: 300 дана.

Редакцияның мекенжайы: 050010, Алматы қ., Шевченко көш., 28; 219, 220 бөл.; тел.: 272-13-19; 272-13-

http://chemistry-technology.kz/index.php/en/arhiv

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Редакцияның мекенжайы: 050100, Алматы қ., Қонаев к-сі, 142, «Д. В. Сокольский атындағы отын, катализ және электрохимия институты» АҚ, каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Типографияның мекенжайы: «NurNaz GRACE», Алматы қ., Рысқұлов көш., 103.

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«Известия НАН РК. Серия химии и технологий».

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Собственник: Республиканское общественное объединение «Национальная академия наук Республики Казахстан» (г. Алматы).

Свидетельство о постановке на учет периодического печатного издания в Комитете информации Министерства информации и общественного развития Республики Казахстан № **KZ66VPY00025419**, выданное 29.07.2020 г.

Тематическая направленность: *публикация приоритетных научных исследований* в области химии и технологий новых материалов.

Периодичность: 6 раз в год. Тираж: 300 экземпляров.

Адрес редакции: 050010, г. Алматы, ул. Шевченко, 28; ком. 219, 220; тел. 272-13-19; 272-13-18,

http://chemistry-technology.kz/index.php/en/arhiv

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Адрес редакции: 050100, г. Алматы, ул. Кунаева, 142, АО «Институт топлива, катализа и электрохимии им. Д.В. Сокольского», каб. 310, тел. 291-62-80, факс 291-57-22, e-mail:orgcat@nursat.kz

Адрес типографии: «NurNaz GRACE», г. Алматы, ул. Рыскулова, 103.

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News of the National Academy of Sciences of the Republic of Kazakhstan. Series of chemistry and technology.

ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Owner: RPA "National Academy of Sciences of the Republic of Kazakhstan" (Almaty).

The certificate of registration of a periodical printed publication in the Committee of information of the Ministry of Information and Social Development of the Republic of Kazakhstan No. KZ66VPY00025419, issued 29.07.2020.

Thematic scope: publication of priority research in the field of chemistry and technology of new materials

Periodicity: 6 times a year. Circulation: 300 copies.

Editorial address: 28, Shevchenko str., of. 219, 220, Almaty, 050010, tel. 272-13-19; 272-13-18,

http://chemistry-technology.kz/index.php/en/arhiv

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Editorial address: JSC «D.V. Sokolsky institute of fuel, catalysis and electrochemistry», 142, Kunayev str., of. 310, Almaty, 050100, tel. 291-62-80, fax 291-57-22, e-mail: orgcat@nursat.kz

Address of printing house: «NurNaz GRACE», 103, Ryskulov str, Almaty.

NEWS

OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN

SERIES CHEMISTRY AND TECHNOLOGY

ISSN 2224-5286

Volume 1, Number 445 (2021), 38 – 46

https://doi.org/10.32014/2021.2518-1491.5

UDC 541.135.7:691.737 IRSTI: 31.15.33

R. N. Nurdillayeva¹, N. Sh. Abdilda¹, A. B. Bayeshov²

¹Khoja Akhmet Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan;
 ²D. V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan.
 E-mail: raushan.nurdillayeva@ayu.edu.kz

ELECTROCHEMICAL BEHAVIOR OF CUPRONICKEL ELECTRODE IN ACIDIC MEDIA

Abstract. The electrochemical properties of the cupronickel electrode polarized by an alternating current in an aqueous solution of hydrochloric acid were studied for the first time. The electrochemical dissolution of cupronickel was carried out in a polarization mode with a frequency of 50 Hz in pairs with a titanium electrode. The current efficiency of dissolution of Cu-Ni alloys dependence on the current density at the titanium (20-120 kA/m²) and cupronickel (200-1200 A/m²) electrodes, the concentration of a hydrochloric acid solution (0.5-5.0 M), the electrolysis duration (0.5-1.75 h) and the alternating current effect (50-300 Hz) were considered. It was observed that the current efficiency of the alloy dissolution decreases linearly with increasing current density at the cupronickel electrode, while the current density at the titanium electrode passes through a maximum value at 60 kA/m². The dependence of the alloy dissolution on the acid concentration was studied, and the reaction order was calculated. The reaction orders for the formation of copper (I) and nickel (II) ions accounted for 0.95 and 0.85, respectively. As the frequency of the alternating current increased, the current efficiency of the cupronickel electrode dissolution changed significantly. It has been shown that high current frequencies do not provide the required anodic half-cycle duration for the oxidation reaction of the metals, as the periods change very rapidly. It was found that electrolysis is effective at a frequency of 50 Hz AC. It was observed that the dissolution rate of the copper-nickel alloy increases with increasing solution temperature. It was found that the dissolution of cupronickel in an aqueous solution of hydrochloric acid by the temperature-kinetic method takes place in the diffusion-kinetic mode. Ideally, the current efficiency values were 59% for Cu (I) ions and 15% for Ni (II) ions.

Key words: cupronickel, Cu-Ni alloy, alternating current, titanium electrode, hydrochloric acid, electrolysis, current density, current efficiency.

Cupronickel is a copper-nickel alloy, usually containing 5-30% nickel, 70-95% copper, and a small amount of 0.8% iron, 1% manganese. A special property of cupronickel is its corrosion resistance to seawater and dry gas atmosphere. Cupronickel contains nickel, it exhibits mechanical strength. The higher the amount of nickel, the higher its strength. Cupronickel alloy containing 30% Ni, 0.8% Fe, 1% Mn, and 68.2% Cu is used as condenser pipes [1], as heat exchanger pipes in the cooling system of nuclear power plants [2]. Cupronickel B10 is an important material used in aviation due to its good electrochemical and mechanical properties (corrosion resistance) [3].

Currently, due to the special mechanical properties of alloys based on Cu-Ni, the study of physicochemical and electrochemical properties of the cupronickel electrode is of interest. The corrosive properties of cupronickel have been studied in a number of scientific papers [1-6]. Corrosive properties of cupronickel alloy studied in permanganic acid [2] and in the aqueous solution of sodium chloride [3-5], in artificial seawater [6,7], and in concentrated LiBr solutions [8]. The corrosion behaviour of cupronickel alloys (Cu 70, Ni 30) is considered in permanganate under acidic conditions. As a result of cyclic polarization, it has been shown that in permanganic acid there is uniform corrosion without pitting (point corrosion) [2].

The corrosive properties of cupronickel alloys containing Cu-Ni (90-10) and Cu-Ni (70-30) have been studied comparatively in brine solutions (NaCl). Cu-Ni (90-10) alloy in 3.5% aqueous solution of NaCl is more corrosion resistant than alloy Cu-Ni (70-30) [1]. The effects of various parameters (temperature, chlorides, carbon dioxide, oxygen) affecting the corrosive properties of Cu-Ni (90-10) alloys in 3.5% NaCl aqueous solution were observed by the electrochemical method [5]. The effect of aluminium on the corrosion action and mechanical properties of Cu-Ni-Fe-Mn alloys in seawater is considered and significant changes in the corrosive and mechanical properties of alloy Cu-7Ni-xAl-1Fe-1Mn are shown [6]. The corrosion resistance of cupronickel (Cu 90-Ni 10) in seawater is provided. During the corrosion process, it was found that CuO, Cu₂O, and Cu(OH)₂ in the corrosion layer of the alloy are converted into CuCl, CuCl₂, and Cu₂(OH)₃Cl [7]. The electrochemical corrosion properties of various copper-based alloys (Cu-10Ni, Cu-Al) in concentrated solutions of LiBr and the corrosion mechanism of cupronickel alloys were studied and discussed [8].

The electrochemical properties of cupronickel alloy are considered in H₂SO₄ acid solution [9] and aqueous LiBr solution [10]. Anodic dissolution of cupronickel alloys in an acidic medium in the presence of electrically active forms of oxygen was studied. Under optimal conditions, at a potential of 0.3 V and a current density of 2.54 mA/cm², a large amount of active oxygen is formed in the process of oxidation, i.e. dissolution [9]. The electrochemical behaviour of the alloy Cu-Ni (70-30) was studied in different concentration of LiBr solution from 0.1 up to 9.0 M. It was found that at low values of the anodic potential (-200V) there is passivation current due to the formation of a doped Cu₂O film involving surface enriched in nickel [10]. The electrochemical properties of Cu metal and Cu-10Ni-10Zn alloys in acidic, neutral, and alkaline solutions were compared. The corrosion rate of the alloy is relatively high in neutral and alkaline solutions in acidic solutions. It was found that the corrosion rate of Cu metal is high in chloride solutions [11]. There was considered thermodynamics of chemical and electrochemical stability of copper-nickel alloys. The chemical stability of cupronickel alloys in the air was determined by nickel, and a phase diagram of the Cu-Ni-O system was constructed [12].

It is known that the use of alternating current accelerates the dissolution of metals prone to passivation, including copper and nickel. The electrochemical properties of copper and nickel in the individual metal states have been studied in several works [13-17]. The mechanism of formation of copper powders in the anodic and cathodic half-periods of industrial AC at a frequency of 50 Hz is considered in sulfuric acid. During electrolysis, round metal powders with a current density of 4000 A/m² of 1-1.5 microns were formed. It was found that ultra disperse copper powders are formed at high current densities [13]. The electrochemical properties of the copper electrode were studied by anodic polarization in an aqueous solution of potassium bromide. The effective value of the formation of copper (I) bromide at the current density of 200 A/m² of the copper electrode reached 72.1% [14]. The electrochemical dissolution of copper in hydrochloric acid was studied. It shows the formation of a film of intermediate compounds of Cu (I) ions during the process, depending on the stability of the chloride complexes Cu (I) [15]. Electrochemical deposition of copper in a solution of sulfuric acid at different potential values at alternating current is considered [16].

Electrochemical dissolution of nickel electrodes in an acid medium, in an aqueous solution of H₂SO₄ acid, was carried out at polarized alternating current. The effect of basic electrochemical parameters on the formation of nickel (II) ions is studied. Rapid dissolution of nickel was observed between potentials - 160 V and + 200 V [17]. The dissolution of nickel in 100 g/L sulfuric acid is studied by cyclic voltammetry. The research data revealed that anode nickel oxide films are destroyed during cathodic polarization as a result of simultaneous redox processes and chemical dissolution of oxides in the electrolyte [18]. Pulse dissolution properties of nickel in rotational processes have been studied, and it has been shown that the dissolution of nickel depends on the rotational speed and that nickel can be efficiently processed at low rotational speeds [19].

The dissolution behaviour of brass in sodium phosphate solutions [20] and the electrochemical properties of the constantine in hydrochloric acid solution [21] polarized by the alternating current are considered. In both research effect of alternating current of 50 Hz parameters on the dissolution of the Cu- based alloys were studied. During electrolysis, optimal parameters of electrochemical dissolution Cu-Zn and Cu-Ni alloys in an aqueous solution were determined [20-21]. Anodic selective dissolution of copper alloys (Cu 65-Ni 35, Cu 35-Ni 65, Cu 63-Zn 37, Cu40-Zn37, Cu50-Al50) in a mixture of

carbonates and chlorides of alkali metals were studied. It was shown the possibility of change of the binary alloy dissolution by changing the kinetic parameters of electrolysis. Due to copper is an electrostatic component in copper chloride alloys, it was found that during dissolution of alloy a nickel-enriched layer is formed on the surface of the alloys galvanostatic mode [22]. The corrosion electrochemical behaviour of Cu based alloys in high-temperature salt electrolytes is studied in the galvanostatic mode. It was found that L63 brass samples have the smallest pore diameter in salt melts thus is the most promising copper-based alloy for the production of nanomaterials [23].

The literature review showed that the electrochemical properties of Cu-Ni based alloys have not been fully studied, although the electrochemical properties of copper and nickel electrodes polarized by alternating current in the individual metal state in aqueous media [12-19] have been studied in detail.

In the presented work the electrochemical dissolution behaviour of an electrolytic polarized cupronickel electrode in an aqueous solution of hydrochloric acid was studied for the first time.

Methods and materials. The electrochemical dissolution behaviour of the cupronickel electrode was studied in the mode of electrolysis of alternating current at industrial frequencies. The main experiments were performed in a 100 ml glass electrolyser without separating the electrode spaces. A plate of cupronickel (containing 67.5% Cu, 27.5% Ni) was used as a working electrode and a titanium wire with a small surface as an auxiliary electrode. The B-24 unit was used as an AC source in the electrochemical circuit. The deviation of the AC sinusoid was determined by using a universal oscillograph C-1-77. In the study, a sound generator GEM was used to obtain different frequencies of alternating current. The amount of copper (II) and nickel (II) ions formed as a result of electrolysis was determined by iodometric, and photocolorimetric methods [24, 25].

During the experiment, the electrochemical dissolution of cupronickel was carried out in combination with a titanium electrode. Preliminary studies have shown that when two cupronickel electrodes are polarized by alternating current, the main processes involved do not take place. When the cupronickel electrode was paired with a titanium electrode, it was observed that the alloy dissolves by forming copper (I), copper (II) and nickel (II) ions. This can be explained by the valve property of the titanium electrode, i.e. the current-correcting property. The valve property is considered to be characteristic of asymmetric resistance, which is mainly due to the formation of an oxide layer that prevents the passage of electricity at the titanium electrode during the anode layer that prevents the passage of electricity at the titanium electrode during the anode half-period [26]. During the cathode half-period, hydrogen is released at the titanium electrode. In this case, the dissolution of the anchored electrode occurs in the anode half-cycle. The dissolution current efficiency (CE) of the cupronickel electrode was calculated for the anode half-cycle of alternating current.

The effects of current densities, electrolyte concentration, solution temperature, electrolysis duration, and AC frequency on the dissolution of Cu-Ni alloys in the alternating current mode were studied. For comparison, the electrochemical dissolution of the alloy was carried out in the mode of direct current electrolysis. Insignificant dissolution of direct current polarized cupronickel electrode was found.

Results and discussion. Dissolution of a cupronickel electrode in a hydrochloric acid aqueous solution polarized with the alternating current can proceed according to the reactions:

$$Cu^0 + Cl^- - e^- \leftrightarrow CuCl E^0 = +0.137 B \tag{1}$$

$$CuCl - e^{-} \leftrightarrow Cu^{2+} + Cl^{-}E^{0} = +0,538 B$$
 (2)

$$Ni^0 - 2e^- \leftrightarrow Ni^{2+} E^0 = -0.250 B$$
 (3)

The formation of copper ions proceeds mainly according to reaction (1) since the rate of reaction (2) is much lower than the first. This is mainly due to the stability of monovalent copper ions in hydrochloric acid solutions, due to the formation of chloride complexes (reactions 4-6), as well as the disproportionate reaction [20]:

$$CuCl + nCl^{-} \rightarrow CuCl_{n+1}^{n-}$$
(4)

$$CuCl + HCl \rightarrow H[CuCl_2]$$
 (5)

$$CuCl + 2HCl \rightarrow H_2[CuCl_3]$$
 (6)

Nickel ions in solution react with chlorine ions to form nickel (II) chloride:

$$Ni^{2+} + 2Cl^{-} \rightarrow NiCl_{2} \tag{7}$$

There was studied the effect of titanium electrode current density on the current efficiency of electrochemical dissolution of a cupronickel electrode polarized by 50 Hz frequency alternating current (figure 1). It is found that when the current density at the titanium electrode is increased from 20 kA/m² to 120 kA/m², the current efficiency of the cupronickel electrode passes through the maximum. However, an increase in the current density at the titanium electrode did not significantly affect the current efficiency of Ni (II) ions. When the current density value is increased up to 60 kA/m², the CE values of Cu (I) and Cu(II) ions increased from 41% to 59% and from 20.5% to 29.5%, respectively, and the current density decreased at 120 kA/m². The increase in current efficiency can be explained by the formation of an oxide layer on the surface of the titanium electrode with valve, i.e. semiconductor properties. If the current density at the titanium electrode is increased further, a decrease in the current efficiency of the cupronickel electrode dissolution is observed. This is due to the formation of titanium oxide layers of different compositions at different current densities, and changes in their valve properties.

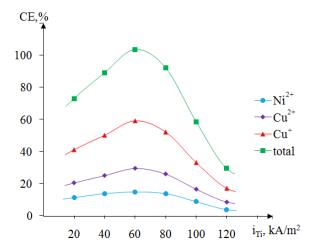


Figure 1 – Effect of titanium electrode current density on the efficiency of the cupronickel electrode dissolution polarized with alternating current: i_{CuNi} = 400 A/m², [HCl] = 0,5 M, τ = 0,5 h.

The reason for the fact that the dissolution of copper-nickel alloys exceeds 100% of the total CE can be explained by the fact that the copper in the alloy is electrochemically dissolved in hydrochloric acid solutions, along with electrochemical dissolution:

$$Cu + Cu^{2+} \rightarrow 2Cu^{+} \tag{8}$$

As a result, copper powders, and cupronickel electrodes formed on the surface of the electrode form a galvanic couple [20], which facilitates the transfer of nickel from the alloy to the solution. These processes lead to a high total CE (CE 100%).

0.5 hours without polarization of the nickel electrode. When placed in an aqueous solution of hydrochloric acid, 0.47 mg of nickel, 1.04mg of copper, and 1.66 mg of cupronickel electrode were dissolved.

The effect of current density on the cupronickel electrode on the dissolution of Cu-Ni alloys polarized by alternating current was studied in the range of $200 \text{ A/m}^2 - 1200 \text{ A/m}^2$ (figure 2). During this experiment, the current density at the titanium electrode was kept constant at 60 kA/m^2 . With an increase in the current density of the cupronickel electrode, there was a significant decrease in the CE of the formation Cu (I) ions from 70% to 10%, the CE for the Cu (II) ions from 35% to 5%, and the CE for the Ni (II) ions from 17.5% to 2.5%. This is due to the increase in current density, the increase in the rate of additional reactions.

Electrolysis by using direct current polarization was also performed for the comparison. It was found that an increase in the current density at the anode reduces the current efficiency of the cupronickel electrode dissolution. This phenomenon was observed by the passivation of the electrode.

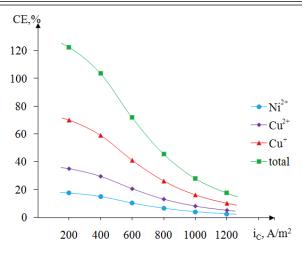


Figure 2 – The effect of the cupronickel electrode current density on the current efficiency of the alternating current polarized Cu-Ni alloy dissolution: $i_{Ti}=60 \text{ kA/m}^2$, [HCl] = 0,5 M, $\tau=0.5 \text{ h}$.

The effect of the concentration of the hydrochloric acid solution on the electrode process during polarization with the alternating current was studied. According to figure 3, with an increase in the concentration of hydrochloric acid by 0.5 M to 5.0 M, the current efficiency value for copper (I), (II), and nickel (II) ions slightly increased. There is observed stable growth in the current efficiency of the dissolution cupronickel electrode from 103% to 128%. This is a natural phenomenon, because as the concentration of the anion increases, so does its oxidizing property.

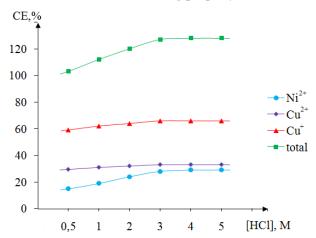


Figure 3 – Effect of hydrochloric acid concentration on the current efficiency of cupronickel electrode dissolution polarized alternating current: i_{CuNi} = 400 A/m², i_{Ti} = 60 kA/m², τ = 0,5 h.

The reaction order was calculated from the dependence of the acid concentration on the cupronickel electrode. The reaction order for the total copper ions accounted for 0.95 and nickel (II) ions - 0.85.

Increasing the duration of electrolysis led to a decrease in the current efficiency of copper-nickel alloys. That is, over time, the electrodes become passivated by the products of electrolysis. When the electrolysis time exceeded 1 hour, the formation of copper powders was observed at the titanium electrode of the electrolyte. As a result of the accumulation of copper powders in the titanium electrode, the current-correcting properties of the titanium electrode decrease.

Figure 5 shows the effect of electrolyte temperature on the current dissolution rate of the cupronickel electrode polarized by an alternating current. According to the results of the study, a substantial dissolution of copper-nickel alloys was observed with increasing electrolyte temperature. The value of CE for total copper and nickel (II) ions increased linearly as well as for total dissolution of Cu-Ni alloy. When the temperature of the solution was increased from 20 up to 60°C, the CE for nickel (II) ions increased from 5% to 18.6%, the CE for total copper ions elevated vastly from 22.5% to 132%.

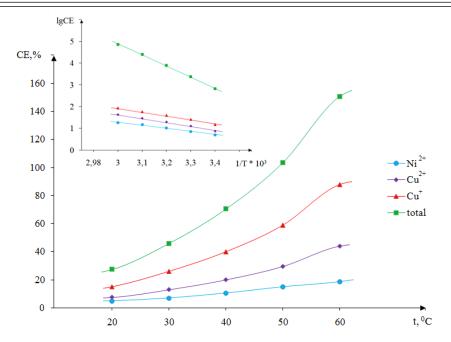


Figure 4 – The electrolyte temperature effect on the current efficiency of cupronickel electrode dissolution polarized alternating current, and inverse dependence of the logarithm of the current efficiency of the cupronickel electrode dissolution on temperature i_{CuNi} = 400 A/m², i_{Ti} = 60 kA/m², i_{Ti} = 60 kA/m², i_{Ti} = 0,5 M, i_{Ti} = 0,5 h.

It is known that the rate of chemical reactions is determined by the energy of activation. The activation energy of electrochemical reactions was found depending on the angular coefficient of the linear image (figure 4). The average value of the activation energy of total copper ions, and nickel (II) ions determined by the temperature-kinetic method ($lgCE-1/T*10^3$) was $E_{act} = 9.31$ kJ/mol, and $E_{act} = 21.73$ kJ/mol, respectively. This indicates that the ongoing electrochemical reaction takes place in a diffusion-kinetic mode.

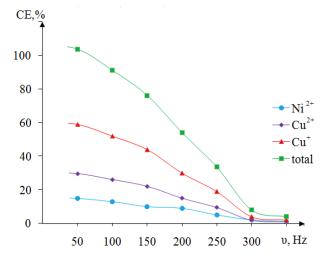


Figure 5 – AC requencies effect on the current efficiency of cupronickel electrode dissolution polarized with alternating current: i_{CuNi} = 400 A/m², i_{Ti} = 60 κ A/m², [HCl] = 0,5 M, τ = 0,5 h.

As can be seen in figure 5, the effect of AC frequency on the dissolution of Cu-Ni alloys polarized by the alternating current is significant. The effect of AC frequency on the polarization of the cupronickel electrode in a hydrochloric acid solution was studied at a current frequency in the range of 50-350 Hz. Increasing the value of the AC frequency, the total current efficiency dissolution of the Cu-Ni alloys is reduced from 103.5% up to 8%, respectively, and the dissolution of the cupronickel electrode at 350 Hz

almost completely stopped. It can be concluded that the decrease in current efficiency with increasing frequency is caused by the inhibition of the ionization process, i.e. the lack of time required for the oxidation reaction in the anode half-cycle. Due to the fact that the periods change very rapidly at high current frequencies, the alloy components do not have time to oxidize copper, and nickel in the anode half-period. In this case, only hydrogen ions are involved in the electrode process. It can be assumed that in the cathode half-period hydrogen ions are reduced to the active atomic state, and in the anodic half-period, they have oxidized again to the H⁺ state. It can also be explained by the regularity of the decrease in the effect of current density with increasing current frequency, a decrease in the actual polarization at the electrodes.

Conclusion. The electrochemical dissolution behaviour of a cupronickel electrode in an aqueous solution of hydrochloric acid under polarization with a 50 Hz frequency alternating current was systematically studied. On the basis of electrochemical experiments, the influence of the current density at the titanium and cupronickel electrodes, the hydrochloric acid solution concentration, the electrolyte temperature, the electrolysis duration and the alternating current frequency on the alloy dissolution behavior with formation of Cu(I), Cu(II), Ni(II) ions were established. Optimal conditions for electrochemical dissolution of cupronickel alloy in hydrochloric acid medium in the mode of industrial AC electrolysis were determined: i_{Ti} = 60 kA/m², i_{CuNi} = 200 A/m², [HCl] = 2.0 M, τ = 0.5 h, t = 50° C, v = 50 Hz). Under optimal conditions, the formation of Cu (I), Cu (II), and Ni (II) ions accounted for 59%, 29.6%, and 15%, respectively, and the total dissolution of the alloy reached 103.6%.

Р. Н. Нұрділлаева¹, Н. Ш. Әбділда¹, А. Б. Баешов²

 1 Қожа Ахмет Ясауи атындағы Халықаралық қазақ-түрік университеті, Түркістан, Қазақстан; 2 Д. В. Сокольский атындағы жанармай, катализ және электрохимия институты, Алматы, Қазақстан

МЕЛЬХИОР ЭЛЕКТРОДЫНЫҢ ҚЫШҚЫЛ ОРТАДАҒЫ ЭЛЕКТРОХИМИЯЛЫҚ ҚАСИЕТІ

Аннотация. Мельхиор құймасының беріктік және коррозиялық тұрақтылық қасиеті жоғары болғандықтан, өндіріс орындарында конденсаторлық және жылуалмастырғыш құбырлар, медициналық құралдар мен тұрмыстық жабдықтар жасауда кеңінен қолданылады. Си-Nі негізіндегі құймалардың қолданылу аясы кең, әрі ерекше механикалық қасиеттеріне байланысты мельхиордың электрохимиялық қасиеттерін зерттеудің маңызы үлкен. Ұсынылып отырған жұмыста өндірістік жиіліктегі айнымалы токпен поляризацияланған мельхиор электродының электрохимиялық қасиеті тұз қышқылының сулы ерітіндісінде алғаш рет зерттелді. Алдын ала жүргізілген зерттеу нәтижелері екі мельхиор электродын айнымалы токпен поляризациялағанда бағытталған негізгі үдерістердің іс жүзінде жүрмейтіндігін көрсетті. Алайды, мельхиор электродын титан электродымен жұптастырғанда құйманың мыс (I), мыс (II), және никель (II) иондарын түзе, қарқынды еритіндігі байқалды. Осыған орай, мельхиордың электрохимиялық еруі титан электродымен жұптастырылып жиілігі 50 Гц айнымалы токты электролиз режимінде жүргізілді. Си-Nі құймасының еруінің ток бойынша шығымына титан ($20-120 \text{ кA/м}^2$) және мельхиор ($200-1200 \text{ A/m}^2$) электродындағы ток тығыздығының, тұз қышқылы ерітіндісі концентрациясының (0,5-5,0 М), электролиздің журу уақытының (0,5-1,75 сағ.) және айнымалы ток жиілігінің (50-300 Гц) әсерлері қарастырылды.Салыстыру мақсатында құйманың электрохимиялық еруі тұрақты ток электролиз режимінде де жүргізілді. Тұрақты токпен поляризацияланған мельхиор электродының мардымсыз еритіндігі анықталды.

Құйманың электрохимиялық еру жылдамдығына титан электродындағы ток тығыздығының әсер ететіндігі анықталды. Мельхиор электроды еруінің ток бойынша шығымы титан электродындағы ток тығыздығы 60 кА/м²-та максимум арқылы өтіп, жоғары ток тығыздығында едәуір төмендейді. Бұл титан бетінде 20-120 кА/м² ток тығыздығында түрлі құрамдағы титан оксиді қабаттары түзіліп, олардың вентильдік қасиетінің өзгеруі негізінде түсіндіріледі. Си-Nі құймасының электрохимиялық еруінің ток бойынша шығымы мельхиор электродындағы ток тығыздығын жоғарылатқанда қосымша реакциялар жылдамдығының өсуі әсерінен сызықты түрде төмендегені байқалды.

Құйма еруінің қышқыл концентрациясына тәуелділігі зерттеліп, реакция реті есептелді. Жалпы мыс иондары түзілуінің реакция реті 0.95, никель (ІІ) иондарының түзілуінің реакция реті 0.85 мәнді көрсетті.

Түйін сөздер: мельхиор, Сu-Ni құймасы, айнымалы ток, титан электроды, тұз қышқылы, электролиз, ток тығыздығы, ток бойынша шығым.

Р. Н. Нурдиллаева¹, Н. Ш. Абдилда¹, А. Б. Баешов²

¹Международный казахско-турецкий университет им. Ходжи Ахмеда Ясави, Туркестан, Казахстан; ²АО «Институт топлива, катализа и электрохимии им. Д. В. Сокольского», Алматы, Казахстан

ЭЛЕКТРОХИМИЧЕСКОЕ ПОВЕДЕНИЕ МЕЛЬХИОРОВОГО ЭЛЕКТРОДА В КИСЛОЙ СРЕДЕ

Аннотация. Мельхиоровый сплав имеет высокую прочность и коррозионную стойкость, широко используется в производстве конденсаторных и теплообменных труб, медицинских инструментов и бытового оборудования. Сплав Cu-Ni имеет широкий спектр применения, и в связи с уникальными механическими свойствами большое значение имеют исследования, посвященные электрохимическому поведению мельхиора. В данной работе впервые исследовано электрохимическое поведение мельхиорового электрода при поляризации переменным током промышленной частоты в водном растворе соляной кислоты. Результаты предварительного исследования показали, что при поляризации двух мельхиоровых электродов переменным током практически не происходят основные направленные процессы. Однако при применении мельхиорового электрода в паре с титановым электродом наблюдалось интенсивное растворение сплава с образованием ионов меди (I), меди (II) и никеля (II). В связи с этим электрохимическое растворение мельхиора проводили в режиме электролиза под действием переменного тока с частотой 50 Гц в паре с титановым электродом. Рассмотрено влияние плотности тока на титановом (20-120 кА/м²) и мельхиоровом $(200-1200 \text{ A/m}^2)$ электроде, концентрации раствора соляной кислоты (0,5-5,0 M), продолжительности электролиза (0,5-1,75 ч.) и частоты переменного тока (50-300 Гц) на выход по току растворения сплава Сu-Ni. С целью сравнения электрохимическое растворение сплава проводилось также в режиме электролиза под действием постоянного тока. Установлено, что при поляризации под действием постоянного тока мельхиоровый электрод растворяется незначительно.

Установлено, что плотность тока на титановом электроде значительно влияет на скорость электрохимического растворения сплава. Выход по току растворения мельхиорового электрода проходит через максимум при плотности тока $60~\text{кA/m}^2$ и существенно уменьшается при высокой плотности тока на титановом электроде. Это объясняется тем, что при плотностях тока на титане $20\text{-}120~\text{kA/m}^2$ образуются слои оксида титана различного состава и изменяются их вентильные свойства.

Изучен процесс растворения сплава в зависимости от концентрации кислоты и определен порядок реакции. Общий порядок реакции образования ионов меди составил 0,95 и порядок реакции образования ионов никеля (II) 0,85.

Ключевые слова: мельхиор, сплав Cu-Ni, переменный ток, титановый электрод, соляная кислота, электролиз, выход по току, плотность тока.

Information about authors:

Nurdillayeva Raushan N., Candidate of Chemistry Science, Associate Professor, Head of Ecology and Chemistry Department of Natural Sciences Faculty, Khoja Akhmet Yassawi International Kazakh-Turkish University, Turkestan, Kazakhstan; raushan.nurdillayeva@ayu.edu.kz; https://orcid.org/0000-0001-9444-737X

Abdilda Nazerke Sh., Khoja Akhmet Yassawi International Kazakh-Turkish University, master student of educational program 7M05324-Chemistry, II course, Turkestan, Kazakhstan; abdilda_nazerke@mail.ru; https://orcid.org/0000-0001-5978-4477

Bayeshov Abdualy, Doctor of Chemistry Science, Professor, Academician of the National Academy of Sciences of the Republic of Kazakhstan, D.V. Sokolsky Institute of Fuel, Catalysis and Electrochemistry, Almaty, Kazakhstan; bayeshov@mail.ru; https://orcid.org/0000-0003-0745-039X

REFERENCES

- [1] Gaber G.A., Hussein W.A., Ahmed A.S. (2020). Comparative study of electrochemical corrosion of novel designs of 90/10 and 70/30 copper-nickel alloys in brine solutions // Egyptian Journal of Chemistry. Vol. 63, N 4. P. 19-20. DOI: 10.21608/ejchem.2019.16389.2001 (in Eng.).
- [2] Subramanian V., Chandramohan P., Srinivasan M.P., Velmurugan S., Narasimhan S.V. (2007). Corrosion of cupronickel alloy in permanganate under acidic condition // Corrosion science. Vol. 49, N 2. P. 620-636. DOI: 10.1016/j.corsci.2006.06.001 (in Eng.).
- [3] Lei N., Xu D. (2017). Deformation temperature and material constitutive model of cupronickel B10 // Journal of Mechanical Science and Technology. Vol. 31, N 8. P. 3761-3767. DOI: 10.1007/s12206-017-0719-7 (in Eng.).

- [4] Ekerenam O.O., Ma A., Zhang Y., Emori W. (2017) Electrochemical behavior of three 90Cu-10Ni tubes from different manufactures after immersion in 3.5% NaCl solution // Journal of Materials Engineering and Performance. Vol. 26, N 4. P. 1701-1716. DOI: 10.1007/s11665-017-2566-1 (in Eng.).
- [5] Ezuber H.M., Al Shater A. (2016) Influence of environmental parameters on the corrosion behavior of 90/10 cupronickel tubes in 3.5% NaCl // Desalination and Water Tratment. Vol. 57, N 15. P. 6670-6679. DOI: 10.1080/19443994.2015.1024743 (in Eng.).
- [6] Yang R., Wen J., Zhou Y., Song K., Song Z. (2018) Effect of Al element on the microstructure and properties of Cu-Ni-Fe-Mn alloys // Materials. Vol. 11, N 9. P. 1777. DOI: 10.3390/ma11091777 (in Eng.).
- [7] Jin T., Zhang W., Li N., Liu X., Han L., Dai W. (2019) Surface characterization and corrosion behavior of 90/10 copper-nickel alloy in marine environment // Materials. Vol. 12, N 11. P. 1869. DOI: 10.3390/ma12111869 (in Eng.).
- [8] El Warreky A.A., Abd El Hamid S.E., Sherif E.S.M. (2020) Electrochemical Corrosion Behaviour of different Cu-Base Alloys in Concentrated LiBr solutions: Part I-Cu/10Ni and A-bronze alloys // International Journal of Electrochemical science. Vol. 15, N 3. P. 2243-2260. DOI: 10.20964/2020/03/72 (in Eng.).
- [9] Wang Y., Xue Y., Zhang C. (2019) Enhanced anodic dissolution of cupronickel alloy scraps by electro-generated reactive oxygen species in acid media // Journal of Alloys and Compounds. Vol. 806. P. 106-112. DOI: 10.1016/j.jallcom.2019.07.276 (in Eng.).
- [10] El Warraky A.A., El Meleigy A.E., Abd El S.E. (2016) The electrochemical behavior of 70-30 Cu-Ni alloy in LiBr solutions // Egyptian Journal of Chemistry. Vol. 59, N 5. P. 833-850. https://journals.ekb.eg/article_1471_9b52c28c76df22e65462a856357d2f63.pdf (in Eng.).
- [11] Badawy W.A., El-Rabiei M.M., Nady H.M., Samy M.A. (2015) Comparison of electrochemical behavior of Cu-10Ni-10Zn alloy and Cu in aqueous solutions // Zeitschriftfur physikalis chemie. Vol. 229, N 3. P. 351-363. DOI: 10.1515/zpch-2014-0627 (in Eng.).
- [12] Nikolaychuk P.A., Tyurin A.G. (2012) Thermodynamics of chemical and electrochemical stability of copper-nickel alloys // Protection of Metals and Physical Chemistry of Surfaces. Vol. 48, N 4. P. 462-476. DOI: 10.1134/S2070205112040132 (in Eng.).
- [13] Nurdillayeva R.N., Bayeshov A.B., Serik G.S. (2018) Production of copper bromide at polarization by an alternating current // News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. Vol. 2. P. 36-43. ISSN 2518-1491 (online), ISSN 2224-5286 (Print) (in Eng.).
- [14] Nurdillayeva R.N., Bayeshov A.B., Serik G.S. (2018) The elaboration of copper bromide synthesis by electrochemical method // News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. Vol. 1, N 371. P. 73-80. ISSN 2518-1467(Online), ISSN 1991-3494(Print) (in Eng.).
- [15] Ovchinnikova S.N., Aleksandrova T.P., Vais A.A. (2004) Copper in acid chloride solutions: electrochemical behavior by quartz micrograyimetry and voltammetry // Russian Journal of Electrochemistry. Vol. 40, N 7. P. 755-759. DOI: 10.1023/B:RUEL.0000035261.95595.e9 (in Eng.).
- [16] Cuenca A., Agrisuelas J., Garcia-Jareno J.J., Vicente F. (2017) Alternating current electrogravimetry of copper electrodissolution in a sulfuric acid solution // Electrochemical Acta, N 235. P. 374-383. DOI: 10.1016/j.electacta.2017.03.079 (in Eng.).
- [17] Bayeshov A.B., Yegeubayeva S.S., Bayeshova A.K., Zhurinov M.Z. (2017) Dissolution of bipolar nickel electrode in sulfuric acid solution at polarization with industrial alternating current // News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. N 1. P. 41-47. ISSN 2518-1491 (Online), ISSN 2224-5286 (Print) (in Eng.).
- [18] Kuznetsova O.G., Levin A.M., Tsybin O.I., Sevostyano M.A., Bryukin V.A., Bolshikh A.O. (2018) Effect of cathodic polarization on the Depassivation of Oxidized Nickel // Russian Metallurgy (Metally). N 7. P. 651-654. DOI: 10.1134/S0036029518070078b (in Eng.).
- [19] He B., Wang D., Li J., Zhu D. (2019) Investigation of Pusating Electrochemical Dissolution of Nickel in rotating processes // Journal of The Electrochemical Society. Vol. 166, N 12. 375 p. (in Eng.).
- [20] Nurdillayeva R.N., Bayeshov A.B., Sunatullayeva L.A., Zhylyabayeva G.N. (2019) Dissolution behavior of brass polarized by alternating current in sodium phosphate aqueous solution // News of the National Academy of Sciences of the Republic of Kazakhstan. Series of Chemistry and Technology. N 3. P. 77-83. ISSN 2518-1491(Online), ISSN 2224-5286 (Print), DOI: 10.32014/2019.2518-1491.33 (in Eng.).
- [21] Nurdillayeva R.N., Kadirbayeva A. (2013) Investigation of the features of electrochemical dissolution of a Cobstantin electrode under alternating current polarization // Chemical Bulletin of Kazakh National University. N 1. P. 51-58 (in Eng.).
- [22] Nikitina E.V., Karfidov E.A., Kazakovceeva N.A. (2020) Anodic selective dissolution of copper alloys in chloride and carbonate melts // Journal of Alloys and Compounds, 845, 156238. DOI: 10.1016/j.jallcom.2020.156238 (in Eng.).
- [23] Karfidov E.A., Nikitina E.V., Kazakovtseva N.A., Babushkina L.M. (2020) Character of selective anodic dissolution. Influence of the Alloy Composition. Russian Metallurgy (Metally). N 2. P. 127-132. DOI: 10.1134/s003602952002007x (in Eng.).
- [24] Anatolyevna P.E., Georgievna L.L., Dmitrievna F.T. (2014) Chemical methods of analysis (workshop on analytical chemistry). [Himicheskie metody analiza (proktikym po analiticheskoi himii)] https://lib.nsu.ru/xmlui/handle/nsu/9271 (in Russ.).
- [25] Dudareva, G. N., Tuan, N. A. (2010) Photometric determination of Nickel with dimethyloxime in the presence of iodine. [Fotometricheskoe opredelenie nikelia s dimetilglioksimom v prisytstvii ioda] // Bulletin of Irkutsk state technical University. Vol. 4, N 44 (in Russ.).
- [26] Bayeshov A.B., Nurdillayeva R.N., Khabibullayeva Sh.H. (2019) Effect of the bromide ions on the titanium electrode dissolution polarized by alternating current in aqueous solutions // News of the National Academy of Sciences of the Republic of Kazakhstan. Series Chemistry and Technology. N 2. 434 p. ISSN 2518-491 (Online), ISSN 2224-5286 (Print), DOI: 10.32014/2019.2518-1491.21 (in Eng.).

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ISSN 2518-1491 (Online), ISSN 2224-5286 (Print)

Редакторы: М. С. Ахметова, Д. С. Аленов, А. Ахметова Верстка на компьютере Д. А. Абдрахимовой

Подписано в печать 01.02. 2021. Формат 60х881/8. Бумага офсетная. Печать – ризограф. 9,5 п.л. Тираж 300. Заказ 1.