N E W S
OF THE NATIONAL ACADEMY OF SCIENCES OF THE REPUBLIC OF KAZAKHSTAN
SERIES OF GEOLOGY AND TECHNICAL SCIENCES
ISSN 2224-5278
Volume 6, Number 426 (2017), 178 – 185

UDC 541.13; 546.74

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RESEARCH OF REGULARITIES OF ELECTROREDUCTION OF NICKEL POWDERS AT POLARIZATION BY THE CATHODIC IMPULSE CURRENT IN THE ULTRASONIC FIELD

Abstract. The process of formation of nickel powders by the electrochemical method has beeninvestigated. The regularity of electroreduction of nickel at polarization by cathodicimpulse current in an ultrasonic field (frequency 35 kHz) is studied. Under these conditions, the effect of the titanium current density on the reduction of nickel ions has been investigated. It is shown that, depending on the current density values, nickel coatings or powders of gray or black color may be produced. At low current densities of the titanium electrode, the nickel powders of gray color and a metal coating are formed. At high current densities of the titanium electrode, black powders are formed. It is established that the total current output of nickel powders and coatings is 83.5%. The effect of the nickel current density on the current output of the formation of its powder has been investigated. It is shown that the maximum current output (64.4%) is observed at a current density of 1000 A/m^2 on nickel. Photomicrographs of the obtained powders and coatings of nickel have beenmade. It is shown that the formed powders consist of dendritic and globular particles. The effect of the concentration of the solution ($NiSO_4 \cdot 6H_2O$+NaCl) on the current output ofnickel recovery has been investigated. It was found that with increasing of $NiSO_4 \cdot 6H_2O$ concentration from 1 to 20 g/l, the current output of nickel powder formation increases from 7.47 to 46.6%. With increasing of concentration of sodium chloride, the current output of nickel powder formation also increases.
Keywords: electrochemistry, nickel, powder, reduction, cathode, impulse, ultrasound, polarization, microphotograph, frequency.

The growing interest in metallic nickel and its powders is due to the continuous increase in the consumption of this metal in new fields of technology [1-5]. Nickel, as a cheaper metal than palladium and platinum, is widely used as a catalyst in hydrogenation processes [6-8]. For these purposes, it is reasonably to use nickel in the form of a powder. Powdered nickel is also consumed in the production of nickel alloys and as a binder in the manufacture of solid and supersolid materials [9]. Nickel electrodes made of the finest powders are also used in fuel cells.

There are a lot of methods for obtaining metallic powders. Such methods are atomization, restitution in the combustion regime, and others [10, 11]. However, all of them are multi-stage, labor-intensive and sometimes expensive. Therefore, the development of new alternative, more economical and simple methods for producing metallic powders is of great interest.

The production of nickel powders by the electrochemical method has a number of advantages such as minimal energy (the process is carried out at room temperature), and other costs (the use of readily available reagents), the simplicity of the equipment used, and the relatively high environmental friendliness of the process.

In the proposedpaper we investigated the process of formation of nickel powders by an electrochemical method. In our previous papers in the study of the formation of platinum powders under the influence of alternating current, the efficiency of using the electrochemical method for this purpose is shown [12-19].

The goal of this paper was to study the regularities of electroreduction of nickel powders at polarization by cathodic impulse current in an ultrasonic field.

Experimental technique. Titanium and nickel electrodes were used for the experiments. The impulse current is connected to the electrochemical circuit using diodes of ED 214A brand. A mixed solution of the following compounds was used as the electrolyte: $NiSO_4 \cdot 6H_2O$, $(NH_4)_2SO_4$and NaCl. A ultrasonic bath with a frequency of 35 kHz, Proskit SS-803 F brand, was used to create an ultrasonic field. The current output (CO) of nickel powder formation under cathodic polarization is calculated for the cathodic half-cycle of alternating current. Photomicrographs of the produced nickel powders were taken with a JEOL JSM-6610LV scanning electron microscope.

Experimental procedure. The influence of the titanium electrode current density on the reduction of nickel ions with the subsequent formation of its powders at polarization by the cathode impulse current in an ultrasonic field has been investigated.

Table 1 provides the results obtained from the investigation of the influence of the titanium electrode density on the reduction of nickel ions polarized by a cathodic impulse current in an ultrasonic field at a frequency of 35 kHz

With a constant current density on the nickel electrode of 4000 A/m^2, when the current density on the titanium electrode varies from 4,000 to 30,000 A/m^2, the bright coatings form on the surface of the electrode, the CO of which decreases with increasing the current density. With increasing the current density up to 40000 A/m^2, the formation of coatings on the electrode is not observed.

In the range of current densities of the titanium electrode, equal to 4000-40000 A/m^2, along with the coatings, the gray powders are formed, the CO of which, with increasing the current density, passes through a maximum. The highest CO is observed at i_{Ti} = 20,000 A/m^{2}and is equal to 34.0%. The results of elemental analysis showed that the purity of the obtained gray nickel powder is 84.85%.

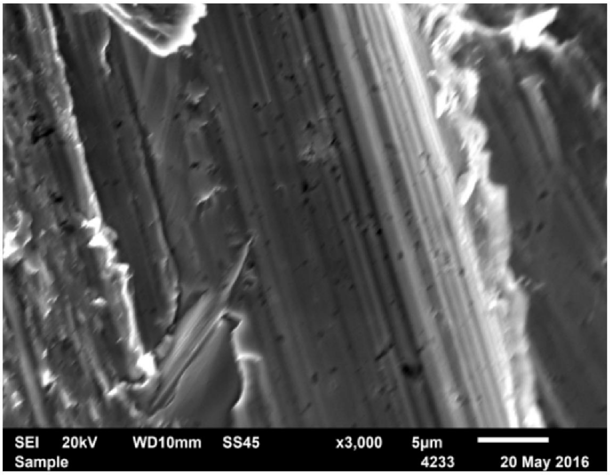
Beginning with i_{Ti} = 20000 A/m^{2}black nickel powders are formed, CO of which increases linearly with increasing the current density on titanium. Based on the purity elemental analysis of the produced nickel powders, it is found that it is 93.36%.

Thus, the total CO of formation of coatings and nickel powder is 83.5%.

Table 1 – Effect of the titanium current density on the CO reduction of nickel polarized by the cathode impulse current in an ultrasonic field at a frequency of 35 kHz: t = 25°C; i_{Ni} = 4000 A/m^2; C (20 g/l $NiSO_4 \cdot 6H_2O$ + 20 g/l $(NH_4)_2SO_4$+ 10 g/L NaCl)

i_{Ti}, A/m^2	Cathodic CO, %			Total cathodic CO, %
	Coating of CO	Gray powder CO	Black powder CO	
4000	74,5	9,0	–	83,5
7500	41,48	14,9	–	56,4
10000	26,8	27,0	–	53,8
20000	8,0	34,0	17,0	59,0
30000	3,0	28,0	18,2	49,2
40000	–	26,6	20,0	46,6

JEOL JSM-6610 LV scanning electron microscope tookthe microphotographs of produced nickel coatings and powders. Figure 1 shows the enlarged 3000-fold microphotographs of nickel coatings produced by polarization with a cathodic impulse current. As was mentioned above, in this case, the bright nickel coatingsare formed ontitanium surface.

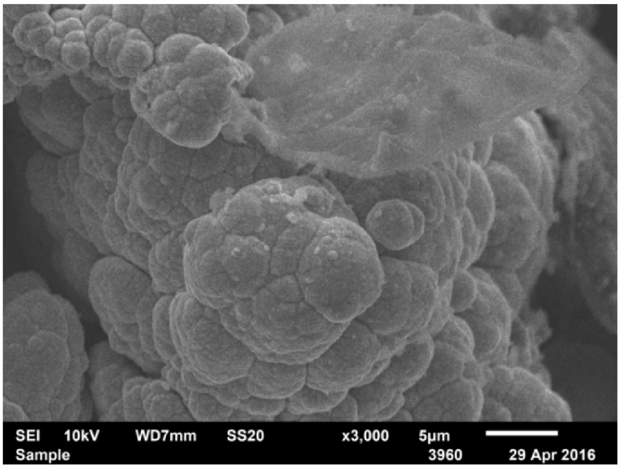


t = 25 °C; i_{Ni}= 4000 A/m^2; i_{Ti}= 20000 A/m^2; C (20 g/l $NiSO_4 \cdot 6H_2O$ + 20 g/l $(NH_4)_2SO_4$ + 10 g/l NaCl)

Figure 1 – A microphotographof nickel coatings producedat polarization with aimpulse cathodic current in an ultrasonic field at a frequency of 35 kHz

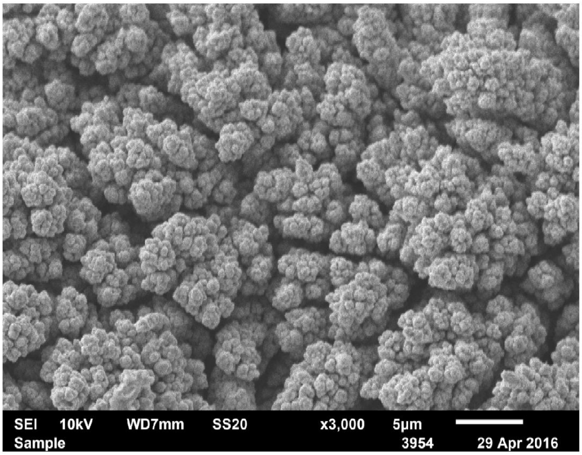
Figures 2 and 3 show the microphotographsof nickel powders, also producedat polarization with a cathodic impulse current in an ultrasonic field with a frequency of 35 kHz. It should be noted again that the nickel powders formed in the electrolyzer space are black (Figure 3), while the powders formed on the surface of the electrode are gray (Figure 2). In this case, the nickel products formed after electrolysis (coating, powders of gray and black color) are easily separated from each other.

In order to establish the optimal parameters for the reduction of nickel with the formation of a powder, the influence of the current density of a nickel electrode on the CO of metal powder formation at polarization by a cathodicimpulse current in a ultrasonic field with a frequency of 35 kHz was investigated (Table 2). With a titanium constant current density of 40,000 A/m^2 and varying the nickel current density from 500 A/m^{2}to 6000 A/m^2, the CO curve of the formation of metal powders passes through a maximum.



t = 25 °C; i_{Ni}= 4000 A/m^2; i_{Ti}= 20000 A/m^2; C (20 g/l $NiSO_4 \cdot 6H_2O$ + 20 g/l $(NH_4)_2SO_4$+ 10 g/l NaCl)

Figure 2 – A microphotographof a gray nickel powder producedat polarization with impulse cathodic current in an ultrasonic field at a frequency of 35 kHz



t = 25 °C; i_{Ni}= 4000 A/m^2; i_{Ti}= 20000 A/m^2; C (20 g/l $NiSO_4 \cdot 6H_2O$ + 20 g/l$(NH_4)_2SO_4$+ 10 g/l NaCl)

Figure 3 – A microphotographof black nickel powder producedat polarization with impulse cathodic current in an ultrasonic field at a frequency of 35 kHz

Table 2 – Effect of the nickel current density on the CO of its reduction at polarized by a cathodic impulse current in an ultrasonic field at a frequency of 35 kHz C (20 g/l $NiSO_4 \cdot 6H_2O$, 20 g/l $(NH_4)_2SO_4$, 10 g/l NaCl); t = 25 °C , i_{Ti}= 40000 A/m^2

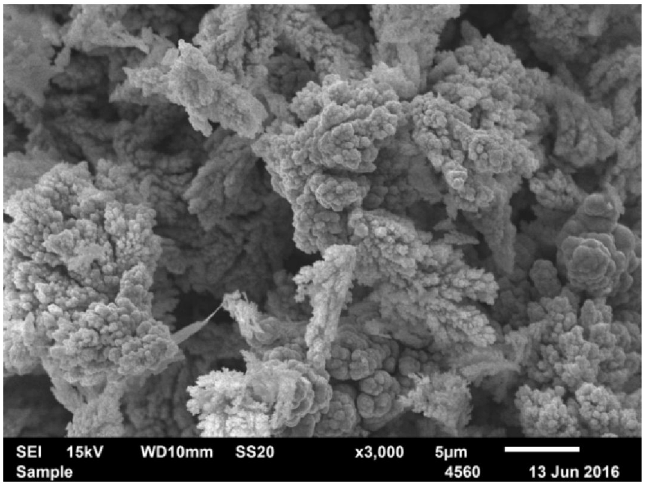
i_{Ni} , A/m^2	500	1000	2000	4000	6000
BT, %	31,1	64,4	48,6	48,7	48,7

The maximum CO is observed at i_{Ni}= 1000 A/m^{2}and is equal to 64.4%. It should be noted that at densities of the current on the nickel electrode of 500-1000 A/m^2, a bright black nickel powder is formed, distinguishing in metallic luster. With increasing the current density i_{Ni}> 1000A/m^2, the powder brightness gradually disappears. Apparently, at low current densities, plate powdersare formed, while at high densities, flake powders are formed. With increasing current density on the nickel, the main part of the current is consumed for gas evolution, which leads to a decrease in the CO.

Figure 4 shows a microphotographof a black bright nickel powder producedat polarizationof nickel electrode with a cathode impulse current (i_{Ni} = 1000 A/m^{2}and i_{Ti} = 40000 A/m^2) in an ultrasonic field at a frequency of 35 kHz. Analysis of the microphotographof the produced powders showed that they consist of dendritic and globular particles. The results of elemental analysis showed that the metal powders obtained at i_{Ni} = 1000 A/m^{2}and i_{Ti} = 40000 A/m^2 correspond to 94.43% of nickel.

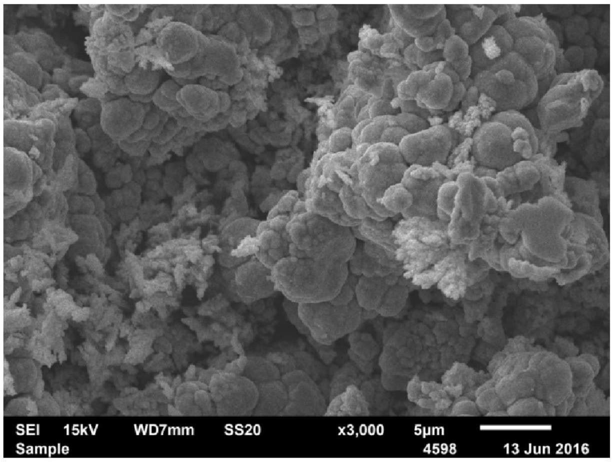
Figure 5 shows a microphotographof a black but not bright nickel powder producedat polarization of the nickel electrode with a cathode impulse current (i_{Ni}= 6000 A/m^{2}and i_{Ti}= 40000 A/m^2) in an ultrasonic field at a frequency of 35 kHz. In this case, the formation of a powder consisting of dendritic and globular particles is also observed. It should be noted that in this case an increase in the number of globular particles is observed. According to elemental analysis, the metal powders produced at i_{Ni} = 6000 A/m^2 и i_{Ti} = 40000 A/m^{2}correspond to 94.43% of nickel.

The effect of the concentration of the solution ($NiSO_4 \cdot 6H_2O$+NaCl) on the COof recovery of a nickel electrode polarized by the cathode impulse current using an ultrasonic field at a frequency of 35 kHz was studied. As can be seen from Figure 6, with increasing $NiSO_4 \cdot 6H_2O$concentration from 1 g/l to 20 g/l, an increase in the CO of nickel powder formation from 7.47% to 46.6%is observed. Further increase in concentration leads to a decrease in CO, because at high concentrations of the $NiSO_4 \cdot 6H_2O$solution, nickel $Ni(OH)_2$is also formed along with the metal powders, which confirms the coloration of the solution in green color.



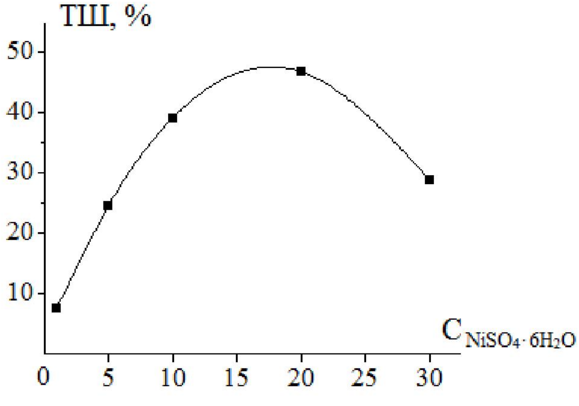
t = 25 ºC; i_{Ni}= 1000 A/m^2;i_{Ti}= 40000 A/m^2; C (20 g/l $NiSO_4\cdot 6H_2O$, 20g/l $(NH_4)_2SO_4$, 10 g/l NaCl)

Figure 4 – A microphotographof a black bright nickel powder producedat polarizationof nickel electrode with a cathodic impulse current in an ultrasonic field at a frequency of 35 kHz



t = 25 ºC; i_{Ni}= 6000 A/m^2;i_{Ti}= 40000 A/m^2; C (20 g/l $NiSO_4\cdot 6H_2O$, 20g/l $(NH_4)_2SO_4$, 10 g/l NaCl)

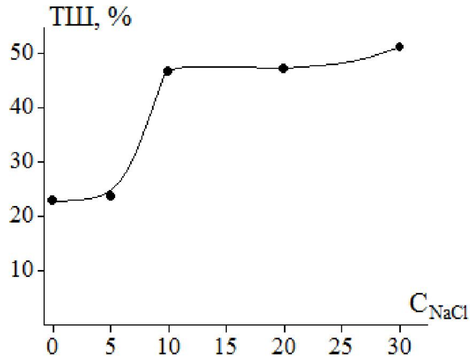
Figure 5 – A microphotographof a black, not bright nickel powder producedat polarization ofnickel electrode with a cathodic impulse current in an ultrasonic field at a frequency of 35 kHz



t = 25 ºC; i_{Ni}= 4000 A/m^2, i_{Ti} = 40000 A/m^2;
C, g/l (x $NiSO_4\cdot 6H_2O$ + 20$(NH_4)_2SO_4$ +10 NaCl)

Figure 6 – Effect of $NiSO_4\cdot 6H_2O$ concentration on the CO of nickel recovery at polarization by cathodic impulse current in an ultrasonic field at a frequency of 35 kHz

Figure 7 shows the results of effect of the sodium chloride solution concentration on the CO ofnickel powder formation atpolarization ofelectrodes by cathodicimpulse current in an ultrasonic field at a frequency of 35 kHz. With an increase in the concentration of sodium chloride, CO ofnickel powder formation also increases. The maximum CO of nickel powder formation is 51.1% and is observed at a NaCl concentration of 30 g/l. Such picture of the dependence of the current outputof the nickel powders formation on the concentration is observed in paper [20], where the positive effect of sodium chloride on the formation of metal powders is noted, which is expressed in an increase in the current outputof the nickel powders formation.



t = 25 ºC; i_{Ni}= 4000 A/m^2, i_{Ti} = 40000 A/m^2;
C, g/l (20 $NiSO_4 \cdot 6H_2O$ + 20 $(NH_4)_2SO_4$ + x NaCl)

Figure 7 – Effect of NaCl concentration on the CO of nickel recovery at polarization by cathodic impulse current in an ultrasonic field at a frequency of 35 kHz

It should be noted that at current densities below 7500 A/m^2 the nickel coating is formed. At i_{Ti}> 30000 A/m^2, nickel hydroxide is formed along with the black nickel powder. As the results of X-ray phase analysis (Figure 8) showed, the reflexes 4.7; 2.70 and 2.34 Å of the product produced correspond to $Ni(OH)_2$, reflections 2.03Å correspond to Ni.

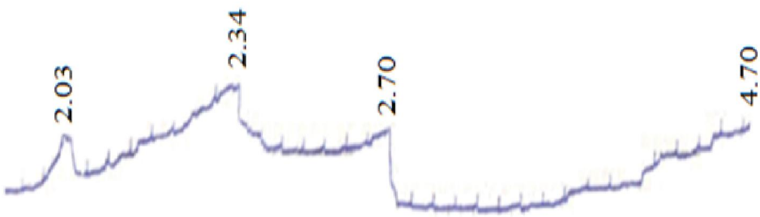


Figure 8 – X-ray photogram $Ni(OH)_2$

Thus, the results of the obtained data have shown the possibility of applying the transient current for producing nickel powder. It is shown that nickel powders of predominantly dendritic form are formed during electrolysis. It has been established that when using an ultrasonic field in the electrolysis process, the dentritic forms of the nickel powder are destroyed, which promotes the production of more dispersed forms of the said powder.

REFERENCES

[1] Beregovskiy V.I. Nickel and its significance for the national economy. Moscow: Metallurgiya, 1964. 405 p.

[2] Dodin D.A. The world market of non-ferrous metals and Russia's position in it // Non-ferrous metals. 2007. N 10. P. 10-13.

[3] Nitridation enhancement of $TiSi_2$ powders by addition of nikel / Roger J., Nouvian L., Le Petitcorps Y. et al. Journal of alloys and compounds. 2017. Vol. 724. P. 249-257.

[4] Kubassov V.L., Bannikov V.V. Electrochemical technology of inorganic substances / Textbook for technical schools of chemistry technological specialties. Moscow: Chemistry, 1989. 288 p.

[5] Gran T.V., Krylov A.S. Electrolytic refining of nickel. Publ. Metallurgiya, 1970. 96 p.

[6] Sabirova Z.A., Danilova M.M., Zaikovskiy V.I. et al. Nickel catalysts based on porous nickel for the reaction of methane vapor conversion // Kinetics and catalysis. 2008. Vol. 49, N 3. P. 449-456.

[7] Danilova M.M., Sabirova Z.A., Kuzin N.A., et al. Nickel and nickel-platinum-containing reinforced catalysts for conducting heat-combined reactions of methane vapor conversion and hydrogen oxidation // Kinetics and catalysis. 2007. Vol. 48, N 1. P. 123-131.
[8] TitovaYu.Yu., BelykhL.B., ShmidtF.K. Nickel hydrogenation catalystsof the Ziegler type: the effect of water content in the nickel precursor on the size and nature of the particles formed // Kinetics and catalysis. 2016. Vol. 57, N 3. P. 392. DOI:10.7868/S0453881116030138
[9] Nickel, its properties and alloys / http://www.cniga.com.ua/index.files/niccolum.htm
[10] Yamukyan M.A., Manukyan Kh.V., Kharatyan S.L. Production of powdered nickel by reduction of the basic nickel carbonate in the combustionregime // Chemical Journal of Armenia. 2008. Vol. 61, N 2. P. 159-166.
[11] LapsinaP.V., KagakinYe.I., DodonovV.G. et al. Nanostructured nickel powders: production and some properties // Polzunovsky News. 2014. N 3. P. 147-150.
[12] Platinum powder formation AT polarization indiced by impulse alternating current in the presence of quadrivalent titanium ions // Int. J. Chem. Sci.: 11(2), 2013, 825-832 / A.B. Bayeshov, B.E. Myrzabekov, N.S. Ivanov, A.K. Bayeshova, M.Zh. Zhurynov.
[13] Bayeshov A., Myrzabekov B.E., Zhurinov M.Zh.Reduction of platinum ions (IV) with the formation of ultradispersed powders in a solution of sulfuric acid by a cathodicimpulse current // Reports NAS RK. 2012. N 5. P. 19.
[14] Bayeshov A., Myrzabekov B.E. Ivanov N.S. Bayeshova A. Reduction of platinum ions (IV) with the formation of ultra-dispersed powders in sulfuric acid solution by impulse current // News of KazNU. Chemical series. 2011. N 1(61). P. 450-456.
[15] Bayeshov A., Zhurinov M.Zh. Nogerbekov B.Yu., Ivanov N.S. MyrzabekovB.E. Komashko L.V. Cathodic formation of platinum powder in phosphate electrolytes // News of NAS RK. 2011. N 1. P. 10-14.
[16] Bayeshov A., Myrzabekov B.E., Ivanov N.S. Electrochemical reduction of platinum (IV) with the formation of nano-sized powders // Abstracts of the XIX Mendeleyev Congress on General and Applied Chemistry. Volgograd, 2011. Vol. 3. P. 35-36.
[17] Bayeshov A., Myrzabekov B.E. Influence of various parameters on the composition and structure of platinum powders // Proceedings of the "Heterogeneous processes in enrichment and metallurgy" International Scientific and Practical Conference. Karaganda, 2011. P. 198-200.
[18] Bayeshov A., Myrzabekov B.E., Ivanov N.S. Electrochemical method for the reduction of platinum (IV) at polarization by an impulse current with the formation of ultradisperse powder // Proceedings of the I-Russian-Kazakhstan Conference on Chemistry and Chemical Technology. Tomsk, 2011. P. 8-11.
[19] Bayeshov A., Myrzabekov B., Ivanov N.S., Zhurinov M.Zh. Investigation of the formation of nanosized platinum powders in the sulfuric acid medium // Reports of NAS RK. 2010. N 6. P. 46-51.
[20] Kudra O., Gitman E. Electrolytic production of metallic powders. Kiev, 1952. 144 p.

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УЛЬТРАДЫБЫСТЫ ӨРІСТЕ КАТОДТЫ ИМПУЛЬСТІ ТОКПЕН ПОЛЯРИЗАЦИЯЛАУ АРҚЫЛЫ НИКЕЛЬ ҰНТАҚТАРЫНЫҢ ЭЛЕКТРОТОТЫҚСЫЗДАНУ ЗАҢДЫЛЫҚТАРЫН ЗЕРТТЕУ

Аннотация. Электрохимиялық әдіс арқылы никель ұнтақтарының түзілу процессі зерттелді. Ультрадыбысты өрісте (5 кГц) катодты импульсті токпен поляризациялау кезінде никельдің электртотығу заңдылықтары зерттелді. Аталған шарттарда никель иондарының тотықсыздануына титандағы ток тығыздығының әсері зерттелді. Ток тығыздығының әр түрлі көрсеткіштерінде никельдің қаптамалары немесе қара және сұр түсті ұнтақтарын алуға болатындығы көрсетілді. Титан электродының төменгі ток тығыздықтарында никельдің сұр түсті ұнтақтары және никель қаптамасы түзілетіндігі көрсетілді. Титан электродының жоғарғы ток тығыздықтарында никельдің қара түсті ұнтақтары түзілетіндігі көрсетілді. Никельдің қаптамалары және ұнтақтары түзілуінің ток бойынша шығымдарының қосынды мәні 83,5 %-ға тең болатындығы анықталды. Никель ұтақтарының түзілуіне никельдегі ток тығыздығының әсері зерттеліп, оның максималды ток бойынша шығымы 1000 А/м^2-де 64,4-ға жететіндігі көрсетілді. Алынған қаптама және ұнтақтардың микрофотосуреттері түсірілді. Түзілген ұнтақтар дендритті және глобула түріндегі бөлшектерден тұратындығы анықталды. Никельдің тотықсыздануының ток бойынша шығымына ерітінді ($NiSO_4 \cdot 6H_2O$+NaCl) концентрациясының әсері зерттелді. $NiSO_4 \cdot 6H_2O$ ерітіндісінің концентрациясының 1 г/л-ден 20 г/л-ге дейін өсуі никельдің ұнтақтарының түзілуінің ток бойынша шығымының 7,47 %-дан 46,6 %-ға дейін өсуіне алып келді. Натрий хлориді концентрациясының өсуімен никельдің ұнтақтарының түзілуінің ток бойынша шығымы да өсетіндігі көрсетілді.

Түйін сөздер: электрохимия, никель, ұнтақ, тотықсыздану, катод, импульс, ультразвук, поляризация, микрофотография, жиілік.

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ИССЛЕДОВАНИЕ ЗАКОНОМЕРНОСТЕЙ ЭЛЕКТРОВОССТАНОВЛЕНИЯ НИКЕЛЕВЫХ ПОРОШКОВ ПРИ ПОЛЯРИЗАЦИИ КАТОДНЫМ ИМПУЛЬСНЫМ ТОКОМ В УЛЬТРАЗВУКОВОМ ПОЛЕ

Аннотация. Исследован процесс образования никелевых порошков электрохимическим методом. Изучена закономерность электровосстановления никеля при поляризации катодным импульсным током в ультразвуковом поле (частота 35 кГц). В указанных условиях исследовано влияние плотности тока на титане на восстановление ионов никеля. Показано, что в зависимости от значений плотности тока можно получать никелевые покрытия или порошки серого либо черного цвета. При низких плотностях тока титанового электрода образуются никелевые порошки серого цвета и покрытие металла. При высоких плотностях тока титанового электрода формируются порошки черного цвета. Установлено, что суммарный выход по току образования порошков и покрытий никеля составляет 83,5 %. Исследовано влияние плотности тока на никеле на выход по току формирования его порошка. Показано, что максимальный выход по току (64,4 %) наблюдается при плотности тока на никеле 1000 А/м^2. Сняты микрофотографии полученных порошков и покрытий никеля. Показано, что образованные порошки состоят из дендритных и глобуловидных частиц. Исследовано влияние концентрации раствора ($NiSO_4 \cdot 6H_2O + NaCl$) на выход по току восстановления никеля. Установлено, что с увеличением концентрации $NiSO_4 \cdot 6H_2O$ от 1 до 20 г/л выход по току образования порошка никеля увеличивается с 7,47 до 46,6 %. С увеличением концентрации хлорида натрия выход по току образования порошка никеля также увеличивается.

Ключевые слова: электрохимия, никель, порошок, восстановление, катод, импульс, ультразвук, поляризация, микрофотография, частота.