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THE EFFECT OF TEMPERATURE ON THE DEGREE OF PURITY OF INDIUM AT ITS ELECTROREFINING

Abstract. The object of the study was rough indium produced in Kazakhstan. To optimize the conditions for its electrorefining, the effect of temperature on the electrodeposition of indium on a titanium electrode in chloride electrolytes was studied in this paper.From the calculated values of the activation energy of the studied process, it was established that the electroreduction of indium on titanium occurs in a mixed mode (E_a = 35.7 kJ/mol). The optimum temperature regime of the process 30-40°C was found, which promotes the formation of qualitative cathode sediments and an increase in their purity during electrolysis (99.9992%).

Keywords: indium, electrolysis, indium electrorefining, cathodic polarization, purity of indium

Introduction. The temperature regime is one of the most important conditions for electrolytic refining of metals. The increase in temperature entails a number of changes: the solubility of salts and the electrical conductivity of the solution are increased, and the passivation of anodes is decreased. In addition, there is a change in the ion discharge potential, namely, reducing the overvoltage of hydrogen and metal evolution. In turn, each of these changes affects the quality of precipitation, so the effect of temperature is complex and under different conditions of electrolysis manifests itself in different ways [1, 2].

The temperature has a double effect on the electrodeposition of metals. With increasing temperature, the diffusion of ions increases, this makes it possible to increase the current density at which the formation of dendrites and spongy deposits is not yet observed. An increase in the temperature of the electrolyte leads to an increase in the growth rate of the crystals, which favors the appearance of a coarse-grained structure [3]. At not too high temperatures, the influence of the first of the factors considered prevails, so that the quality of the coatings is improved. At high temperatures, coatings of inferior quality are formed.

In practice, when examining the effect of the electrolyte temperature on the electrolysis performance, the optimal temperature is selected, at which the maximum possible current output and the minimum power consumption are observed. Usually, the temperature of the electrolyte in the baths is maintained in the range of 36-40 ° C. At this temperature, the electrolysis performance is stable, the energy consumption is small and the cathode precipitates are qualitative [4].

In [5], the effect of temperature on the cathodic and anodic yields on current during the electrodeposition of indium on a copper electrode in sulfuric acid solutions was studied. Brilliant dense precipitation of indium is obtained at higher current densities and elevated temperatures. The temperature does not have a significant effect on the anode current output. The authors of [6] established the influence of the temperature and acidity of the solution on the stability of monovalent indium in sulfuric acid solutions.

When studying the influence of temperature on the processes of electrochemical refining of metals, classical nonstationary methods are used - chronoamperometry and chronopotentiometry. In this paper, the effect of temperature on the kinetics of indium electroreduction on a titanium electrode, the cathode current yield, and the quality of cathodic precipitation are studied.

EXPERIMENTAL PART

The experiments were carried out in a thermostated cell made of organic glass with a volume of 300 cm^3 (figure 1). The cathode was a titanium electrode with an area of 40 cm^2, the anode was indium, and as a reference electrode, chloride-silver electrode was used, connected with the working solution by a salt bridge. The temperature of the electrolyte (30, 40, 50°C) was maintained by thermostating with an accuracy of 0.10°C. Before each measurement, the surface of the titanium electrode was cleaned out with a micron skin, degreased with alcohol and washed with bidistillate. The surface of the anode was renewed by removing the thin layer with a ceramic knife and rinsing with bidistilled water. The pH values of the electrolyte were maintained in the range of 1.5-2.0. The electrolyte was 1 mol/l sodium chloride solution containing 0.5 mol/l indium chloride. The choice of chloride electrolytes is explained by their high electrical conductivity, the activating action on the anode processes and the high rate of discharge-ionization of indium in them.

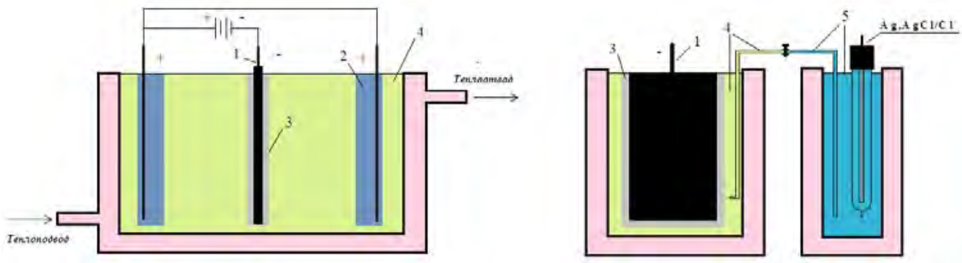


Figure 1 – Electrolysis installation: 1 – Cathode (Titan); 2 – Anode (Rough Indium); 3 – Cathode precipitate (Refined indium); 4 – Electrolyte; 5 – 3.5 M KCl

Analysis of the surfaces of the titanium electrode after cathodic polarization with temperature variation was performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectral analysis (EDX).

Electrolysis was performed in galvanostatic mode. Samples for analysis by ICP-MSmethod were prepared as follows: after electrolysis, the electrodeposited indium was dissolved in nitric acid (high purity) and diluted with bidistilled water to a certain volume.

Electrochemical measurements were performed on the device Autolab PGSTAT 302N.

RESULTS AND DISCUSSION

To determine the optimum electrolysis temperature, chronoamperometric measurements of the electrolytic deposition of indium on a titanium electrode at different temperatures were carried out (figure 2).

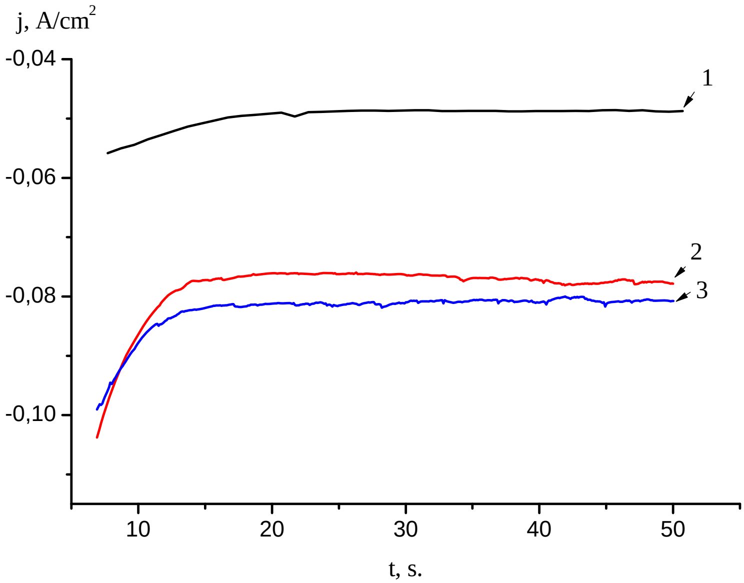


Figure 2 – Chronoamperogram of indium precipitation
at a potential of -0.9 V at various temperatures:
1 - 30 ^{0}C; 2 - 40 ^{0}C; 3 - 50 ^{0}C

As the figure shows, with an increase in temperature there is a significant increase in cathodic currents. The chronoamperogram is characterized by the presence of two sections, in the time interva l 0÷15 s the discharge reaction proceeds in the kinetic regime, and the limiting diffusion current is observed with time. To quantify the effect of temperature on the rate of reduction of indium from chloride electrolytes at a total deposition potential (-0.9 V rel. to the chloride-silver electrode), the values of the activation energy of the process were calculated. For this purpose, the values of the exchange currents were calculated on the basis of the dependence of the magnitude of the current on time.At infinitesimal values of time, the current tends to an infinitely large value, which indicates a high rate of supply of material to the surface of the electrode. Under these conditions, the slowness of the nondiffusive stages of the electrode process is clearly manifested. At sufficiently small values of time, the dependence of i on √t is linear and allows using the extrapolation method to determine the exchange currents. The linear dependencies shown in figure 3 can be described by the following equation:

$$i = b\sqrt{t} + a\ . \quad (1)$$

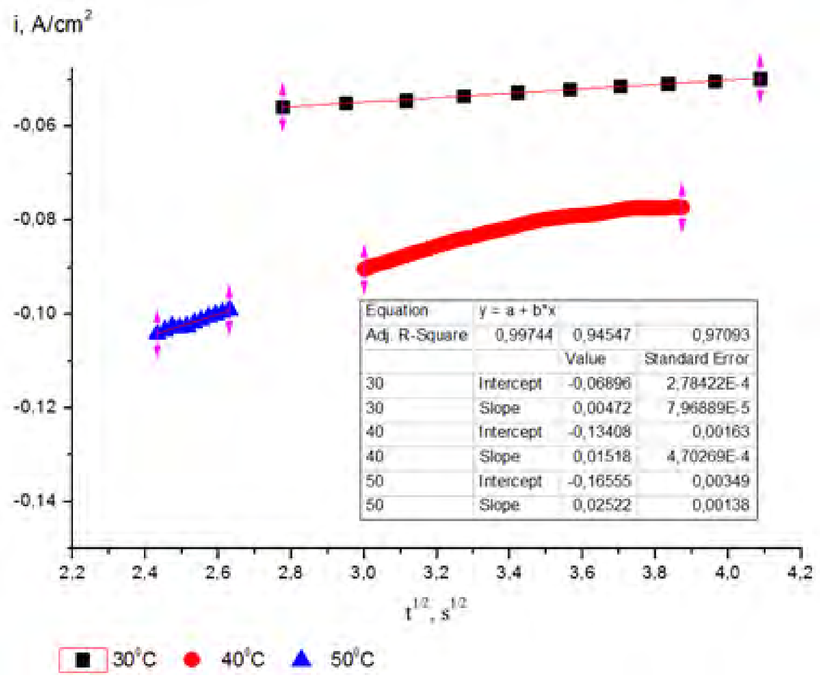


Figure 3 – Chronoamperograms of indium recovery
at small values of time on a titanium electrode

The results of processing chronoamperograms are presented in table 1.

Table 1 – The values of the constants a and b, exchange currents (i_0)
and correlation coefficients at different temperatures

T, ^{0}C	1/T, 10^{-3} K^{-1}	i_0, A/см^2	lg($-i_0$), A/см^2	B	a, 10^{-3}	R^2
30	3,300	-0,069	-1,161	-0,069	4,72	0,99
40	3,194	-0,134	-0,873	-0,134	15,18	0,95
50	3,095	-0,166	-0,781	-0,166	25,22	0,97

Then the values of the activation energy of the process under study at different temperatures were calculated from the exchange currents:

$$lgi = B - Ea / (2.3\ RT)\ . \quad (2)$$

The graph of the dependence lgi_0 -1/T allows us to calculate the value of the activation energy (figure 4), which was 35.7 kJ/mol. The value of the activation energy indicates the course of electroreduction of indium on a titanium electrode in a mixed mode.

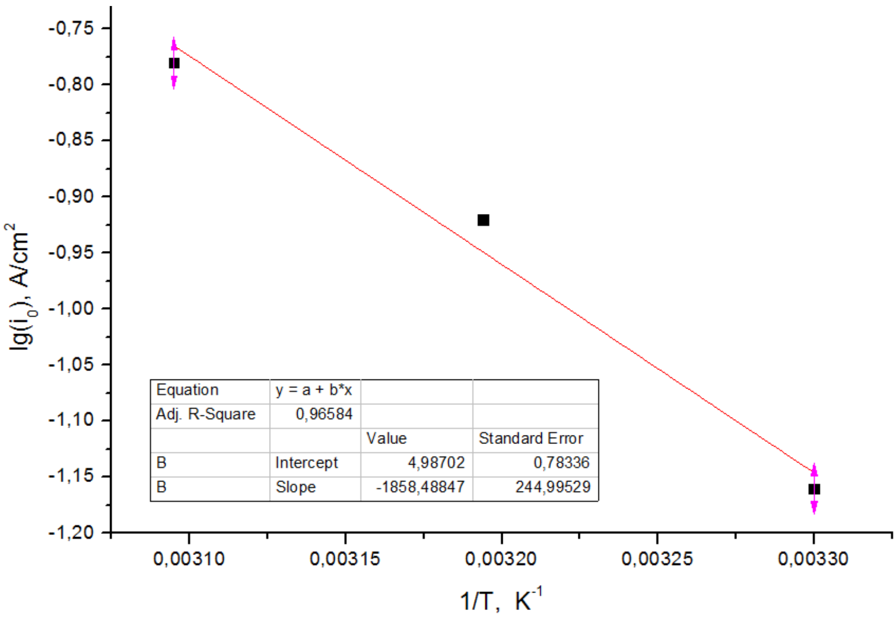


Figure 4 – Dependence of the logarithm of the exchange current lg i_0
on the reciprocal of the temperature 1/T

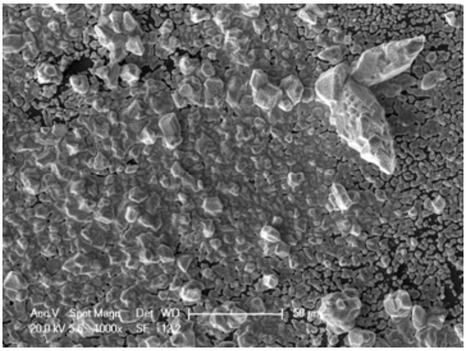
The obtained value of the activation energy is in good agreement with the value found from cyclic voltammograms of this process [7]. The obtained results can be used to calculate the rate of the process of electrodeposition of indium on a titanium electrode at other temperatures, which will allow us to optimize the choice of the temperature regime of electrolysis.

To determine the quality of cathode sediments obtained at different tempe-ratures, their analysis was performed by scanning electron microscopy (SEM) and energy dispersive X-ray spectral methods (figure 5).

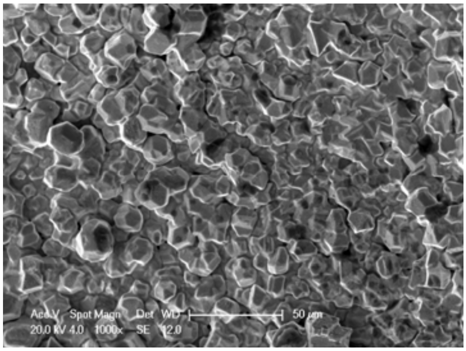
As can be seen from the photomicrograph, a small increase in temperature accelerates the rate of nucleation, precipitates coarse-grained sediments, which should lead to a decrease in impurities in the precipitated metal. The increase in temperature promotes the consolidation of precipitation, but at a temperature above 40 ° C they become rough and amorphous. This, apparently, is due to the course of the associated hydrogen evolution [8].

In an investigation of the discharge-ionization of indium on a titanium elec-trode, an optimal range of pH values of the electrolyte was found [9]in the refi-ning of indium (1.5-2.5). This is explained by the fact that the interfering effect of

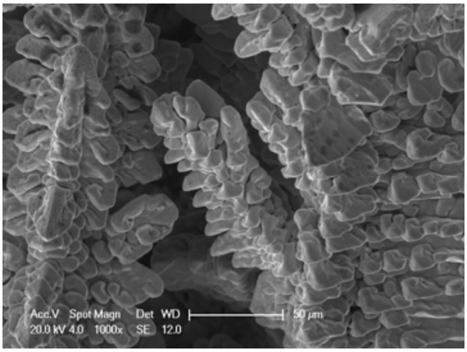
25 ^{0}C



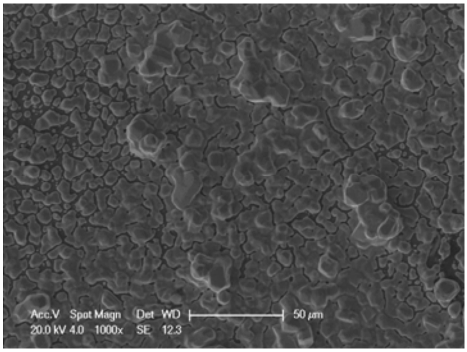
30 ^{0}C



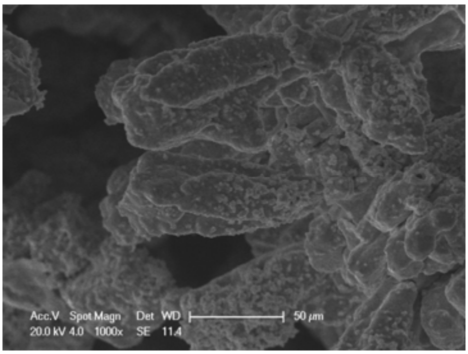
40 ^{0}C



50 ^{0}C



60 ^{0}C



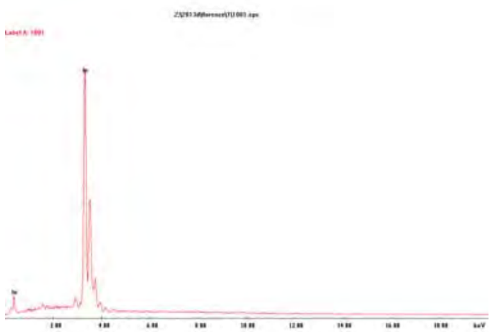


Figure 5 –Microphotographs of the surface
of a titanium electrode after cathodic polarization,
with temperature variation by SEM and EDX methods

reducing hydrogen ions is enhanced in a strongly acidic medium, and at pH above 3, indium hydroxide is formed. In the same work, the optimum current density (0.01 A/cm^2) was determined during electrolytic refining of indium.

The content of impurity metals and the degree of purity of electrified indium are determined by mass spectrometry (ICP-MS) methods with inductively coupled plasma. The cathode sediments of three experiments on electrolytic purification of rough indium were analyzed in order to evaluate the reproducibility of the experimental results. The results of the analysis are presented in table 2.

Table 2 – Results of analysis of precipitated indium samples by the ICP-MS method

№	The composition of the electrolyte	pH of the medium	The cathode potential (rel.chloride-silver electrode), V	Temperature, ^0C	VT catode, %	Degree of purity, %
1	0,5M $InCl_3$ + + 1,0M NaCl	1,5	-0,9	30	100,4	99,9992
					99,8	99,9989
					99,5	99,9990
2				40	100,1	99,9991
					99,7	99,9993
					99,4	99,9994
3				50	114,7	99,9982
					112,5	99,9984
					111,3	99,9987
Rough Indium IN-2						99,9840

As can be seen from the obtained results, there is a significant increase in the purity of cathode sediments during electrolytic refining of indium on a titanium electrode from chloride electrolytes in the temperature range 30-40 ^0C, which allows us to recommend these conditions as optimal.

Conclusion. The effect of temperature on the electroreduction of indium on a titanium electrode in chloride electrolytes was studied and the optimum temperature regime was determined. It was found that an increase in temperature to 40 °C leads to the enlargement of cathodic sediments and an increase in their purity. Further temperature increases impair the quality of the precipitated indium.

The value of the activation energy (Ea = 35.7 kJ/mol) of indium electroreduction on titanium, indicating the course of the process in a mixed mode, is determined.

Electrorefining of rough indium at a temperature of 30 and 40 ^0C was carried out and the purity of indium cathode precipitation was determined, the average value of which was 99.9992%.

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Резюме

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ЭЛЕКТРОРАФИНИРЛЕУ КЕЗІНДЕГІ
ИНДИЙДІҢ ТАЗАЛЫҚ ДӘРЕЖЕСІНЕ ТЕМПЕРАТУРАНЫҢ ӘСЕРІ

Зерттеу нысаны ретінде Қазақстанда өндірілетін қаралашты индий болды. Оның электрорафинирлеу кезіндегі шарттарын оңтайландыру үшін бұл жұмыста титан электродында хлоридті ерітінділерде индий электртұнуына температураның әсері зерттелді. Зерттелетін үрдістің активтену энергиясы несептелген мәндерінен индийдің титанда электртотықсыздануы аралас режимде жүретіні анықталды (E_a = 35,7 кДж/моль). Үрдістің оңтайлы темпералық режимі табылды – 30-40^{0}С. Бұл режим катодты тұнбалардың түзілуіне жақсы әсер етіп, олардың электролиз кезіндегі тазалық дәрежесін арттырады (99,9992%).

Түйін сөздер: индий, электролиз, индий рафинирлеуі, катодтық поляризация, индий тазалығы.

Резюме

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ВЛИЯНИЕ ТЕМПЕРАТУРЫ НА СТЕПЕНЬ ЧИСТОТЫ ИНДИЯ
ПРИ ЕГО ЭЛЕКТРОРАФИНИРОВАНИИ

Объектом исследования являлся черновой индий, производимый в Казахстане. Для оптимизации условий его электрорафинирования, изучено влияние температуры на электроосаждение индия на титановом электроде в хлоридных электролитах. Из расчитанных значений энергии активации исследуемого процесса установлено, что электровосстановление индия на титане протекает в смешанном режиме (E_a = 35,7 кДж/моль). Найден оптимальный температурный режим процесса 30-40^{0}С, способствующий образованию качественных катодных осадков и повышению их степени чистоты при электролизе (99,9992%).

Ключевые слова: индий, электролиз, рафинирование индия, катодная поляризация, чистота индия.