MATHEMATICAL MODELING OF THE PROCESS OF ELECTROCHEMICAL DEPOSITION OF Mo-Re

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Abstract: *The paper reports the results of mathematical modeling and optimization of the process of obtaining thin films based on Mo-Re alloy by electrodeposition. The study of electrodeposition of Mo-Re alloys was carried out using methods of potentiodynamic, galvanostatic, and cyclic voltammetry under different conditions on a Pt electrode. Studies have been conducted using the method of planning experiments and a regression equation is obtained. Based on the experimental data, the obtained regression equation was analyzed, the Fisher criterion was calculated and the significance of the regression coefficients was estimated. To confirm the experimental results, based on the data obtained, the coefficients of the regression equation were refined, and the criteria of significance and adequacy were calculated. The calculations based on the experimental data indicate that the regression equation adequately describes the process of co-deposition of rhenium with molybdenum.*
Keywords: *rhenium molybdenum alloys, regression equation, Fisher criteria, mathematical modeling, electrochemical deposition*
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Introductıon

Currently, with the development of science and technology, the production of alloys with special and defined (semiconductor, optical, radioactive, etc.) properties is becoming increasingly important. Such materials include rhenium and its alloys, which have many specific physical properties and are used in various areas of semiconductor production [1-3].

In recent years, the scope of use of these elements and their compounds has expanded significantly: space technology, radio engineering, automation, electronics, etc. There is also a need to study their chemical and physical properties and develop a technology for producing new alloys based on these elements. Significant mechanical strength, hardness, high electrical resistance, and other properties make it possible to use rhenium and its alloys in various technology areas widely. Rhenium alloys with several metals are used in electronic, electrical, and nuclear engineering, and in the production of special-value coatings [4-6]. The combination of unique physicochemical properties of rhenium makes this metal promising for use in high-tech industries such as aviation, rocket engine production, nuclear power, biomedicine, and heterogeneous catalysis.

By now, a sufficient number of works in the literature [7-9] are devoted to the electrochemical deposition of rhenium and molybdenum from various aqueous electrolytes. Since both molybdenum and rhenium are refractory metals, mixing these two elements in the form of alloys provides for achieving a double advantage of both the high-temperature physical properties of rhenium and the excellent mechanical properties of molybdenum; thus, the overall characteristics of the alloy are significantly improved.

The solution to most problems in chemistry and chemical engineering is associated with complex and expensive experiments. Hence, the importance of optimal experimental planning methods is clear, which in some cases allow for a significant reduction in the time and material costs of research. Mathematical modeling of new materials allows for a significant increase in the speed of development of new versions of products. For the first time, attempts to apply mathematical methods for optimal experimental planning were made by the English mathematician R. Fisher. The theory of experimental planning began to develop at a particularly rapid pace after the appearance of the works of D. Box and K. Wilson [10].

Methods of optimal experimental planning allow the use of mathematical apparatus not only at the stage of processing measurement results but also in the preparation and implementation of experiments. Compiling a mathematical model of the studied process based on the obtained results decreases the number of experiments, helps to reduce the number of reagents, and accordingly, the time spent on research is reduced [11]. Construction of a mathematical model of the process by choosing the most optimal parameters and expressing them as a mathematical function can help to increase the production output and reduce its cost. Therefore, the mathematical model should not only accurately describe the actual process, but also be simple and ensure the accuracy of calculations [12]. Based on the study of the process results using methods of mathematical statistics, it is easy to determine the influence of the main parameters (concentration of the initial components, temperature, current density) on its course and determine the pattern of the reaction, as well as the optimal mode for its implementation. To confirm the obtained experimental results, a regression equation is constructed, and the criterion of significance and adequacy is calculated [13]. For optimization of multifactorial experimental problems, the most interesting is the method of experimental planning.

This work is devoted to the results of mathematical modeling and optimization of the process of obtaining thin films based on Mo-Re alloy by the method of electrodeposition.

Experimental part

For electrodeposition of Mo-Re alloy, the electrolyte of the following composition was selected: sodium molybdate - Na_2MoO_4, potassium perrhenate - $KReO_4$, sulfuric acid - H_2SO_4. An electrode with a visible surface of 0.07 cm^2 was used as the working electrode. The three-electrode cell contained the electrode under study, the platinum auxiliary electrode with an area of 4 cm^2, and a silver chloride reference electrode. Volt-ampere curves were recorded without stirring. Deposition of films for studying the structure and composition was carried out on Pt and Ni substrates with an area of 2.0 cm^2. The kinetics of the processes were monitored using cyclic voltammetry measurements on the IVIUMSTAT device. To study the morphology of the films on the platinum substrate, the electrode surface was examined using a JEOL JSM7600F scanning electron microscope at various magnifications.

Results and discussion

For electrodeposition of the Mo-Re alloy, the electrolyte of the following composition was selected: sodium molybdate Na_2MoO_4, potassium perrhenate $KReO_4$, and sulfuric acid H_2SO_4; pH = 0.4. Z_1 and Z_2 are concentrations (M) of rhenium and molybdenum in the electrolyte, Z_3 is current density (A/dm^2). The optimization parameter was the percentage of rhenium in deposit Y. Based on preliminary experiments, the factor variation intervals were selected so that the optimization parameter values were in the range of 40-90% rhenium.

The required number of experiments N with FFE is determined by the formula

$$N = n^k$$

where N is the number of experiments in the plan; n is the number of levels (mainly two); k is the number of factors.

A three-factor experiment (k = 3), N = 8 was used in the work. The experimental conditions, the planning matrix and the experimental results are presented in Table 1.

Table 1. Planning matrix

№	Factors			Coded values of factors			Y_{exp}, %	Y_{cal}, %	Relative error, (%) $\lvert y_{exp}-y_{cal}\rvert / y_{exp}$
	Z_1(Re)	Z_2(Mo)	Z_3	x_1	x_2	x_3			
1	0.003	0.0015	0.5	-1	-1	-1	43	43.5	**1.2**
2	0.003	0.0015	2	-1	-1	+1	58	59.5	**2.6**
3	0.003	0.04	0.5	-1	+1	-1	52	49	**5.8**
4	0.003	0.04	2	-1	+1	+1	64	65	**1.6**
5	0.004	0.0015	0.5	+1	-1	-1	69	69.5	**0.7**
6	0.004	0.0015	2	+1	-1	+1	88	87.5	**0.6**
7	0.004	0.04	0.5	+1	+1	-1	73	75	**2.7**
8	0.004	0.04	2	+1	+1	+1	91	91	**0**
Ave-rage	*0.0035*	*0.02075*	*1.25*				*67.25*	*67.50*	

Using formula (1):

$$Z_i^0 = \frac{z_i^{max}+z_i^{min}}{2} \qquad \Delta Z_i = \frac{z_i^{max}-z_i^{min}}{2} \qquad (1)$$

For all factors the values of Z have been calculated:

$$Z_1^0 = \frac{0.003+0.004}{2} = 0.0035\ ;\ \Delta Z_1 = \frac{0.004-0.003}{2} = 0.0005\ ;\ Z_2^0 = 0.0207\ ;\ \Delta Z_2 = 0.0192;$$

$$Z_3^0 = 3; \quad \Delta Z_3 = 1;$$

$$x_i = \frac{Z_i - Z_i^0}{\Delta Z_i} \qquad (2)$$

at $Z_1 = 0.003$, the value of $x_1 = \frac{0.003-0.0035}{0.005} = -1$

The coefficient in the regression equation b_j is determined by the scalar product of the y column and the corresponding x_j column, divided by the number of experiments in the design matrix (N = 16).

$$b_j = \frac{1}{8}\sum_{i=1}^{8} x_{ji} y_i$$

b_1=13 b_0=67.25; b_1=13; b_2=2.75; b_3=8

Substituting the values of the above calculated coefficients into the regression equation $y = b_0 + b_1x_1 + b_2x_2 + b_3x_3$, the following expression is obtained:

$$y=67.25+13x_1+2.75x_2+8x_3$$

The optimization parameter of a three-component system is determined by the Box-Wilson equation using the following expression

$$y= b_0+b_1x_1+b_2x_2+b_3x_3+b_{12}x_1x_2+b_{13}x_1x_3+b_{23}x2x_3+b_{123}x_1x_2x_3 \qquad (3)$$

To obtain a more complete regression equation effects of paired and triple interactions are taken into account

$$b_{12} = \frac{\sum_{i=1}^{8}(x_1x_2)_i y_i}{8} = -1$$

The remaining coefficients are determined in a similar way

$$b_{12}=-1;\ b_{13} = 1.25;\ b_{23} = -0.5\ b_{123} = 0.25$$

After conducting three additional parallel experiments the following values have been obtained

$$\mathbf{y_1}= 42.7;\ \mathbf{y_2}=42.3;\ \mathbf{y_3}=42.9$$

$$\bar{y}^0 = \frac{\sum_{n=1}^{3} y_n^0}{3} = 42{,}6$$

$$S_{Sreprod}^2 = \frac{\sum_{n=1}^{3}(y_n^0 - \bar{y}^0)^2}{3} = \frac{0{,}01 + 0{,}09 + 0{,}09}{3} = 0{,}063$$

$$y^0 = \frac{\sum_{n=1}^{n} y^0}{n}$$

$$S_{Bi} = S_{sreprod}^2/\sqrt{N}$$

$$S_b = \sqrt{0{,}063} = 0{,}25$$

$$S_b = 0{,}25/\sqrt{8} = 0{,}09$$

Assessment of the significance of the co-efficients is made according to the Student criterion:

$$t_i = \frac{B_i}{S_{bi}} \qquad (4)$$

In accordance with the table of critical values for Student's *t*-distribution (f = 3, P = 0.05), t = (3.18)

then $S_b \cdot t = 0.09\ 3.18 = 0.286$

It is clear that all regression coefficients are significant, with the exception of $b_{123} = 0.25$. Then we consider the following expression:

$$y= 67{,}25+13x_1+2{,}75x_2+8x_3 - x_1x_2+1.25x_1x_3-0.5x_2x_3 \qquad (5)$$

It is necessary to check the adequacy of the obtained regression equation using the Fisher criterion.

$$F = \frac{S_{sost}^2}{S_{sreprod}^2} \qquad (6)$$

The residual variance is calculated using the formula

$$S^2_{sost}\frac{\sum(yi-yj)^2}{N-l} \qquad (7)$$

$$S^2_{sost}=\frac{2{,}125}{4}=0{,}53 \text{ then } F=\frac{0{,}53}{0{,}063}=8{,}43$$

The calculated value is less than the table value, so the resulting regression equation adequately describes the experiment.

The transition from dimensionless scale to natural size can be done using the formula below.

$$x_i=\frac{Z_i-Z_i^0}{\Delta Z_i}$$

as a result the following equation is obtained

$$y= -50+18500Z_1+221Z_2 +0.75Z_3-Z_1Z_2+2500Z_1Z_3 - 26Z_2Z_3$$

The values of parameters Z_1=0.004, Z_2=0.04 and Z_3=2.5 provide the maximum value of the objective function (y_{max})=90%.

To find the average approximation error, the following calculations were performed, the results of which are presented in the table below.

The average approximation error is calculated using the formula:

$$A=\frac{1}{k}\sum_{1=1}^{k}\frac{y_i-y_j}{y_i}\cdot 100\%$$
$$A= 2{,}03\ \%$$

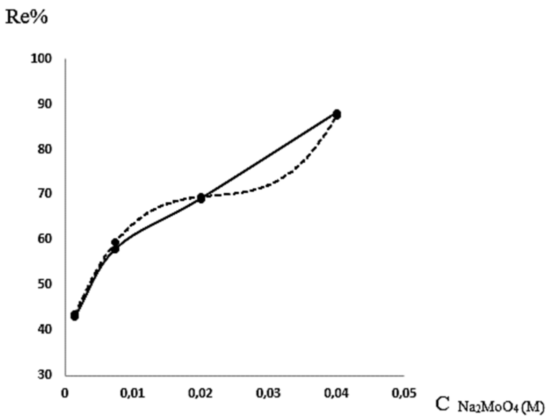

Fig. 1. Dependence of the rhenium content in the deposits on the concentration of Na_2MoO_4 in the electrolyte (solid lines are calculated data, dashed lines are experimental values). Electrolyte composition (M): 0.004 $KReO_4$ + 2.0 H_2SO_4; pH=0.4, i_k = 2.5 A/dm^2, T=298 K.

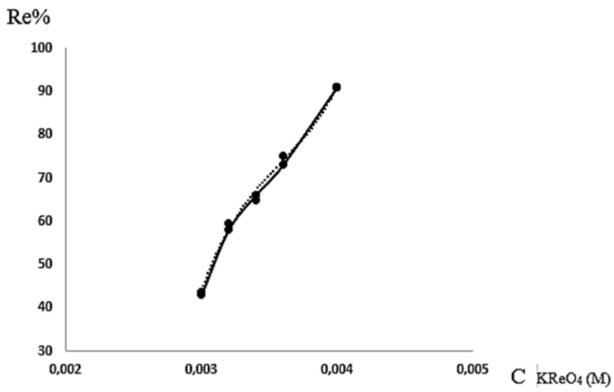

Fig. 2. Dependence of the rhenium content in the deposits on the concentration of $KReO_4$ in the electrolyte (solid lines are calculated data, dashed lines are experimental values). Electrolyte composition (M): 0.04 Na_2MoO_4 +2.0 H_2SO_4; pH=0.4, i_k = 2.5 A/dm^2, pH= 0.4 T=298 K.

Based on the experimental data, it was found that at rhenium and molybdenum concentration values of 0.003 and 0.04 M and a current density of 0.5 A/dm^2, the value of ε_{max} is 0.057. That is, the point with the maximum relative error corresponds to the third line of Table 1.

To verify that the developed mathematical model accurately describes the process of co-deposition of rhenium and molybdenum, graphs were constructed reflecting the dependence of the alloy composition on the concentration of rhenium, molybdenum, and the current density.

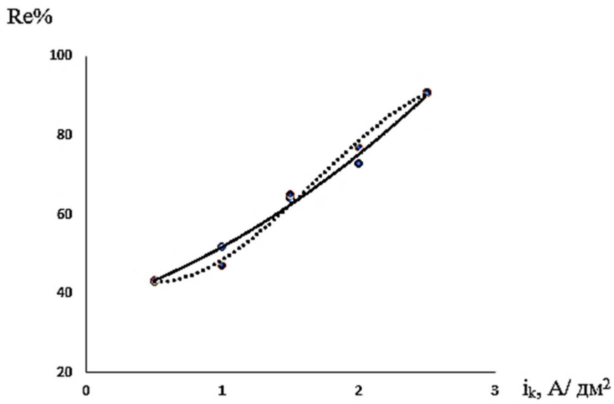

Fig. 3. Dependence of the rhenium content on current density (solid lines are calculated data, dashed lines are experimental values). Electrolyte composition (M): 0.04 Na_2MoO_4 + 0.004 $KReO_4$+ 2.0 H_2SO_4; pH=0.4; T=298 K.

Conclusıon

Based on the experimental data, the regression equation is obtained, the Fisher criterion is calculated, and the significance of the regression coefficients is estimated. It was found that the developed model allows us to adequately determine the optimal co-deposition mode. When comparing the calculated and experimental results, it was found that the accuracy of the regression equation is 2%. Thus, the obtained regression equation allows us to determine the relationship between the alloy composition, the electrolysis parameters, and the electrolyte composition.

References

1. James E. *Renium; Propereties, uses and occurrence*, Nova Science Pub Inc. 2016. 130 p.
2. Naor A., Eliaz N., Burstein L., Gileadi E. Direct Experimental Support for the Catalitic Effect of Iron-Group Metals on Electrodeposition of Rhenium. *Elec.Sol. State Let.* 2010*,* **Vol.13(12)**, p. 91 – 93. DOI: 10.1149/1.3489532
3. Pallant A.A. *Monograph Metallurgy of rhenium*. Nauka. 2007. 29 p.
4. Seleznev V.A., Tarkhov M.A., Voronov B.M., Milostnaya I.I., Lyakhno V.Yu., Garbuz A.S., Mikhailov M.Yu., Zhigalina O.M., Gol'tsman G.N. Deposition and characterization of few-nanometers-thick superconducting Mo–Re films. *J. Superconductor Science and Technology*. 2008, **Vol. 21(11)**, 115006. DOI: 10.1088/0953-2048/21/11/115006
5. Andreone A., Barone A., Di Chiara A., Mascolo G., Palmieri V., Peluso G., Scotti di Uccio U. Mo-Re superconducting thin films by single target magnetron sputtering. *J. IEEE Transactions on Magnetics.* 1989, **Vol. 25(2)**, p. 1972-1975. DOI: 10.1109/20.92695
6. Yapontseva Yu.S., Kublanovsky V.S., Vyshnevskyi O.A. Electrodeposition of CoMoRe alloys from a citrate electrolyte. *Journal of Alloys and Compounds.* 2018, **Vol. 766**, p. 894-901. DOI: 10.1016/j.jallcom.2018.07.018
7. Trefon-Radziejewska D., Juszczyk J., Fleming A., Podwórny J., Chirtoc M., Horny N., Wrona A., Lis M., Mazur M., Wojcieszak D., Kaczmarek D., Bodzenta J. Thermophysical properties of refractory W-50.4%Re and Mo-39.5%Re thin alloy layers deposited on silicon and silica substrates. *International Journal of Refractory Metals and Hard Materials*. 2020, **no**

. **87**, p.105-147. DOI: 10.1016/j.ijrmhm.2019.105147

8. Liu Q., Huang Q. Electrodeposition of ReMo alloys. *J. Electrochimica Acta*. 2024, **Vol. 500**, 144761. DOI: 10.1016/j.electacta.2024.144761
9. Alizade Y.E., Salahova E.A., Kalantarova P.E., Heybatova A.F., Hajiyeva K.I., Khankishiyeva N.N., Tagiev D.B. Electr odeposition of thin molybdenum coatings from sulphate solutions. *Azerbaijan Chemical Journal*. 2023, **no. 2**, p. 47-54. DOI: 10.32737/0005-2531-2023-2-47-53
10. Sautin S.N. *Experiment planning in chemistry and in chemical technology*, Leningrad: Chemistry. 1975. p. 31.
11. Звонаров С.В. *Основы математического моделирования*. Екатеринбург: Издательство Уральского университета. 2019. с.112
12. Самарский А.А. *Математическое моделирование*. Москва: Наука. 1997. с. 320
13. Линдеман О.О. *Математические модели в химии*. Москва: Химия. 1999. с. 194