About one counterexample of applying method of splitting in modeling of plating processes

D S Solovjev¹², I A Solovjeva², Yu V Litovka³, I L Korobova²

¹ Tambov State University named after G.R. Derzhavin, 33, Internatsionalnaya, Tambov, 392000, Russia
² Tambov State Technical University, 106, Sovetskaya, Tambov, 392000, Russia
³ E-mail: solovjevdenis@mail.ru

Abstract. The paper presents the main factors that affect the uniformity of the thickness distribution of plating on the surface of the product. The experimental search for the optimal values of these factors is expensive and time-consuming. The problem of adequate simulation of coating processes is very relevant. The finite-difference approximation using seven-point and five-point templates in combination with the splitting method is considered as solution methods for the equations of the model. To study the correctness of the solution of equations of the mathematical model by these methods, the experiments were conducted on plating with a flat anode and cathode, which relative position was not changed in the bath. The studies have shown that the solution using the splitting method was up to 1.5 times faster, but it did not give adequate results due to the geometric features of the task under the given boundary conditions.

1. Introduction

Galvanic coatings are applied for improving the surface’s wear resistance, for protection against corrosion and for giving the product’s presentation. The plating quality has a very strong influence on the operating characteristics of the finished products. Reducing unevenness plating is difficult due to different scattering ability of the electrolyte and the «boundary effect» [1]. Uneven thickness of the coating layer can lead to such negative factors as defects, an increase in power consumption and metal. Also subsequent mechanical processing of the finished product can be required. Technological and constructive factors influence the quality of galvanic coatings. Articles [2-4] study the influence on technological factors (such as current density, temperature, acidity and concentration of electrolyte components), on the quality of the plating. In articles [5, 6], authors solved problems of searching a non-conductive screens’ position and the number of additional anodes. As a rule, these problems are solved experimentally. However, the high cost of electrolytes, metals and energy does not allow numerous experiments. Mathematical modeling of electroplating processes is the way out. An important question, which arose after the formation of the equations of the mathematical model, is the choice of the solution methods. This is especially true in the case of using differential equations in partial derivatives.

The aim of this work is studying the correctness using two variants of the implicit grid method (with seven-point and five-point templates in combination with the splitting method) for solving differential equations in partial derivatives of mathematical models of plating processes.
2. Mathematical model of plating processes

The unevenness of the coating thickness can be estimated by criteria proposed by L. I. Kadaner [7]. The unevenness is determined from the formula:

\[ R = \int_{S_c} \frac{\delta(x, y, z)}{\delta_{\text{min}}} \, dS, \]

where \( \delta_{\text{min}} \) is the minimum according to the regulations thickness of the coating; \( \delta(x, y, z) \) – the thickness of the coating at the point of the surface with coordinates \( x, y, z \); \( S_c \) – surface area of the detail.

The thickness of the coating at the point of the surface with coordinates \( x, y, z \) can be calculated using M. Faraday’s law:

\[ \delta(x, y, z) = \eta \cdot \left( \frac{i_a(x, y, z) \cdot T \cdot E}{\rho} \right), \]

where \( E \) is the electrochemical equivalent of the metal of the coating; \( T \) – the duration of the plating process; \( \rho \) is the density of the coating metal; \( \eta \) – the outcome of the metal by the electric current, which depends, as a rule, on the current density at the point of the surface with coordinates \( x, y, z \), temperature \( t \) of the electrolyte and the concentration of \( f \)-th component \( C_f \) of the electrolyte.

The current density on the electrode surface is calculated from the law of G. S. Ohm:

\[ i_a(x, y, z) = \chi \cdot \text{grad} \phi(x, y, z) |_{S_a}, \]
\[ i_c(x, y, z) = -\chi \cdot \text{grad} \phi(x, y, z) |_{S_c}, \]

where \( \chi \) is the specific conductivity of the electrolyte; \( S_a \) – surface of the anode; \( \phi \) is the potential of the electric field in the volume of the plating bath.

The distribution of the potential of the electric field is defined by the differential equation in partial derivatives by P.-S. Laplace [8]:

\[ \frac{\partial^2 \phi(x, y, z)}{\partial x^2} + \frac{\partial^2 \phi(x, y, z)}{\partial y^2} + \frac{\partial^2 \phi(x, y, z)}{\partial z^2} = 0, \]

with boundary conditions on the border «electrolyte-insulator»:

\[ \frac{\partial \phi(x, y, z)}{\partial n} |_{S_{\text{ins}}} = 0, \]

with boundary conditions on the border «electrolyte-anode»:

\[ \phi(x, y, z) + F_a(i_a(x, y, z)) |_{S_a} = U, \]

with boundary conditions on the border «electrolyte-cathode»:

\[ \phi(x, y, z) + F_c(i_c(x, y, z)) |_{S_c} = 0, \]

where \( S_{\text{ins}}, S_a, S_c \) – surface of the wall of the galvanic bath; \( n \) – normal to the surface of the wall of the bath; \( U \) – voltage; \( F_a, F_c \) – functions of the anode and cathode polarization, respectively.

An approximation difference scheme with a seven-point template «cross» is used for the numerical solution of equation (5). The approximation error is equal to \( O(h_x^2 + h_y^2 + h_z^2) \), where \( h_x, h_y, h_z \) – the steps of the template along axes \( X, Y \) and \( Z \). Solving the systems of network equations is found by the numerical method of upper relaxation, which provides a high rate of convergence [9].

In the book [10] the method of splitting is used to reduce the dimensionality of the problem (5)-(8) and the calculation’s numbers. The volume of the plating bath is replaced by \( n_1 \) horizontal and \( n_2 \) vertical cross sections that are parallel to planes \( XOY \) and \( YOZ \) in the method of splitting. For each section, the two-dimensional problems are solved in the following form:

\[ \frac{\partial^2 \phi(x, y)}{\partial x^2} + \frac{\partial^2 \phi(x, y)}{\partial y^2} = 0, \]
\[ \phi(x, y) + F_a(i_a(x, y)) |_{S_{\text{an}}} = U, \]
\[ \phi(x, y) + F_c(i_c(x, y)) |_{S_{\text{cn}}} = 0, \]
\[ \frac{\partial \phi(x, y)}{\partial n} |_{S_{\text{an}}} = 0. \]

Then the solution of problem (5)-(8) will be defined as:

\[ \phi(x, y, z) = 0.5 \cdot \left( \phi^x(x, y) + \phi^v(y, z) \right), \]

where \( h = 0, 1, \ldots, n_1; v = 0, 1, \ldots, n_2 \). Approximation of difference schemes used for the numerical solution of equations (9)-(12) and (13)-(16).
Let us examine the correctness of the solution of the equations of mathematical models of processes of electroplating using: 1) a seven-point template, 2) a five-point template in combination with the splitting method.

3. Materials and methods
A series of experiments by deposition nickel plating was carried out in the bath with the size of 30x40x30 cm (XxYxZ) to examine the correctness of the solution of the equations of the mathematical model. In the series of experiments, there were four possible options for the location of the anode and cathode in the plating bath (figure 1). The dimensions of the surfaces of anode $S_a$ and cathode $S_c$ are: a – 25x25 cm and 15x15 cm; b – 10x25 cm and 10x25 cm; c – 15x15 cm and 25x25 cm; d – 10x10 cm and 10x10 cm. The coating was deposition in sulphate electrolyte of the Watts with pH= 2.5-3 and the concentration of components $C$, g/l: NiSO$_4$ – 200-250; NiCl$_2$ – 30-60; H$_3$BO$_3$ – 25-40. Temperature $t$ of the electrolyte was maintained in the range of 40-45°C. Voltage was $U = 6$V. Processing’s time $T$ was 30 min.

![Diagram](image1.png)

Figure 1. The electrode arrangement in space of the plating bath:
a – symmetric coaxial ($S_a > S_c$); b – asymmetric coaxial ($S_a = S_c$);
c – symmetric coaxial ($S_a < S_c$); d – asymmetric non-axial ($S_a = S_c$).
The measurement of average values of the deposited Nickel coatings was carried out according to GOST 9.302-88 with a thickness gauge «Constant K5». The thickness gauge has a measurement error of ± 1 µm in the range of 0...100 µm. Each experiment was repeated 3 times. After that, the average value of measured coating thickness was calculated in geometrically equivalent points on the surface of the parts to reduce the influence of random factors.

4. Results and discussion
The results of experimental studies and mathematical modeling of processes of applying Nickel plating is given in table 1 and in figures 2, 3.

| Variant of arrangement of electrodes in figure 1. | Experiment | Seven-point template in combination with splitting method | Seven-point template in combination with splitting method |
|-------------------------------------------------|------------|--------------------------------------------------------|--------------------------------------------------------|
| δ_{min}, µm | R | δ_{min}, µm | R | δ_{min}, µm | R |
| a | 5.6  | 1.148  | 5.679  | 1.212  | 6.981  | 1.196  | 26 | 15 |
| b | 4.3  | 1.216  | 4.544  | 1.224  | 3.383  | 1.165  | 32 | 20 |
| c | 3.4  | 1.146  | 3.583  | 1.134  | 2.479  | 1.853  | 21 | 12 |
| d | 5.1  | 1.271  | 5.311  | 1.311  | 2.364  | 1.148  | 30 | 19 |

**Figure 2.** The distribution of coating thickness δ along surface S_c for one of the cross sections along the length of L_x: 1 – experiment; 2 – seven-point template; 3 – five-point template in combination with the splitting method.
In mathematical modeling, using the five-point template with the splitting method, the largest discrepancy between the theoretical thickness distribution and the experimental one is given. The speed of calculations by this method was higher. These results can be explained by the difference of potential distribution $\varphi$ in the space of a plating bath (figure 3), which is obtained by solving equations (5)-(8) and equations (9)-(12), (13)-(16) with the subsequent averaging of the result (17).

Figure 3. The distribution of potential $\varphi$ in the space of the bath along horizontal cross sections $A_{a}B_{a}C_{a}D_{a}$: a, c, e, g – seven-point template; b, d, f, h – five-point template in combination with the splitting method.
If in the space of the bath, there is at least one $A_h B_h C_h D_h$ horizontal cross section or vertical cross section $E_v F_v G_v H_v$, that contains $S$, or simultaneously does not contain $S$, the splitting method cannot be used, because boundary conditions (10) or (14) are never met.

5. Conclusion

The study showed that the solution of the equations of the mathematical model of the process of plating using the method of splitting does not give correct results even in the most simple geometric configurations of the used anode and cathode. Mathematical modeling of platings using figure anodes, and additional anodes is generally impossible.

Simultaneous accounting of the three spatial coordinates (seven-point template) gives the most appropriate results in mathematical modeling of processes of electroplating, although it is the most time-consuming.

References

[1] Kudryavtsev N T 1975 *Applied electrochemistry* (Moscow: Chemistry)
[2] Dini J W and Johnson H R 1980 The properties of gold deposits produced by DC, pulse and asymmetric AC plating *Gold Bulletin* 13(1) 31-34
[3] Antikhovich I V, Chernik A A, Zharskii I M and Bolvako A K 2015 Electrodeposition of a nickel coating from a low-temperature acetate-chloride nickel-plating electrolyte *Russian Journal of Electrochemistry* 51(3) 281-285
[4] Karahan I H 2015 Effect of pH values on the characterization of electrodeposited Zn-Mn coatings in chloride-based acidic environment *International Journal of Electrochemical Science* 10(6) 4513-4522
[5] Purcar M, Topa V, Munteanu C, Chereches R, Avram A and Grindei L 2012 Optimization of the layer thickness distribution in electrochemical processes using the level set method *IET Science, Measurement & Technology* 6(5) 376-385
[6] Solovjev D S and Litovka Yu V 2013 Mathematical modeling and optimal control of electrodeposition in a multi-anode bath taking into account the change in the concentration of the electrolyte components *Computer Research and Modeling* 5(2) 193-203
[7] Kadaner L I 1961 *The uniformity of electroplated coatings* (Kharkov: Kharkov State University)
[8] Deconinck J 1994 Mathematical modelling of electrode growth *Journal of Applied Electrochemistry* 24(3) 212-218
[9] Marchuk G I 1989 *Methods of Computational Mathematics* (Moscow: Science)
[10] Marchuk G I 1988 *Splitting methods* (Moscow: Science)