UNIFORMITY OF THE DISTRIBUTION OF THICKNESS OF COATINGS IN THE CASE OF NONSTATIONARY SYSTEMS OF ELECTROLYSIS

1. CURRENT REVERSAL

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Current reversal is widely used in electroplating for intensifying the processes of electrodeposition and improving the microstructure and quality of galvanic deposits. It is also known that in certain cases current reversal exerts a favorable influence upon the uniformity of the macrodistribution of metal [1]. This permits the use of current reversal to reduce the superfluous consumption of nonferrous metals, which, for example, in the case of cadmium comprise an average of about 35% [2]. Let us consider the uniformity of the distribution of metal in the case of reversal in greater detail in order to determine the optimum ratio of the durations of the cathodic and anodic periods at which the amount of excess applied metal will be the least.

It is known that the uniformity of the distribution of the coating thickness over the surface of the part (in the case of a 100% current yield) is determined by the properties of the solution (its scattering power R) and the geometry of the system. Therefore, with all other conditions equal, the value of the optimum ratio of the anodic and cathodic periods will also depend upon the geometry of the part and the electrolyzer. In view of the exceptional variety of geometric forms and sizes of parts, it is impossible to determine this ratio in general. However, the problem can be somewhat narrowed, and a solution can be sought for a definite class of parts, possessing the same geometrical characteristics. Let us assume that the geometry of the system of part and electrolyzer can be approximately characterized by two quantities: by the ratio D_{max}/D_{min} of the maximum current density to the minimum in the original field, depending upon the "degree of contour of the part," and by the distance l_0 between the points with the greatest and least current density – the "size of the part." Then the uniformity of the distribution of the deposit on parts of a given class (in particular, in the case of reversal), can be approximately judged by studying the distribution of metal in any reference cell with the same geometrical characteristics. The latter may be considered as an approximate model of a given class of parts.

One of the most convenient reference cells is the slit cell, the secondary distribution of current in which has already been calculated [3]. The schematic distribution of the current along the electrode of a slit bath in the cathodic and anodic periods is shown in Fig. 1. From the figure it is evident that both in the cathodic and in the anodic period, the current density is a maximum at point 1 and a minimum at point 2. But since the anodic distribution of the current is usually less uniform than the cathodic distribution, the close-lying portions of the cathode will dissolve most intensively in the anodic period. As a result, the part of the metal superfluously applied in the cathodic period dissolves in the anodic period. The problem reduces to seeking a ratio of the cathodic and anodic periods at which the amount of usefully consumed metal will be a maximum. This condition can be written in the form of the requirement of a maximum value of the following criterion [4]:

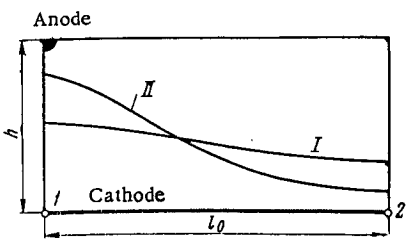

Fig. 1. Scheme of slit cell and distribution of current along the electrode in the cathodic and anodic periods. I) Cathodic; II) anodic distribution.

$$K_p = \frac{\delta_{min}}{\delta_{av}} = \max, \qquad (1)$$

where δ_{min} and δ_{av} are the minimum and average thicknesses of the coating, respectively.

The minimum thickness of the coating during the period, in accord with the Faraday law, is determined by the equation:

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$$\delta_{min} = \frac{k}{\gamma_s}(D_к\tau_к - D_a \cdot \tau_a), \quad (2)$$

where k is the electrochemical equivalent of the metal deposited; D_k and D_a are the cathodic and anodic current densities at the point with minimum thickness of the deposit, respectively; τ_k and τ_a are the durations of the cathodic and anodic periods, γ is the specific gravity, s is the area of the coating.

To simplify Eq. (2), let us represent the current densities D_k and D_a in the form of products of the average current densities $D_{k\,av}$ and $D_{a\,av}$ by their dimensionless values D_k and D_a. As a result we obtain:

$$= \frac{k}{\gamma s} D_{к\,av}\tau_к(D_к - \alpha D_a). \quad (3)$$

Here $\alpha = \frac{D_{a\,av} \cdot \tau_a}{D_{к\,av} \cdot \tau_к}$ represents the ratio of the amounts of electricity passed through in the anodic and cathodic periods. The average thickness of the coating in the case of current reversal is determined by an analogous expression:

$$\delta_{ср} = \frac{k}{\gamma s} D_{к\,av}\tau_к(1 - \alpha). \quad (4)$$

Substituting for example, (3) and (4) into (1), we obtain:

$$K_p = \frac{D_к - \alpha D_a}{1 - \alpha}. \quad (5)$$

For a rigorous solution of the problem posed, the function $K_p = f(\alpha)$ (5) must be investigated for a maximum. The difficulty lies in the fact that the position of the point with maximum thickness of the coating varies with α. Therefore, to find an optimum system of reversal at set polarization curves, it is necessary to calculate the anodic and cathodic current distribution. Then, having set a series of values of $\alpha (0 < \alpha < 1)$, we must seek points with a minimum thickness of the coating, comparing them with one another and selecting the value of α at which the minimum thickness is the greatest.

The solution of the problem is appreciably simplified if the nonlinear polarization curves in a given interval of current densities are replaced by linear curves and the available formulas for the secondary distribution of current in the slit bath are used. In addition, it should be considered that the geometry of the slit bath is such, that, depending upon α, the minimum thickness of the coating may lie either at point 1 or at point 2. If the thickness of the deposit is a minimum at point 1, then in Eq. (5) we should substitute the values of D_k and D_a at this point. Let $D_{1k} = 1.5$, $D_{1a} = 2.5$; then the dependence of K_p upon α is expressed by curve 1 of Fig. 2. As can be seen from the figure, with increasing α the value of K_p decreases continuously. If, on the other hand, the thickness of the deposit is a minimum at point 2, then by substituting the current densities at this point $D_{2k} = 0.66$ and $D_{2a} = 0.2$, into Eq. (5), we ascertain that in this case K_p increases monotonically with increasing α (Fig. 2, curve 2). Thus, at low values of α the coating will be the thinnest at point 2. However, with increasing α, the thickness of the coating at point 1 decreases so much that it becomes equal to, and then even less than the thickness of the coating at point 2. The optimum value of α can be determined from the condition of equality of the thickness of the coating at the extreme points of the electrode:

$$\frac{k}{\gamma s} D_{к\,av}\tau_к(D_{1к} - \alpha D_{1a}) = \frac{k}{\gamma s} D_{к\,av}\tau_к(D_{2к} - \alpha D_{2a}), \quad (6)$$

from which

$$\alpha_{opt} = \frac{D_{1к} - D_{2к}}{D_{1a} - D_{2a}}. \quad (7)$$

In the case of a sufficient duration of the anodic and cathodic periods, the current distribution on the electrode is determined by the slope of the stationary polarization curves and by the specific resistance of the solution. Knowing the stationary values of the index of scattering power R, for a calculation of the secondary current densities at points 1 and 2 we can use the following equation [3]:

$$D = 1 + \frac{a_i b_i}{b_i + a_i El}, \quad (8)$$

where $El = R/l_0$ is the criterion of electrochemical similarity; a_i and b_i are coefficients depending upon the geometry of the cell and position of the point on the electrode. The numerical values of these coefficients for points 1 and 2, calculated for four different slit baths, are cited in [3].

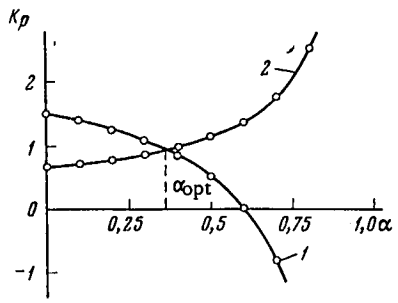

Fig. 2. Dependence of the criterion of uniformity of distribution of the metal during reversion on the ratio of the duration of the anodic and cathodic periods. 1) At point 1; 2) at point 2.

TABLE 1. Dependence of the Optimum Ratio of the Duration of the Anodic Period to the Cathodic Period on the Geometrical Characteristics of the Slit Bath: I) $l_0/h = 1.3$; II) 1.9; III) 2.35; IV) 2.8

l_0, cm	R_k, cm	R_a, cm	Cell			
			I	II	III	IV
10	3	0.25	0.544	0.565	0.576	0.575
10	3	0	0.517	0.526	0.536	0.535
5	3	0.25	0.402	0.411	0.42	0.42
5	3	0	0.347	0.357	0.366	0.365
2	3	0.25	0.25	0.243	0.255	0.259
2	3	0	0.176	0.176	0.195	0.189
1	3	0.25	0.172	0.177	0.18	0.181
1	3	0	0.096	0.1	0.104	0.105

After expressing the current densities entering into Eq. (7) as a function of El, in accord with (8), we finally obtain

$$\alpha_{opt} = \frac{\dfrac{a_1 b_1}{b_1 + a_1 E l_k} - \dfrac{a_2 b_2}{b_2 + a_2 E l_k}}{\dfrac{a_1 b_1}{b_1 + a_1 E l_a} - \dfrac{a_2 b_2}{b_2 + a_2 E l_a}}. \qquad (9)$$

If we know the geometrical characteristics of the cell (length of the cathode l_0 and distance between the cathode and partition h) and the values of the cathodic and anodic indices of the scattering power of the electrolyte, Eq. (9) permits us to calculate the optimum ratio of the anodic and cathodic periods at which the thickness of the metal at the extreme points of the electrode will be the same. We calculated the values of α_{opt} for the following conditions: $R_k = 3$ cm; $R_a = 0.25$ and 0 cm. The results of the calculation for four slit cells, characterizing parts of different sizes and different degrees of shape irregularity, are cited in Table 1.

As can be seen from Table 1, the optimum duration of the anodic period drops sharply with decreasing linear dimensions of the electrode and increases negligibly when its degree of shape irregularity increases.

The distribution of the current on the electrode in the cathodic and anodic periods and the resultant distribution of the current calculated for the optimum value of α during reversal are shown in Fig. 3. The shaded areas between the corresponding current distribution curves and the maximum current density are proportional to the amounts of superfluously applied metal. As can be seen from the figure, in the case of reversal the amount of superfluously applied metal is the most reduced. The relative fraction of usefully consumed metal, equal to δ_{min}/δ_{av}, calculated in the case of deposition by direct current and in the case of an optimum system of reversal, can be used for a quantitative estimation of the effectiveness of reversal. The data of the calculation ($R_k = 3$ cm; $R_a = 0.25$ cm), cited in Table 2, show that current reversal permits a three-to eight-fold reduction of the amount of superfluously applied metal, depending upon the geometry of the part. In the case of the same linear dimensions, the effectiveness of reversal increases with increasing degree of shape irregularity of the part. Thus, on the basis of the data of Tables 1 and 2, it can be concluded that the utilization of current reversal to improve the macrodistribution of the metal is the most expedient for complex contoured small parts. It should be mentioned that the use of large values of α (> 0.2-0.3) is inadvisable, not only on account of an increased consumption of electrical power, but also because the porosity of the coating on the immersed end may be appreciably increased as a result of local nonuniformity of the anodic dissolution of the metal.

EXPERIMENTAL SECTION

An experimental verification of Eq. (9) was performed in slit cell IV at $l_0 = 5$ cm. A freshly prepared copper sulfate electrolyte and an ammonium sulfate electrolyte for cadmium plating were used.*

* The electrolyte was developed by N. P. Gnusin, Z. Ya. Firsova, and V. Ya. Bartenev at the Laboratory of Electrochemistry, Institute of the Physicochemical Bases of Reprocessing of Mineral Raw Materials, Siberian Section of the Academy of Sciences of the USSR.

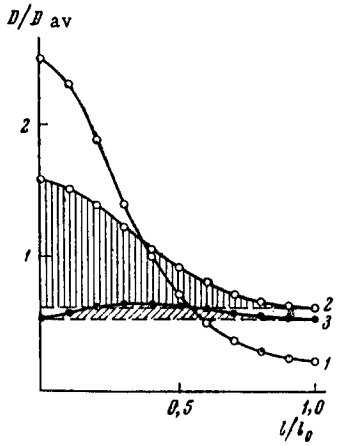

Fig. 3. Anodic (1), cathodic (2), and resultant current distribution during reversal, calculated for the optimum value of $\alpha(3)$. $El_a = 0.05$; $El_k = 0.6$; $\alpha = 0.415$; $l_0/h = 2{\cdot}8$.

TABLE 2. Dependence of the Fraction of Usefully Consumed Metal in the Case of Direct Electrolysis and Optimum System of Reversal Upon the Degree of Shape Irregularity of the Cell and its Dimensions

l_0, cm	K_p					
	Cell II		Cell III		Cell IV	
	Without reversal	Reversal	Without reversal	Reversal	Without reversal	Reversal
10	0.65	0 92	0.55	0,874	0,45	0,824
5	0.76	0,977	0.69	0,956	0.60	0,894
2	0,875	0,99	0.83	0.982	0.79	0.96
1	0.93	0,995	0,9	0.988	0.87	0.97

The composition of the solutions, system of electrolysis, and value of the index of scattering power in the cathodic and anodic periods are indicated in Table 3.

Current reversal was carried out with an electromagnetic relay. The relay was turned on and off with a contact disk, coupled to an electric motor, fed from a low-frequency generator. The cathode was mechanically polished stainless steel, while the anode was copper or cadmium, depending upon the electrolyte. Before application of the deposit under a set system of reversal, the cathode was preliminarily coated (10 μ) in a plane parallel field. After the deposition, the coating was removed from the base, cut into 10 equal parts, and weighed.

The index of scattering power was measured by the method described earlier [5], using a slit cell with cut-out cathode. The optimum value of α was calculated according to the measured values of R from Eq. (9), and then established on the contact disk of the reverser. The distribution of thickness of the metal obtained under the calculated systems of reversal is shown in Fig. 4, a and b. As can be seen in the case of both coatings, the thickness of the metal at the extreme points of the electrode is approximately the same, which corresponds to the calculation. However, the calculated values proved somewhat

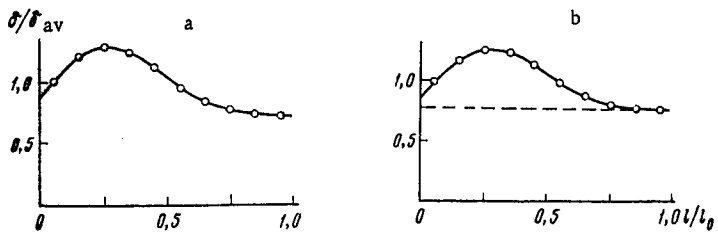

Fig. 4. Distribution of the relative thickness of the coating obtained at the calculated optimum value of α. a) Deposition from an acid copper electrolyte; b) from an ammonium sulfate electrolyte for cadmium plating.

TABLE 3.

Composition of electrolyte	D_{av}, A/dm^2	R_K, cm	R_a, cm	α_{opt}	τ_k, sec
$CuSO_4 \cdot 5H_2O$—100 g/liter H_2SO_4—200 g/liter	2.2	3	0.25	0.42	67
$CdSO_4 \cdot \frac{8}{3} H_2O$—80 g/liter; Amino-1-$(NH_4)_2SO_4$—300 g/liter, acid 5 g/liter	1.5	1.9	0.1	0.5	71

low in both cases. As a result, the experimental value of K_p, for example, in the case of a copper electrolyte, was 0.78, instead of the calculated 0.89. This is evidently explained by the fact that at the beginning of each cathodic period, as a result of the appreciable decrease in the polarizability, the distribution of current is more nonuniform than corresponds to the stationary value of the index of scattering power R_k, entering into Eq. (9).

CONCLUSIONS

1. For a slit cell in the case when the distribution of current in the cathodic and anodic periods is determined by the stationary value of the index of scattering power, we obtained an approximate equation for the optimum ratio (α) of the durations of the cathodic and anodic periods at which the thickness of the deposit is the same at the extreme points of the cathode.

2. A calculation of the optimum value of α for slit cells with different degrees of shape irregularity and different linear dimensions indicated that the use of reversal to improve the macrodistribution of the metal is the most expedient for complex-contoured small parts.

3. An experimental verification of the equation obtained indicated that the calculated values of α are somewhat low. The cause of this is explained by the more uniform distribution of current at the beginning of each cathodic period in comparison with the stationary value, which enters into the equation.

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