JOURNAL OF APPLIED ELECTROCHEMISTRY 3 (1973) 161–167

Time optimal electrodeposition of metals with a pulsating current

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Received 18 July 1972

A method of input current shape synthesis, applied to the process of the electrodeposition of metals, is given. It is shown that the optimal control theory can be successfully applied to this kind of problem. Essentials of the mathematics of the method and the computer program flow chart are also given.

Theory is checked using experiments on the electrodeposition of copper. The agreement between theoretical and experimental results is satisfactory.

1. Introduction

It is well known that irregular forms of metal deposits are obtained when electrodeposition under diffusion control is occurring [1–5]. The effect of the diffusion control can be decreased by applying pulsating or reversal currents [6–11], or completely avoided by applying pulsating potential [12, 13], when, with the high efficiency of the process, rather good quality metal deposits can be obtained. However, on the basis of these results, nothing can be concluded in advance concerning the specific shapes of input currents or potentials to employ.

This paper attempts to provide a method of input current synthesis for the electrodeposition process to obtain a specified amount of metal deposit in the shortest possible time without forcing the system into diffusion control.

2. Mathematical model, statement and solution of the problem

The electrodeposition process with pulsating current described by Equations 1–5 is considered as a time optimal control problem:

$$\frac{\partial C}{\partial t} = D \frac{\partial^2 C}{\partial x^2} \tag{1}$$

$$C(o,x) = C_0 \tag{2}$$

$$C(t,\delta) = C_0 \tag{3}$$

$$\left.\frac{\partial C}{\partial x}\right|_{x=0} = \frac{I(t)}{nFD} \tag{4}$$

$$\frac{dQ}{dt} = I(t) \tag{5}$$

where: C = Concentration
D = Diffusion coefficient
C_0 = Bulk concentration
δ = Diffusion layer thickness
I = Input current

It is desired to find an input current $I(t)$ which transfers the system for minimal time T from the initial state $C(o,x) = C_0$ and $Q(o) = 0$ to a specified final state

$$C(T,x) = C_s + (C_0 - C_s)\frac{x}{\delta} \tag{6}$$

$$Q(T) = Q_d \tag{7}$$

without violating the physical constraints

$$C(o,t) \geqslant C_s \tag{8}$$

$$O \leqslant I(t) \leqslant I_{max} \tag{9}$$
$$t \varepsilon [o,T]$$

where: C_s = critical surface concentration
Q_d = quantity of electricity corresponding to the specified thickness of a metal deposit
I_{max} = maximum permitted current

There are a number of methods for solving the problem stated above, such as: dynamic programming [14], maximum principle [15], and method of moments [16]. In the Appendix A, a specific method which does not require a background in these methods, but only a knowledge of the diffusion equation solution, is presented. The method is in fact a simplified version of the general method of moments.

Applying this method, one arrives at the following expression for the optimal input current:

$$I(t) = \frac{I_{max}}{2}\left\{1 + \text{sign}\left[\sum_{m=1}^{\infty} \lambda_m^0 G_m(T,t) + \mu^0\right]\right\} \tag{10}$$

where the parameters λ_m^0 and μ^0 have to be obtained by minimizing the expression

$$1/l = \min_{\lambda_m,\mu}\left[\int_0^T \left|\sum_{m=1}^{\infty} \lambda_m G_m + \mu\right| dt + \int_0^T \left(\sum_{m=1}^{\infty} \lambda_m G_m + \mu\right) dt\right] \tag{11}$$

subject to the constraint

$$\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu Q_d = 1 \tag{12}$$

where:

$$G_m(t,T) = \frac{1}{nF}\exp\left[-(2m-1)^2 D\pi^2 (T-t)/4\delta^2\right] \tag{13}$$

$$e_{1dm} = \frac{2}{\delta}\int_0^{\delta} (C_s - C_0)\left(1 - \frac{x}{\delta}\right)\cos\frac{(2m-1)\pi x}{2\delta}\, dx \tag{14}$$

The algorithm for solving the minimization problem (11) and (12), and the corresponding computer program are given in the Appendix B.

For computational purposes the series in (10), (11) and (12) have to be truncated at some finite N giving generally arbitrary close approximation of the optimal input current.

The algorithm described in the Appendix B does not include directly the constraint (8). Instead, it has been assumed that the maximal permitted current I_{max} for the optimal law (10) will not force the system to the diffusion-controlled conditions.

3. Computer results

Using the computer program described in the Appendix B, the optimal input current synthesis has been performed. The solution of the diffusion equation has been truncated at $N = 7$ terms. The following values of physical constants are used:

$$D = 3{\cdot}2 \times 10^{-6}\,\text{cm}^2\,\text{s}^{-1}$$
$$\delta = 5{\cdot}5 \times 10^{-2}\,\text{cm}$$
$$C_0 = 5 \times 10^{-6}\,\text{mol}\,\text{cm}^{-3}$$
$$C_s = 0{\cdot}1\, C_0$$
$$n.F = 2 \times 10^5\,\text{A}\,\text{s}\,\text{mol}^{-1}$$
$$I_{max} = 1{\cdot}5 \times 10^{-4}\,\text{A}\,\text{cm}^{-2}$$
$$Q_d = 0{\cdot}054\,\text{A}\,\text{s}\,\text{cm}^{-2}$$

The optimal input shape of current is given in Fig. 1. The desired final state of the system and the state obtained by applying optimal input current are provided in Fig. 2. The discrepancies are due to the finite number of terms included, and are more emphasized in the vicinity of the electrode surface. The maximum number of terms accepted is limited by the convergence of the method used for solving the system of transcendental Equations (B.4), which is included in the algorithm. The algorithm has been success-

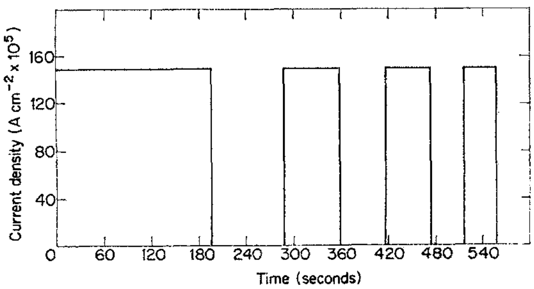

Fig. 1. Optimal input current.

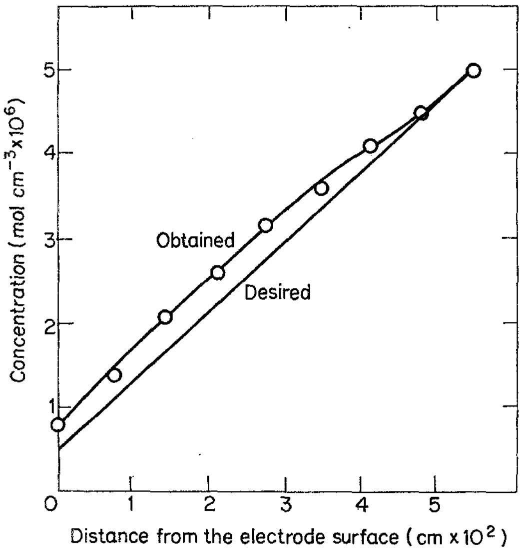

Fig. 2. The diffusion layer concentration distribution.

fully applied for $N = 11$, but for experimental purposes $N = 7$ was sufficient.

4. Experimental

Principally, the electrode on which copper is electrodeposited has been designed in the following manner: a piece of nickel sheet has been covered with a defined layer of agar-agar gel, prepared from the solution which has been used for the electrodeposition of copper (5×10^{-3}M $CuSO_4$ with 5×10^{-2}M Na_2SO_4 as supporting electrolyte). The electrode assembly is described elsewhere [17]. A quantity of agar-agar solution, sufficient for all measurements in one set of experiments, is prepared. In this way, the same quality of gel is maintained. In all experiments, chemicals of p.a. quality and distilled water are used.

A standard galvanostatic circuit is used. A copper counter-reference electrode of about 50 times larger area than the working electrode is used. Copper is deposited using the input current shape theoretically specified in the preceding section. Electrolysis was performed at 25·0±0·1°C.

Polarization curve and overpotential–time relationships have been plotted.

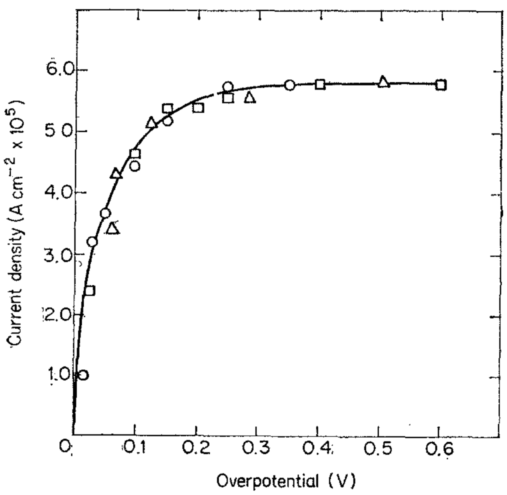

Fig. 3. The polarization curve of the electrode used.

5. Results and discussion

The polarization curve for the electrodeposition of copper in the system already described is presented in Fig. 3. The limiting diffusion current for the electrodeposition is used to calculate

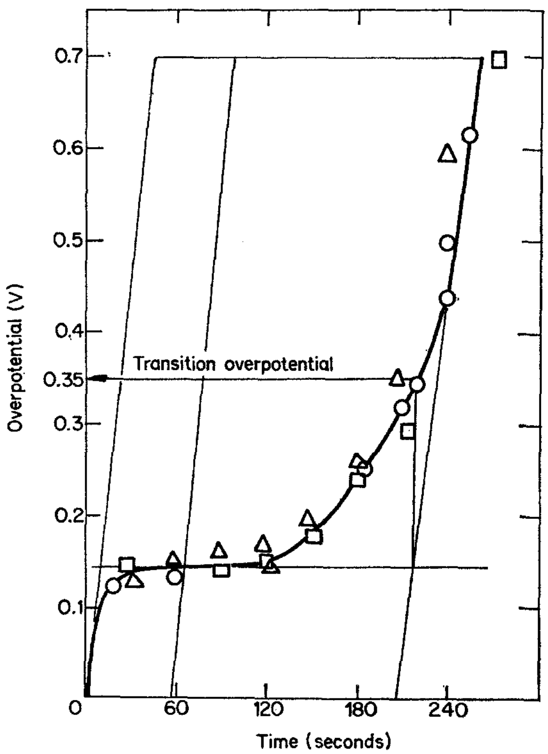

Fig. 4. The determination of the transition time in the case of a current the magnitude of which is equal to the amplitude value.

Table 1. The results of the application of the optimal deposition regime on a model system

Input current shape	*Calculated*	*Experiment I*	*Experiment II*	*Experiment III*
I Pulse (sec)	200	200	200	200
I Pause (sec)	89	89	89	89
II Pulse (sec)	67	67	67	67
II Pause (sec)	57	57	57	57
III Pulse (sec)	60	48	43	50
III Pause (sec)	42	42	42	42
IV Pulse (sec)	42	38	35	35
Total time (sec)	557	541	533	540
Relative error of total time %	—	−2·9	−4·3	−3·1

the diffusion coefficient of the Cu(II) cation. A value of $3{\cdot}2\times10^{-6}$ cm^2 sec^{-1} is thus obtained. Therefore, the input shape of current could be calculated using the previously described method.

An overpotential–time relationship for the electrodeposition of copper with a fixed maximum current density of $1{\cdot}5\times10^{-4}$ A cm^{-2} is presented in Fig. 4. The transition time of 216 sec and transition overpotential of 0·350 V, at which potential the process is diffusion-controlled, were graphically determined using the procedure given in [18].

The values of the transition time and the overpotential, at which diffusion control of the process starts, were used for experimental checking of the applied current input shapes. So, whenever the overpotential of the process equalled the value of 0·350 V, the pulse was switched off to avoid diffusion-controlled electrodeposition. The results for the electrodeposition of copper performed in this way are given in Table 1. It should be noted that experimental and theoretically-predicted results are overlapping up to the third pulse. From the third pulse onwards discrepancies appear, due to simplifications on the mathematical model of the system.

Finally, the electrodeposition of copper was performed with the effective* d.c. current density to check whether it is possible to get the same amount of deposit for a total time of 557 sec, assuming the process is not diffusion-controlled.

An overpotential–time relationship, for the electrodeposition of copper, with $I_{eff}=9{\cdot}9\times10^{-5}$ A cm^{-2}, is presented in Fig. 5. The transition time is reached at 456 sec indicating that the process is diffusion-controlled for a shorter period of time than in the case of electrolysis with applied currents of specified input shape (cf. Table 1).

It may be concluded that the electrodeposition of thin layers of metals, using input currents of

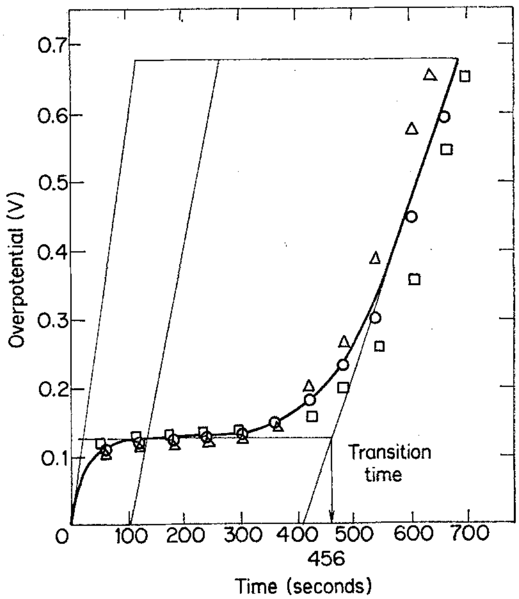

Fig. 5. The determination of the transition time in the case of a current the magnitude of which is equal to the effective value.

* It is easily calculated that for the given current input shape

$$I_{eff} = 0{\cdot}66\, I_{max}.$$

shape programmed in the manner described in this paper, can be carried out with currents higher than the limiting diffusion current without the process becoming diffusion-controlled. The times of electrolyses programmed in this way exceed the transition times for corresponding effective d.c. current densities. These results might be practically applied in plating technology.

6. Conclusion

It is shown that the optimal control theory can be successfully applied to the electrodeposition of metals with pulsating current. A method for synthesizing the desired shape of input current, based on the minimum time criterion, is given.

Experiments on the electrodeposition of copper performed with calculated current input shape fit the theory satisfactorily.

Acknowledgement

The authors would like to thank Dr D. B. Šepa for helpful discussion during the preparation of this paper.

Appendix A

Introducing the substitution

$$I(t) = i(t) + kl \tag{A1}$$

where $-1 < k < 1$

$$l = ||i(t)|| = \sup_{t\varepsilon[0,t_1]} |i(t)| \tag{A2}$$

is the maximal absolute value of the current $i(t)$ on the interval $[0,t_1]$ (norm in Banach L^∞ or M space [16]), the constraint (9) becomes

$$|i(t)| \leqslant l \tag{A3}$$

and solutions of the Equations (1)–(6) at $t = t_1$ become:

$$C(x,t_1) = C_0 - \sum_{m=1}^{\infty} \int_0^{t_1} H_m(\tau,t_1,x)[i(t)+kl]\mathrm{d}\tau \tag{A4}$$

$$Q(t_1) = \int_0^{t_1} [i(\tau)+kl]\mathrm{d}\tau \tag{A5}$$

where

$$H_m(\tau,t_1,x) = \frac{1}{nFD} \exp\left[-\frac{(2m-1)^2 D\pi^2}{4\delta^2}(t_1-\tau)\right] \cos\frac{(2m-1)\pi x}{2\delta} \tag{A6}$$

Let us introduce the following notations

$$e_1(x,t_1) = C(x,t_1) - C_0 \qquad e_{1d} = (C_s - C_0)\left(1 - \frac{x}{\delta}\right)$$

$$e_2(t_1) = Q(t_1) \qquad e_{2d} = Q_0$$

It is useful to restate the problem in the following way (minimum norm control problem): Given the initial state $e_1(x,o) = 0$, $e_2(o) = 0$ find the input current $i(t)$ which takes the system to the desired state

$$e_1(x,t_1) = e_{1d} \tag{A7}$$

$$e_2(t_1) = e_{2d} \tag{A8}$$

and which minimizes the norm l.

The relationships (A7) and (A8) will be satisfied if the relationship

$$\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu e_{2d} = \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m(\tau,t_1) + \mu\right] i(\tau)\mathrm{d}\tau + kl \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m(\tau,t_1) + \mu\right] \mathrm{d}\tau \tag{A9}$$

is satisfied for arbitrary $\mu \neq 0$ $\lambda_m \neq 0$ (m = 1,2,...).

From the definition (A2) it follows

$$\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu_2 e_{2d} \leqslant l\left\{\int_0^{t_1} \left|\sum_{m=1}^{\infty} \lambda_m G_m(\tau,t_1) + \mu\right| \mathrm{d}\tau + k\int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m(\tau,t_1) + \mu\right] \mathrm{d}\tau\right\} \tag{A10}$$

or

$$||i|| = l \geqslant \frac{\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu e_{2d}}{\int_0^{t_1} \left|\sum_{m=1}^{\infty} \lambda_m G_m + \mu\right| \mathrm{d}\tau + k\int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m + \mu\right] \mathrm{d}\tau} \tag{A11}$$

The relation (A11) in particular must be satisfied for λ and μ which maximize the right-hand side of (A11)

$$l \leqslant \max_{\lambda_m,\, \mu \neq 0} \frac{\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu_2 e_{2d}}{\int_0^{t_1} \left| \sum_{m=1}^{\infty} \lambda_m G_m + \mu \right| d\tau + k \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m + \mu \right] d\tau}$$

or

$$l \geqslant \max_{\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu e_{2d} = 1} \left[\frac{1}{\int_0^{t_1} \left| \sum_{m=1}^{\infty} \lambda_m G_m + \mu \right| d\tau + k \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m + \mu \right] d\tau} \right] \tag{A12}$$

This means that one has to minimize the expression

$$\frac{1}{l} = \lambda_m^{\min}, \mu \quad \left[\int_0^{t_1} \left| \sum_{m=1}^{\infty} \lambda_m G_m + \mu \right| d\tau + k \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m G_m + \mu \right] d\tau \right] \tag{A13}$$

under the equality constraint

$$\sum_{m=1}^{\infty} \lambda_m e_{1dm} + \mu e_{2d} = 1 \tag{A14}$$

Thus, any input current $i(t)$ which makes $e_1(x,t_1) = e_{1d}$ and $e_2(t_1) = e_{2d}$ must satisfy (A12) and the current with minimum l must satisfy (A12) with the equality sign.

Denoting the optimal values of λ_m and μ with λ_m^0 and μ^0 and taking into account relations (A9), (A10) and (A13), one can come to the following equation

$$\int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m + \mu^0 \right] i^0(\tau) d\tau + lk \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m + \mu^0 \right] d\tau = l \int_0^{t_1} \left| \sum_{m=1}^{\infty} \lambda_m^0 G_m + \mu^0 \right| d\tau + lk \int_0^{t_1} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m + \mu^0 \right] d\tau \tag{A15}$$

From (A15) it follows directly that

$$i^0(t) = l \operatorname{sign} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m(t_1, t) + \mu^0 \right] \tag{A16}$$

or taking into account the substitution (A1)

$$I^0(t) = l \left\{ k + \operatorname{sign} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m(t, t_1) + \mu^0 \right] \right\} \tag{A17}$$

From the statement of the auxiliary problem, one can conclude that for $k = 1$, the current $I(t)$ which takes the system during the time interval (o,t_1) to the desired final state, must have a minimum amplitude equal to 2 l. If $2l > I_{max}$ the time interval can be decreased, otherwise it must be increased. When, by iterations, the time $t_1 = T$ is found such that $2l = I_{max}$, the input current

$$I^0(t) = \frac{I_{max}}{2} \left\{ 1 + \operatorname{sign} \left[\sum_{m=1}^{\infty} \lambda_m^0 G_m(t,T) + \mu_0 \right] \right\} \tag{A18}$$

is the solution of the minimum time problem.

This means that the iterative algorithm for solving the minimization problem (A13) and (A14) with different final times t_1 until $2l = I_{max}$ have to be formulated. Such an algorithm is described in the Appendix B.

Appendix B

If the series in (A13) and (A14) is truncated at N terms, from Equation (A14) it follows that

$$\mu = \frac{1 - \sum_{m=1}^{\infty} \lambda_m e_{1dm}}{e_{2d}} \tag{B1}$$

Subs tituting (B1) into (A13) one gets

$$\min_{\lambda_1 \ldots \lambda_N} J(\lambda_1 \ldots \lambda_N) = \min_{\lambda_1 \ldots \lambda_N} \left[\int_0^{t_1} \left| F(\lambda, t_1, \tau \right| d\tau + k \int_0^{t_1} F(\lambda, t_1, \tau) d\tau \right]$$

where:

$$F(\lambda,t_1,\tau) = \frac{1}{e_{2d}} + \sum_{m=1}^{N} \lambda_m \left[G_m(t_1,\tau) - \frac{e_{1dm}}{e_{2d}} \right]$$

Since the function $F(\lambda,t,\tau)$ may have a maximum of N zeros, $\tau_1, \tau_2, \ldots \tau_N$ it follows that

$$J(\lambda_1, \ldots \lambda_N) = \pm \left[\int_0^{\tau} F(\lambda,t_1,\tau)d\tau - \int_{\tau_1}^{\tau_2} F(\lambda,t_1,\tau)d\tau + \ldots \pm \int_{\tau_N}^{t_1} F(\lambda,t_1,\tau)d\tau \right] + k \int_0^{t_1} F(\lambda,t_1,\tau)d\tau \quad \text{(B3)}$$

(the positive sign corresponds to a positive value of $F(\lambda,t_1,\tau)$ in the first interval $[o,\tau_1]$ .From $\partial J/\partial \lambda_i = 0$ ($i = 1,2, \ldots N$) one can come to the following system of transcendental equations:

$$\psi_K = \left[\int_0^{t_1} \frac{\partial F}{\partial \lambda_i} d\tau - \int_{\tau_1}^{\tau_2} \frac{\partial F}{\partial \lambda_i} d\tau + \ldots \pm \int_{\tau_N}^{t_1} \frac{\partial F}{\partial \lambda_i} d\tau \right] + k \int_0^{t_1} \frac{\partial F}{\partial \lambda_i} d\tau = 0 \quad (B4)$$

$$(i = 1,2, \ldots, N)$$

from which the zeros $\tau_1, \ldots, \tau_N$ of the function $F(\lambda,t_1,\tau)$ can be determined.

From the system of algebraic equations

$$F(\lambda_1, t_1, \tau_i) = 0 \quad (i = 1,2,\ldots,N) \quad (B5)$$

the optimal values of parameters λ_i can be

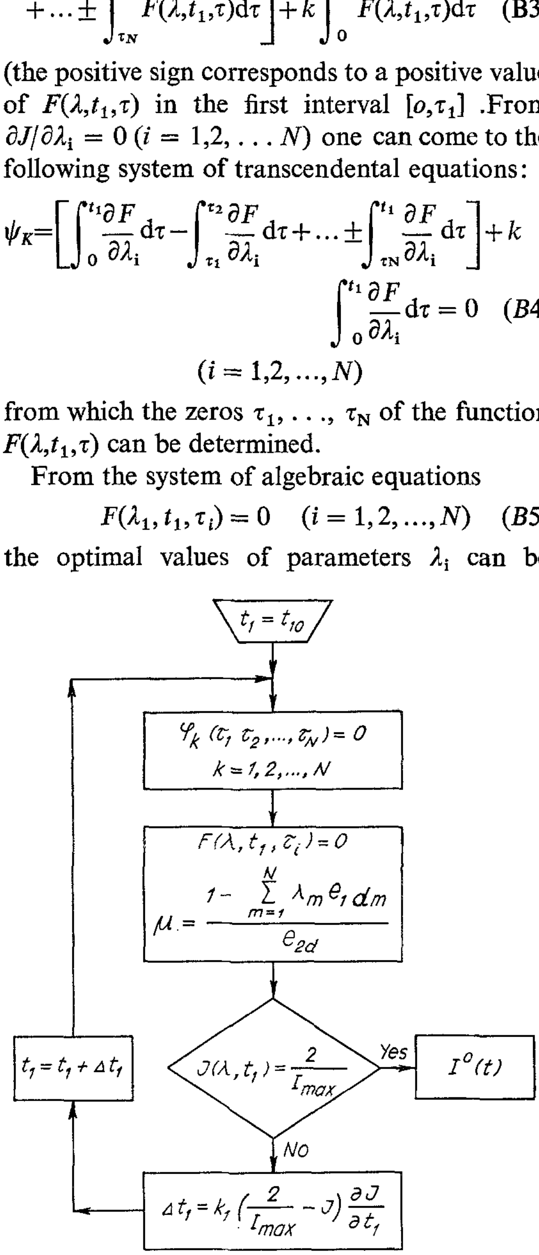

Fig. 6. Computer programme flow chart.

determined, while the optimal value of μ is obtained from Equation (B1). Through the Equations (B4) and (B5), the solution of the auxiliary problem for assumed t_1 is obtained. Using the gradient technique, the expression

$$\Delta t_1 = k_1 \left[\frac{2}{I_{max}} - J(\lambda^0, t_1) \right] \frac{\partial J(\lambda^0, t_1)}{\partial t_1}$$

will provide the increment Δt_1 which will lead the iterative procedure to the desired condition

$$I_{max} = 2l$$

The flow chart of the corresponding computer program is given in Fig. 6.

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