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MATHEMATICAL SIMULATION OF INTERACTIVE PHYSICAL PROCESSES IN HIGH TEMPERATURE ELECTROCHEMICAL DEVICES[①]

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ABSTRACT

A mathematical analogue of interactive mass transfer in some electrochemical processes has been considered. A programme has been developed which calculates thermal and electrical phenomena in high temperature electrochemical devices, with the influence of magnetic fields being taken into consideration.

Key words: mathematical analogue mass transfer electrochemical process

1 INTRODUCTION

As is known, in many electrochemical systems there occur complicated processes involving mass transfer and electrical charges. Studying these processes plays a decisive role in analyzing the effciency of many technochemical devices. One of the most general expressions for the mass flow J_i of the i-th component in a mixture has the form[1]:

$$J_i = c_i\omega - D_i\mathrm{grad}c_i + \gamma'_i z_i c_i E \qquad (1)$$

Thus, in formula (1), the mass flow consists of convection, diffusion and migration components. If there are other physical processes (except for diffusion and electric current). The expression for the migration current,

$$J_{\mathrm{migr}} = \gamma_i z_i c_i E = \gamma_i z_i c_i \mathrm{grad}\varphi \qquad (2)$$

will be more complicated. This paper considers mathemactical analogues for computing the electrical field intensity E and migration flow, respectively, in a three-dimensional case in association with some physical processes accompanying mass transfer (namely, thermal and magnetic fields).

2 ANALOGUE FOR CALCULATING ELECTROMAGNETIC FIELD WITH A TEMPERATURE GRADIENT

If the electrical field intensity is due to electrical and thermal causes only, the formula describing it can be presented in the form[2]:

$$E = j/\sigma + \alpha\mathrm{grad}T \qquad (3)$$

Thus, for calculating E it is necessary to solve the equation system of thermal and electrical fields together. In this case the thermal current density I and the electrical current density j are given by the formulae[2]:

$$I = (\varphi + \alpha\mathrm{grad}T)j - \lambda\mathrm{grad}T \qquad (4)$$

$$j = -\sigma\alpha\mathrm{grad}T - \sigma\mathrm{grad}\varphi \qquad (5)$$

From the definitions (j and I) it

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should be noted that the interrelation between j and E through thermal and electrical fields will be taken into account in equations and boundary conditions. At the inner boundaries of the region the analogue will describe the Peltier, Seebeck and Thomson effects[2].

The analysis and the calculations of interrelated thermal and electrical processes have been made in a one- dimensional case[3,4] and in a two-dimensional one[5,6].

It is known[2] that in describing processes taking place in the presence of the external magnetic field the formulation of the symmetry principle for kinetic coefficients, which underlies the formulae (3) ~ (5) changes. In this case kinetic coefficients are dependent on magnetic field strength. Considering only this linear relationship, instead of (3)~(5) we obtain[2]:

$$E = j/\sigma + a\nabla T + R[H \times j] + N[H \times \nabla T] \quad (6)$$

$$I = (\varphi + aT) j - \lambda\nabla T + NT[H \times j] + L[H \times \nabla T] \quad (7)$$

$$j + \sigma R[H \times j] = -\sigma\nabla\varphi - \sigma a\nabla T - \sigma N[H \times \nabla T] \quad (8)$$

The addend $R\,[H \times j]$ describes the Hall effect (the influence of magnetic fields on electric ones); $N\,[H \times \nabla T]$ is the Nernst effect (the influence of magnetic fields on the thermoelectromotive force); $L[H \times \nabla T]$ is the Leduc-Rigy effect (the influence of magnetic fields on heat conductivity); $NT[H \times j]$ is the Ettingshausen effect (the influence of magnetic fields on the Peltier effect).

Substituting equations (7) and (8) into the conservation laws

$$\operatorname{div} I = j \cdot E \quad (9)$$

$$\operatorname{div} j = 0 \quad (10)$$

as did as ref. [2], neglecting the second order members connected with H we get the system of equations

$$\operatorname{div}(\sigma(T)\nabla\varphi) = -\operatorname{div}(\sigma(T)a(T)\nabla T) - \sigma Rj \cdot j + [j \times H] \times \nabla(\sigma R) - \sigma Nj \cdot \nabla T \quad (11)$$

$$\operatorname{div}(\lambda(T)\nabla T) = -j \cdot j/\sigma(T) + Tj \cdot \nabla a + NTj \cdot j + Lj \cdot \nabla T - (1/\sigma T) \cdot \nabla T \times (d/dT)(\sigma NT^2)\,[j \times H] \quad (12)$$

In deducing equations (11) and (12) Maxwell's equation was assumed to be valid

$$\operatorname{rot} H = j \quad (13)$$

Thus, the present analogue only takes account of the magnetic field which is caused by the current flowing in this region. If the circulation effects on heat and electricity transfer are taken into consideration, the equations are still more complicated:

$$\operatorname{div}(\sigma(T)\nabla\varphi) = -\operatorname{div}(\sigma(T)a(T)\nabla T) + \operatorname{div}(\mu\sigma(T)[\omega \times H]) - \sigma Rj \cdot j + [j \times H] \times \nabla(\sigma R) - \sigma Nj \cdot \nabla T \quad (14)$$

$$\operatorname{div}(\lambda(T)\nabla T) = \rho c_p \omega \cdot \nabla T - j \cdot j/\sigma(T) + Tj \cdot \nabla a + NTj \cdot j + Lj \cdot \nabla T - (1/\sigma T) \times (d/dT)(\sigma NT^2)\,[j \times H] \cdot \nabla T \quad (15)$$

If σ and λ do not depend upon temperature, instead of (14) and (15) we get the system of equations:

$$\triangle\varphi = \mu(H \cdot \omega - \omega \cdot j) - \operatorname{div}(a\nabla T) - Rj \cdot j + [j \times H] \cdot \nabla R - Nj \cdot \nabla T \quad (16)$$

$$\triangle T = \rho c_p \omega \nabla T/\lambda - j \cdot j/\sigma\lambda + Tj \cdot \nabla a/\lambda - 1/(\lambda T)(d/dT)(NT^2)[j \times H] \cdot \nabla T + N/\lambda Tj \cdot j + L/\lambda j \cdot \nabla T \quad (17)$$

If all the coefficients mentioned above are constatns, for calculating φ and J we have the following analogue:

$$\triangle\varphi = \mu(H \cdot \omega - \omega \cdot j) - a\triangle T - Rj \cdot j - Nj \cdot \nabla T \quad (18)$$

$$\triangle T = \rho c_p \omega \cdot \nabla T/\lambda - j \cdot j/\sigma\lambda - 2N[j \times H] \cdot \nabla T/\lambda + NTj \cdot j/\lambda + Lj \cdot \nabla T/\lambda \quad (19)$$

The magnetic field is calculated by introducing the magnetic vector potential A

$$H = \mathrm{rot}A/\mu \quad (20)$$

on the basis of solving the equation

$$\mathrm{rot}(\mathrm{rot}\ A/\mu) = j \quad (21)$$

or (in case of a homogeneous medium)

$$\triangle A = \mathrm{grad\ div}\ A - \mu j \quad (22)$$

3 STATEMENT OF THE PROBLEM

As an analogous problem, consider the problem of investigating the interactive electromagnetic and thermal fields in the electrolyte of some electrochemical system. The field of calculation is a rectangular parallelepiped $x = (x_1, x_2, x_3)$, $\Omega = \{0 \leqslant x_i \leqslant l_i \quad i = 1,2,3\}$

The system of equations (18), (19), and (22) were considered as the analogue of the electromagnetic and thermal processes in this region. On the lower side of Ω a zero electric potential was given and on the upper one an electric current was given:

$$j \cdot n|_{x_3 = l_3} = j_0(x_1 x_2)$$

On all the lateral surfaces the condition of zero electric current was laid down. On all the sides of Ω the boundary conditions for the thermal fields describe heat exchange according to the linear law:

$$j \cdot n|_{S_i} = \alpha_i^* (T - T^0)$$

4 CALCULATION RESULTS

For solving the problem raised, the method of finite differences has been applied. For solving the system of algebraic equations, the combination of an iteration method and a fast Fourier transform were used. Some calculation results obtained on the basis of the analogue and the algorithm described above are listed in Table 1 and shown in Figs. 1, 2, 3.

The limiting values of Ω as well as the thermal and electric characteristics were given so that the analogue would describe transfer processes in the electrolyte of an aluminium electrolyzer. Interrelated thermal and electromagnetic fields are known to be of decisive importance on the characteristics of aluminium electrolysis.

Table 1 shows the response of the analogue on changing the parameters α, N, L, R listed in the table are the limiting values of these coeffcients within the accuracy of one order, i. e. those values which resulted in more or less marked deviations of the result

Table 1 Results of the electromagnetic and thermal characteristics design

Design parameters	$\alpha = 0$ $N = 0$ $L = 0$ $R = 0$	$\alpha = 10^{-1}$ $N = 0$ $L = 0$ $R = 0$	$\alpha = 0$ $N = 10^{-12}$ $L = 0$ $R = 0$	$\alpha = 0$ $N = 0$ $L = 10^{-7}$ $R = 0$	$\alpha = 0$ $N = 0$ $L = 0$ $R = 10^{-11}$
maximal potential difference/mW	1 102	1 102	1 100	1 102	1 100
Maximal value of jx_1/Am−2	240	797	221	240	377
Maximal value of jx_2/Am−2	198	681	221	198	310
Maximal value of jx_3/Am−2	6 110	6 380	6 380	6 410	6 680
Average temperature/℃	932	932	933	934	932
Maximal temperature/℃	946	946	948	952	946
Measuring range of Bx_1,G	[−25.9, 28.01]	[27.0, 29.2]	[−26.0, 28.1]	[−25.9, 28.0]	[−26.1, 28.1]
Measuring range of Bx_2,G	[24.3, 26.9]	[−25.9, 28.2]	[−21.7, 27.2]	[−24.3, 26.9]	[−21.5, 27.0
Measuring range of x_3,G	[−0.8, 0.8]	[−0.8, 0.8]	[0.9, 0.8]	[−0.8, 0.8]	−0.8, 0.8]

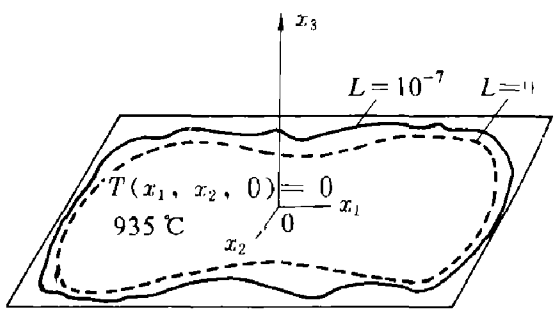

Fig. 1 Calculation results for thermal field

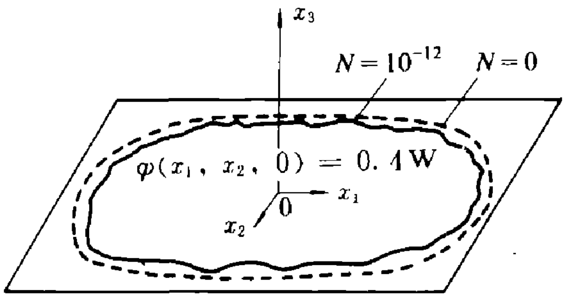

Fig. 2 Calculation results for electric potential

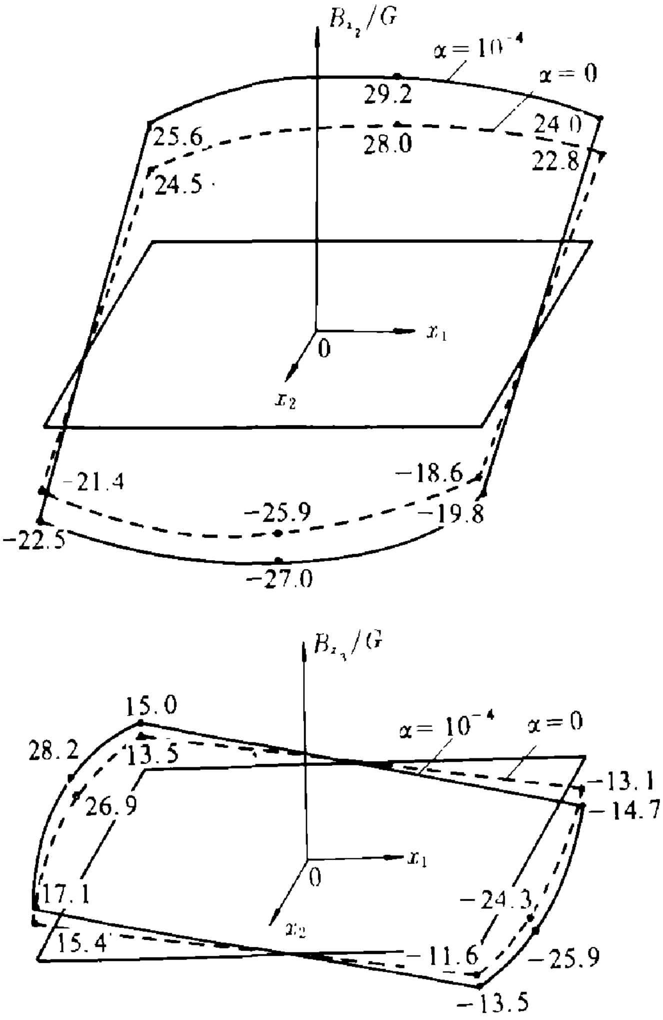

Fig. 3 Calculation results for magnetic fields

obtained(of order 1%).

The change of α leads to the redistribution on electric current and was practically on effect on the maximal and average temperatures. On the contrary, the coefficient L is only in the right part of the thermal field equation and therefore influences only $T(x)$. The parameters N and R change potential differences(and hence E). In all cases, electric current deflections cause magnetic field changes. Note that the maximal values of the calculated fields given in Table 1 do not show all the changes in the distributions of $T(x)$, $\varphi(x)$, $b(x)$. The greatest variation are in the lateral magnetic field. Likewisely in the central part of Ω, where $B(x) \approx 0$ there was practically no response of the analogue to deviations in N, L and R.

Symbols

J_i —mass flow in i-th component, c_i —concentration, D_i — diffusion factor, γ_i —mobility, z_i —charge, ω —liquid circulation velocity, E —electric field intensity, φ —electirc potential, j — electric current density, α— coefficient of thermoelectromotive force, σ —electric conductivity coefficient, λ — thermal conductivity coefficient, I —density of thermal flow, T —temperature, ρ —density, c_p — heat capacity, H —magnetic field intensity, R —hall coefficient, N —Nernst coefficient, L —Leduc-Rigy coefficient, μ — magnetic permeability, ω —rotω-velocity rotation.

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