HEAT EXCHANGE PARAMETERS IN ANODIC ELECTROLYTIC HEATING

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The use of boundary conditions of the third sort for description of heat exchange between an anode and its vapor-gas envelope is justified.

Use of high temperature heating of metals in electrolyte solutions for chemothermal processing requires the ability to control the basic parameters of such a process — the heating rate and temperature. For anodic electrolytic heating the measured input parameters are the voltage, and solution concentration and temperature. Output parameters are the temperature of the part heated, the anode, and the current. The function $Q_c(U)$ is usually determined experimentally for each type of part processed. Under step heating conditions where the voltage changes abruptly, it is also necessary to know the rate of change of temperatures including the surface temperature, as functions of time. In light of the fact that the "heating" elements in the solution—vapor-gas envelope—anode is the envelope [1-3], its thermal properties obviously determine the dependences mentioned above.

Direct measurements within the envelope are quite difficult because of its small thickness (~10-100) μ high temperature (to 1000°C), and the dissolving of the anode surface, and thus, that of any sensor mounted thereon, which occurs. However the present study does not require a precise knowledge of processes occurring in the envelope, and it will suffice to introduce relatively simple and convenient parameters which will permit calculation of the thermal state of the anode with sufficient accuracy at any voltage and any moment of time. Since the envelope provides the boundary conditions for the anode, study of the former's nonsteady-state thermal conductivity can recreate these boundary conditions and their relationship to the anodic heating parameters, i.e., produce a solution of the external converse thermal conductivity problem. Since the boundary conditions are not defined uniquely by the temperature field of the body, there is some arbitrariness in their final selection. For definiteness, we will assume that heat exchange between the envelope and the anode surface is described by a law [1]

$$Q_{\rm c} = \alpha [T_{\rm m} - T_{\rm s}(t)]. \tag{1}$$

The problem then reduces to measurement of the functions $T_s(t)$ and $Q_c(t)$ for various input parameters; in the present study we use voltages of 90-270 V and concentrations of 10-28%.

Experiment. The anodes used were vertically oriented bars of medium carbon steel 230 mm long and 20 mm in diameter, with lateral surface thermally insulated by asbestos fiber. Thickness of the thermal insulation was 10 mm. A chromel—alumel thermocouple was attached to the side surface of the bar 5 mm from its face, which later was placed in contact with the electrolyte — solution of NH_4NO_3 in distilled water. The nonsteady-state temperature and current were recorded by a potentiometer.

The converse thermal conductivity problem for the bar was solved by the method of least squares described in [4]. The thermal flux through the bar face was approximated by a polynomial

$$Q_{\mathbf{c}}(t) = \sum_{n=-1}^{p} A_n t^{n/2}.$$
 (2)

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Time, sec	Anode tempera- ture, °C	Current density, A/cm	Thermal flux into anode,	Anode surface tem- perature °C	Maximum tempera- ture in envel- ope, °C	Env- elope thick- ness	Product of current dens- ity × envel- ope thickness 10 ⁻⁴ A/cm
Voltage 110 V							
30 60 90 120 150 180 210 240 270	299 366 401 423 437 448 456 464 470	$\begin{array}{c} 2,61 \\ 2,42 \\ 2,36 \\ 2,33 \\ 2,29 \\ 2,29 \\ 2,26 \\ 2,26 \\ 2,26 \\ 2,26 \end{array}$	$ \begin{array}{r} 6,5\\ 5,1\\ 4,3\\ 3,8\\ 3,4\\ 3,1\\ 2,9\\ 2,7\\ 2,6\\ \end{array} $	- 389 442 469 485 503 509 514 520	$\begin{array}{r} 408\\ 456\\ 480\\ 493\\ 502\\ 508\\ 514\\ 519\\ 524\\ \end{array}$	13 16 17 17 17 17 17 17 18	33,9 38,7 40,1 39,6 38,9 38,9 38,9 38,4 38,4 38,4 40,7
Voltage 250 V							
30 60 90 120 150 180 210 240 270	$\begin{array}{c} 371 \\ 483 \\ 541 \\ 576 \\ 598 \\ 614 \\ 626 \\ 637 \\ 649 \end{array}$	1,56 1,43 1,34 1,31 1,27 1,24 1,24 1,21 1,21 1,21	9,3 7,4 6,2 5,4 4,8 4,4 4,1 3,9 3,7	507 599 643 667 682 692 700 709 718	537 623 662 682 694 703 710 718 727	16 21 25 25 26 26 27 27	25,0 30,0 32,2 32,8 31,8 32,2 32,2 32,2 32,7 32,7
		7 m 300 - 700 - 500 - 500 - 3		50 190	230	с - 27Л //	

TABLE 1. Experimental and Calculated Data for Anode Heating

Fig. 1. Medium temperature (°C) vs voltage (V).

In accordance with the superposition principle

$$T_{\mathbf{c}}(x, t) = \sum_{n=-1}^{p} A_n T_{\nu}(x, t),$$
(3)

i.e., the bar temperature field is determined by thermal fields $T_n(x, t)$, created by heat flux elements $q_n(t) = t^{n/2}$; the x-axis coincides with the bar axis and is directed upward from the face. The form of the function $T_n(x, t)$ presented in [5], which solved the nonsteady-state thermal conductivity equation for a semi-infinite bar with insulated side surface and boundary conditions: $T_n(x, 0) = T_0 - \lambda \partial T(0, t) / \partial x = q_n(t)$,

$$T_n(x, t) = \frac{Va}{\lambda} \Gamma\left(\frac{n+2}{2}\right) (4t)^{(n+1)/2} t^{n+1} \Phi^*\left(\frac{x}{2 Vat}\right).$$
(4)

The coefficients A_n can be determined from the condition of a minimum in the functional

$$\Lambda = \sum_{k=1}^{b} [T_{\mathbf{c}}(x, t_k) - T_{\mathbf{a}}(x, t_k)]^2$$
(5)

more precisely, the greater the number of times considered. In the present experiments values $17 \le b \le 22$ were used.

In view of its small thickness the envelope can be considered a body with negligible thermal resistance, and the temperature distribution in the envelope at each moment in time can be described by a steady-state thermal conductivity equation as was done in [3]. Then the envelope thickness

$$\delta(t) = \gamma \lambda_0' \frac{[T_{\rm s}(t) + 1/\gamma]^2 - 1/\gamma^2}{j(t) U - 2Q_{\rm c}(t)} .$$
(6)

Thus, after processing the experimental data a series of functions $Q_c(t)$, $T_s(t)$, j(t), and $\delta(t)$ were obtained.

Results. It follows from the data obtained (Table 1) that the maximum temperature in the envelope increases together with anode temperature and cannot be treated as the temperature of the heating medium in the sense of Eq. (1). On the other hand, upon formal calculation with Eq. (1) from the relationship $Q_c(t_1)/Q_c(t_2)$ we obtain values of T_m differing from each other for any pair t_1 and t_2 by not more than 10%. Results of such calculations performed for different voltages are presented in Fig. 1. No dependence of T_m on solution concentration was observed.

To clarify the meaning of the quantity T_m defined in this manner, we will consider the mechanism for scattering of the current source energy in the vapor-gas medium of the envelope. We average the electric field intensity distribution obtained in [3]

$$E_{\mathbf{mp}} = \frac{\varepsilon \varepsilon_0 \mu}{3j\delta} \left[\left(\frac{2j\delta}{\varepsilon \varepsilon_0 \mu} + E_0^2 \right)^{3/2} - E_0^3 \right].$$
(7)

Here E_0 is the threshold field [2]. It is evident from Eq. (7) that in the process of heating the field should not change greatly, all the more so since the product $j\delta$ (see Table 1) remains constant — increase in δ is compensated by decrease in *j*. For electrolytes of sufficiently high concentration or for high voltages the condition $E_0 \ll (2j\delta/\epsilon\epsilon_0\mu)^{\frac{1}{2}}$ is satisfied, corresponding to the limiting case of complete screening of the phase boundary surface potential by the net potential of the space charge within the envelope [3]. In this case to determine the mean field we use the expression $E_{\rm mp} \approx \mu/\delta$, which yields an upper limit of ~10⁷ V/m. Assuming that the charge carriers are electrolyte ions (ion complexes) [2], we will evaluate their energy. In a high field thermal energy can be neglected and it may be assumed that the ion has the energy it would take on in the field in free flight, given that the mass of the ion is close to that of a neutral molecule. The ion free path length is ~10⁻⁸ m, consequently, its energy, expressed in temperature units, is ~10³°C. In view of the fact that the ion "temperature" in the anode heating process remains constant (constant field) and coincides in order of magnitude with the measured temperature of the medium $T_{\rm m}$, we feel these quantities can be identified with each other.

The heat liberation coefficient was calculated from Eq. (1) for known $T_{\rm m}$, its value of (2500 ± 500 W/(m²·K)) being close to that determined in [1]. No dependence of α on voltage or solution concentration was observed.

The results obtained permit the conclusion that the nonsteady-state stage of anodic electrolytic heating is described satisfactorily by boundary conditions of the third type with the heat liberation coefficient and the temperature of the medium, as defined by the voltage, as constants.

NOTATION

Here t is time; U, system voltage; j, current flowing through envelope; T_c , T_a , calculated and measured anode temperatures; T_s , anode surface temperature; T_m , temperature of medium in envelope; Q_A , thermal flux in anode; a, λ , thermal diffusivity and conductivity of anode material; δ , envelope thickness; Γ gamma function; $i^{n+1}\Phi^*$, (n + 1)-th integral of error function Φ^* ; λ'_0 , vapor thermal conductivity at 100°C, γ , coefficient in temperature dependence of vapor thermal conductivity; μ , ion mobility; α , heat liberation coefficient.

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