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QUASI-ONE-DIMENSIONAL MODEL OF HEAT AND MASS TRANSFER DURING SUBLIMATION OF A MOLECULAR CRYSTAL PLATE IN A PLANE CHANNEL

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An unsteady quasi-one-dimensional model is constructed for the process of sublimation of a monocrystalline plate of β-diketonate in a uniform flow of an indifferent gas. A method of collocations and least squares is developed for solving heat-transfer problems. In contrast to the previous variants of the method, the algorithm proposed is designed for solving unsteady equations in partial derivatives with a phase transition. Numerical calculations are performed for various regimes of sublimation of chromium β-diketonate; the results are in good agreement with the data of a physical experiment.

Key words: *sublimation, chemical deposition, β-diketonate, heat and mass transfer, simulation.*

Introduction. The technology of chemical vapor deposition (CVD technology) is currently used to obtain various types of coatings in microelectronics and optical industry, in production of high-temperature crucibles and catalysts, etc. The limited use of the CVD technology in obtaining metal coatings is caused by the lack of precursors themselves (volatile chemical compounds) and data on their thermal characteristics. There are practically no quantitative data on mass transfer of both individual components and their mixtures in an inert-gas flow. There are a few papers where sublimation of β-diketonates is considered on the basis of the convective mass-transfer theory [1, 2].

To use volatile β-diketonates in CVD processes effectively, one has to solve some problems; most important of them are the control of stoichimetry and reproducibility of film growth. The composition of the growing film and its quality can be controlled by managing the processes of evaporation, transportation (or transfer), decomposition of initial substances, and film deposition itself [3]. This requires a detailed analysis of transfer phenomena in sublimation of molecular crystals in the flow of an inert carrier gas. The most effective method of studying these processes is mathematical simulation, since experimental investigations involve significant methodical and technical difficulties. For this purpose, however, one needs mathematical models that adequately describe the processes mentioned. A quasi-one-dimensional unsteady mathematical model of sublimation of one-species molecular crystals in the flow of an inert gas (argon) is proposed below.

1. Mathematical Model. We consider sublimation of metal β-diketonate in a plane slotted channel with a given wall temperature maintained constant. The plate of monocrystalline β-diketonate with an initial thickness δ_{10} is mounted on a plane holder located inside the channel on the lower wall (Fig. 1). The longitudinal and transverse sizes of the plate are much greater than its thickness δ_{10}. A heated inert gas with prescribed values of the flow rate $Q_{\rm g}$ and temperature $T_{\rm g}$ equal to the temperature of the upper wall moves along the channel. The initial height of the upper chamber of the slotted channel is $H_{{\rm s},0}$ and its transverse and longitudinal sizes are much greater than δ_{10}; therefore, tip effects and changes in the gas-flow velocity can be neglected. The plate of β-diketonate is heated owing to convective heat transfer from the gas, radiation of the upper wall of the channel, and heat transfer from

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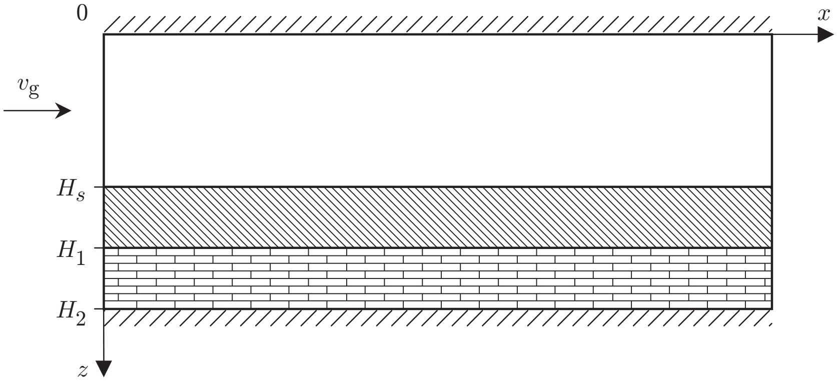

Fig. 1. Computational domain.

the lower wall, which results in sublimation of the substance. Since the total thermal resistance R_1 of the layer between the upper wall of the channel and sublimation front is much higher than the thermal resistance R_2 between the front and the lower wall ($R_1/R_2 > 330$), convective heat transfer between the gas and the upper wall can be neglected.

We choose a Cartesian coordinate system (x, z) with the x axis in the plane of the upper wall of the channel and the z axis in the plane of the channel entrance. The direction of the x axis coincides with the gas-flow direction, and the z axis is directed downward. Assuming that the thermophysical parameters of β-diketonate are constant and equal to their mean values in the considered range of temperature variation, we write the equations of heat transfer in the β-diketonate specimen and in the holder:

$$c_1\rho_1 \frac{\partial T}{\partial t} = \lambda_1 \frac{\partial^2 T}{\partial z^2}, \qquad H_\mathrm{s} < z < H_1; \tag{1}$$

$$c_2\rho_2 \frac{\partial T}{\partial t} = \lambda_2 \frac{\partial^2 T}{\partial z^2}, \qquad H_1 < z < H_2. \tag{2}$$

The boundary conditions are

$$-\lambda_1 \frac{\partial T}{\partial z}\Big|_{z=H_\mathrm{s}(t)} = \alpha_\mathrm{s}(T_\mathrm{g} - T_\mathrm{s}) - æ_\mathrm{s}\dot{M}; \tag{3}$$

$$\lambda_1 \frac{\partial T}{\partial z}\Big|_{z=H_1^-} = \lambda_2 \frac{\partial T}{\partial z}\Big|_{z=H_1^+} = -\alpha_1(T_{H_1^-} - T_{H_1^+}); \tag{4}$$

$$-\lambda_2 \frac{\partial T}{\partial z}\Big|_{z=H_2} = \alpha_2(T_{H_2} - T_2); \tag{5}$$

$$T\Big|_{t=0} = T_0, \qquad H_\mathrm{s}\Big|_{t=0} = H_{\mathrm{s},0}. \tag{6}$$

Here c_1, ρ_1, and λ_1 are the heat capacity, density, and thermal conductivity of β-diketonate, T_2 is the temperature of the lower wall of the channel, $H_\mathrm{s} = H_\mathrm{s}(t)$ is the coordinate of the sublimation surface, H_1 and H_2 are the distances from the upper wall of the channel to the upper and lower surfaces of the holder, respectively, $\alpha_\mathrm{s} = \alpha_{\mathrm{s,conv}} + \alpha_{\mathrm{s,rad}}$ is the total coefficient of heat transfer due to convective heat transfer between the gas and crystallization front and radiative heat transfer from the upper wall to the front, α_1 and α_2 are the coefficients of heat transfer at the contact boundaries of the plate with the upper surface of the holder and of the lower surface of the holder with the lower wall, respectively, $æ_\mathrm{s}$ is the sublimation heat, which is assumed to be temperature-independent, and $\dot{M}$ is the mass rate of substance sublimation from a unit surface. Equation (3) determines the heat balance on the sublimation surface; Eqs. (4) and (5) determine the conditions of contact heat transfer between the plate made of β-diketonate and the upper surface of the holder and also between the lower surface of the holder and lower wall of the channel, respectively. The values of $\alpha_{\rm s,conv}$ and $\alpha_{\rm s,rad}$ are determined by the expressions

$$\alpha_{\rm s,conv} = {\rm Nu}\,\lambda_{\rm g}/(2H_{\rm s,0}), \qquad \alpha_{\rm s,rad} = \varepsilon\sigma_0(T_{\rm g}^2 + T_{\rm s}^2)(T_{\rm g} + T_{\rm s}), \qquad T_{\rm s} = T(H_{\rm s}, t),$$

where ε is the reduced emissivity factor for the plate made of β-diketonate and the channel wall, σ_0 is the Stefan–Boltzmann constant, Nu is the Nusselt number determined, in accordance to [3], by the dependence ${\rm Nu} = 0.75\,{\rm Re}^{0.43}\,{\rm Pr}^{1/3}$, ${\rm Re} = 2H_{\rm s,0}v_{\rm g}/\nu_{\rm g}$ is the Reynolds number, ${\rm Pr} = \nu_{\rm g}/a_{\rm g}$ is the Prandtl number, $v_{\rm g}$ is the gas velocity in the channel, and $\nu_{\rm g}$ and $a_{\rm g}$ are the kinematic viscosity and thermal diffusivity of the gas, respectively.

Radiative heat transfer between the contacting surfaces can be neglected because it is small as compared to heat transfer due to thermal conductivity. Then, for α_1 and α_2, we have

$$\alpha_1 = \lambda_{\rm g}/\delta_{\rm gap1}, \qquad \alpha_2 = \lambda_{\rm g}/\delta_{\rm gap2},$$

where $\lambda_{\rm g}$ is the thermal conductivity of the gas (argon); $\delta_{\rm gap1}$ and $\delta_{\rm gap2}$ are the widths of the gaps between the contacting surfaces of the plate and the holder and of the holder and the lower wall of the channel, respectively.

Equations (1)–(6) are supplemented by the relation that describes convective heat transfer between the gas and the plate made of β-diketonate ($z = H_{\rm s}$). Neglecting the concentration of β-diketonate vapors in the gas volume, we write

$$\dot M = \beta\mu_1 C. \tag{7}$$

Here β is the mass-transfer coefficient, μ_1 is the molecular weight of β-diketonate, C is the molecular concentration of β-diketonate vapors, related to the vapor saturation pressure $P_{\rm s}$ and sublimation temperature $T_{\rm s}$ by

$$C = P_{\rm s}/(RT_{\rm s}) = P_{\rm t}\,{\rm e}^{-(æ_{\rm s}/R)(T_{\rm s}^{-1} - T_{\rm t}^{-1})}/(RT_{\rm s}), \tag{8}$$

R is the universal gas constant, and $P_{\rm t}$ and $T_{\rm t}$ are the vapor saturation pressure and temperature at the triple point. Substituting Eq. (7), with allowance for (8), into Eq. (3), we obtain

$$-\lambda_1 \frac{\partial T}{\partial z}\Big|_{z=H_{\rm s}(t)} = \alpha_{\rm s}(T_{\rm g} - T_{\rm s}) - æ_{\rm s}\beta\mu_{\rm s}\frac{P_{\rm t}}{RT_{\rm s}}\,{\rm e}^{-(æ_{\rm s}/R)(T_{\rm s}^{-1} - T_{\rm t}^{-1})}. \tag{9}$$

Now we pass to dimensionless variables using $T_{\rm g}$, λ_1, $\delta_{10} = H_1 - H_{\rm s,0}$, $t_0 = \delta_{10}^2/a_1$, and $a_1 = \lambda_1/(c_1\rho_1)$ as reference parameters. After simple transformations, from (1), (2), (4)–(6), and (9), we obtain

$$\frac{\partial\theta}{\partial\tau} = \frac{\partial^2\theta}{\partial y^2}, \quad Y_{\rm s} \leqslant y \leqslant Y_1, \qquad \frac{\partial\theta}{\partial\tau} = \bar a_2\frac{\partial^2\theta}{\partial y^2}, \quad Y_1 \leqslant y \leqslant Y_2,$$

$$-\frac{\partial\theta}{\partial y}\Big|_{y=Y_{\rm s}(\tau)} = {\rm Bi}_{\rm s}(1 - \theta_{\rm s}) - \bar\delta_{10}\,{\rm St}\,{\rm Sh}\,{\rm Le}\,\bar P_{\rm t}\,\frac{{\rm e}^{-{\rm St}\,\bar c_1(1/\theta_{\rm s} - 1/\theta_{\rm t})}}{\theta_{\rm s}},$$

$$\frac{\partial\theta}{\partial y}\Big|_{y=Y_1^-} = \bar\lambda_2\frac{\partial\theta}{\partial y}\Big|_{y=Y_1^+} = -\,{\rm Bi}_1(\theta_{Y_1^-} - \theta_{Y_1^+}),$$

$$-\frac{\partial\theta}{\partial y}\Big|_{y=Y_2} = {\rm Bi}_2(\theta_{Y_2} - \theta_2);$$

$$\theta\Big|_{\tau=0} = \theta_0, \qquad Y_{\rm s}(0) = Y_{\rm s,0}, \tag{10}$$

where ${\rm Bi}_{\rm s} = \alpha_{\rm s}\delta_{10}/\lambda_1$, ${\rm Bi}_1 = \alpha_1\delta_{10}/\lambda_1$, and ${\rm Bi}_2 = \alpha_2\delta_{10}/\lambda_2$ are the Biot numbers, ${\rm St} = æ_{\rm s}/(c_1T_{\rm g})$ is the Stefan number, ${\rm Le} = D/a_1$ is an analog of the Lewis number, ${\rm Sh} = 2\beta H_{\rm s,0}/D$ is the Sherwood number, $\bar a_2 = a_2/a_1$, $a_2 = \lambda_2/(c_2\rho_2)$, $\bar\lambda_2 = \lambda_2/\lambda_1$, $\bar c_1 = c_1/R$, $\theta = T/T_{\rm g}$, $\bar P_{\rm t} = \mu_1P_{\rm t}/(\rho_1RT_{\rm g})$, and $\bar\delta_{10} = \delta_{10}/(2H_{\rm s,0})$.

The velocity of motion of the sublimation surface is described by the equation

$$\dot Y = \bar\delta_{10}\,{\rm Sh}\,{\rm Le}\,\bar P_{\rm t}\theta_{\rm s}^{-1}\,{\rm e}^{-{\rm St}\,\bar c_1(\theta_{\rm s}^{-1} - \theta_{\rm t}^{-1})},$$

which is integrated after determining the dependence $\theta_{\rm s}(\tau)$ under the initial condition (10). The mass-transfer coefficient β is determined by the Sherwood number by the formula $\beta = {\rm Sh}\,D/(2H_{\rm s,0})$. Using the analogy between the heat- and mass-transfer processes, we determine the Sherwood number by the expression ${\rm Sh} = 0.75\,{\rm Re}^{0.43}\,{\rm Sc}^{1/3}$, where ${\rm Sc} = \nu_{\rm g}/D$ is the Schmidt number and D is the coefficient of diffusion of β-diketonate vapors in the argon flow.

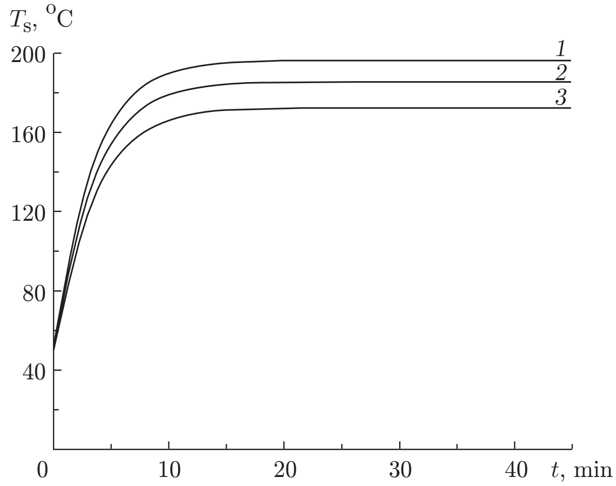

Fig. 2

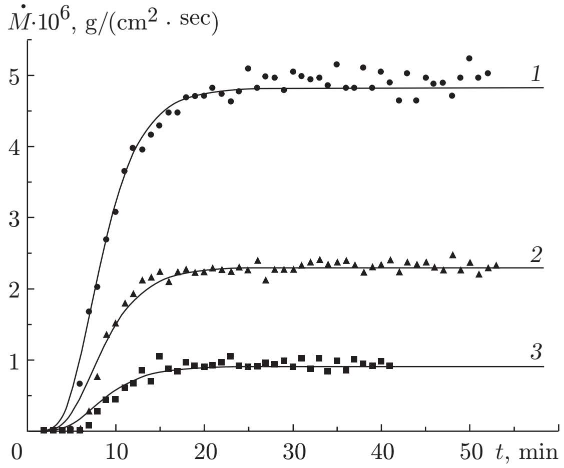

Fig. 3

Fig. 2. Calculated dependence of sublimation temperature on time ($v_0 = 3.6 \cdot 10^{-3}$ m/sec) for $T_g = 197$ (1), 186 (2), and 173°C (3).

Fig. 3. Calculated (curves) and experimental [3] (points) dependences of the mass rate of sublimation on time ($v_0 = 3.6 \cdot 10^{-3}$ m/sec) for $T_g = 197$ (1), 186 (2), and 173°C (3).

2. Brief Description of the Algorithm. In accordance with the proposed mathematical model on the basis of the method of collocations with least squares [4, 5], a numerical algorithm was developed for solving the problem of heat and mass transfer in the process of β-diketonate sublimation. In the model considered, the domain on whose external moving boundary sublimation occurs is divided into two subdomains: holder and plate made of β-diketonate. In each subdomain, we solve the initial-boundary problem (10) for the heat-transfer equation with different thermal diffusivities corresponding to holder and plate materials. For this purpose, the computational domain is covered by the grid (y_i, τ_j). At each time layer τ_j, the solution of the problem is sought in the form of a piecewise-polynomial function of the spatial coordinate y; in each spatial interval (y_i, y_{i-1}), the solution is determined in the form of a linear combination of the basis functions

$$\bar{\theta}^j = \sum c_k^j \varphi_k,$$

where φ_k are the basis functions, c_k are unknown parameters, $\bar{\theta}^j(\bar{y}) = \theta(y, \tau_j)$, and $\bar{y}$ is the local coordinate in the interval. The basis functions are chosen to belong to the space of second-order polynomials, which ensures the order of space approximation of the solution equal to $O(h^3)$. The derivative with respect to time is approximated in the first order as follows:

$$\frac{\partial \theta}{\partial \tau} \approx \frac{\theta^j - \theta^{j-1}}{\Delta \tau}, \qquad \Delta \tau = \tau_j - \tau_{j-1};$$

therefore, at each time layer, we solved the equation

$$\frac{\theta^j - \theta^{j-1}}{\Delta \tau} = A\,\frac{\partial^2 \theta^j}{\partial y^2} \qquad (A_1 = 1,\ A_2 = \bar{a}_2). \tag{11}$$

The coefficients c_k were determined from the conditions of collocation of Eq. (11), boundary conditions, and conditions of matching of the numerical solution at interval boundaries. As a result, in each interval, we obtain an overdetermined system of linear algebraic equations with respect to unknowns c_k. Its solution is determined from the condition of the minimum sum of the squared residuals of equations that enter into this system. Minimization yields a system of three equations with respect to three unknown parameters c_k. This system is solved analytically for different conditions at the interval boundaries. Symbolic expressions for all c_k are obtained. To calculate the amount of the evaporating mass of β-diketonate, we integrate the equation of motion of the boundary, since the velocity of its motion is determined by the parameters of the process at each time layer. Thus, the position of the boundary is explicitly determined in chosen nodes of the grid in time.

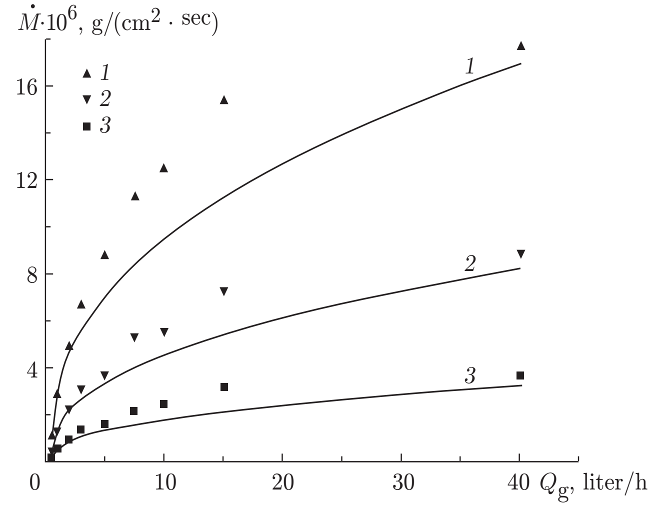

Fig. 4. Experimental [3] (points) and calculated (curves) dependences of the mass rate of sublimation on the volume velocity of the argon flow for $T_{\rm g} = 197$ (1), 186 (2), and 173°C(3).

3. Results of Numerical Calculations. As an example, we consider the process of sublimation of chromium β-diketonate $[\mathrm{Cr(CH_3COCHOH_3)_3}]$ in an argon flow with different values of its temperature. The following initial data were used. The gas parameters were $\nu_{\rm g} = 1.37 \cdot 10^{-5}(T_{\rm g}/298)^{1.75}$ m^2/sec, $a_{\rm g} = 2.04 \times 10^{-5}(T_{\rm g}/298)^{1.75}$ m^2/sec, $\lambda_{\rm g} = 1.54 \cdot 10^{-3} T_{\rm g}^{3/2}/(T_{\rm g} + 160)$ W/(m · K), and $v_{\rm g} = v_0(T_{\rm g}/298)$ m/sec. The chromium β-diketonate parameters were $c_1 = 1637.4$ J/(kg · K), $\rho_1 = 1374$ kg/m^3, $\lambda_1 = 10$ W/(m · K), $\text{æ}_{\rm s} = 1.197 \cdot 10^5$ J/mole, $\mu_1 = 349.33$ g/mole, $D = 6.37 \cdot 10^{-6}(T_{\rm g}/298)^{1.75}$ m^2/sec, $P_{\rm t} = 1419.61$ Pa, $T_{\rm t} = 489$ K, and $\delta_{10} = 0.002$ m. The reactor parameters were $H_{\rm s,0} = 0.01$ m, $H_2 - H_1 = 0.005$ m, $\delta_{\rm gap1} = 2 \cdot 10^{-5}$ m, and $\delta_{\rm gap2} = 5 \cdot 10^{-5}$ m.

Figures 2 and 3 show the dependences of temperature and mass rate of sublimation $\dot{M}$ on time for different temperatures of the gas. After a transitional sector caused by specimen heating up to the gas temperature, a quasisteady regime is established, in which the above-mentioned parameters remain almost constant. The time needed to reach the quasisteady regime is 15–20 min. It follows from Fig. 3 that the calculated values of the mass rate of sublimation are in good agreement with the results of the physical experiment [3]. The disagreement of experimental and numerical data observed before the quasisteady regime is caused by the threshold sensitivity of the balance used, which does not exceed $5 \cdot 10^{-5}$ g. As a result, a delay of mass registration is observed at the initial stages of the experiment if the mass-variation rate is low.

The dependence of the specific mass rate of sublimation in the quasisteady evaporation regime on the argon-flow velocity for different temperatures is plotted in Fig. 4. With increasing flow velocity, the sublimation rate increases; the increase is most intense in the range of flow velocities from 0 to 15 liters/h. The good agreement with experimental data, as in Fig. 3, verifies that the dependences used to calculate the heat- and mass-transfer coefficients give an adequate description of the heat- and mass-transfer phenomena on the sublimation surface. The difference in experimental and calculated data (up to 20%) observed in the range of volume velocities of the argon flow 5–30 liters/h is, apparently, related to the specific features of the reactor (cylindrical reactor with a semi-cylindrical holder for the specimen) used in the experiments of [3].

Thus, a quasi-one-dimensional unsteady model for sublimation of metal β-diketonate in a uniform steady flow of an inert gas and a numerical algorithm for solving heat-conduction equations with a phase-transition boundary are developed, which offer an adequate description for the process of evaporation of a solid volatile (chromium β-diketonate).

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