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THERMAL REGIMES OF CHEMICAL GAS-PHASE DEPOSITION  
OF CONDENSED PRODUCTS ON A MOVING SUBSTRATE  
HEATED WITH AN ELECTRIC CURRENT

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A nonstationary model is constructed for gas-phase formation of coatings on a moving fiber heated with an electric current.

Setups in which zonal electric heating of a moving substrate wire in a chemically active medium is realized are now widely employed for producing fibers from inorganic substances by the method of chemical gas-phase deposition. In the ohmic-heating zone deposition of condensed product on a substrate, as a result of which the transverse cross section of the substrate changes, occurs as a result of heterogeneous chemical transformations. The change in the transverse cross section of the substrate wire affects, through the electric resistance, both the electric power released in a given cross section of the specimen and the conditions of heat transfer. Thus, the case at hand the heating and deposition of condensed product on the substrate are determined by a collection of interrelated factors: chemical reactions, electric heating, and heat emission into the surrounding medium.

In this paper we give a mathematical description of this process for the purpose of constructing an algorithm for controlling the condensation regimes when preparing continuous fibers by the method of chemical gas-phase deposition.

1. Mathematical Model of the Deposition Process. A substrate filament with radius  $r_0$  is heated on the section  $X = 0-l$  with a stable electric current ( $I = \text{const}$ ); the current is stabilized with the help of tracking devices. The filament moves with velocity  $U$  in the laboratory coordinate system. In the heating zone heterogeneous chemical condensation occurs on the surface of the filament; this changes the transverse size of the specimen as a

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result of the accumulation of a layer of the product, whose electrophysical and thermophysical properties are different from those of the substrate. It is assumed that the chemical condensation process is itself thermally neutral, and the intensity of heat removal from the side surface of the specimen is much lower than internal heat transfer ( $Bi \ll 1$  - the temperature distribution over the cross section of the specimen is insignificant).

We now derive an equation describing the heating of a moving filament as the condensed product settles on it. Umov's equation [1-3] is satisfied for a body with a time-dependent volume:

$$\frac{\partial H}{\partial t} + \text{div}(j + UH) = I_+ - I_- \quad (1)$$

For cylindrical symmetry, taking into account the differences between the thermophysical characteristics of the substrate and the layer it is easy to obtain

$$H = [c_1 \rho_1 (r_0/r)^2 + c_2 \rho_2 (1 - (r_0/r)^2)] T. \quad (2)$$

Volume heating is caused by Joule heating, for which, in the case when the substrate and layer conduct in parallel,

$$I_+ = \frac{0.239 I^2 \sigma_1 \sigma_2}{\pi^2 r^2 [\sigma_1 (r^2 - r_0^2) + \sigma_2 r_0^2]}. \quad (3)$$

When the conductivity of the product is of a metallic character the temperature dependences of the resistivity of the substrate ( $i = 1$ ) and layer ( $i = 2$ ) are determined by the relation  $\sigma_i = \sigma_{i0} (1 + \gamma_i T)^{m_i}$ . For a product with semiconductor properties  $\sigma_2 = \sigma_{20} \exp(A/T)$ .

Heat losses from the specimen are caused by convective and radiative heat transfer from the side surface (they depend on the transverse dimensions of the specimen) and conductive heat removal from the ends:

$$I_- = 2\alpha(r)(T - T_0)/r + 2\epsilon\sigma(T^4 - T_0^4)/r, \quad (4)$$

where  $\alpha = \alpha_0 (r/r_0)^{n-1}$  is the coefficient of convective heat transfer, and  $n \leq 1$ . Substituting Eqs. (2)-(4) into Eq. (1), we obtain the heat-conduction equation sought:

$$\begin{aligned} & \frac{\partial}{\partial t} \left[ \frac{c_1 \rho_1 r_0^2 + c_2 \rho_2 (r^2 - r_0^2)}{r^2} T \right] = \lambda \frac{\partial^2 T}{\partial X^2} - \\ & - U \frac{\partial}{\partial x} \left[ \frac{c_1 \rho_1 r_0^2}{r^2} T - \frac{c_2 \rho_2 (r^2 - r_0^2)}{r^2} T \right] - \frac{2\alpha(r)}{r} (T - T_0) - \frac{2\epsilon\sigma}{r} (T^4 - T_0^4) + \frac{0.239 I^2 \sigma_1(T) \sigma_2(T)}{\pi^2 r^2 [\sigma_1(T)(r^2 - r_0^2) + \sigma_2(T)r_0^2]}. \end{aligned} \quad (5)$$

The change in the transverse size of the specimen owing to chemical condensation is described by the expression

$$\frac{\partial r}{\partial t} = K_0 \exp(-E/RT) - U \frac{\partial r}{\partial X}, \quad (6)$$

the meaning of which is that at a fixed point the cross section of the filament changes as a result of both the chemical process, which is exponentially dependent on the temperature, and the longitudinal displacement of the specimen of variable thickness.

It is assumed that initially the substrate is heated up to the temperature of the surrounding medium and that boundary conditions of the first kind are realized at the points of electric contact (because of conductive heat removal into the massive electric contacts the temperature of the specimen is constant and equal to the temperature of the surrounding medium). The rate of the deposition process at temperature  $T_0$  is insignificant. These assumptions are reflected by the following conditions:

$$\text{at } t = 0 \quad T = T_0; \quad (7)$$

$$\text{at } X = 0 \quad T = T_0, \quad r = r_0; \quad (8)$$

$$\text{at } X = l \quad T = T_0, \quad r = r(t). \quad (9)$$

The system (5)-(9) makes it possible to describe the process of chemical condensation on a moving substrate heated with a stabilized electric current.

For convenience in solving and analyzing the system we write it in dimensionless form. Introducing the dimensionless variables we transform the system (5)-(9) into the form

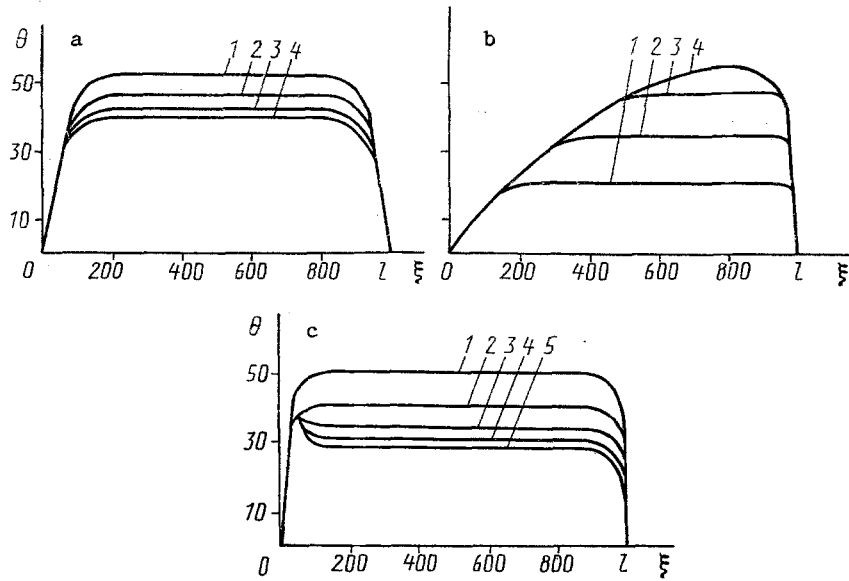


Fig. 1. Nonstationary temperature profiles along the specimen for different  $Da$  numbers: a)  $Da=10^{-4}$  ( $1-\tau=2,86 \cdot 10^{-7}$ ;  $2-3,34 \cdot 10^{-5}$ ;  $3-6,67 \cdot 10^{-5}$ ;  $4-3,50 \cdot 10^{-4}$ ); b)  $Da=5 \cdot 10^{-10}$  ( $1-\tau=10^{-9}$ ;  $2-10^{-8}$ ;  $3-10^{-7}$ ;  $4-3,4 \cdot 10^{-7}$ ); c)  $Da=1$  ( $1-\tau=2,43 \cdot 10^{-7}$ ;  $2-2,13 \cdot 10^{-5}$ ;  $3-4,25 \cdot 10^{-5}$ ;  $4-6,38 \cdot 10^{-5}$ ;  $5-8,50 \cdot 10^{-5}$ )

$$\frac{\partial \theta}{\partial \tau} = \frac{\delta z^2}{\beta [1 + \omega_c (z^2 - 1)]} \frac{\partial^2 \theta}{\partial \xi^2} - \frac{2(\omega_c - 1)(1 + \beta \theta)}{[1 + \omega_c (z^2 - 1)] \beta z} \exp(\theta/(1 + \beta \theta)) - \quad (10)$$

$$\frac{1}{Da} \frac{\partial \theta}{\partial \xi} - \frac{\alpha z^n \theta}{[1 + \omega_c (z^2 - 1)] \beta} - \frac{\varepsilon [(1 + \beta \theta)^4 - 1] z}{\beta (1 + \omega_c (z^2 - 1))} + \frac{l}{\beta [1 + \omega_c (z^2 - 1)]} \frac{[1 + \gamma_1 (1 + \beta \theta)]^{m_1}}{[1 + \sigma_0 \varphi_0(\theta) (z^2 - 1)]}, \quad (11)$$

$$\frac{\partial z}{\partial \tau} = \exp(\theta/(1 + \beta \theta)) - \frac{1}{Da} \frac{\partial z}{\partial \xi}, \quad (12)$$

$$\text{at } \tau = 0 \quad \theta = 0, \quad z = 1; \quad (13)$$

$$\text{at } \xi = 0 \quad \theta = 0, \quad z = 1; \quad (14)$$

$$\text{at } \xi = l \quad \theta = 0. \quad (14)$$

In the case when the conductivity of the layer is of a metallic character

$$\varphi_0(\theta) = \frac{[1 + \gamma_1 (1 + \beta \theta)]^{m_1}}{[1 + \gamma_2 (1 + \beta \theta)]^{m_2}},$$

and in the case when the conductivity is of a semiconductor character

$$\varphi_0(\theta) = \frac{[1 + \gamma_1 (1 + \beta \theta)]^{m_1}}{\exp(A/(1 + \beta \theta))}.$$

The system (10)-(14) was solved on a computer with the help of an implicit difference scheme by the method of forward and backward sweep.

**2. Computational Results.** Heating of the moving filament from the initial temperature up to its equilibrium value starts when the electric current is switched on ( $t = 0$ ). The heating is completed when a stationary (quasistationary) distribution of the temperature and thickness of the layer formed in the zone of heating, which are functions of the parameters, are established. Criterional analysis of the system and the numerical calculations showed that three different regimes of heating of the filament are possible (see Fig. 1). The possibility of realization of these regimes is determined by the Damkohler number, which in the present case can be written in the form  $Da = \tau_*/\tau_{**}$ .

In the limit  $Da \rightarrow \infty$  (Fig. 1a) the motion of the specimen does not have a decisive effect on the character of the temperature profiles in the heating zone. The effect reduces to the appearance of asymmetry in the temperature distribution (the temperature maximum is displaced relative to the center of the heating zone in the direction of motion of the speci-

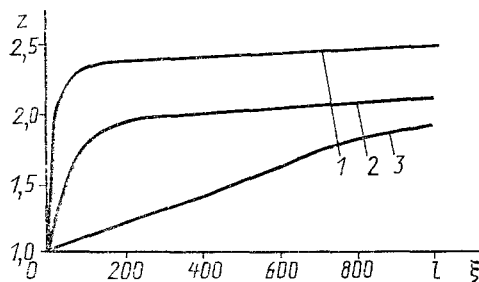


Fig. 2. Stationary distribution of the thickness of product along the specimen for different Da numbers:  $Da = 10^{-7}$  (1),  $10^{-3}$  (2), and  $10^{-1}$  (3).

men). At all points of the heating zone the temperature increases with time and approaches asymptotically the stationary value. The rate of heating of the filament is determined by the Joule power and the resulting heat losses (primarily from the side surfaces).

Curve 1 in Fig. 2 illustrates for the case  $Da \rightarrow \infty$  the character of the distribution of the thickness of the film grown in the heating zone in the stationary state.

In the other limiting case  $Da \rightarrow 0$  (Fig. 1b), which corresponds to high drawing velocities or low reaction rates, the motion of the specimen has the decisive effect on the temperature profile in the heating zone. In this case the thermal inertia of the fiber, which results in the appearance of a longitudinal temperature gradient (the intensity of the heat losses through the side boundaries is comparable to heat losses from the ends), plays an appreciable role. The distribution of the thickness of the product layer formed in the heating zone in the stationary state has an S shape (curve 2, Fig. 2), which is all the more distinct the smaller the value of Da.

For values of  $Da \approx 1$  (the characteristic drawing and reaction times are comparable), in contrast to the cases studied above, there arise qualitatively new regimes of heating of the moving filament (Fig. 1c). When the electric current is switched on, initially (when the temperature of the filament is still low and the reaction is not significant) the specimen is heated according to the laws of chemically inert bodies and the temperature increases with time everywhere in the heating zone. The increase in temperature in turn intensifies the deposition process and the cross section of the specimen varies along the heating zone. Because of the change in electric power the variation in the cross section of the specimen results in a redistribution of temperature, as a result of which the temperature reaches a maximum on the input section of the specimen while other sections cool to some stationary value of the temperature. Thus, here, with the exception of the input sections, the temperature of the specimen passes with time through a maximum and the character of the distribution of the film thickness along the heating zone (in the steady state) corresponds to the curve 3 in Fig. 2.

The thermophysical properties of the product formed and the conditions of heat transfer have a significant effect on the thermal conditions of deposition. The parameter  $w_c$ , which in real situations falls in the range  $w_c = 0-10$ , characterizes the role of the volume heat capacity of the deposited layer. As one can see from the system (10)(14), the parameter  $w_c$  affects both the rate of heating of the specimen and the longitudinal temperature gradient. An increase of  $w_c$  (increase of the volume heat capacity of the product formed) results in an increase of the duration of the nonstationary stage. The effect of  $w_c$  on the character of the temperature distribution along the specimen is more complicated. For the kinetic regime of deposition ( $Da \approx 1$ ) numerical calculations show (Fig. 3) that when  $w_c$  increases the stationary temperature in the heating zone decreases; this is connected with the increase in the overall heat capacity of the specimen. A temperature maximum appears in the heating zone only for  $w_c > 1$  (the heat capacity of the product is higher than that of the substrate). The magnitude of the local heating\* of the specimen  $\Delta\theta = \theta_{\max} - \theta_{st}$  passes through a maximum

\*The temperature on the temperature plateau for the steady state regime at the point  $\xi = 0.75l$  was taken as the stationary value of the temperature  $\theta_{st}$  (see Fig. 1b).

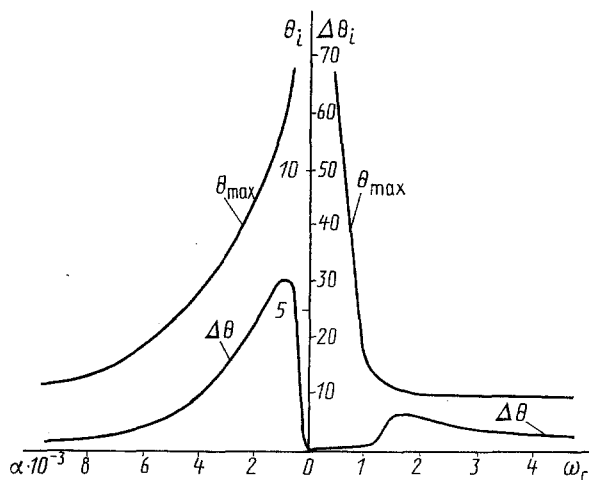


Fig. 3. Effect of the thermophysical parameters on the non-uniformity of heating of the specimen.

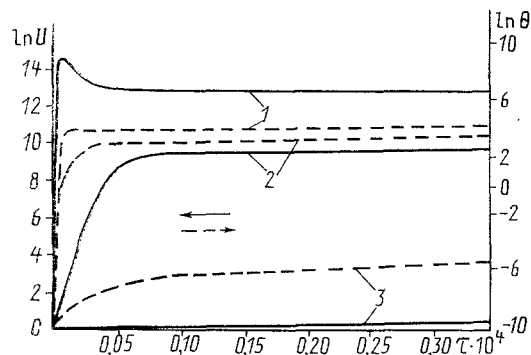


Fig. 4. Change in temperature and the effect of electric conductivity of the product on the rate of deposition ( $\xi = 0.5 \text{ \AA}$ ): 1) metal; 2) semiconductor; 3) dielectric.

as  $w_c$  increases. This type of dependence  $\Delta\theta(w_c)$  is associated with the character of the change in the thickness of the specimen on the input sections of the heating zone.

An increase in heat losses from the side surfaces of the filament also results in an extremal dependence of the nonuniform heating along the specimen (Fig. 3). This is a consequence of the temperature dependence of the coefficient of convective heat transfer.

The character of the distribution of the temperature and the thickness of the film formed on the heated section of the substrate are closely related with the electric conductivity of the reaction products. When the electric current is stabilized the variation of the Joule heating along the specimen is determined by the character of the change of the resistivity of the specimen. Accordingly, here we can study three cases: metallic, semiconductor, and dielectric films.

It is well known that semiconductors are characterized by electric conductivities falling between the values for metals ( $10^6$ - $10^4 \text{ \Omega}^{-1} \cdot \text{cm}^{-1}$ ) and good dielectrics ( $10^{-10}$ - $10^{-12} \text{ \Omega}^{-1} \cdot \text{cm}^{-1}$  at room temperature). A characteristic feature of semiconductors, which distinguishes them from metals, is that the electric conductivity increases with temperature, and as a rule the increase is exponential in a quite wide range of temperatures. As the temperature increases the electron density in the conduction band increases and with the same current strength the time dependence of the rate of growth of the film will be different for metallic, films (Fig. 4). The film will grow at the slowest rate in the case of dielectrics, because their resistivity is high and the specimen will be heated to a lower temperature. Metals are heated significantly more strongly with the same current strength and drawing velocity, and because of the extremal dependence of  $\theta(\xi)$  here the rate of growth of the film also passes through a maximum. Initially the behavior of semiconductor films is identical to that of dielectric films. With time, once a quite high temperature is reached, the rate of growth

of the film increases and the stationary (quasistationary) rate of growth of the film becomes close to the rate in the case of metals (Fig. 4).

Thus under conditions of heterophase condensation on a moving substrate heated with an electric current there appear a number of effects that must be taken into account when describing the regimes of reactions of practical importance. The assumption that there is no transverse distribution of the temperature is not strict, but in real situations it can apparently be used for sufficiently thin substrates. Thus in the case when compounds of the type  $\text{Si}_3\text{N}_4$  and  $\text{SiC}$  are deposited on a 10- $\mu\text{m}$ -in-diameter substrate with  $\alpha = 10^{-2}$  cal/( $\text{cm}^2 \cdot \text{sec} \cdot \text{deg}$ )  $\text{Bi} \approx 10^{-2}$  for a ten-fold increase of the initial diameter of the specimen, i.e., it can be assumed that there is no transverse temperature gradient in the process.

#### NOTATION

Here the dimensional variables are: the time  $t$ , the longitudinal coordinate  $x$ , the velocity of the filament  $U$ ;  $\text{Bi}$ , Biot's number;  $H$ , specific enthalpy;  $j$ , conductive heat flux;  $I_+$ , rate of volume heating;  $I_-$ , rate of volume heat absorption;  $c_i$  and  $\rho_i$ , specific heat capacity and density of the substrate ( $i = 1$ ) and layer ( $i = 2$ );  $\sigma_i$ , resistivity;  $\rho$ , outer radius of the specimen;  $r_0$ , radius of the substrate filament;  $I$ , current strength;  $\epsilon$ , emissivity of the specimen;  $\sigma$ , Stefan-Boltzmann constant;  $\alpha$ , coefficient of convective heat transfer;  $\lambda$ , effective thermal conductivity of the specimen;  $E$ , activation energy;  $K_0$ , preexponential factor;  $T_0$ , temperature of the surrounding medium;  $T$ , temperature of the deposited specimen;  $R$ , universal gas constant;  $l$ , length of the zone of electric heating. Dimensionless variables:  $\theta = E/(RT_0^2)(T - T_0)$ , is the temperature;  $\tau = K_0 \exp(-E/RT_0)/r_0$  is the time;  $\xi = X/r_0$  is the longitudinal coordinate;  $z = r/r_0$  is the transverse size of the film;  $\text{Da} = K_0 \exp(-E/RT_0)/U$ , is Damkoehler's number;  $\tau_* = r_0/U$ , is the characteristic drawing time;  $\tau_{**} = r_0/(K_0 \exp(-E/RT_0))$ , is the reaction time; and,  $\omega_c = c_2 \rho_2 / (c_1 \rho_1)$ , is the ratio of the volume heat capacity of the product to the volume heat capacity of the substrate.

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