

FLOW OF CHEMICALLY NONEQUILIBRIUM GAS MIXTURES WITH  
SPONTANEOUS CONDENSATION AT LOW MACH NUMBERS

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UDC 541.24:532.5:621.372.8

Vapor deposition methods, which have found broad application in industry (see, e.g., [1-3]) are based on slow flows of multicomponent, chemically reacting gas mixtures with spontaneous condensation of the reaction products. The authors of [4] proposed a method for obtaining equations for essentially subsonic flows of nonequilibrium gas mixtures in the presence of arbitrary finite changes in density. The same concept was used in [5] to study flows with an equilibrium concentration of the reaction products.

Here we generalize the model in [5] and consider the kinetics of condensation in order to determine the concentration of condensate particles and their diameter. We also discuss the formulation of the problem of modeling the MCVF method of obtaining semifinished optical fibers, the method of solving this problem, and the results of a study of the features of gas dynamics and mass transfer.

1. The basic system of equations of the dynamics of a multicomponent two-phase mixture, modeling the methods of chemical vapor-phase deposition, is written in a one-temperature, one-velocity approximation based on the small sizes of the condensate particles ( $\sim 5 \cdot 10^{-8}$  m). The problem is subsequently simplified with respect to two small parameters characteristic of the deposition conditions (see [1-3]): the Mach number (characteristic mean-mass velocity of the mixture  $\leq 1$  m/sec) and the volume fraction of condensate.

This system can then be written in the following dimensionless form:

$$\rho_c \frac{d\mathbf{v}}{dt} = -\nabla \tilde{p} + \frac{1}{\text{Re}} \left[ 2\mathbf{V} \cdot (\mu \mathbf{S}) - \frac{2}{3} \nabla (\mu \mathbf{V} \cdot \mathbf{v}) \right] + \frac{\rho_c - 1}{\text{Fr}} \mathbf{j}; \quad (1.1)$$

$$\rho_c \frac{dH}{dt} = \frac{1}{\text{Re Pr}} \nabla \cdot (\lambda \nabla T) - \frac{1}{\text{Sc Re}} \sum_{i=1}^N \nabla \cdot (\rho Y_i h_i \mathbf{V}_i); \quad (1.2)$$

$$\rho \frac{dY_i}{dt} = W_i^x - W_i^c - \frac{1}{\text{Sc Re}} \nabla \cdot (\rho Y_i \mathbf{V}_i) + Y_i W^c, \quad i = 1, 2, \dots, N, \quad (1.3)$$

$$\frac{\partial \rho_c}{\partial t} + \nabla \cdot (\rho_c \mathbf{v}) = 0; \quad (1.4)$$

$$\frac{\partial \rho_j^c}{\partial t} + \nabla \cdot (\rho_j^c \mathbf{v}) = W_j^c, \quad j = 1, \dots, m; \quad (1.5)$$

$$\rho T = M_g, \quad \rho_c = \rho + \sum_{j=1}^m \rho_j^c; \quad (1.6)$$

$$\frac{dX_n}{dt} = I_0 r_{\text{cr}}^n + n B_* \dot{r}_c X_{n-1}, \quad n = 0, 1, 2; \quad (1.7)$$

$$W_j^c = D_* (B_* \dot{r}_j X_2 + (1/3) r_{\text{cr}}^3 I_0 \delta_{1j}), \quad W^c = \sum_{j=1}^m W_j^c; \quad (1.8)$$

Here,  $t$  is time;  $\rho_c$ ,  $\mathbf{v}$ ,  $H$ ,  $T$ ,  $\mathbf{S}$ ,  $\mu$ ,  $\lambda$ , and  $c_p$ , density, velocity vector, specific enthalpy, temperature, strain-rate tensor, viscosity, thermal conductivity, and isobaric heat capacity for the mixture;  $Y_i$ ,  $h_i$ ,  $\mathbf{V}_i$ ,  $M_i$ , and  $W_i^x$ , mass fraction, enthalpy, rate of diffusion, molecular weight, and chemical reaction rate for the  $i$ -th gaseous component;  $\tilde{p}$ , excess pressure;  $M_g$ , molecular weight of the mixture of gaseous components;  $\rho_j^c$  and  $W_j^c$ , density and source of mass of the  $j$ -th component in the condensed phase;  $m$ , quantity of the condensing components;  $\text{Re}$ ,  $\text{Fr}$ ,  $\text{Pr}$ , and  $\text{Sc}$  are the Reynolds, Froude, Prandtl, and Schmidt numbers;  $X_n$  is the  $n$ -th order moment of

the condensate particle-size distribution function;  $r_{cr}$  and  $I_0$ , radius of the critical cluster and the rate of formation of these clusters in a unit volume;  $\delta_{1j}$ , Kronecker symbol;  $\dot{r}_j$  and  $\dot{r}_c$ , rate of growth of the particles due to condensation of the  $j$ -th component and the total rate of growth of the particles;  $B_*$  and  $D_*$ , dimensionless parameters characterizing processes involved in the formation of clusters of critical size and macroscopic condensation.

In Eqs. (1.7) and (1.8),  $r_{cr}$  and  $I_0$  are calculated from relations of the Frenkel-Zeldovich [6, 7] classical theory of nucleation. The quantities characterizing mass exchange between the phases ( $\dot{r}_j$  and  $\dot{r}_c$ ) were calculated from formulas for homogeneous-heterogeneous condensation for the free-molecular regime of particle flow [8].

The  $n$ -th order moments of the particle-size distribution function  $f(t, x, r)$  are determined by the equality

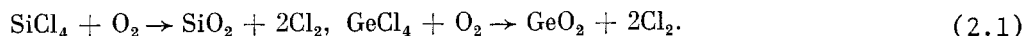
$$X_n = \int_{r_{cr}}^{\infty} r^n f(t, x, r) dr, \quad n = 0, 1, 2,$$

which suggests their physical meaning:  $X_0 = N_p$  - the concentration of condensate particles,  $X_1 = \langle r \rangle N_p$ ,  $X_2 = \langle r^2 \rangle N_p$ , where  $\langle r \rangle$  and  $\langle r^2 \rangle$  are the mean and squared values of particle radius, respectively.

2. Formulation of a Problem for the MCVD Method. This method has come into wide use due to its relative simplicity. We will briefly discuss its general features.

An initial mixture of chlorides of silicon and germanium in excess oxygen (characteristic values of their mass fractions -0.2, 0.1, 0.7) are fed at atmospheric pressure and the temperature  $T_0 \approx 300$  K into a substrate tube of fused quartz rotating about its own axis ( $\omega \sim 5$  rad/sec). The length of the tube is about 1 mm, its diameter  $d = 2 \cdot 10^{-2}$  m, and the mean-mass velocity of the incoming gas  $u_0 \leq 0.1$  m/sec. Chemical reactions are initiated by supplying energy from an external moving oxygen-hydrogen burner (velocity  $\sim 5 \cdot 10^{-3}$  m/sec, with the velocity of the burner coinciding with  $u_0$  in terms of direction). The supply of energy creates a region of finite length in which significant heating occurs (the maximum temperature of the tube wall is about 1900 K).

When the local temperature of the initial gas mixture is above 1200 K, the following chloride oxidation reactions take place in it:



The silicon and germanium oxides are in the supersaturated state and condense in the volume with the formation of highly disperse particles. Their interaction with the carrier gas leads to partial deposition on the inside surface of the tube downflow from the heated zone and to the formation of a porous layer  $\sim 10^{-5}$  m thick. An increase in temperature in this layer due to movement of the external burner leads to sintering and vitrification of the particles. By changing the consumption of the alloying addition ( $\text{GeCl}_4$ ) in each cycle of burner movement, it is possible to obtain the necessary distribution of the refractive index in the cross section of the forming semifinished product. From 10 to 100 such layers are usually deposited, depending on the type of fiber being made.

The required semifinished product, in the form of a solid transparent cylinder, is obtained by collapse of the hollow cylinder due to surface tension during its heating to a temperature  $\geq 2000$  K.

Low deposition efficiency and the low productivity of the above method have stimulated efforts to model it and search for ways of optimizing it. However, the published studies have either covered only individual parts of the process [9, 10] or have involved the introduction of unsubstantiable simplifying assumptions [11]: stationariness of the process, narrow-channel approximation, absence of gravity and rotation of the substrate tube, equilibrium of the chemical reactions and condensation. On the other hand, the system of equations presented in Sec. 1 makes it possible to conduct a thorough study of the MCVD method.

To this end, we write Eqs. (1.1)-(1.8) in a cylindrical coordinate system and we add the following boundary conditions: a) at the inlet of the substrate tube, we assign a parabolic velocity profile for a mixture of the specified composition, having a dimensionless temperature equal to 1; b) flexible boundary conditions are established for all of the unknowns at the outlet of the tube; c) the condition of symmetry for all unknowns is satisfied on the tube axis; d) on the inside surface of the tube:

for projections of the velocity vector

$$v_z = 0, v_r = 0, v_\phi = Re_\omega/Re,$$

for temperature

$$\lambda \partial T / \partial r = -K(t, z)[T_w - T_0(t, z)],$$

for the mass fraction of the gaseous components

$$\partial Y_i / \partial r = 0, i = 1, 2, \dots, N,$$

for the condensed phase, the flow to the wall is determined by the rate of thermophoresis  $v_t^c$ :

$$J_w^c = \rho^c v_t^c.$$

Here,  $Re_\omega = \omega d^2 / (4\nu)$  is the Reynolds number calculated from the angular velocity;  $T_w$  is the temperature of the inside surface;  $T_0$  is the temperature of the outside surface of the tube, the distribution of this temperature along the longitudinal coordinate being taken from an experiment and the time dependence being determined by the displacement of the burner;  $K(t, z) = 2\lambda_{*} / [\lambda_0 \ln(1 + h/d)]$  is the thermal conductivity of the tube wall, of thickness  $h$ ;  $\lambda_{*}$  is the effective thermal conductivity of quartz with allowance for the radiative component.

Analysis of the kinetics of the overall chemical reactions involving oxidation of the chlorides (2.1) shows [12] that they can be modeled with sufficient accuracy by first-order kinetic equations. Then the reaction rate for the  $i$ -th component can be calculated from the relation

$$W_i^x = \sum_{r=1}^{N_x} \frac{1}{Dam_r} v_{ir} \frac{M_i}{M_r} Y_r \frac{k_r^0(T)}{k_r^0(T_r^*)} \exp \left\{ -\frac{E_{ar}}{T_0 R} \left( \frac{1}{T} - \frac{1}{T_r^*} \right) \right\},$$

where  $Dam_r$ ,  $k_r^0$ ,  $T_r^*$ , and  $E_{ar}$  are the Damköhler number, the preexponential multiplier, the critical temperature, and the activation energy for the  $r$ -th reaction;  $v_{ir}$  is the stoichiometric coefficient of the  $i$ -th component in the  $r$ -th reaction;  $k_r^0$  and  $E_{ar}$  are found from analyzing empirical data [12].

Comparison of numerical values of  $W_i^x$  at different temperatures suggests that during spontaneous condensation of the reaction products, clusters of the critical size are formed by the combination of  $SiO_2$  molecules — since the rate of the silicon chloride oxidation reaction is higher. In connection with this, the radius of the nuclei and the rate of their formation per unit volume are calculated in terms of the parameters of silicon dioxide.

3. Numerical Method. The numerical method to be used to solve the problem is based on branching of physical processes. We will use  $A_1$  to denote the operator which describes the evolution of the gas with "frozen" reactions and condensation. The quantity  $A_2$  represents an operator corresponding to chemical reactions and phase transformation in the absence of convective and molecular transport. Then the complete step for integration over time can be represented in the form

$$A(2\Delta t) = A_1(\Delta t)A_2(\Delta t)A_2(\Delta t)A_1(\Delta t)$$

( $\Delta t$  is the time step).

The operator  $A_1$  is the Chorin-Hurt modification of the well-known MAC method [13] and consists of three stages. In the first stage, an explicit scheme is used to calculate velocity projections from an assigned pressure field. In the second stage, we construct an iterative process in which the values found for pressure and velocity are corrected until continuity equation (1.4) is satisfied with a prescribed accuracy. Then the explicit scheme is used to solve Eqs. (1.2), (1.3), (1.5), and (1.7) with "frozen" reactions and condensation.

Let us examine the operator  $A_2$ . Here we use an implicit scheme to simultaneously solve the equations for the enthalpy of the mixture, the mass fractions of the components in the gas and condensed phases, and the moments of the particle-size distribution functions with "frozen" convective and molecular transport. Although the first of these does not contain

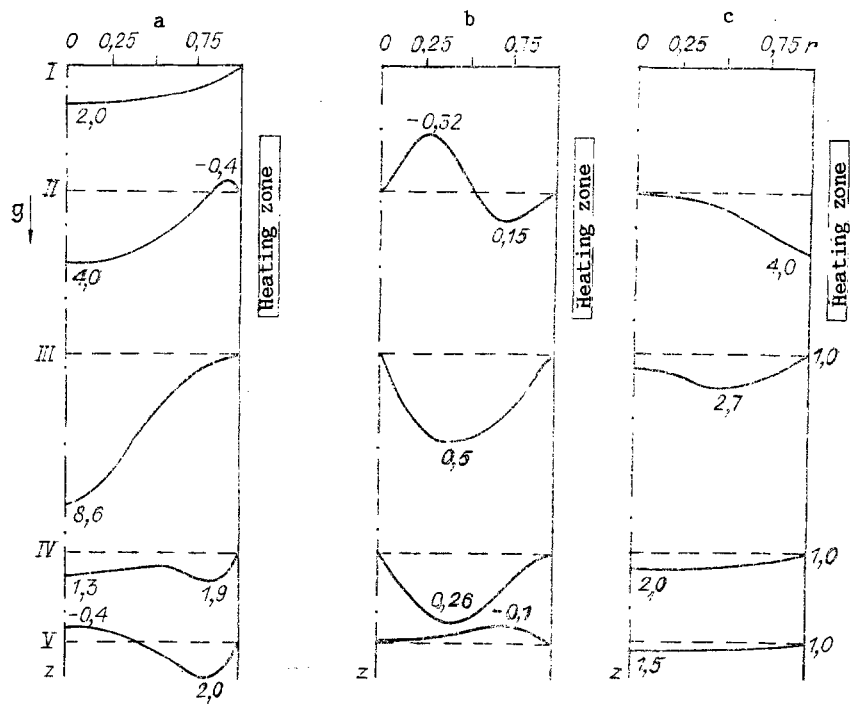


Fig. 1

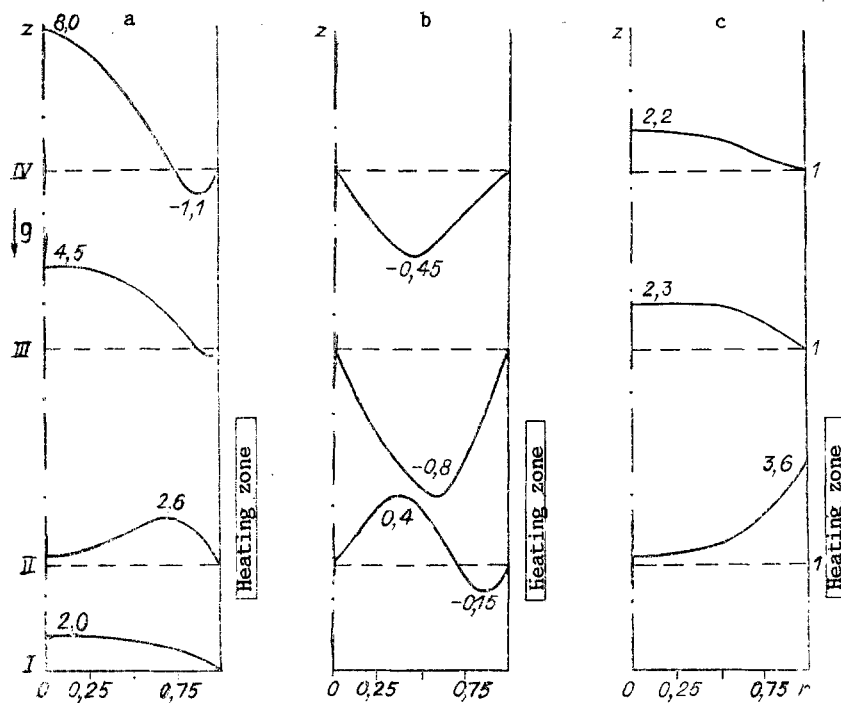


Fig. 2

the source, it is nonetheless included in the system to allow for the temperature change connected with the processes of chemical reaction and condensation. The nonlinear finite-difference equations are solved by using an iterative process constructed on the basis of a Newton linearization.

In problems in which it is unnecessary to have a detailed description of processes with characteristic times shorter than the characteristic gas dynamic time, it is natural to select an integration step on the order of the latter (from the condition of stability of operator  $A_1$ ). Here, the changes in temperature and mass fraction at one time step may be quite substantial. The method of solution used here consists of limiting the increments of the unknowns during the iterations while allowing for their physical ranges [14].

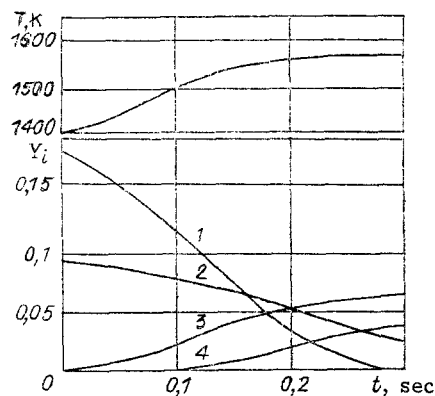


Fig. 3

4. Results of Calculations. Calculations were performed for different orientations of the substrate tube and different Re and Fr. In the present case, Re and Fr are not similarity criteria but are determined by the composition and flow rate of the mixture at the inlet.

It should be noted that when the tube is positioned horizontally, buoyancy causes the flow to be three-dimensional in character. In connection with this, we performed qualitative calculations in a plane approximation in order to obtain the regions of Re and Fr in which natural convection has a significant effect on the flow pattern.

Analysis of the calculated results shows that at  $Re < 150$  and  $Fr < 0.1$ , mixed-convective flow is realized in the horizontal channel. In the region of significant superheating, the transverse velocities reach ~15-20% of the maximum longitudinal velocity. Regions of recirculatory flow (at  $Re \sim 40$  and  $Fr \sim 0.01$ ) develop at the inlet and outlet of the heating zone near the top and bottom walls, respectively. If the conditions at the inlet are such that  $Re > 150$  and  $Fr > 0.1$ , then the effect of buoyancy on the dynamics of the flow can be ignored and the flow can be considered axisymmetric.

When the substrate tube is positioned vertically, the structure of the axisymmetric flow is determined by the direction in which the gas mixture is pumped, other conditions being equal. As an example, Fig. 1 illustrates the distribution of the longitudinal (a) and radial (b) components of the velocity vector, as well as the temperature of the mixture (c) at different stations in the case of descending flow and  $Re = 40$ ,  $Fr = 0.01$ .

The distortion of the longitudinal velocity profile from parabolic form in section I is attributable to the effect of buoyancy and acceleration of the flow due to the energy supplied in the heating zone. We should point out the substantial radial velocities in sections II and III and the formation of two recirculation regions: at the inlet of the heating zone near the surface of the wall; below this zone, downflow in the central part of the tube (sections II and V). After section IV, the radial component of the velocity vector changes sign

Figure 2 shows the distribution of the main gas dynamic parameters of an ascending flow with the same values of Re and Fr. In this case, buoyancy leads to additional acceleration of the heated volumes of the mixture (sections II-IV, Fig. 2a). It should be noted that the radial velocity in sections III and IV, located downflow from the heating zone, is directed toward the axis of the channel. This makes the scheme based on ascending flow of the mixture unpromising for the MCVD method of obtaining semifinished products.

Thus, a fairly complex flow regime is realized in the substrate tube (the flow being mixed-convective for certain values of the parameters), while chemical reactions and condensation of the reaction products occur against the background of this flow.

The chemical reactions are endothermic, while heat is given off during the phase transformation. The overall effect is positive. Calculations show that the temperature of the mixture is increased by an average of 8-12% as a result of these processes. This fact can be clearly seen in the example of a spatially uniform problem. Thus, Fig. 3 shows the changes in the temperature of the system with time from the initial value  $T = 1400$  K. Also shown are the mass fractions of the silicon and germanium chlorides and their oxides in the condensed phase (lines 1-4 correspond to  $SiCl_4$ ,  $GeCl_4$ ,  $SiO_2$ , and  $GeO_2$ ). The figure reflects the nonequilibrium character of reactions that take place in the system, since the gas dynamic time scale is equal to  $d/u_0 = 0.2$  sec.

Examination of the deposited powder under an electron microscope showed that the condensate particles are nearly spherical. Their diameters are distributed mainly in the range from  $10^{-8}$  to  $9 \cdot 10^{-8}$ , with a maximum at  $d_p \sim 5 \cdot 10^{-8}$  m. Similarly to [7], by comparing theoretical values of particle diameter with this distribution we were able to find the temperature dependence of the empirical parameter  $\beta$  which enters into the relation for the rate of formation of clusters of critical size ( $\beta = -5.75 + 0.005T$ ). This dependence qualitatively demonstrates the agreement between the theoretical and experimental results.

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