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HIGH-TEMPERATURE DEPOSITION OF CARBON FILMS

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A mathematical model of growth of a carbon film in high-temperature deposition has been constructed in the approximation of the Stefan problem. The influence of different factors on the maximum thickness of the film has been analyzed. It has been shown that the porosity of the film is a factor of fundamental importance which determines the dynamics of its growth in terms of the effective thermal conductivity.

Introduction. Deposition of carbon films has aroused constantly growing interest among specialists, which is due to the unique properties of such films and their numerous applications. It is assumed that the fields of application of carbon films will further be extended. In this work, consideration is given to the high-temperature deposition of carbon films. This process occurs under the action of high-density energy fluxes [1] on carbon materials when the evaporated carbon atoms are deposited on a colder substrate beyond the region of direct action. In particular, such deposition must be taken into account in developing reactors for thermonuclear fusion [2–4] and in the technologies of laser [5], beam [6], and plasma treatment of materials.

Mathematical Model. Let us consider a fairly large cloud of carbon vapor with temperature T_v and with number density N_v above a substrate of temperature T_s. As is well known, here we also have condensation of the vapor on a cold substrate and the growth of a condensed-material film. The radiative heat exchange between the gas and the growing film is of importance; the transfer of heat through the film to the cold substrate is also significant. The film is heated as a consequence of the liberation of the latent heat of phase transition in vapor condensation and radiative heating by the external radiation.

In the free molecular regime [7], the equation describing a change in the film thickness h has the form

$$\frac{dh}{dt} = \frac{km}{\rho_f \sqrt{2\pi mk}} \left[\frac{T_v N_v}{\sqrt{T_v}} - \frac{T_f N_s (T_f)}{\sqrt{T_f}} \right] = v . \quad (1)$$

In the approximation of a very high thermal conductivity of the film material when the surface temperature of the film is equal to the temperature of the substrate and the contribution of the evaporation can be disregarded, the approximate solution of (1) yields the following expression for the thickness of the deposited film:

$$h(\tau) \sim \frac{\tau}{\rho_f} \sqrt{\frac{T_v km}{2\pi}}\, N_v .$$

For the conditions where $N_v = 10^{22}$ atoms/m^3 and $T_v = 4000$ K, the thickness of a carbon film deposited during 1 μsec is 70 nm. The flux of carbon atoms per unit area is equal to $7 \cdot 10^{24}$ atoms/(m^2·sec).

We will consider the growth of the carbon film on the cold substrate as the Stefan problem. The surface temperature of the film T_f is described by the equation representing the law of conservation of energy (the x axis is directed orthogonally to the film surface):

$$a \frac{dT_f(t)}{dx} = F_m + F_r - v c_f \rho_f T_f(t) . \quad (2)$$

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According to the kinetic theory of gases [7], F_m can be calculated as

$$F_m = \sqrt{\frac{k}{2\pi m}} \left[N_v T_v^{0.5} (2kT_v + U) - N_f (T_f) T_f^{0.5} (2kT_f + U) \right]. \quad (3)$$

We employ for F_r the following simplified expression:

$$E_r = W - \sigma\gamma T_s^4 . \quad (4)$$

The quantity γ is equal to about 0.9 for carbon films.

The temperature field in the film $T(x, t)$ is described by the heat-conduction equation

$$c_f \rho_f \partial_t T(x, t) = \partial_x [a (T(x, t)) \partial_x T(x, t)] \quad (5)$$

with boundary conditions $T(x, t) = T_1$ on the substrate and $T(h(t), t) = T_f(h, t)$ on the film surface.

It is easy to show that for relatively thin films with $h < 5 \cdot 10^{-5}$ m [8] the time of reaching of the steady-state asymptotics by the unsteady solution is of the order of several microseconds. Therefore, below we will employ only the steady-state solution of Eq. (5). Since the thermal conductivity depends on temperature, the steady-state profile of temperature in the film differs from the linear profile.

Employing Eq. (1), we write (2) in the following manner:

$$\frac{dT_f}{dt} = \frac{v}{a} [F_m (T_f (h)) + F_r - v c_f \rho_f T_f (h)] . \quad (6)$$

Equations (1) and (6) describe the growth of the film and the change in the film-surface temperature as a consequence of the condensation and evaporation of carbon molecules and the radiative heat exchange. The initial conditions for the system of ordinary differential equations (1) and (6) have the form

$$h (0) = h_0 \quad (7)$$

and

$$T_f (0) = T_s . \quad (8)$$

The numerical experiments conducted have confirmed the conclusion drawn in [9, 10] that most of the energy flux incident on a thin film is removed from it by heat conduction. The radiation flux exerts a substantial influence on the film growth only in the case where it makes up an appreciable part of the molecular flux. One can use for evaluations the values of the incident fluxes that are characteristic of the radiation from a cloud of carbon plasma with a temperature of the order of 1 eV.

Limiting Thickness of the Deposited Film. The mathematical model presented above enables one to investigate the dynamics of growth of the film as a function of all parameters with the use of standard computational systems of the Mathcad or Mathsoft type. It seems very useful to find the maximum film thicknesses irrespective of the regime of deposition (pulse, pulse-periodic, and steady-state). This maximum thickness will be called limiting and will be denoted as h_1. To find it we solve the system of equations (1) and (6) until we attain a constant thickness of the film. Indeed, as the thickness of the film increases, the efficiency of removal of the energy liberated on the film surface by heat conduction decreases, as a result of which the surface temperature of the film increases and finally attains a value for which the flux of evaporating molecules becomes equal to the flux of condensing molecules and the film ceases to grow.

The thickness of the film and the surface temperature as functions of the deposition time are shown in Fig. 1; the condensation coefficient is considered to be equal to unity.

We note that the rate of growth of the film for porous graphite is higher than that for standard graphite because of the lower density of the former. However, the limiting thickness of the film is higher in standard graphite by

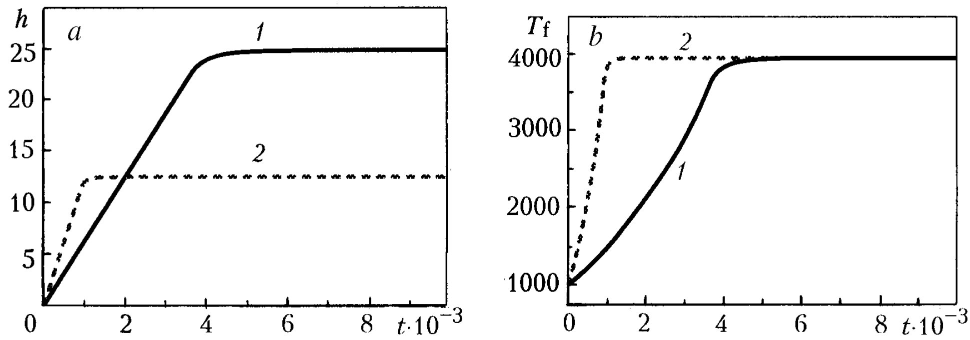

Fig. 1. Thickness (a) and surface temperature (b) of the film vs. deposition time: 1) standard graphite; 2) porous graphite with a porosity of 0.5. T_s = 1000 K and T_v = 4000 K. t, sec; h, μm; T_f, K.

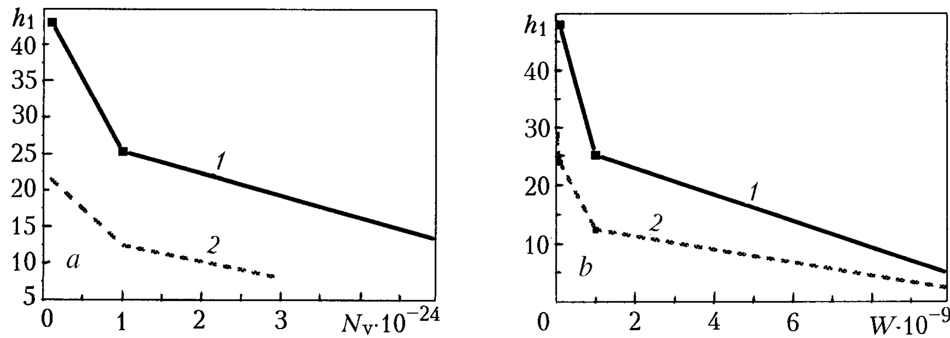

Fig. 2. Influence of the number density of a carbon gas (a) and the power of the radiation flux (b) on the limiting thickness of the film. The notation is the same as in Fig. 1. h_1, μm; W, W/m^2; N_v, atoms/m^3.

virtue of the more efficient removal of heat by the mechanism of heat conduction. It has been assumed in calculations that the porosity of the film is equal to 0.5; the effective thermal conductivity and the specific density of the porous-graphite film are half as high as those of the standard-graphite film.

The lower heat capacity and thermal conductivity of the porous-graphite film (principal factor) lead to a more intense temperature growth as compared to the film of standard graphite. It is obvious that if the substrate temperature is lower, the limiting thickness is larger by virtue of the increase in the temperature gradient. Figure 2 shows the dependences of the limiting thickness on the density of the vapor N_v and the value of the external radiation flux W.

The increase in the density of the flux of molecules incident on the substrate (this density is in direct proportion to N_v) leads to an increase in the rate of liberation of the latent heat of phase transition and consequently to a decrease in the limiting thickness of the film. This effect is more pronounced for porous graphite because of the lower value of the thermal conductivity.

We note that an increase of two orders of magnitude in W decreases the limiting thickness only by about an order of magnitude. We emphasize that the limiting thickness of the deposited film is independent of the value of the condensation coefficient.

Discussion of the Results. The developed mathematical model of a high-temperature growth of a carbon film describes the interrelated processes of condensation, evaporation, and radiative and conductive heat exchange through the film. The notion of a limiting thickness of the film for specified deposition conditions has been introduced. In particular, it has been shown that the limiting thickness of the deposited film decreases with increase in the density of a carbon vapor.

Rapid growth of a carbon film during the redeposition leads to an inhomogeneous structure of the film [11, 12], including the formation of vacancies, dislocations, and pores. The main reason for the appearance of the inhomogeneous structure is the temperature gradient in the direction of growth of the film during the high-temperature deposition, whose value can be of the order of 10^8 K/m. This gradient continuously changes the lattice parameters in the

newly formed condensed phase without leaving time for relaxation. It has been shown that the radiation energy flux can substantially decrease the thickness of the film during the high-temperature deposition.

The porosity of high-quality graphite is known to be equal to about 0.1 [13]. As the processing of the experimental results presented in [4] has shown, the porosity of a carbon film can attain 0.64 during the redeposition. The high porosity of the film material leads to a change in the thermal conductivity [14, 15], which can decrease by an order of magnitude or more as compared to the corresponding value for standard graphite. A porous carbon film with a pore radius of the order of $5 \cdot 10^{-7}$ m can be optically transparent. This effect has also been observed in [4]. At sufficiently high temperatures, the mobility of carbon atoms in the condensed phase, which is exponentially dependent on temperature, increases to the extent that it can "heal" the pores. This effect leads to the fact that the pore radius can decrease near the surface or the pore can disappear. This results in a nonuniform distribution of the pores over the thickness of the deposited film (such a distribution has been observed in [4]).

Based on the results of our modeling, we can draw the conclusion that under redeposition conditions the limiting thickness of the film cannot be larger than 10^{-5}. In so doing, only relatively high-quality carbon films can attain such a size, whereas high-porosity films will be strongly heated even at thicknesses of the order of several microns and will then evaporate. In other words, only low-porosity films with a high thermal conductivity can stably exist as a result of redeposition in experimental setups at sites of fairly intense energy liberation. In fact, the growth of such films represents a stochastic series of processes of deposition and macroscopic evaporation if a high-porosity structure has been formed. Under these conditions, a low-porosity film is formed only as a result of fluctuations. It is natural to expect that in such a regime of growth the thickness of a low-porosity film is much smaller than that of a high-porosity film, since the time of its effective growth is shorter. At sites with a low density of energy fluxes, there can stably exist high-porosity films with a much larger thickness than low-porosity films. It is precisely such a situation that is observed in the experiment [4].

The quality of the deposited film can be influenced by the mechanical stresses occurring due to the temperature gradients. A large temperature gradient in the film leads to the appearance of relatively large internal stresses. In particular, for a carbon film with a thickness of 20 μm and a pressure difference of $\Delta T \sim 3000$ K, evaluation of the stress P according to the formula $p \sim E\alpha\Delta T$ yields $P \sim 0.2$ GPa ($E \sim 30 \cdot 10^{9}$ Pa). Such stresses must lead to its cracking.

The presence of a small amount of a carrier gas virtually has no effect on the growth of the carbon film. However the presence of hydrogen in the carbon plasma leads to the fact that hydrogen undergoes a chemical reaction with carbon [6, 11, 12]. Allowance for such effects necessitates further development of the mathematical model proposed in this work.

When the partial pressures of the carrier gas above the substrate are sufficiently high, a transition zone is formed in the gas phase; in this region, there appears a temperature gradient of the vapor-gas cloud, which results in a high supersaturation of the carbon vapor and spontaneous formation of clusters. The deposition of the clusters influences the structure of the film, in particular, by increasing its porosity, and affects the dynamics of deposition in terms of the thermal conductivity.

CONCLUSIONS

The mathematical model presented can also be employed for investigation of the high-temperature deposition not only of a carbon vapor but also of the vapor of other substances and their mixtures after obvious changes in the values of the basic parameters.

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NOTATION

h, film thickness, m; t, time, sec; v, rate of growth of the film thickness, m/sec; k, Boltzmann constant; m, mass of a carbon atom, kg; τ, deposition time, sec; T_s, substrate temperature, K; T_f, film-surface temperature, K; T_v

and N_v, temperature and number density of a carbon vapor, K and atoms/m^3; F_m and F_r, energy fluxes related to molecular transfer and radiative transfer respectively, W/m^2; ρ_f and c_f, density and specific heat of a carbon film, kg/m^3 and J/(kg·K); a, thermal conductivity of the film, W/(m·K); U, latent heat of phase transition per atom, J/atom; W, flux of the radiation energy incident on the film, W/m^2; γ, emissivity factor; σ, Stefan–Boltzmann coefficient; h_1, limiting thickness of the redeposited film, m; E, Young modulus, Pa; α, coefficient of thermal expansion of the film material, m/K; P, stress, Pa·m; ΔT, temperature difference between the substrate and the film surface, K. Subscripts: s, substrate; f, film; v, carbon vapor; r, radiation; m, molecular.

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