changes, where

$$r_{12}/F_1 = r_{21}/F_2, \quad r_{23}/F_2 = r_{32}/F_3.$$

This method agrees with the results in [7] obtained for molecular fluxes by virtue of their analogy to radiant fluxes. In contrast to [7], the channel is made complicated while the jumps in the potential are determined on its elements. The heat flux is obtained by summing the jumps.

NOTATION

k, attenuation coefficient, m^{-1}; r, thermal resistance to radiant flux, dimensionless; q, resultant flux density, W/m^2; $\Theta \equiv n^2\sigma T^4$; A, endface absorptivity; $R = 1 - A$; F, channel section area, m^2; Q, resultant flux power in the channel, W; T, temperature, K; ρ, radius, m; τ_0, optical thickness of a layer of the medium.

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OPTIMIZATION OF THE THERMAL MODE OF POLYMER SUBSTRATES DURING THEIR VACUUM METALLIZATION

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An analytic expression is obtained for the specific heat of the vacuum metallization process. Optimal values of the evaporation temperature are determined for a number of metals and maximal deposition rates are estimated at which thermal rupture of the polymer materials does not occur.

Utilization of the highly productive technology of vacuum metallization of polymer materials by the method of evaporation and condensation of metal atoms is constrained to a significant extent by their relatively low thermal stability and the substantial change in their physicochemical properties during heating. The multivariety of the thermal action to which a substrate is subjected during vacuum metallization and the complex nature of the change in the system thermophysical properties during metal film growth produce a number of difficulties in the strict formulation and resolution of the appropriate transport equations [1-3]. To a considerable extent this circumstance governs the lack of a simple method, but sufficiently completely reflecting the features of metallization, for computing the substrate temperature and determining the influence of fundamental technological parameters of coating superposition on its values. An approach is developed in this paper for the selection of the technological metallization modes that are optimal in the energetic action on the substrate that is based on utilization of the specific heat of the process.

In the general case, the energy obtained by the substrate for any method of producing the vapor phase of a metal consists of the energy of radiation of the surface of the metal being evaporated, and the energy of the phase transitions of the coating material. Since the metallization process proceeds at low pressure, heat transmission from the evaporator to the substrate because of convection and heat conduction is negligible. Then if there is no chemical interaction in the formation of the coating then the heat flux density perceived by the substrate can be determined from the relationship

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TABLE 1. Values of $T_{e,0}$ and $q_{j,0}$ for a Number of Metals for Different ε

Metal	ε	$T_{e,0}$, K	$q_{j,0}$, 10^{-6} J/kg
Copper	0,04	2080	5,9051
	0,1	2200	5,9746
	0,4	2410	6,1000
Aluminum	0,04	1920	13,089
	0,1	2040	13,230
	0,4	2230	13,483
Lead	0,06	1340	1,0502
	0,1	1385	1,0582
	0,4	1540	1,0838
Gold	0,025	2205	2,0140
	0,06	2330	2,0363
	0,1	2415	2,0507
Cadmium	0,04	606	1,0329
	0,1	637	1,0419
	0,4	690	1,0577
Tin	0,07	2225	3,4572
	0,1	2285	3,4746
Silver	0,03	1700	2,8627
	0,06	1770	2,8890
	0,1	1830	2,9101

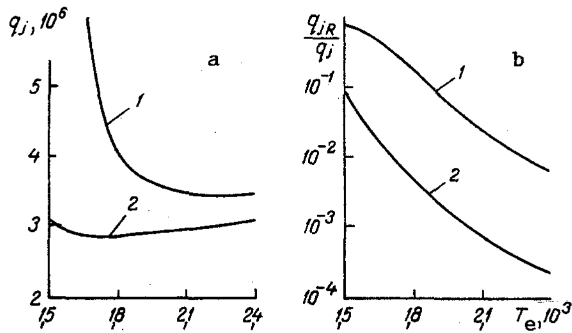

Fig. 1. Dependence of the specific heat of the metallization process (a) and fraction of the radiation component in the specific heat (b) on the evaporation temperature of tin (1) and silver (2).

$$q = b\varepsilon\sigma T_e^4 + Kj\left(\int_{T_m}^{T_e} C_1 dT + \int_{T_s}^{T_m} C_2 dT + \alpha + r\right). \quad (1)$$

The coefficient of metal atom condensation on the polymer surface in the initial stages of precipitation changes in time and depends on the temperature T_s [4]. However, for coating thicknesses greater than 15 nm the nature of the substrate does not affect the kinetics of metallic phase growth and $K \approx 1$.

Let us note that utilization of the expression (1) to compute the heat flux during metallization assumes the simultaneous action of radiation and phase transition energies on the substrate surface. Analysis of the features of the processes that proceed shows that for $j = \text{const}$ the essential difference between the computed and the true values of q will be observed only in the initial stages of coating formation when $t \lesssim \tau_p$. Since τ_p is of the magnitude $\sim 10^{-13}$-10^{-11} sec [5] and the energy being liberated during substrate material recrystallization in the later stages of coating formation is considerably less than q then the heat flux in the stage of continuous film formation is stationary in practice and the nature of its redistribution because of the low thermal resistance of the thin metal film is determined only by the thermophysical properties of the polymer substrate.

Let us introduce into the considerations the specific heat of the metallization process by defining it as the quantity of energy being liberated on the substrate surface during condensation of unit mass of metal, i.e., $q_j = q/Kj$. Then on the basis of (1) and the analogy of the mass flux distribution of the evaporated substance and the flux of radiation, from which $b = j/v_e$ [6] follows, we obtain

$$q_j = \frac{\varepsilon\sigma T_e^4}{Kv_e} + \int_{T_m}^{T_e} C_1 dT + \int_{T_s}^{T_m} C_2 dT + \alpha + r. \quad (2)$$

Analysis of the relationship (2) shows that q_j is a function just of the thermophysical properties of the coating material and is independent of the geometric parameters of the evaporator—substrate system, which makes it universal and useful for analysis of the thermal mode of the characteristic. The expression (2) contains quantities determined sufficiently exactly, in contrast to the relationship presented in [7], which permits its utilization to compute specific systems and to estimate the influence of the technological parameters of the process on the magnitude of substrate surface heating. Only values of the emission characteristics can be selected with a certain uncertainty. Under real conditions, the emission parameters vary even during the evaporation process because of the presence of thin oxide films on the surface of the metal melt, as well as crucible material, and different aftercharges.

The metal evaporation temperatur exerts significant influence on the quantity q_j.

Let us take into account that in conformity with [8]

$$v_e = \frac{A}{\sqrt{T_e}} \exp\left(-\frac{B}{T_e}\right). \tag{3}$$

Computations performed on the basis of (2) and (3) showed that the dependence $q_j(T_e)$ is nonmonotonic (Fig. 1a). The highest thermal fluxes for an identical concentration rate is perceived by a substrate with low evaporation temperatures. The main contribution to q_j is introduced by the metal melt surface radiation (Fig. 1b). As the temperature rises q_j diminishes and the minimal value $q_{j,0}$ is achieved for a certain value $T_e = T_{e,0}$ that is optimal from the viewpoint of thermal action on the substrate. The search for the optimal value $T_{e,0}$ is carried out by the method of tangents, which is effective for the minimization of convex functions [9] (it can be shown that the function $q_j(T_e)$ is convex). Presented in Table 1 are values of $q_{j,0}$ and $T_{e,0}$ for metals most often used as coatings. Let us note that the change ε does not affect the values of $q_{j,0}$ in practice. The optimal temperature $T_{e,0}$ as ε increases shifts toward the domain of higher values. For $T_e = T_{e,0}$ the radiation flux is on the order of 1% of the integrated heat flux acting on the surface.

The obtained values of q_j permit estimation of the polymer surface heating that occurs during metallic film precipitation thereon and calculation of the limit values of the precipitation rate by the known value of the substrate thermostability temperature.

The maximal temperature of a flat substrate can be determined in a consideration of the stationary problem [10] as a result of solving the system of equations

$$\begin{gathered} q_j Kj + \varepsilon_m q_p = \varepsilon_m \sigma T_1^4 + \frac{\lambda}{l}(T_1 - T_2), \\ \frac{\lambda}{l}(T_1 - T_2) + \varepsilon_m q_p = \varepsilon_s \sigma T_2^4. \end{gathered} \tag{4}$$

In a linear approximation which is sufficiently well-founded for $T_1 - T_2 \ll T_1$, there follows from (4)

$$\begin{gathered} T_1 = T_{av} + \frac{\varepsilon_s^2 q_j Kj}{(\varepsilon_m + \varepsilon_s)\left[(\varepsilon_m + \varepsilon_s)\frac{\lambda}{l} + 4\varepsilon_m \varepsilon_s \sigma T_{av}^3\right]}, \\ T_2 = T_{av} - \frac{\varepsilon_m \varepsilon_s q_j Kj}{(\varepsilon_m + \varepsilon_s)\left[(\varepsilon_m + \varepsilon_s)\frac{\lambda}{l} + 4\varepsilon_m \varepsilon_s \sigma T_{av}^3\right]}. \end{gathered} \tag{5}$$

Here $T_{av} = \sqrt[4]{\frac{(\varepsilon_m + \varepsilon_s) q_p + q_j Kj}{(\varepsilon_m + \varepsilon_s)\sigma}}$ and it is the temperature achievable on the substrate surface for $\lambda/\ell \to \infty$.

The maximal error induced by linearization occurs as $\lambda/\ell \to 0$. We then obtain from (4) that

$$T_1 = \sqrt[4]{\frac{q_j Kj + \varepsilon_m q_p}{\varepsilon_m \sigma}}. \tag{6}$$

TABLE 2. Values of v_{max} for $T_e = T_{e,0}$, m/sec

Metal	Polymer substrate								
	polyethylene			polytetrafluoroethylene			polyethylene terephthalate		
	substrate thickness, mm								
	0,05	0,2	1	0,05	0,2	1	0,05	0,2	1
Copper	$\frac{1{,}21\cdot10^{-8}}{9{,}35\cdot10^{-6}}$	$\frac{1{,}21\cdot10^{-8}}{2{,}33\cdot10^{-6}}$	$\frac{1{,}17\cdot10^{-8}}{4{,}67\cdot10^{-7}}$	$\frac{1{,}23\cdot10^{-7}}{3{,}52\cdot10^{-5}}$	$\frac{1{,}20\cdot10^{-7}}{8{,}88\cdot10^{-6}}$	$\frac{1{,}08\cdot10^{-8}}{1{,}78\cdot10^{-6}}$	$\frac{2{,}39\cdot10^{-8}}{1{,}5\cdot10^{-5}}$	$\frac{2{,}37\cdot10^{-8}}{3{,}76\cdot10^{-6}}$	$\frac{2{,}29\cdot10^{-8}}{7{,}53\cdot10^{-7}}$
Aluminum	$\frac{1{,}79\cdot10^{-8}}{1{,}38\cdot10^{-5}}$	$\frac{1{,}79\cdot10^{-8}}{3{,}45\cdot10^{-6}}$	$\frac{1{,}73\cdot10^{-8}}{6{,}91\cdot10^{-7}}$	$\frac{1{,}81\cdot10^{-7}}{5{,}2\cdot10^{-5}}$	$\frac{1{,}78\cdot10^{-7}}{1{,}31\cdot10^{-5}}$	$\frac{1{,}6\cdot10^{-7}}{2{,}63\cdot10^{-6}}$	$\frac{3{,}53\cdot10^{-8}}{2{,}22\cdot10^{-5}}$	$\frac{3{,}51\cdot10^{-8}}{5{,}56\cdot10^{-6}}$	$\frac{3{,}38\cdot10^{-8}}{1{,}11\cdot10^{-6}}$
Silver	$\frac{2{,}1\cdot10^{-8}}{1{,}63\cdot10^{-5}}$	$\frac{2{,}1\cdot10^{-8}}{4{,}08\cdot10^{-6}}$	$\frac{2{,}02\cdot10^{-8}}{8{,}17\cdot10^{-7}}$	$\frac{2{,}12\cdot10^{-7}}{6{,}2\cdot10^{-5}}$	$\frac{2{,}08\cdot10^{-7}}{1{,}55\cdot10^{-5}}$	$\frac{1{,}87\cdot10^{-7}}{3{,}11\cdot10^{-6}}$	$\frac{4{,}13\cdot10^{-8}}{2{,}63\cdot10^{-5}}$	$\frac{4{,}11\cdot10^{-8}}{6{,}57\cdot10^{-6}}$	$\frac{3{,}95\cdot10^{-8}}{1{,}32\cdot10^{-6}}$
Tin	$\frac{3{,}27\cdot10^{-8}}{2{,}46\cdot10^{-5}}$	$\frac{3{,}27\cdot10^{-8}}{6{,}13\cdot10^{-6}}$	$\frac{3{,}17\cdot10^{-8}}{1{,}23\cdot10^{-6}}$	$\frac{3{,}33\cdot10^{-7}}{9{,}32\cdot10^{-5}}$	$\frac{3{,}26\cdot10^{-7}}{2{,}33\cdot10^{-5}}$	$\frac{2{,}95\cdot10^{-7}}{4{,}67\cdot10^{-6}}$	$\frac{6{,}48\cdot10^{-8}}{3{,}95\cdot10^{-5}}$	$\frac{6{,}44\cdot10^{-8}}{9{,}87\cdot10^{-6}}$	$\frac{6{,}20\cdot10^{-8}}{1{,}98\cdot10^{-6}}$

Remark. Values for the free polymer film in the numerator and for a film in contact with the surface that has the constant temperature T = 290 K in the denominator.

Estimates show that the difference in the values of T_1 determined from (5) and (6) does not exceed 8% in the case when $\lambda/\ell = 0$ for metallization modes realizable in practice.

Let us note that in conformity with known methodologies [1, 3], the thermal computation reduces to determining the values of the temperature T_{av}. Moreover, computations executed by using (5) for different λ/ℓ and q indicate the possible existence of temperatures T_1 different from T_{av}. The difference $T_1 - T_{av}$ grows as the precipitation rate, the specific heat of the process, and the thickness of the polymer substrate increase.

The relationships obtained are used to determine the maximal rate of precipitation of a metallic coating on a polymer film. It is here considered that the ultimate temperature achievable on the polymer surface should not exceed the value of the thermal stability temperature. Presented in Table 2 are results of computing v_{max} for the two process schemes utilized most often: metallization of a free film, and metallization of a film making contact with a cooled surface (T_2 = const).

As is seen, cooling the polymer substrate surface is a sufficiently effective technological method of acting on the metallization thermal mode for thin polymer films. Precipitation of a metallic film is here possible with a substantially higher velocity and conservation of the quality of the system being obtained.

NOTATION

q, heat flux density, $W\cdot m^{-2}$; b, a geometric factor taking account of the size and shape of the evaporator-substrate system; ε, reduced integral emissivity of the metal being evaporated; σ, Stefan–Boltzmann constant, $W\cdot m^{-2}\cdot K^{-4}$; T_e, temperature of the metal being evaporated, K; j, mass flux density, $kg\cdot m^{-2}\cdot sec^{-1}$; C_1, specific heat of the metal in the liquid state, $J\cdot kg^{-1}\cdot K^{-1}$; T_m, metal melting point, K; T_s, substrate surface temperature, °K; r, specific heat of vapor formation, $J\cdot kg^{-1}$; α, specific heat of melting, $J\cdot kg^{-1}$; K, condensation coefficient; τ_p, time of thermal metal atom relaxation, sec; q_j, specific heat of the metallization process, $J\cdot kg^{-1}$; v_e, mass flow rate of metal evaporation, $kg\cdot m^{-2}\cdot sec^{-1}$; A, B, constants; $T_{e,0}$, optimal temperature of the metal being evaporated, °K; $q_{j,0}$, minimal specific heat of the metallization process, $J\cdot kg^{-1}$; ε_m, emissivity of the metal film; ε_s, emissivity of the substrate; λ, heat conduction coefficient of the substrate material, $W\cdot m^{-1}\cdot K^{-1}$; ℓ, substrate thickness, m; T_1, substrate surface temperature on the growing film side, °K; T_2, substrate surface temperature on the reverse side, °K; q_p, equilibrium heat flux density from the vacuum chamber walls, $W\cdot m^{-2}$; $q_{jR} = \varepsilon\sigma T_e^4/kV_e$, radiation component of the specific heat of the metallization process, $J\cdot kg^{-1}$.

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