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DECOMPOSITION TEMPERATURE AND MECHANISM OF POLYMER MATERIALS IN ARC-DISCHARGE PLASMA JET

A. Z. Skorokhod, S. F. Zhandarov, and O. R. Yurkevich

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The decomposition temperatures of disperse polymers moving in a plasma jet are determined. The mechanism of thermal destruction is discussed, as well as the influence exerted by physical factors in the fast heating of polymer materials in conditions of nonsteady ablation.

The use of gas-thermal methods of applying anticorrosional protective coatings poses a number of problems. It is known that coatings obtained by gas-thermal – in particular, plasma – methods are not continuous enough for operation in aggressive media [1]. The traditional approach to increasing the operational life of such coatings is to use a thicker layer, so as to eliminate pores which run through the whole coating. However, this leads to increase in weight of the components and increased consumption of expensive materials.

An alternative approach is to use metal–polymer coatings which do not contain through porosity, combining the application of the inorganic and organic components in a single technological cycle. The successful realization of this process using plasma technology entails studying the influence of plasma on polymer particles, in particular, determining the fusibility of the particles and obtaining quantitative estimates of the mass loss from the surface as they move in the plasma jet. The basic factors influencing the fusibility of the particles is the thermal conductivity of the polymer material under shock treatment by a thermal front, the duration of this tratment, and the surface temperature. In [2, 3], this temperature was taken to be equal to the destruction temperature of the given polymer materials at low heating rates. However, in conditions of plasma treatment accompanied by ablation of the polymer, the surface temperature of the particle may significantly exceed the decomposition temperature determined by the standard procedure, even in the case of steady ablation [4]. The competition between ablation and heat-flux motion within the particle determines the fusibility of the particle and the effectiveness of the material in coating application. Thus, a key element in determining the effectiveness of disperse polymer materials for coating application by plasma technology is to establish the decomposition temperature of the polymer-particle surface T_w. However, at its current level of development, the theory of the thermal properties of solids – in particular, high-molecular compounds of complex structure – does not permit the calculation of values of the thermophysical characteristics solely on the basis of data on the structure of the material. Therefore, the thermophysical characteristics of materials required for engineering calculations are determined experimentally.

In the present work, the decomposition temperature of the polymer surface T_w in particle motion in a high-enthalpy gas flow is estimated on the basis of experimental data on the linear ablation rate v_∞ and the temperature at the point of plasma entry T_e; the rate of mass loss is analyzed as a function of various physical factors. An arc-discharge plasma jet

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is created by a UMP-6 plasmotron with the following energy characteristics: arc current 320 A; working potential 50 V; flow rate of plasma-forming gas (argon) 0.9 g/sec. Disperse high-density polyethylene (HDPE) of grade 20906-040 (All-Union State Standard GOST 16338-77) and polytetrafluoroethylene (PTFE) corresponding to GOST 2422-80 are used. Both materials are linear partially crystalline polymers; they differ significantly in their thermophysical properties. Data obtained in differential thermal analysis at a heating rate of 25 deg/min indicate that the decomposition temperature is 703 K for PTFE and 596 K for HDPE.

Tests of polymer materials in steady conditions with a temperature gradient in the sample which is constant over time are used in determining the melting depth of disperse polymers in coating application by a plasma method. The heat-flux balance equation for a particle moving in a plasma jet in quasi-steady conditions takes the form [4]

$$\lambda_s \frac{d^2T}{dy^2} - B\rho\Delta Q_{\text{subl}} \exp(-E/RT) + \rho c_s v_\infty \frac{dT}{dy} = 0. \tag{1}$$

The first term in Eq. (1) corresponds to the heat flux on account of the heat conduction of the material, the second to the heat flux in destruction, and the third to the heat flux taking account of the specific heat of the material. Numerical methods must be used to solve Eq. (1), but the third term may be neglected since the heat of destruction is significantly greater than that absorbed on account of the specific heat. Then Eq. (1) takes the form

$$\frac{d^2T}{dy^2} = \frac{B\Delta Q_{\text{subl}} \exp(-E/RT)}{\lambda_s}\rho. \tag{2}$$

In addition, the linear ablation rate may be described by the expression [4]

$$v_\infty = \frac{G_\Sigma}{\rho} = \int_0^\infty B \exp(-E/RT)\,dy \tag{3}$$

with the boundary conditions

$$T|_{y=0} = T_w,\quad T|_{y\to\infty} = T_0. \tag{4}$$

Simultaneous solution of Eqs. (2) and (3), taking account of Eq. (4), gives

$$G_\Sigma = \frac{\sqrt{B\rho \frac{R}{E} \lambda_s \exp(-E/RT)\, T_w}}{\sqrt{H^* - \frac{\Delta Q_{\text{subl}}}{2}}}. \tag{5}$$

Replacing G_Σ by ρv_∞ and the total heat of decomposition by $c_s(T_p - T_0) + \Delta Q_{\text{subl}}$, Eq. (5) may be reduced to the form

$$T_w = \frac{\sqrt{c_s(T_p - T_0) + \frac{\Delta Q_{\text{subl}}}{2}}\; v_\infty \sqrt{E/R}}{\sqrt{\frac{B}{\rho} \lambda_s \exp(-E/RT)}}. \tag{6}$$

It follows from Eq. (6) that calculation of T_w entails knowing v_∞. Since T_w and v_∞ depend on the heating rate, the plasma-flare temperature T_e at the point of entry of the polymer material must be estimated to solve the problem. To this end, the ionic current at different points along the plasma-jet axis is measured using a probe and an F-118 nanovoltammeter (Fig. 1), which yields a lower bound for the ionic concentration at the probe surface. The results obtained are substituted into the kinetic equation describing the change in state of the plasma. It is assumed here that the plasma is quasi-neutral, i.e., $n_e = n_i$. In the arc zone, the gas layer next to the plasma is heated to several thousand degrees by conduction, leading to thermal ionization of the gas and discharge development [5]. In nonequilibrium conditions, this mechanism does not apply because of the inadequate gas heating (~10^3 K) behind the discharge front.

The thermodynamic equilibrium of the system at the given temperature is constant, and the relation between the temperature and the concentration of plasma ions is described by the Saha equation [6]. However, radiative recombination must be taken into account for more

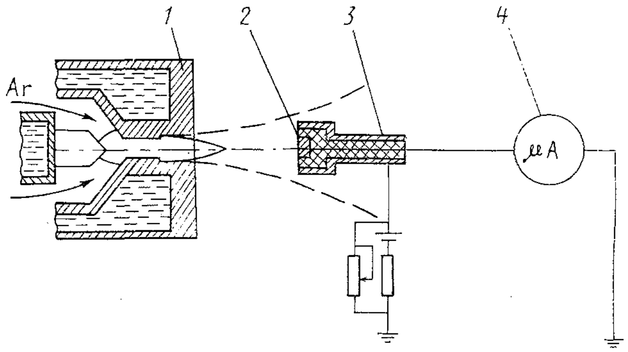

Fig. 1. Scheme for measuring the ionic current density: 1) piasmotron; 2) probe collector; 3) screen; 4) measuring instrument.

accurate description of charged-particle creation and destruction. Suppose that charged-particle creation and destruction occur predominantly within a cylinder of radius R' and length L, where R' ≫ L, i.e., $n_0 k_i(T_e) \gg 1/(\Lambda_D^2)D$. According to [7], the following channels are possible:

ionization

$$e + \mathrm{Ar} \xrightarrow{k_i} \mathrm{Ar}^+ + 2e,\quad \mathrm{Ar}^* + \mathrm{Ar} \xrightarrow{k_*} \mathrm{Ar}_2^+ + e,\quad \mathrm{Ar}^* + e \xrightarrow{k} \mathrm{Ar}^+ + 2e,$$

recombination

$$\mathrm{Ar}^+ + 2e \xrightarrow{k_{ei}} e + \mathrm{Ar}^*,\quad \mathrm{Ar}_2^+ + e \xrightarrow{k_d} \mathrm{Ar} + \mathrm{Ar}^*,\quad \mathrm{Ar}^+ + e \xrightarrow{k_r} \mathrm{Ar} + h\omega.$$

Then the kinetic equation takes the form

$$\frac{dn_e}{dt} = k_i n_0 n_e + k_* n_0 n_* + k n_e n_* - k_{ei} n_e^2 n_i - k_d n_e n_{\mathrm{Ar}_2^+} - k_r n_e n_i. \tag{7}$$

The second, third, and fifth terms in Eq. (7) are negligibly small with respect to the others, and may be neglected. Then Eq. (7) takes the form

$$\frac{dn_e}{dt} = k_i n_0 n_e - k_{ei} n_e^2 n_i - k_r n_e n_i. \tag{8}$$

Equation (8) decribes the formation of ions by direct electron impact and the destruction of charged particles on account of three-particle and radiative recombination. If the energy distribution function of the electrons is Maxwellian, the expression for k_i is [7]

$$k_i(T_e) = \sqrt{\frac{8T_e}{\pi m}}\,\sigma_0 \exp(-I/T_e). \tag{9}$$

For argon, σ_0 is $3 \cdot 10^{-20}$ m^2 [7]. The following values of k_{ei} and k_r are used in the calculations [7]

$$k_{ei} = (\sigma_0/I) \cdot 10^{-14} (I/T_e)^{9/2}, \tag{10}$$

$$k_r \sim 10^{-18}\ \mathrm{m}^3/\mathrm{sec}. \tag{11}$$

In the steady case, $dn_e/dt = 0$ in conditions of steady plasmotron operation. Hence, Eq. (8) takes the form

$$k_i n_0 = k_{ei} n_e^2 + k_r n_e. \tag{12}$$

Substitution of Eqs. (9)-(11) into Eq. (12) gives

$$\sqrt{\frac{8T_e}{\pi m}}\,\sigma_0 \exp\left(\frac{I}{T_e}\right) n_0 = \frac{\sigma_0}{I} \cdot 10^{-14} \left(\frac{I}{T_e}\right)^{9/2} n_e^2 + 10^{-18} n_e. \tag{13}$$

After simple manipulations, Eq. (13) may be reduced to recurrence form with respect to T_e

TABLE 1. Variation in Ionic Current and Electron Temperature along Plasmotron Axis

No.	S, mm	$i\cdot 10^{-6}$, A	T_e, K
1	25	36,0	8700
2	50	18,5	6900
3	75	6,3	6052
4	100	3,5	5320
5	150	1,9	4760

$$\exp\left(-\frac{I}{T_e}\right)=\frac{10^{-14}}{I}\left(\frac{I}{T_e}\right)^{9/2}T_e^{-3/2}\frac{i^2Pm^2}{e^2m_r^2}\sqrt{\frac{\pi m}{8}}+\frac{10^{-18}im}{\sigma_0 em_g}T_e^{-1/2}\sqrt{\frac{\pi m}{8}}. \qquad (14)$$

Substituting numerical values into Eq. (14), T_e is calculated at five points along the plasmotron axis by successive approximation (Table 1). Since i in Eq. (14) corresponds to the lower bound on the ionic concentration, the values of T_e obtained represent the lower bound on the electron temperature. However, since T_e is not very sensitive to change in i according to Eq. (14), the real values of T_e are only 30-50 K higher than the theroretical values. According to [8], the quasi-equilibrium of the plasma ($T_i \approx T_e$) is disrupted at a distance of >75 mm from the plasmotron; therefore, the values of T_e at 100 and 150 mm may be somewhat too low.

Substitution of i = 320 A (the arc current) into Eq. (14) gives $T_e \sim 29{,}000$ K, which corresponds to the arc temperature [1, 8].

The linear ablation rate v_∞ in steady conditions is determined from the time at which a hole appears in a plate of the given material placed in different zones of the plasma flux. The initial and final times of hole formation are determined from the combustion of two thin (~50 μm) wires placed on the two sides of the plate. The experimental data are shown in Table 2.

Substituting the results for v_∞ into Eq. (6) (the other numerical values are taken from [4]; $B = 7\cdot 10^{18}$ sec^{-1} here), the solution is found by successive approximation. The values of T_w are sufficiently close for PTFE (1080 K) and HDPE (1165 K). Thus, the difference in chemical structure and rheological properties of the two polymers has no significant influence on the surface temperature of the materials in steady ablation.

Is it correct to substitute v_∞ into Eq. (6)? Essentially, two problems are being considered: the internal problem — the burning-through of the plate; and the external problem — flow of the plasma jet around the particle, which moves in the acceleration section relative to the jet. However, as shown in [9], the temperature variation of the particles occurs in a very narrow surface layer, the depth of which is much less than the particle radius. The surface temperature of the particle T_w increases very rapidly, whereas that at the center of the particle remains practically constant. Assuming that T_w is the same at all points of the surface (particle rotation also facilitates equalization of T_w), the problem for $y \ll r$ may be considered in a plane approximation.

The rate of mass loss from the particle surface for nonsteady ablation is determined by means of a model experiment. A spherical metal particle (diameter 5 mm) is covered with a polymer film (thickness 500 μm) by an electrostatic method [10]. The particles undergo circular rotation in a plane perpendicular to the symmetry axis of the plasmotron, at a distance of 25 mm from its end. The center of the sphere passes through the axial line of the plasma flare in each rotation. The particle is weighed after each passage through the plasma

TABLE 2. Experimental Data on the Linear Rate of Steady Ablation

Material	T_e, K	l, mm	τ, sec	v_∞, m/sec
PTFE	8700	2,50	2,8	$8{,}9\cdot 10^{-4}$
HDPE	8700	3,21	2,0	$1{,}6\cdot 10^{-3}$

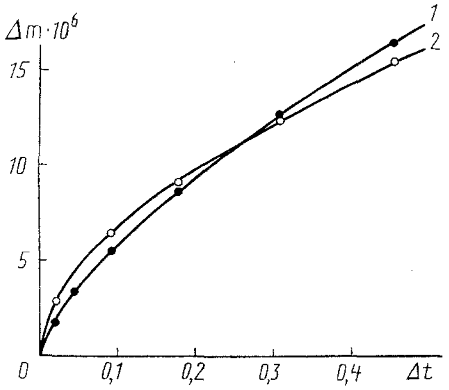

Fig. 2. Dependence of the mass loss on the residence time of the model particle in the plasma flow: 1) PTFE: 2) HDPE. Δm, kg; Δt, sec.

flare, yielding the dependence $\Delta m = f(\Delta t)$ (Fig. 2). In each rotation, the particle is in the plasma jet for $6.4 \cdot 10^{-2}$ sec; this is much less than the time for the establishment of steady ablation and exceeds the time in which the high-temperature flare zone acts on the polymer particles in coating application.

It is known that the mechanisms of thermal destruction for HDPE and PTFE are different [11]. The destruction of PTFE begins with free-radical initiation and occurs predominantly by successive rupture of the basic chain. Fragments of more than monomeric size are unable to enter the gas phase here. The decomposition of HDPE is by the free-radical mechanism, and the monomer content in the decomposition products is slight. However, the curves of the mass loss as a function of the residence time of the model particles in the plasma flare are the same for PTFE and HDPE, within the limits of experimental error. Thus, the temperatures of surface decomposition for PTFE and HDPE particles are sufficiently close even in conditions of nonsteady ablation. The greater or lesser deviation of the mass-loss characteristics from the steady curves may be explained by inertia of the heating and decomposition of the materials. The degree of inertia of these processes depends on the type of material, i.e., on the predominance of particular failure mechanisms and the thickness of the decomposition zone. With increase in heating rate because of the inertia of these processes in the material, the deviation of the characteristics from the steady case must increase, as confirmed by experiment. The failure zone of these materials in conditions of nonsteady ablation is concentrated into a narrow surface layer, and the failure mechanisms characteristic of the particular polymers are rapidly modified and converge because of the changing external conditons. This indicates that the rate of mass loss of polymer materials in the given process is not determined solely by the thermal mechanism of destruction. Evidently, the influence of physical and other factors (geometric, structural, diffusional, mechanical, etc.), which may play a decisive role in some cases, is superimposed on the kinetic dependence of the thermal decomposition of the materials.

Thus, on introducing the polymer particles in the high-temperature zone of the plasma flare, their surface temperature takes a value 300-500 K greater than the temperature of thermal destruction, and the failure of materials of different chemical structure is described by similar kinetic dependences. Intense mass loss from the particle surface in conditions of nonsteady ablation prevents their melting, and therefore high-quality layer formation on a cold substrate cannot be expected; the application of coatings of inorganic and organic components in a single technological cycle distinguishes itself in this context, since the polymer material acquires additional heat for the formation of a molten film from the layer of inorganic component already applied.

NOTATION

v_∞) linear ablation rate; T_e) electron temperature; T_w) decomposition temperature of material in steady ablation; λ_s) thermal conductivity of material; B) rate constant of destruction, $\sec^{-1}$; ρ) density of material; ΔQ_{subl}) heat of sublimation of material; E) activation energy of destruction process; R) universal gas constant; T) temperature; c_s) specific heat of material; y) current coordinate; r) particle radius; G_Σ) rate of mass loss from unit surface; T_0) ambient temperature; H^*) total enthalpy of failure; n_e, n_i, n_0) concentration of electrons, ions, and neutral particles, respectively; Λ_D) Debye length; D) diffusion coefficient; k_i, k_*, k, k_{ei}, k_d, k_r) rate constants of ionization by electron impact, associative ionization, step ionization, three-particle recombination, dissociative recombination, and radiative recombination, respectively; n_*) concentration of excited atoms; I) ionization potential; σ_0) effective cross section of ionization by electron impact; i) ionic current at the probe; m_g) mass flow rate of plasma-forming gas; P) pressure in plasma jet; e) elementary charge; m) mass of argon molecule; S) distance from nozzle cross section of plasmotron; l) plate thickness; τ) time of plate burnthrough.

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CALCULATION OF THE DRYING OF MOIST PARTICLES IN APPARATUS CONTAINING OPPOSED SWIRLED STREAMS

I. Kh. Enikeev

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A method is suggested that enables one, in the model of interpenetrating continua, to investigate heat and mass transfer between a gas and moist particles in swirled streams. Similarity criteria are obtained for modeling an extensive class of problems of chemical engineering.

Swirled flows of multiphase media are used extensively in modern technology (chemical engineering apparatus, turbomachines, cryogenics, etc.) to intensify processes of heat and mass transfer and separation. Two types of heterogeneous media are used most often in industrial devices: 1) gas–drop and vapor–drop streams; 2) gas suspensions (a gas containing dessicant or moist solid particles in a suspended state).

Whereas the theory for the first class of flows and methods of calculating heat and mass transfer have been presented fairly completely in [1-3], for a gas containing moist solid particles in a suspended state, models of heat and mass transfer have been developed only for the case of a low mass content of the disperse phase. The approaches developed in [4-6] to investiate the theory of heat and mass transfer between moist solid particles and a gas stream (drying theory) do not enable one to model and calculate the drying process for a high content of the disperse phase, when the influence of the particles on the motion of the carrier gas must be taken into account. In the present paper, therefore, it is proposed to investigate the drying process in a model of interpenetrating continua, enabling us to model that process in a wide range of variation of the mass concentration of particles.

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