HEATING OF POLYMER PARTICLES IN PLASMA-JET SPUTTERING

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The heating of polymer particles on interaction with a high-temperature plasma-jet flux is considered. The distribution of the particle temperature fields at various Biot numbers is established.

The technological applications of low-temperature plasma jets have been sufficiently studied and successfully realized in the sputtering of disperse inorganic material: metals, alloys, ceramics [1, 2]. At the same time, there are very limited data on the use of plasma jets for the processing of polymer materials and the creation of metal—polymer systems [3, 4]. As is known [5], the plasma sputtering of disperse inorganic materials includes more than 60 controllable parameters. In the plasma sputtering of polymer materials, the number of interrelated factors greatly increases. Since this process is multifactorial, the formation of a high-quality polymer layer on the surface of a part is a complex problem. Therefore, the mathematical modeling of the processes occurring in the plasma processing of polymers is both scientifically interesting and essential for practical applications.

Investigations show [1, 3] that the quality of the sputtered layer depends on the thermophysical state of the particles when they reach the surface of the part, i.e., on the conditions of polymer melting in the plasma jet (where its residence time is 10^{-3}-10^{-4} sec).

Models of the heat transfer of polydisperse particles of inorganic materials with plasma jets have been mathematically described in [1, 6-12]. In most cases, a heat-conduction equation of parabolic type for spherical particles is used [9]

$$\frac{\partial [rT(r,\ \tau)]}{\partial r} = a\,\frac{\partial^2 [rT(r,\ T)]}{\partial r^2}\,. \tag{1}$$

In determining the thermal conductivity of crystalline bodies, no significant errors result from neglecting the term $\tau_r\, dq/d\tau$ in the refined heat-propagation equation [10]

$$q = -\lambda \Delta T - \tau_r \frac{dq}{d\tau} \tag{2}$$

and using the approximate Fourier law, since the rate of heat propagation in metals and their alloys, for example, is infinitely large and the relaxation time is sufficiently small ($\tau_r = 10^{-9}$-10^{-11} sec). The solutions obtained indicate adequate agreement between the theoretical and experimental data.

For polymer materials, the solution of the thermophysical and technological problems is complicated by the temperature gradient along the particle radius resulting from the low thermal diffusivity of the polymer, the agglomeration of small particles in plasma-jet deposition, the need to take not only the melting points but also the characteristic yield temperatures into account, and the intense mass losses with a narrow interval between them.

Therefore, the description of the thermal physics is only possible by creating models which correspond to the processes actually occurring in the interaction of the material being sputtered and the plasma flux, with subsequent analysis by computational techniques.

Earlier [11], for the example of polytetrafluoroethylene (PTFE, Ft-4), it was shown that 150-μm particles do not melt in the plasma jet with the specified technological conditions of sputtering. It was found in [12] that the optimal degree of dispersity of the powder polymer materials must be determined to obtain a monolithic protective film and form a strong adhesional contact between the polymer and the metal. Without detailed consideration of the factors influencing the heat transfer of the polymer particle with the plasma jet, it may be noted that the plasma-jet temperature was regarded as the parameter determining this

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process in [11, 12]. It will be supposed that heat transfer occurs on account of heat conduction. The particles in the plasma jet are assumed to be spehres of fixed radius R.

Since a heat-conduction equation of parabolic type for spherical particles is used to determine the temperature field of a particle in a high-temperature gas medium, the applicability of this equation must be considered, taking the relaxational character of the viscoelastic polymer properties into account. To this end, the relaxation period of the heat transfer τ_r is estimated, and the time of particle melting is established experimentally.

The relaxation period τ_r is related to the thermal diffusion coefficient a (the thermal diffusivity) as follows [9]

$$\tau_r = \frac{a}{w^2}. \tag{3}$$

On the basis of the moment of particle interaction with plasma [12] and the penetration depth of the heat, which is determined by the dimensions of the completely molten particle, the relaxation time of the heat flux is calculated.

The character of polymer melting directly in the plasma jet is tested experimentally by sputtering individual particles of ND polyethylene (NDPE) into water and also onto glass substrates which are motionless and moving at high speed transverse to the jet. The photograph in Fig. 1 and studies of the formation of spherulitic supermolecular structures in polymer particles during plasma sputtering directly into water indicate that melting of the particle occurs in the plasma jet, and the relaxation time of the viscofluid state is less than the time of particle interaction with the plasma jet. Calculations confirm that the relaxation time differs from the interaction time by 2-3 orders of magnitude.

High heating rates (10^4-10^6 K/sec) evidently have a great influence on the spectrum of polymer relaxation times. As noted in [13], the polychromatic kinetics becomes monochromatic at sufficiently high temperatures (heating rates). This means that the broad distribution of relaxation times associated with the molecular-mobility distribution of the reacting particles tends to a definite minimum value. Hence, the heat-conduction equation of parabolic type may be used in the first approximation to solve practical problems of optimizing the plasma sputtering of powder polymer materials.

The solution of Eq. (1) with boundary conditions of the first kind, where the surface temperature T_s is constant, was considered in [1].

However, in the general case, the particle surface does not reach the temperature T_s instantaneously, but after some time $\Delta\tau$. The parameter characterizing the heat transfer of the polymer particle with the plasma jet is the Biot number [1].

Taking account of the Biot number, calculation of the temperature field within the polymer particle over time reduces to solving Eq. (1) with boundary conditions of the third kind

$$T(r, 0) = T_0 = \mathrm{const};\ T_c = 2273\ \mathrm{K};\ -\frac{1}{\mathrm{Bi}}\frac{\partial T(r, \tau)}{\partial r} + \frac{1}{R}[T_c - T(R, \tau)] = 0;\ T(0, \tau) \neq \infty;\ \frac{\partial T(0, \tau)}{\partial r} = 0. \tag{4}$$

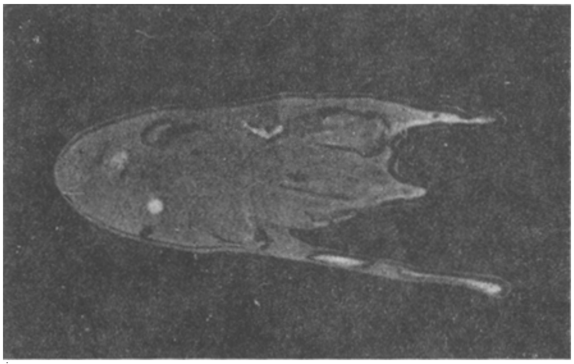

Fig. 1. Photograph of NDPE particle sputtered by a plasma jet onto a glass substrate (×500).

TABLE 1. Values of Biot Number for Polymer Particles of Various Sizes (T_{me} = 2273 K, v_{me} = 43.67·20^{-5} m^2/sec)

Particle size, μm	v_{rel}, m/sec	Re	Nu	α, M^2·K	Bi	
					NDPE	PTFE
40	100 50 10	9,16 4,58 0,92	3,73 3,23 2,55	11190 9690 7650	0,59 0,51 0,40	0,96 0,83 0,66
60	100 50 10	13,74 6,87 1,37	4,11 3,49 2,67	8220 6980 5340	1,3 1,1 0,84	2,13 1,8 1,38
80	100 50 10	18,32 9,16 1,83	4,44 3,73 2,77	6660 5595 4155	0,7 0,6 0,44	1,14 0,96 0,71
100	100 50 10	33 11,5 2,3	4,73 3,93 2,86	5676 4716 3432	0,75 0,62 0,45	1,22 1 0,74

The solutions of Eqs. (4) and (5) in dimensionless form was obtained in [9]

$$\Theta = 1 - \sum_{n=1}^{\infty} A_n \frac{R \sin \frac{\mu_n r}{R}}{r \mu_n} \exp(-\mu_n^2 \mathrm{Fo}), \tag{5}$$

where

$$A_n = (-1)^{n+1} \frac{2\mathrm{Bi} \sqrt{\mu_n^2 + (\mathrm{Bi}-1)^2}}{\mu_n^2 + \mathrm{Bi}^2 - \mathrm{Bi}}; \tag{6}$$

$$\Theta = \frac{T - T_0}{T_c - T_0}; \ \mathrm{Bi} = \frac{\alpha R}{\lambda}; \ \mathrm{Fo} = \frac{a\tau}{R^2}. \tag{7}$$

The error in calculating the Biot number undoubtedly has an influence on the results given by Eq. (5), since the multifactorial influence of various properties of the plasma itself and the particle on the heat-transfer coefficient means that this parameter is very difficult to determine at high heating rates in plasma jets.

In fact, approximate estimation of the Biot number from Eq. (7), taking account of the temperature dependence of the thermophysical properties of the plasma, gives a value of the order of one for particles of up to 160 μm, although Bi may be greater or less than one in specific conditions (Table 1). In obtaining the Biot number for NDPE and PTFE, the properties of the plasma and the polymer particles are taken into account.

For metal particles, Bi → 0, and hence all the A_n are zero (except A_1 = 1), and $\mu_1 \approx$ 3Bi. Then Eq. (2) may be simplified

$$\Theta = 1 - \frac{R \sin \sqrt{3\mathrm{Bi}} \frac{r}{R}}{r \sqrt{3\mathrm{Bi}}} \exp(-3\mathrm{Bi}\,\mathrm{Fo}). \tag{8}$$

For polymer particles, the general solution in Eq. (2) must be used, determining the characteristic roots of the equation

$$\mathrm{tg}\,\mu = -\frac{\mu}{\mathrm{Bi}-1} \tag{9}$$

for each Bi. In this case, computerization of the calculation yields more complete and complex information on the heat transfer between the polymer particles and the plasma jet.

The general solution of Eq. (5) when Bi = 1 is now sought

$$\mu_n = (2n-1)\frac{\pi}{2}; \ A_n = (-1)^{n+1} \frac{2}{\mu_n}. \tag{10}$$

Taking account of Eq. (7), Eq. (5) is written in the form

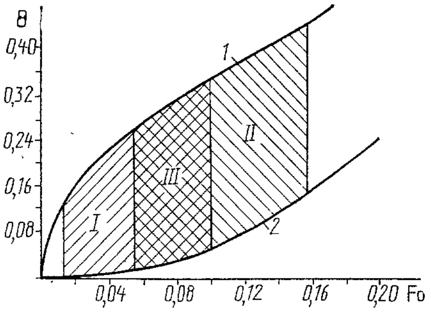

Fig. 2

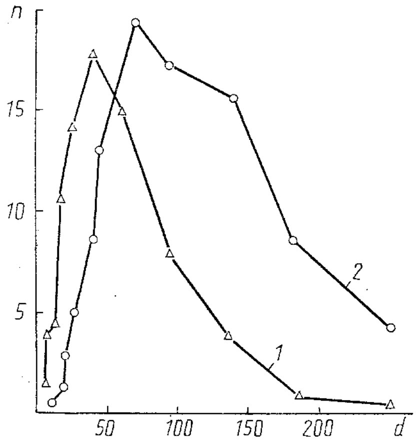

Fig. 3

Fig. 2. Curves of the distribution of the temperature field at the surface (1) and in the center (2) of NDPE and PTFE particles: I) NDPE treatment zone; II) PTFE treatment zone; III) common tratment zone of NDPE and PTFE.

Fig. 3. Distribution curves of granulometric composition of NDPE: 1) initial; 2) deposited by plasma jet. n, %; d, μm.

$$\Theta = 1 - \sum_{n=1}^{\infty} (-1)^{n+1} \frac{4}{(2n-1)\pi} \frac{\sin (2n-1)\frac{\pi r}{2R}}{(2n-1)\frac{\pi r}{2R}} \exp\left[-\frac{\pi^2}{4}(2n-1)^2 \mathrm{Fo}\right]. \tag{11}$$

For the center of the particle, as r → 0

$$\Theta_{ce} = 1 - \sum_{n=1}^{\infty} (-1)^{n+1} \frac{4}{(2\pi-1)\pi} \exp\left[-\frac{\pi^2}{4}(2n-1)^2 \mathrm{Fo}\right], \tag{12}$$

and for the surface of the particle

$$\Theta_s = 1 - \sum_{n=1}^{\infty} \frac{8}{\pi^2 (2n-1)^2} \exp\left[-\frac{\pi^2}{4}(2n-1)^2 \mathrm{Fo}\right]. \tag{13}$$

The results of calculations on an EC-1022 computer agree with the data of [12] (Fig. 2).

The zones of polymer processing lie between the curves determining the melting point of the center and the onset of surface destruction of the particles, and correspond to Fo = 0.011-0.1 for NDPE and 0.054-0.159 for PTFE. The times corresponding to these Fourier numbers for particles of various sizes are given in Table 2. The presence of the common zone III of polymer treatment for NDPE and PTFE indicates that, in conditions of nonsteady high-intensity heating, the temperature region of polymer treatment expands and, despite the difference in their properties, the technological conditions may partially agree. The optimal treatment conditions for each polymer are determined by its set of rheological and thermophysical characteristics. Note also that the specified value of Bi is not constant in the general case. As shown by calculations, Bi may vary from 0.4 to 1 or even higher in the path of the PTFE and NDPE particles, although Bi ≤ 1 for particles smaller than 100 μm.

Separate calculation of Bi is of particular interest to determine the heat transfer between the particle and the plasma jet. In [1], it was shown that the value of Bi suggests directions for optimizing the preparation of high-quality coatings. For example, when Bi < 1 — in particular, for polymers, Bi < 0.4 — optimization focuses on the particle heating in the plasma jet. If Bi > 1, processes occurring in the interaction of the particle with the substrate (substrate heating, the completion of melting, increase in the loss rate, etc.) must be activated. As shown by experimental data on plasma polymer coatings, their quality increases when the particles are completely molten in the jet itself, which reduces or completely eliminates the additional treatment of the resulting layer by a plasma flare.

TABLE 2. Time Characteristics of the Onset of Melting and Destruction of Polymer Particles of Various Sizes

No.	Thermophysical state of material	NDPE			PTFE		
		Fourier No.	particle radius, μm	time, sec	Fourier No.	particle radius, μm	time, sec
1	Onset of surface melting of particle	0,0025	20	$8\cdot 10^{-6}$	0,018	20	$6,9\cdot 10^{-5}$
			30	$1,7\cdot 10^{-5}$		30	$1,56\cdot 10^{-4}$
			40	$3,1\cdot 10^{-5}$		40	$1,77\cdot 10^{-4}$
			50	$4,8\cdot 10^{-5}$		50	$4,33\cdot 10^{-4}$
2	Onset of surface destruction of particle	0,011	20	$3,4\cdot 10^{-5}$	0,054	20	$2,08\cdot 10^{-4}$
			30	$7,7\cdot 10^{-4}$		30	$4,67\cdot 10^{-4}$
			40	$1,34\cdot 10^{-4}$		40	$8,31\cdot 10^{-4}$
			50	$2,1\cdot 10^{-4}$		50	$1,3\cdot 10^{-3}$
3	Onset of melting at center of particle	0,1	20	$3,1\cdot 10^{-4}$	0,159	20	$6,12\cdot 10^{-4}$
			30	$6,9\cdot 10^{-4}$		30	$1,38\cdot 10^{-4}$
			40	$1,22\cdot 10^{-3}$		40	$2,45\cdot 10^{-3}$
			50	$1,9\cdot 10^{-3}$		50	$3,82\cdot 10^{-3}$
4	Onset of destruction at center of particle	0,139	20	$4,24\cdot 10^{-4}$	0,20	20	$7,69\cdot 10^{-4}$
			30	$9,6\cdot 10^{-4}$		30	$1,73\cdot 10^{-3}$
			40	$1,7\cdot 10^{-3}$		40	$3,1\cdot 10^{-3}$
			50	$2,65\cdot 10^{-3}$		50	$4,8\cdot 10^{-3}$

The tendency of the polymer particles to agglomeration complicates the optimization of their heating in a plasma jet. Large NDPE agglomerates (larger than 80 μm) do not melt in the plasma jet. On sputtering particles of such materials, melting is completed in some period at the substrate. The distribution curves of the granulometric composition obtained by means of an Epiquant automatic structural analyzer indicate the presence of agglomeration (Fig. 3).

In analyzing the heat transfer of such large agglomerates with a plasma jet, their nonspherical shape must be taken into account. As shown in [14], the problem of heating a body of complex form may be reduced to the problem of heating a body of basic form (plate, cylinder, sphere) by introducing the criterion of approximate similarity.

Thus, mathematical modeling permits sufficiently complete description of the thermophysical interaction of polymer particles with a high-temperature plasma-jet flux. The results obtained facilitate the directed search for optimal technological conditions of polymer treatment by plasma sputtering.

NOTATION

a) thermal diffusivity; r) current particle radius; R) initial particle radius; τ) time; T) particle temperature; τ_r) relaxation period of heat transfer; w) rate of heat propagation; T_c) temperature of medium; Bi) Biot number; α) heat-transfer coefficient; Fo) Fourier number; λ) thermal conductivity of the material; Nu) Nusselt number; Re) Reynolds number; v) particle velocity.

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

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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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