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MUTUAL THERMAL EFFECT OF DEPOSITED PARTICLES ON THE STRENGTH OF A PLASMA COATING

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UDC 621.039.61

An analytical expression is derived for the strength of a coating to resist separation. The probability density of incidence of the deposited particles is given as a function of position on the basis of a known experimental dependence.

Particles adhering to a substrate have roughly the shape of a disk of radius R and height h with R/h ~ 100 [1]. The adhesion strength Σ per unit base area of such a disk is greater the longer the solidification time t_0 of the disk and the higher the contact temperature T_K [1]. If the flow rate G (kg/sec) of the plasmatron is high, then some of the particles are not able to cool off prior to subsequent particles impinging onto them. Therefore, the cooling time of the deposited layer is increased, which leads to an increase in Σ. Below, we calculate Σ allowing for the mutual thermal influence of the deposited particles.

Let the deposited coating consist of N disks of particles and their projection onto the substrate lie in the deposition spot S(x, y), where x and y are the coordinates on the substrate. For the convenience of further calculations, we shall introduce the auxiliary unitary functions E_i and $\Phi(N; A_k)$, i, k = 1, 2, ..., N. Let

$$E_i = \begin{cases} 1, & \text{if} \quad (x, y) \in C_R(\xi_i, \eta_i), \\ 0, & \text{if} \quad (x, y) \notin C_R(\xi_i, \eta_i), \end{cases} \tag{1}$$

where ξ_i, η_i are coordinates on the substrate of the projection of the center of the disk $C_R(\xi_i, \eta_i)$ of radius R.

Let

$$\Phi(N; A_k) = (1 - |e_{a_1 a_2 \ldots a_N}|) \prod_{j=1}^{K} E_{a_j} \prod_{S=k+1}^{N} (1 - E_{a_S}), \tag{2}$$

where $e_{a_1 a_2 \ldots aN}$ is the Levi–Civita symbol, the absolute value of which is equal to unity if there are identical indices and zero if all indices are different, $A_k = (a_1, a_2, \ldots, a_k)$, and a_k is the number of disks. From Eqs. (1) and (2) it follows that $\Phi(N; A_k)$ equals unity only in the vicinity of the intersections of the projections of disks $a_1, a_2, \ldots, a_k$ and equals zero over all the remaining regions S(x, y).

As an example, Fig. 1 shows a picture of intersection of the projection of three disks in the deposition spot S(x, y) for N = 3. In this case, the following functions Φ are not identically zero:

$$k = 1{:}\ \Phi(3; 1) = E_1(1 - E_2)(1 - E_3);\ \Phi(3; 2) = (1 - E_1) E_2 (1 - E_3);$$
$$\Phi(3; 3) = (1 - E_1)(1 - E_2) E_3;$$
$$k = 2{:}\ \Phi(3;\ 1, 2) = \Phi(3;\ 2, 1) = E_1 E_2 (1 - E_3);\ \Phi(3;\ 1, 3) =$$
$$= \Phi(3;\ 3, 1) = E_1(1 - E_2) E_3;\ \Phi(3;\ 2, 3) = \Phi(3;\ 3, 2) = (1 - E_1) E_2 E_3;$$
$$k = 3{:}\ \Phi(3;\ 1, 2, 3) = \Phi(3;\ 3, 2, 1) = \Phi(3;\ 2, 1, 3) =$$
$$= \Phi(3;\ 2, 3, 1) = \Phi(3;\ 1, 3, 2) = \Phi(3;\ 3, 1, 2) = E_1 E_2 E_3.$$

Tomsk Division of the Institute of Structural Macrokinetics, Academy of Sciences of the USSR. Translated from Inzhenerno-fizicheskii Zhurnal, Vol. 62, No. 1, pp. 51-56, January, 1992. Original article submitted February 14, 1991.

1062-0125/92/6201-0039$12.50

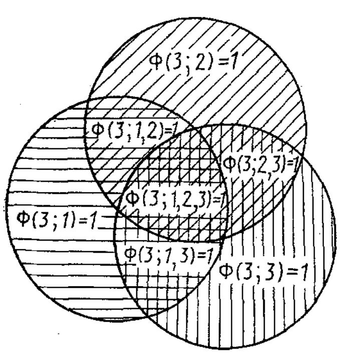

Fig. 1

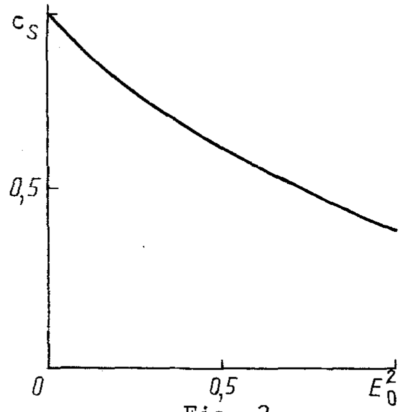

Fig. 2

Fig. 1. Intersection pattern of the projections of three particle disks at the deposition spot.

Fig. 2. Variation of the surface porosity ε_S with dimensionless parameter E_0^2 (the quantities Φ, ε_S, and E_0^2 are dimensionless on the figures).

Each of these functions equals unity in the region of intersection of the disks, the number of which are indicated in the designation of the argument of the function after the semicolon. In $k = 1$ regions, the adhesion strength is formed during the cooling of a disk of height h. In $k = 2$ regions, the upper disk, which changes t_0 and T_K of the lower disk also affects the adhesion strength; in this case the amount of time between the incidence on the substrate of the upper and lower disks is important. In region $k = 3$ the two upper disks exert a thermal influence on the adhesion strength of the lower disk. The overall force of adhesion of the three disks in Fig. 1 equals

$$F = \iint_{S(x,\,y)} \{[\Phi(3;\ 1) + \Phi(3;\ 2) + \Phi(3;\ 3)]\,\sigma_1(1) + \Phi(3;\ 1,\ 2)\,\sigma_2(1,\ 2) + \\ + \Phi(3;\ 1,\ 3)\,\sigma_2(1,\ 3) + \Phi(3;\ 2,\ 3)\,\sigma_2(2,\ 3) + \Phi(3;\ 1,\ 2,\ 3)\,\sigma_3(1,\ 2,\ 3)\}\,dxdy,$$

where $\sigma_k(A_k)$ is the strength of adhesion per unit area of the base of the layer formed by the deposition of k disks $a_1, a_2, \ldots, a_k$.

Since $N \sim 10^4$-10^5 during deposition, the pattern of intersection of the projections of the disks onto the substrate is significantly more complicated than in Fig. 1. We shall enumerate the disks of the deposited layer such that the number of disk a_i corresponds to the point in time $t(a_i)$ incidence of the particles onto the substrate. Thus, if $a_i < a_j$, then $t(a_i) \leq t(a_j)$, therefore a disk with a lower number lies in the region of the intersection of disks closer to the substrate. The quantity

$$F(\mathrm{A}_k) = \iint_{S(x,\,y)} \Phi(N;\ \mathrm{A}_k)\,\sigma_k(\mathrm{A}_k)\,dxdy$$

is equal to the force of adhesion with the substrate of the region of the disks that is the intersection only of disks $a_1, a_2, \ldots, a_k$. Let F_k be the adhesion force of layers formed by all possible intersections of only k disks, then

$$F_k = \frac{1}{k!\,(N-k)!} \sum_{a_1=1}^{N} \sum_{a_2=1}^{N} \cdots \sum_{a_N=1}^{N} F(\mathrm{A}_k),$$

where the factor in front of the summation indicates that $F(A_k)$ is unchanged either when the indices $a_1, a_2, \ldots, a_k$ are interchanged, or when $a_{k+1}, a_{k+2}, \ldots, a_N$ are interchanged. The number of these permutations is $k!(N - k)!$.

The overall adhesion force F of the deposited layer with region S(x, y) is equal to

$$F = \sum_{k=1}^{N} \iint_{S(\xi_1,\,\eta_1)} p(\xi_1,\ \eta_1)\,d\xi_1 d\eta_1 \cdots \iint_{S(\xi_N,\,\eta_N)} p(\xi_N,\ \eta_N)\,F_k d\xi_N d\eta_N, \tag{3}$$

where p(x, y) is the probability density function for the incidence of the center of the particle disk to the point (x, y). By definition

$$\iint\limits_{S(x,\,y)} p(x,\,y)\,dxdy = 1.$$

Assuming that all functions in Eq. (3) are piecewise continuous and the multiple integral uniformly converges, we can interchange the order of integration and then replace the $k!(N-k)!$ identical terms in the multiple summation by one, then

$$F = \iint\limits_{S(x,\,y)} \left\{\sum_{k=1}^{N} \frac{1}{k!\,(N-k)!} I^k (1-I)^{N-k} \sum_{a_1=1}^{N} \sum_{a_2=1}^{N} \cdots \sum_{a_N=1}^{N} (1 - \right.$$

$$\left. - |e_{a_1 a_2 \ldots a_N}|)\, \sigma_k(\mathbf{A}_k)\right\} dxdy = \left\{ \iint\limits_{S(x,\,y)} \sum_{k=1}^{N} I^k (1-I)^{N-k} \sum_{a_1=1}^{N-k+1} \sum_{a_2=1+a_1}^{N-k+2} \cdots \sum_{a_k=1+a_{k-1}}^{N} \sigma_k(\mathbf{A}_k)\right\} dxdy, \tag{4}$$

where

$$I = I(x,\,y) = \iint\limits_{S(\xi_i,\,\eta_i)} p(\xi_i,\,\eta_i) E_i \, d\xi_i d\eta_i = \iint\limits_{C_R(x,\,y)} p(\xi,\,\eta)\, d\xi d\eta. \tag{5}$$

With the aim of practical use of Eq. (4), it is natural to propose that the thermal influence on the adhesion strength turns out to be due to predominantly the two first layers of deposited particles, i.e., in Eq. (4)

$$\sigma_k(\mathbf{A}_k) \ \text{replace by} \ \sigma_2(\mathbf{A}_2), \ \text{for} \ k > 2. \tag{6}$$

For simplicity in the following calculations we shall assume that the particles impinge on the substrate in equal time intervals Δt, $\Delta t = t_N/N$, t_N is the time of deposition of N particles. Since to calculate $\sigma_k(\mathbf{A}_k)$ it is sufficient to know only the time intervals over which the disks adhere, and not the moment in time of deposition, then

$$\sigma_2(\mathbf{A}_2) = \Sigma_2(l), \tag{7}$$

where $\ell = a_2 - a_1$, and $t_l = \Delta t \ell$ is the time interval over which disk a_2 adheres to disk a_1. From Eqs. (4), (6), (7), changing the order of summation, we get

$$F = N \Sigma_1 J_{1\,N-1} + \iint\limits_{S(x,\,y)} \left[\sum_{l=1}^{N-1} \Sigma_2(l) \sum_{k=2}^{N-(l-1)} R(N,\,k,\,l)\, I^k (1-I)^{N-k}\right] dxdy, \tag{8}$$

where Σ_1 is the specific adhesion strength resulting from the cooling of a disk of thickness h;

$$J_{ik} = \iint\limits_{S(x,\,y)} I^i (1-I)^{N-k}\, dxdy; \tag{9}$$

$$R(N,\,k,\,l) = \sum_{a_1=1}^{N-(k-1)-(l-1)} \ \sum_{a_3=1+a_1+l}^{N-k+3} \ \sum_{a_4=1+a_3}^{N-k+4} \cdots \sum_{a_k=1+a_{k-1}}^{N} 1. \tag{10}$$

From Eq. (10) it is clear that $R(N,\,k,\,\ell) = C_{k-1}^{N-\ell}$, where $C_{k-1}^{N-\ell}$ are binomial coefficients. Using Newton's binomial formula, from Eqs. (8) and (9) we obtain

$$\Sigma = F/S = \Sigma_1 (1 - \varepsilon_N) + \sum_{l=1}^{N-1} (\Sigma_2(l) - \Sigma_1)(\varepsilon_N - \varepsilon_{N-1} - \varepsilon_l + \varepsilon_{l-1}), \tag{11}$$

where S is the area of S(x, y); Σ is the specific adhesion strength against separation, and

$$\varepsilon_l = \iint\limits_{S(x,\,y)} (1-I)^l\, dxdy/S, \ l = 1,\,2,\,\ldots,\,N. \tag{12}$$

We shall show that ε_N is the specific area of the pores (porosity) in the deposition spot of N deposited particles. Actually, from Eq. (3), assuming $\sigma_k(\mathbf{A}_k) = 1$ and using Newton's binomial formula, we obtain

$$S_N = S(1 - \varepsilon_N), \tag{13}$$

where S_N is the contact area of N deposited particles. Thus, ε_ℓ, $\ell = 1, 2, \ldots, N$, are equal to the porosities of the ℓ first deposited particles.

The first term in Eq. (11) is equal to the specific strength without allowing for the thermal influence of the deposited particles, and the thermal influence is included in the second term in the assumption that only the first two layers of deposited particles predominantly influence the adhesion strength.

Since $p(\xi, \eta) \leq 1$, and the radius of the deposition spot $\rho \sim 10^{-2}$ m, from Eq. (5) it follows that $I \sim E^2 = R^2/\rho^2 \ll 1$. Taking this into account and the fact that

$$\lim_{I \to 0} (1 - I)^{-\frac{1}{I}} = e,$$

from Eq. (12) we get

$$\varepsilon_l = \varepsilon(t_l) = \iint\limits_{S(x,\,y)} \exp(-It_l/\Delta t)\,dxdy/S. \tag{14}$$

Note that from Eq. (14) it follows that $\varepsilon(t)$ is the porosity in the spot at time t.

We denote $\sigma(t_\ell) = \Sigma_2(\ell)$, then from Eqs. (11) and (14)

$$\Sigma = \Sigma_1(1 - \varepsilon(t_N)) + \sum_{l=1}^{N-1} (\sigma(t_l) - \Sigma_1)[\varepsilon'(t_N) - \varepsilon'(t_l)]\,\Delta t = \Sigma_1(1 - \varepsilon(t_N)) + \int_0^{t_N} (\sigma(t) - \Sigma_1)(\varepsilon'(t_N) - \varepsilon'(t))\,dt, \tag{15}$$

where $\varepsilon'(t_i) = (\varepsilon_\ell - \varepsilon_{\ell-1})/\Delta t$.

We now calculate Δt, t_N, Σ_1, and σ. The quantity Δt is found from the condition that one particle is deposited during time Δt:

$$4\pi R_0^3\gamma/3 = \beta G \Delta t, \tag{16}$$

where R_0 is the radius of the equal volume of spherical particles being deposited.

For further calculations, we shall define the function $p(x, y)$ in Eq. (5). For plasma deposition, the probability density of the incidence of a particle at the point (x, y) of the region $0 \leq x^2 + y^2 < \infty$ has the form [1]

$$p_\infty(x, y) = \frac{1}{\pi\rho^2} \exp\left(-\frac{x^2 + y^2}{\rho^2}\right). \tag{17}$$

We take as $S(x, y)$ the region $C_\rho(0, 0)$. Normalizing $\rho_\infty(x, y)$ in the region $C_\rho(0, 0)$, we obtain the following probability density function:

$$p(x, y) = \frac{e}{e - 1} p_\infty(x, y). \tag{18}$$

To calculate Eq. (5), we introduce the new variable of integration

$$\begin{gathered} \xi = \xi_i - x,\ \eta = \eta_i - y;\ x = r_1 \cos\Theta_1,\ y = r_1 \sin\Theta_1; \\ \xi = r\cos\Theta,\ \eta = r\sin\Theta;\ \varepsilon_1 = \frac{r_1}{\rho},\ \varepsilon = \frac{r}{\rho},\ \varphi = \Theta - \Theta_1. \end{gathered} \tag{19}$$

From Eqs. (5), (15), and (19) accurate to terms of order E^4 (for plasma deposition $E^2 \sim 10^{-4}$)

$$\begin{gathered} I = \frac{e}{\pi(e-1)} \exp(-\varepsilon_1^2) \int_0^E \exp(-\varepsilon^2) \int_0^{2\pi} \exp(-2\varepsilon\varepsilon_1 \cos\varphi)\,d\varphi\varepsilon d\varepsilon = \frac{e}{e-1} E^2 \exp(-\varepsilon_1^2), \\ \varepsilon'(t) = (\exp(-\mu) - \exp(e\mu))/t,\ \mu = tE^2/(\Delta t(e-1)). \end{gathered} \tag{20}$$

The quantity t_N is calculated from the condition $\varepsilon_N = \varepsilon_S$, where ε_S is the surface porosity of the deposited coating on the substrate. From Eqs. (14) and (20)

$$\varepsilon_S = \varepsilon_S(t_N) = \mathrm{Ei}\left(-\frac{eE_0^2}{e-1}\right) - \mathrm{Ei}\left(\frac{E_0^2}{e-1}\right),\ E_0^2(t_N) = E_0^2 = E^2\frac{t_N}{\Delta t}, \tag{21}$$

where

$$\mathrm{Ei}(x) = \int_{-\infty}^{x} \frac{\exp x}{x}\,dx,\ x < 0,$$

is an integral exponential function.

We shall borrow the expression for Σ_1 from [1]:

$$\frac{\Sigma_1}{\Sigma_m} = 1 - \exp\left(\frac{\nu t_p}{\exp\left(E_a/(kT_{\text{к}})\right)}\right), \quad t_p = \frac{h^2}{\alpha^2 a_1}, \tag{22}$$

where Σ_m is the maximum porosity, t_p is the reaction time during the chemical interaction of the material particles and the substrate (this time in this case is chosen, as in [1], equal to the cooling time of the particles t_0); ν is the intrinsic frequency of atomic vibrations, E_a is the activation energy, a_1 is the coefficient of temperature conductivity of the molten material of the particles, and α is a dimensionless parameter determined from the nomogram in [1].

The function $\sigma(t)$ in Eq. (15) is calculated using the solution of the problem of the cooling of the particles given in [1]. To do this, we note that during the deposition of the upper particles, when the lower particles had still not solidified ($t < t_0$), we can use the solution for the cooling of one particle, but 2h thick, i.e., for $t \le t_0$

$$\sigma(t) = \Sigma_1(2h). \tag{23}$$

For values of $t > t_0$ we use approximately $\sigma(t) = \Sigma_1(h)$, assuming here that the upper particle does not exert a thermal influence on the strength after complete solidification of the lower particle.

From Eqs. (15), (19) and (21)

$$\varepsilon(t_0) = \varepsilon_S(t_0), \tag{24}$$

$$\Sigma = (1 - \varepsilon_S)\Sigma_1(h) + [\Sigma_1(2h) - \Sigma_1(h)]\,[1 - \varepsilon_S(t_0) + t_0\varepsilon'(t_N)]. \tag{25}$$

In Eq. (25), ε_S should be assigned, and t_N is found from Eq. (21) or the graphical dependence of ε_S on E_0^2 can be used (Fig. 2).

Note that the role of the second term in Eq. (25) increases markedly with increasing t_0, and likewise for an increase in the dimensionless parameter $E_0^2(t_0)$, which decreases $\varepsilon_S(t_0)$; this is clear from Eq. (21) and Fig. 2. Equation (25) is the analytic dependence of the strength of a plasma coating on the parameters of the deposition process allowing for the mutual thermal influence of the deposited particles, if the surface porosity ε_S is calculated from the analytical variation (Eq. (21)) with the unitary dimensionless parameter E_0^2. From Eqs. (16) and (21) we have

$$E_0^2 = \frac{3t_N\beta G R^2}{4\pi R_0^3\gamma\rho^2}. \tag{26}$$

The quantity R in Eq. (26) can be determined from the known theoretical and experimental dependencies cited in [1].

NOTATION

R, h, radius and height of the disk; Σ, specific surface strength of adhesion; t_0, solidification time; T_K, contact temperature; G, flow rate of the plasmatron; N, number of deposited disks; E_i, Φ, unitary auxiliary functions; C_k^N, binomial coefficients; ε_ℓ, porosity of the ℓ deposited disks; ρ, radius of deposition spot; γ, density of the material of the particles; β, powder utilization factor; t_p, duration of the reaction during chemical interaction of the materials of the particles and the substrate.

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