Main problems of mathematical modeling high energies plasma technologies

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Abstract. Some fundamental problems of mathematical modeling of processes to get coatings using vacuum ion-plasma method have been formulated. It has been introduce a notion of an active surface zone to describe non-thermal activation. It has been shown that non-thermal activation processes can be explained because of the surface focuson effect. Main evolution stages of conversion of absorbed particles have been described based on probability theory. Some general theoretical relations applied in the theory of formation of a new phase on a surface of a solid body have been defined.

1. Introduction
Plasma technology of high energies (PTHE) for obtaining special coatings in a vacuum of metals, their compositions, and ultra-hard compounds are in ever-growing use to increase operational life and reliability of various engineering products [1, 3-11].

The essence of this technology is the following. Using an electric-arc evaporator or accelerator a plasma jet is developed in a vacuum arc of a cathode form. This plasma jet consists of ions and atoms of a cathode’s metal (or cathode’s metals in a multi arc mode) and electrons. Main features of this plasma jet are high degree of plasma ionization (more than 0.5), high initial ion energy (more than some tens of eV), average multiplicity of ion ionization exceeding unity, and high density of a metal mass flow in a plasma jet (corresponding to a coating growth rate 0.1 … 1 mc/m/min) [1, 2].

After various treatment, this plasma jet is directed to the condensing surface that is under adjustable negative potential 0…2 kV. As a result, ions get additional kinetic energy $e_\pi U_c$ in a Debye layer near the part surface, then after neutralization, they get to a condensing surface. Depending on the part potential value $U_c$, coating formation, ion sputtering of the surface or even ion implantation can happen. While supplying reactant gases into a vacuum chamber it is possible to get a coating of various compounds (nitrides, carbide, oxides, etc.).

Over the past period of development of this technology some fundamental and applied tasks have been stated and solved, they have also allowed to provide its wide introduction into an industry. However, prospects for further development of PTHE as well as other technologies for coatings applying ion-bombardment of a surface are connected with the necessity of solving a range of fundamental, applied and technical problems.

2. Main processes typical for ion-plasma technologies
Mathematical modeling of plasma technologies of high energies (PTHE) is to describe the following
main processes typical for ion-plasma technologies:
1. Interaction of a plasma jet with a ‘cold’ gas while transporting the stream from a cathode to a condensing surface.
2. Electrical exchange of moving non-isothermic quasi-neutral plasma with a solid body surface.
3. Interaction of atomic particles of average energies 10…1000 eV with a solid body surface. Influence of these particles and energies on reaction rate constants of absorption, hemisorption, surface migration, desorption, dissociation and embedding into active growth center of coatings.
4. Influence of technological heredity (initial and acquired during the coating growth) on product properties with coatings, and control of these properties.
5. Optimization of structure complexity to obtain extreme operating properties of multicomponent systems.
6. Influence of basic controlling physical parameters of deposition on physicochemical properties of coatings and engineering-and-economical performances of the deposition process.
7. Rationalization of practical fields of application of multicomponent and multilayer coatings.

Conducted analysis of classical potentials (Born-Mayer, Mare, Bohr, power, etc.) as well as potentials obtained on the basis of statistical methods taking into account electron interaction (Thomas – Fermi – Firsov, Hartree – Fock – Sletter, free electronic gas, etc.) has shown that in the considered energy regions values can differ by an order and more [2]. Absence of reliable experimental data on scattering cross-sections in the energy region 1…500 eV does not allow to take clear choice of the interaction potential, and consequently to base physical process with needed definiteness. Widely used in papers hard spheres approximation could not be reasonable because it does not allow describing the known experimental fact of prevailing scattering at little angles within this energy range. The only excuse for using this approximation in cascades of shifts of a solid body is rather weak dependence of cascade average characteristics on the type of equation for the energy transfer cross-section.

The second essential feature of the considered technology is the fact that coating formation and heterogeneous reactions take place under intensive bombardment of a surface by fast atomic particles with energies essentially higher than thermal energies, but with essentially lower energies considered for calculation of cascades of shifts. Consequently, well-developed methods of statistical physics (thermal interaction region) and method of kinetic equations (region of ion implantation and scattering) cannot be applied without certain clarifications. Therefore, a necessity arises to develop new approaches to description of processes on solid body surfaces when forming coatings under ion bombardment.

One of possible variants of description such processes was suggested by the authors in [4].

The essence of it that the driving force of some processes on the surface is considered as a superposition of impacts based on thermal and non-thermal activation. Thermal and activation is determined by classical equilibrium distributions on energies, and it results in known equations of theory of transition state Eyring-Evans-Polanyi or in formulae of Ya.I. Frenkel type with Boltzmann multiplier.
3. Effect of formation of surface focusons

Non-thermal activation of these processes is stipulated by an ion bombardment of a surface and kinetic energy transfer from fast particles. This kinetic energy is transferred to atoms of a crystal lattice during sequential collisions. It also develops active area inside and on a solid body surface. For the lifetime of this active area, various physical-chemical processes with non-thermal activation by phonons, electrons and photons take place. Without discussing the nature of this activation, we can state that non-thermal activation of a surface process of the given type takes place in some active area \( S_A \), and this area appears under high-energy particle that have impacted the surface. To be more specific, it is assumed that the size of an active area \( S_A \) such that probability of the given type of surface processes is close to unity. Naturally, at a first approximation, size of this area is proportional to the released energy \( W_i \) and inversely proportional to the activation energy \( U_A \) of the considered physical-chemical process. Thus, area value of an active zone can be introduced at a first approximation as:

\[
S_A = A \frac{W_i}{U_A} \cdot \frac{1}{N_i},
\]

where \( n_r \) – reticular density of surface atoms, coefficient \( A \) has a physical meaning of a number of atoms on the surface available for sorption and having obtained energy \( U_A \) sufficient for the activation of physical-chemical processes of the given type.

For example, using introduced notion of a magnitude of an active zone \( S_A \) we determine a reaction constant of non-thermal dissociation of nitrogen molecules adsorbed on a surface with the density \( n \). For some time period \( dt \) a number of high-speed atoms of metal \( N = j_i S dt \) with stream density \( j_i \) fall on the surface with area \( S \). Each of these atoms develops active zone with the area \( S_i \). According to (1) it provides dissociation \( n \cdot N \cdot S_A \) of absorbed nitrogen molecules. Using a definition of a macroscopic reaction rate constant \( \lambda_n \) of non-thermal dissociation of nitrogen, we get:

\[
\lambda_n = A \frac{W_i}{U_A} \cdot \frac{j_i}{n_r},
\]

where \( \tilde{j}_i = j_i/n_r \) - reduced stream density; \( U_A \) – in the given case the energy of activation of molecule dissociation \( n_r \) in absorption state on a surface.

This phenomenological approach was experimentally proved when obtaining coatings of nitrides [4] in the region of low temperatures, but it resulted in necessity of substantiation of physical mechanism of such dissociation. First, physical meaning of a magnitude \( S_A \) – is actually a middle cross-section of interaction of a fast atom with a solid body surface. But obtained experimental magnitude \( S_A \) is evaluated in area occupied from some dozens to some hundreds of surface solid body atoms. Secondly, activation energy of desorption \( N_2 \) is of 0.4...0.8 eV, but the bond energy of nitrogen atoms in a molecule, even taking into account weakening of this bond by the surface interaction, cannot be less than 6...8 eV. Therefore, mechanism of kinetic energy transfer from fast atomic particle to the atoms of active zone and the mechanism of energy transfer from the atoms of active zone to the absorbed molecules of nitrogen is to be such that the possibility of strong bond breakage of atoms in a nitrogen molecule without kinetic energy transfer to the whole molecule (in the direction perpendicular to the surface) would appear, and it would be sufficient for its desorption.

To answer the raised questions the authors have suggested the mechanism of occurrence and development of surface focusons of Silsby type [5]. Really, when the energy of impacting particles is less than 300...500eV, their scattering cross-section on solid body atoms is close to a half of a crystal lattice constant as early as during the first interactions. In this case, focusons develop at certain angles of scattering directions along surface crystallographic axes of a crystal lattice. These focusons provide energy and impulse transfer at very long range (in comparison with interatomic ones) due to consecutive elastic collisions of atoms of the same mass.
In case of such consecutive collisions of surface atoms of a solid body, absorbed molecules and atoms in the potential field of these surface atoms also get certain impulse and kinetic energy along the surface direction of a solid body. If an absorbed atom gets such impulse and energy, it passes to another sorption center. If such an impulse and energy is obtained by the atoms not simultaneously or by one of atoms of an absorbed molecule of nitrogen, bond breakage N-N or excitation of violent oscillations happens along this bond weakened by the surface interaction with subsequent dissociation of a molecule.

Consequently, in both considered cases we deal with non-thermal activation of surface migration processes and with molecule dissociation on a surface. Besides, in contrast to thermal activation, described processes slightly depend on the surface temperature, and absence of impulse component perpendicular to a solid body surface eliminates the problem of keeping particles in absorbed state after obtaining rather high kinetic energy from a focuson.

Quantitative description of influence of effect of surface focusons initiation on coating formation processes, chemisorption, etc. can be done using introduced notion of an active zone of non-thermal activation on a solid body surface [2].

We assume that a fast atom with the energy \( W_i \) that has fallen on the surface is able to develop \( k W_i / W_f \) - surface focusons \( (k \) – efficiency coefficient of surface focusons production with the average energy of their production \( W_i \)). Designating as \( \langle W \rangle \) average losses of focuson’s energy in one act of sequential collisions in a chain (taking into account transfer of part of energy to absorbed atoms and molecules) we get that each of the focusons embraces \( N = W_f / \langle W \rangle \) surface atoms. Magnitude \( N \) can be introduced as \( N = S_{\varphi,1} \cdot n_r \), where \( S_{\varphi,1} \) - effective surface zone area of non-thermal activation produced by a focuson.

Thus, total effective area \( S_A \) of an active zone of non-thermal activation is:

\[
S_A = \frac{k W_i}{W_f} \cdot S_{\varphi,1} = \frac{k W_i}{\langle W \rangle} \cdot \frac{1}{n_r}.
\] (3)

Introducing in (3) the magnitude \( A \) based on relation \( A = k U_A / \langle W \rangle \), we can form (3) similar with relation (1) obtained phenomenologically.

Considered effect of arising of surface focusons is at the initial stage of development, and it requires detailed theoretical and experimental research because of high significance of ion-plasma technologies for practical purposes.

4. Calculation of constants of surface reaction rate in case of plasmachemical synthesis of coatings

For logical completion of analysis of influence of thermal and non-thermal effects on heterogeneous processes, it is necessary to develop a calculation algorithm of rate constants of corresponding surface reactions. In this connection, we consider some features of this calculation with respect to an absorbed molecule \( N_2 \), taking part in formation of a nitride coating.

Molecule \( N_2 \) having undergone thermal accommodation falls on a certain sorption center. This molecule leaves this sorption center in a certain time because of thermal or non-thermal activation. With some probability, it can fall on another sorption center (surface migration) in a similar molecule state or it can desorb from the surface or dissociate into atoms. If a molecule has migrated to the second sorption center, from this center as well as from the first one it can take part in three mentioned above outcomes with a certain probability. Thus, determination of desorption and dissociation rate constant is a probabilistic analysis of molecule behavior at two structural levels. The first level is a possible particle transformation at leaving from this sorption center. The second level is a possible particle transformation if it migrates to different sorption centers.

First, let us consider probabilistic description of possible particle transformations at the first structural level. Suppose in time \( t=0 \) a particle falls on some sorption center, and at some random time
$t=T$ it can leave the center with three possible outcomes. The first outcome is a migration, the second one is desorption from the surface, and the third outcome is dissociation in atoms. Each of these outcomes can be realized with the intensity $\lambda_i$ (i=1, 2, 3) in absence of others.

In case of purely thermal activation, intensity of each outcome can be determined using Ya.I. Frenkel formula or using formulae of transition-state theory:

$$\lambda_{i,T} = v \exp(-U_i/kT),$$

where $U_i$ – activation energy of an appropriate process. To simplify, preexponential factor is taken as $v$ - a frequency of a particle oscillation in a bound state.

In case of atom bombardment of the surface by fast atoms these outcomes for an absorbed molecule $N_2$ happen because of non-thermal activation of an appropriate process mentioned above. Therefore, for the intensity of non-thermal activation of desorption happening due to absorbed molecules sputtering we get [4]:

$$\lambda_{2, H} = \alpha_{p, 2} f_i,$$

where $\alpha_{p, 2}$ – sputtering ratio of absorbed molecules.

Intensity of non-thermal dissociation is determined by (2), and we assume $\lambda_{p, H} = \lambda_{H}.

Thus, having considered each of three possible outcomes separately we can state that the given outcome is realized with intensity $\lambda_{i} = \lambda_{i,H} + \lambda_{i,T}$. These events happen because of accidental, independent, and individual for each event reasons.

Statistical description of a probability of each outcome can be the following. A particle is on the given sorption center for some time $[0,t]$. It can leave it with intensity $\lambda_i$ at some accidental time $T$. Set $\{T\}$ when considering statistically equivalent experiments is a set of random events. We break up $[0,t]$ into $N$ equal parts in length $t/N$. Then possibility of leaving of a particle in any of intervals $t/N$ is $\lambda_i t/N$, and possibility of an opposite event over the whole interval $[0,t]$ is determined as a product probability of this opposite event $(1-\lambda_i t/N)$ at all $N$ intervals:

$$P\{T > t\} = \lim_{N \to \infty} \left(1 - \lambda_i t/N\right)^N = e^{-\lambda_i t}.

Hence, probability that a particle leaves the given sorption center on $i$-reason for the time $t$ is:

$$P\{T < t\} = 1 - e^{-\lambda_i t}.

Consequently, for individual $i$-event we have a demonstrative probability distribution law (7), and its distribution density is:

$$f_i(t) = \lambda_i e^{-\lambda_i t}.

When considering three independent possible outcomes, possibility to discover a particle in the given center for some time that is greater or equal $t$ equals possibility of failure of these three events:

$$P[T_1 > t, T_2 > t, T_3 > t] = P[T_1 > t] P[T_2 > t] P[T_3 > t] = e^{-\lambda_1 t} = e^{-\lambda_2 t} = e^{-\lambda_3 t},

where $\lambda = \lambda_1 + \lambda_2 + \lambda_3$.

It follows that the mean lifetime of a particle on this center (mathematical expectation) is $\tau = 1/\lambda$.

Possibility that the outcome will be the first event (migration) is determined as a possibility of occurrence of the first event earlier then the second and the third ones:

$$P_1 = P[T_1 < T_2, T_1 < T_3] = \int_0^\infty f_1(t_1) \int_0^{t_1} f_2(t_2)dt_2 \cdot \int_0^{t_1} f_3(t_3)dt_3 \, dt_1 = \frac{\lambda_1}{\lambda}

Occurrence of the second and the third outcomes is determined similarly:

$$P_2 = \frac{\lambda_2}{\lambda}, \quad P_3 = \frac{\lambda_3}{\lambda}.

Consequently, possibility that a particle out of sorption state will move to the adjoining center
(i=1), desorb (i=2) or dissociate (i=3) will be:

\[ P_i(t) = P_i \cdot (1 - P[T_1 > t, T_2 > t, T_3 > t]) = \frac{\lambda_i}{\lambda} \cdot (1 - e^{-\lambda t}). \]  

(11)

and appropriate probability densities will be

\[ f_i(t) = \frac{\lambda_i}{\lambda} e^{-\lambda t}. \]  

(12)

Process rates (reaction rate constants \( k^*_i \)) of migration, desorption, and dissociation when the particle is on the same center is determined as mathematical expectations from corresponding intensity distributions:

\[ k^*_i = \int_0^\infty P_i(T_1 > t, T_2 > t, T_3 > t) f_i(t) dt = \frac{\lambda_i^2}{\lambda} = \lambda_i P_i. \]  

(13)

Now let us analyze changes of reaction rate constants of desorption and dissociation taking into account migration of particles over desorption centers.

From each desorption center with the similar bond energy a particle is able to move to the adjoining center with possibility \( P_{11}, P_{22}, P_{33} \) (10) and with intensity \( k^*_1, k^*_2 \) and \( k^*_3 \) (13) to move to the adjoining center, to desorb or to dissociate. There is no need to take into account influence of degree of filling of a surface on these processes when forming coatings in contrast to chemisorption.

Then possibilities of these outcomes from the first sorption center are \( P_{11}, P_{22}, P_{33} \), from the second one possibilities of these outcomes are \( P_{12} = P_{21}, P_{22} = P_{11} P_{22}, P_{32} = P_{31} P_{32}, \) and from some j-center are \( P_{1j} = P^j_1, P_{2j} = P^{j-1}_1 P_2 \) and \( P_{3j} = P^{j-1}_1 P_3 \).

Microscopic rate constants of desorption and dissociation are determined as mathematical expectations of these events:

\[ k_2 = \sum_{j=1}^\infty k^*_2 \cdot P_{2,j} = k^*_2 \sum_{j=1}^\infty P_{2,j} = \frac{\lambda_2^2}{\lambda} \frac{\lambda_2}{\lambda_3 + \lambda_3}, \]  

(14)

\[ k_3 = \sum_{j=1}^\infty k^*_3 \cdot P_{3,j} = k^*_3 \sum_{j=1}^\infty P_{3,j} = \frac{\lambda_3^2}{\lambda} \frac{\lambda_3}{\lambda_2 + \lambda_3}. \]

Relations (14) obtained on the basis of strict probabilistic analysis differ from similar relations used in adsorption and hemisorption theories [6] where it is assumed without proper basis that \( k_2 = \lambda_2 \text{T}. \)

It is justified because in these theories relations including the combination \( k_2/k_3 \), which is proportional (in case of purely thermal activation of the process) to the relation \( \exp(-\left(u_2 - u_3\right)/kT) \) are researched experimentally. Besides, physical picture of the process does not undergo qualitative changes. But, when obtaining coating in conditions of combined effect of thermal and non-thermal activation, qualitative and quantitative physical picture essentially depends on the \( k \) kind [2].

5. Results and discussion

Result analysis of numerical simulation of various variants of kinetics of plasmochemical synthesis of nitride coatings [2] has shown that kinetic schemes with the same energy adsorptive state of molecular nitrogen have the same disadvantage that arises in mathematical modelling of most chemisorption processes. Really, classic calculations with one prechemisorption molecule state [6] due to the quick change of \( k_2 \) under temperature rise allow to describe adequately kinetics of these processes only when \( T \leq T_{kp} \), where \( T_{kp} \) depends on a molecule bond energy in this only prechemisorption state.

For chemisorption of gases with purely thermal activation, such considering often gives satisfactory results because the small temperature interval around active chemisorption temperature is of practical interest. For example, in ion-plasma deposition formation of nitride coatings can be obtained within the range from 300 to 700...800 K. Therefore, development of an adequate
mathematical description in a wide temperature range is of practical interest.

Authors [2] have determined that this problem is eliminated if we take into account possibility of molecule adsorption and possibility of changing of energy magnitude in case of molecule migration on a surface. This also allows to describe adequately kinetics of the process in a wide temperature range. In this case, multiplicity of prechemisorption molecule states (polysorption) and possible transitions between these states can be presented in the following scheme (Figure 1).

![Figure 1. Transition scheme of an adsorbed nitrogen molecule between various energy states.](image)

It may be shown that for the considered scheme (Figure 1), if the surface is slightly filled, the parameter \( y = k_3/k_2 \) may be the following:

\[
y = (z(\alpha))^3 + (\sigma_i)^3 \left( \frac{\lambda_i(\alpha)}{\lambda_2(\alpha)} \right)^3 \phi(\beta_1, \beta_2, \ldots, \beta_n),
\]

(15)

\[
\phi(\beta_1, \beta_2, \ldots, \beta_n) = 1 - \gamma_i^2 \left( z(\beta_i) + \gamma_i^2 + \tilde{\sigma}_i \phi(\beta_2, \ldots, \beta_n) \right)^{-1},
\]

\[
\phi(\beta_1, \ldots, \beta_n) = 1 - \gamma_i^2 \left( z(\beta_i) + \gamma_i^2 + \tilde{\sigma}_i \phi(\beta_1, \ldots, \beta_n) \right)^{-1},
\]

\[
\phi(\beta_n) = 1 - \sigma_{n+1}^2 \left( z(\beta_n) + \sigma_{n+1}^2 \right)^{-1},
\]

\[
z(\alpha) = \lambda_3(\alpha)/\lambda_2(\alpha), \quad z(l) = \lambda_3(l)/\lambda_2(l),
\]

\[
\gamma_i = (1 - \sigma_i)\sigma_i^i, \quad \tilde{\sigma}_i = \sigma_i \sigma_i^i, \quad l = \beta_1, \beta_2, \ldots, \beta_n, \quad i = 2, \ldots, n.
\]

Research has shown that numerical simulation using (15) gives satisfying results when describing kinetics of plasma-chemical formation of nitrides on solid body surfaces for a wide temperature and energy range of incoming particles.

6. Conclusion
Thus, results of this work have allowed to formulate a set of urgent fundamental problems of obtaining coatings under ion bombardment and to outline approaches to their solutions. Moreover, some general relations applied in a theory of a new phase formation on a solid body surface have been specified.

Acknowledgments
The reported study was funded by the Ministry of Science and Higher Education of the Russian Federation.

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