Receiving nanostructural topocomposite coatings in terms of the cascade cross effect

P B Grinberg¹, K N Poleschenko¹, D N Korotaev², P V Orlov², G A Vershinin³, E E Tarasov⁴, E V Ivanova⁵
¹Omsk Scientific Research Institute of Process and Engine Manufacture, 283, street of B. Khmelnytskyyi, Omsk, 644021, Russia
²Siberian State Automobile and Highway University, 5, Mira ave., Omsk, 644080, Russia
³Dostoevsky Omsk State University, 55a, Mira ave., Omsk, 644077, Russia
⁴FGUP Federal Research and Development Centre «Progress», 4, 5th Kordnaya street, Omsk, 644018, Russia
⁵Omsk Tank-Automotive Engineering Institute, 119, 14th military town, Omsk, 644098, Russia

E-mail: korotaevd99@mail.ru

Abstract. The article considers physico-technological aspects of receiving nanostructural topocomposite coatings in terms of the cascade cross effect based on the special cathodic system, making possible ionic-plasma processing simultaneously with the use of three cathodes in a pulse mode. The authors carry out theoretical and experimental researches of forming concentration profiles of element distribution in surface layers of the bilayer “film-base” system. They determine the features of mass transfer processes developing in response to cascade cross effect. It is demonstrated that due to the mutual diffusion of the film and the base elements in the field of the phase boundary in the ”film-base” system a transition area is formed. Its dimensions can be associated with the thickness of the nanofilm. The authors give an example of receiving a multilayer nanostructural composition in terms of cascade cross effect.

1. Introduction
Application of wear-resistant coatings on working surfaces of different products is among the primary ways of increasing their operational characteristics. Among the methods of the surface modification of products, constructional parts and tools condensation of the substance from the plasma phase in vacuum with ionic bombardment of the surface (CIB) is one of the most adapted method for industrial production [1, 2]. At the same time, the necessity of improving the CIB method is caused by performance and reliability assurance of product surfaces operated under high loadings and speeds. Attempts of the problem solution for improving performance properties in the specified conditions were carried out due to the increase in thickness of coatings and creation of multilayer coatings based on carbides, nitrides, borides and other compounds of refractory metals, including the ones with intermediate layers from pure metals, each of which has its own functional purpose [3]. However, in the process of increasing the thickness of coatings with the size of more than 4-5 microns the formation of considerable residual stresses [4] takes place that enhances the probability of brittle failure of coatings under operating conditions. Besides, under the creation of multicoatings there is an
ensuring problem of good adhesion of both the coating against the base and the layers against each other [3]. The solution of the specified problems and the issues of physico-technological character relating to the products working in the conditions of increased temperature-speed modes can be substantially provided using nanostructural topocomposite coatings (NSTCC), characterized by the gradient structure and nanocluster surface morphology [5-8].

2. Problem statement
The key problem of receiving nanostructural topocomposite coatings (NSTCC) is the ensuring of perfect adhesion of the coating to the base material. The specified problem gets a special urgency in case of overlaying a nonmetallic basis (for example, under ion-plasma processing of elastomers and polymers), as the ensuring of good adhesion of the coating is limited by the temperature of its heating. Besides, under operation conditions of modified products the presence of well-defined interface in the "coating base" system, which is a sphere of peak voltage initiation, may cause the loss of their working capacity even initially.

The discussed problem can be solved by receiving NSTCC based on the cascade cross effect (CCE) (fig. 1).

Figure 1. The scheme of an elementary act of the cascade cross effect. Designations: K1, K2 and K3 – cathodes; 1 – ion generated by the cathode K1; 2, 4 – clusters of multicharged ions; 3 – ion generated by the cathode K3; 5 – atom of the film; 6 – adatoms; 7 – atoms of the base material.

The idea of realization of the CCE consists in the ensuring of conditions for development and cascade overlapping of atom-atom collisions concentrated in the boundary layer of the target under pulse ion-plasma action on the processed sample involving three cathodes simultaneously. The thermomechanical pulse under the CCE initiates a variety of the physical phenomena in the surface layers of the samples with coatings. These phenomena are developed for account of high-energy transmission to the bilayer "film base" system by accelerated ions. According to the simulation results, there is a peak value in the field of the interface of the two-phase system on the energy distribution profile (fig. 2). The energy peak under observation promotes the development of diffusion and segregation processes in the field of the interphase boundary. These processes define the composition of elements and the transition area length of forming NSTCC under the cross effect. Thus, the purpose of the given work is theoretical and experimental research of the mass transfer processes, defining the specificity of the interface area formation in the "film-base" system under receiving NSTCC based on the CCE.
Figure 2. Energy distribution profile depending on the depth of penetration of atoms Al. The energy of incident ions $E=35$ keV.

3. Materials and methods
The steel 110M13F was used as a base material in the research. Ion-plasma processing was carried out on the retrofit HHB-6.6 with the use of the specially developed cathodic system$^1$ (See fig. 3). The nanofilm with the INTOM 20$^2$ coating in the order of 30 nm thick was applied on the steel samples after glow-discharge cleaning. The coating is developed on the basis metal of the system Ti-Al-Mo. Under surface supported coating deposition the pulse amplitude was in the order of 5 kV, the pulse duration was in the order of 50–60 $\mu$s, the frequency was 15–25 kHz under constant negative voltage of 1000 V.

Figure 3. The scheme of a cathodic system. Designations: K1, K2, K3 – cathodes; 1 – template; 2 – sample; 3 – sample holder; 4 – reflector; 5 – vacuum chamber; 6 – ion flows.

$^1$ The cathodic system is developed in Omsk Scientific Research Institute of Process and Engine Manufacture.

$^2$ Coating INTOM - 20 (INTOM series) is developed in Omsk Scientific Research Institute of Process and Engine Manufacture.
For the realization of the cross effect high-voltage pulses with the amplitude in the order of 20 kV, the duration of 10-20 µs and the frequency of 10-15 kHz under constant negative voltage of 1000 V were delivered to the substrate. To receive multicharged ion clusters, the reflector of the special structure was used (See fig. 2). The titanic alloy BT5 was used as the material for cathodes; nitrogen was used as a working agent. The chamber pressure was $7 \times 10^{-10}$ mm Hg. The process modeling of profile formation for embedded atoms was carried out by means of the computer program TRIM [9]. The profiles were calculated on the computer IBM-PC/AT-like by processing 10000 trajectories. The initial power of the incident ions was set within 35-50 keV.

The definition of concentration dependences in the field of the interphase boundary was carried out by the method of secondary ion mass spectrometry on the mass spectrometer SAJW-0.5 SIMS. The research of impurity migration processes was carried out using the wave model of mass transfer [10]. To research the structure of the modified layers, the electronic microscope JEOL was used. The researches of the surface morphology after different modes of ion-plasma activation and coating deposition were carried out on the scanning probe microscope NTEGRA Prima in the mode of contact atomic force microscopy (k-AFM).

4. Results and discussion

The simulation results of ion-beam mixing (IBM) are presented in fig. 4. The depth of interpenetration of atoms reaches 5 nm. There is diffusion of both the film atoms into the basis and the iron from the basis material into the film. However, the thickness of the transition area is in the order of 10 nm and it grows with the increase in the ion energy.

![Figure 4](image_url)

**Figure 4.** Distribution of recoil atoms in the “substrate-film” interface vicinity after ion-beam mixing (IBM) by the ions of the titan with the energy of 35 keV (a) and 50 keV (b).

At the same time, the results of the level-by-level analysis of the transition area show (fig. 5) that there is an interpenetration of both the film atoms Ti, Al, Mo and the base atoms Fe, Mn, C. Under the energy of ions E=50 keV the thickness of the layer of nuclear mixing can reach the order of 15-20 nm.
Figure 5. Concentration profiles of element distribution in the field of the interphase boundary for the "film-base" system.

According to the analysis of the experimental results, concentration profiles Ti and Al have peaks, located at the depths, far exceeding the initial depth (fig. 4). This fact gives reason to assume that, besides ion-beam mixing (IBM), wave mechanisms of mass transfer are responsible for the formation of the specified distribution profiles. In accordance with the regulations of the expanded irreversible thermodynamics, using dissipative flows for new independent variables, the basic equation for the description of the wave phenomena in nonequilibrium conditions of the mass transfer is the Maxwell-Cattaneo equation:

\[ J + \tau_D \frac{\partial J}{\partial t} = -D \nabla C, \quad (1) \]

where \( J \) – mass flow, \( \tau_D \) – flow relaxation time, \( D \) – diffusion coefficient, \( C \) – concentration of implanted ions, \( t \) – time.

The contribution of the pressure diffusion into the mass transfer is considered in the generalized equation of diffusion by means of the component \( D_T \frac{\partial P}{\partial x} \), here \( D_T = DV_0/(kT) \) – a thermal diffusion coefficient, \( P \) – pressure, \( V_0 \) – a volume change, which falls on one atom at the expense of the thermal diffusion, \( k \) – Boltzmann constant, \( T \) – an absolute temperature.

The type of the pressure was set in the form of the solitonic pulse,

\[ P(x,t) = P_0 \text{ch}^{-2}((x - st)/x_0), \]

where \( P_0 \) – a shock wave amplitude, \( s \) – propagation velocity, \( x_0 \) - half-width of the wave. The contribution to the change of the components concentration at the expense of the thermal diffusion was considered by means of the component

\[ \frac{k_1}{T} \frac{\partial T}{\partial x} \frac{\partial C}{\partial x}, \]

where \( k_1 \) – thermal diffusion ratio, related to the activation energy of thermal diffusion. The study of the contribution to the radiation-induced mass transfer of the temperature and the pressure gradient was carried out by the variation of the time step \( t \), the shock-wave amplitude \( P_0 \), the period of the pulse initiation \( w_0 \), the number of pulses \( N_i \) and the movement rate \( u_g \) of the flow boundary.

The formula for the coordinate variation of the surface is defined by:
where $u_g(\tau)$ – the speed of the boundary movement at the time $\tau$. The boundary conditions on the moving boundary $w$ were the values of the concentration in the given coordinate at the previous time. The results of qualitative modeling are shown in fig. 6.

Figure 6. Concentration change in the space $x$ and time $t$ coordinates. Simulation modes: a) – the number of pulses $N = 15$; the period of the pulse $f = 5$; the pressure amplitude 30; b) – the number of pulses $N = 25$; the period of the pulse $F = 5$; the pressure amplitude 30.

The findings allow us to note that in each case (fig.6 a, b) the existence of stable dynamical states is observed. According to the simulation results, the transformation of the initial profile reveals a common law, consisting in the formation of expressed maxima at different distances along the surface. All other things being equal to the parameters set, there is a qualitative change in the nature of the profile distribution, namely: the place of the maximum position is shifted deep with the increase in the number of pulses set. Thus, the admixture is localized at a certain depth of the target, depending on the number of pulses.

The analysis of the results shows that under the conditions of the cascade cross-effect the intensification of diffusion processes is observed. Such a manifestation of diffusion phenomena is typical for strongly non-equilibrium conditions. It can be assumed that the PTC creates conditions sufficient for the formation of the thermal spike, in which the local temperature rise can reach the order of ($\approx 10^9$ K/c). Under these conditions, the energy released in the atomic collisions during their existence ($\approx 10^{-12}$ s), does not have time to dissipate from the propagation area of cascades. These factors can contribute to a sharp increase in defects due to the violation of the crystal structure up to the formation of amorphous-crystalline and amorphous structural states that affect the atom mobility because of increasing the diffusion coefficient.

It is known that the grain size has a great influence on the diffusion coefficient [11]. The diffusion coefficient along the grain boundaries can be several orders of magnitude greater than through the
grain. In this regard, the smaller the grain is, the greater the length of the boundaries is, and the more intense the diffusion is. Such influence of grain boundaries is associated with the fact that the crystal lattice at the boundaries is strongly distorted, the boundaries are "loosened" and there is a sufficient number of mobile vacancies. Therefore, the diffusion along the grain boundaries is characterized by lower values of activation energy in comparison with the volume diffusion. In this regard, it can be assumed that the formation of high-defect interfacial and grain boundaries in the cascade cross-effect will contribute to the processes of intense mass transfer. In addition, the observed mass transfer can be carried out by the moving sub-boundaries [10]. In such a case, the contribution of this mechanism will be more significant when they will be present in a greater number. Therefore, the most "beneficial" structure for the enhanced diffusion is a "nanoscale structure". According to the results of the theoretical analysis, carried out in [12], during the relaxation period of grain boundary structures, the creep of the grain boundary dislocations significantly accelerates the diffusion processes, which is characterized by a change in the average diffusion coefficient by 4-5 orders of magnitude. These statements are in good agreement with the results of electron microscopy of multilayer films obtained with the cross-effect. In this case, the thickness of the transition layer can reach the values in the order of 20 nm, commensurate with the thickness of the applied nanofilm, equal to 30 nm (Fig. 7).

![Figure 7](image.png)

*Figure 7.* Electron-microscope image of a multilayer film with the selected fragment of the film layers (1) and the transition layer (2); (×50 000). Designations: 1 – nanofilm area; 2 – transition area between the nanofilms.

5. Conclusion

Based on the theoretical and experimental researches, the peculiarities of formation of nanostructural topocomposite coatings obtained in terms of the cascade cross effect are studied. It is shown that the specificity of the coating formation under these conditions is caused by the intensification of mass transfer processes in the field of the interphase boundary in the “film-base” system. These processes lead to the formation of the transition area due to the mutual diffusion of the film elements and the base, determined by the atomic mixing, the wave mass transfer mechanism and the enhanced grain boundary diffusion. The use of the cascade cross effect significantly extends the technological capabilities of designing and obtaining nanostructural topocomposite coatings, including multilayer ones. When assigning the appropriate modes of the pulse action it is possible to create multilayer compositions of a different structure with the thickness of the transition layers, commensurate with the thickness of the nanofilms. The obtained compositions are characterized by the absence of the expressed interphase boundaries in the "film-base" system, which allows us to reduce the factor of localization of peak voltages in the transition area during the use of products based on the 110M13F steel under dynamic and shock actions.
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