Long-range action effects in the formation of nanostructured topocomposites under the impact of combined ion-plasma flows

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Abstract. The article updates the long-range action effect in the formation of nanostructured topocomposites under the conditions of the ion-plasma impact. The authors study the features of the concentration dependences of the distribution of elements in the boundary layers in the formation of the two-layer system "film-base". They determine that under the conditions of the implementation of the cascade cross-effect at considerable depths in the material of the hard-alloy base, locally inhomogeneous areas are formed, resulting in an increase in the microhardness of the material. Within the framework of the worked out simulation model, the study of factors contributing to the manifestation of the long-range action effect is undertaken. The contribution to the change of concentration dependences of the temperature, different diffusion mechanisms and the pressure gradient is established and differentiated. Based on the synthesis and analysis of the dynamics of the competing processes of "deceleration - acceleration" of the diffusion, the explanation to the formation of the hardened sublayers in the hard-alloy base of topocomposites and their role in the manifestation of the long-range action effect is offered.

1. Introduction

The fundamental and applied significance of the long-range action effect (LRAE) appearing in the interaction of energy flows with the solid surfaces, and consisting in changing the structure and properties of solids at depths significantly exceeding the area of primary energy release [1-7], is on top of its relevancy. LRAE manifestations are associated with an increase in the density of defects at depths significantly exceeding the ion range, abnormal diffusion, change in the microhardness of the material to several hundred micrometers from the surface.

By now, a large experimental material has been accumulated, indicating the manifestation of the long-range action effect in various types of surface treatment of metals and alloys: ion-beam, ion-plasma, laser and others. However, a generalized model of this effect has not been developed yet, and the hypotheses of the proposed mechanisms of LRAE are being discussed by the researchers.

Thus, the authors [1] associate the cause of LRAE with the formation of hypersonic waves when an accelerated ion interacts with the surface due to a "microexplosion" that generates a primary high-frequency acoustic wave. Propagating through the material, the primary wave encounters extended defects on its way, causes their restructuring, which is accompanied by the emission of secondary waves and so on.

In the works [5, 6, 8, 9] it is stated that the long-range action effect is associated with the formation of a developed dislocation structure in the boundary layers of the target and is observed in pure metals with a low yield point, as well as in wrought alloys with a high level of plasticity. According to the authors, static and dynamic stresses are the main cause of LRAE in the implanted materials. The level of static stresses in the doped layer according to the calculated estimates can significantly exceed the yield point of the target material, which, apparently, results in the development of plastic deformation of the deep layers [9]. At the same time, when discussing a number of the results obtained, the researchers note another reason related to the propagation of elastic waves in the material and their interaction with the imperfections of the crystal lattice [10, 11].

From the perspective of the percolation model LRAE is interpreted as a result of the critical behavior of the amorphized (defective) layer. According to the provisions of this model, the defective layer located at the depth of the maximum possible ion range is a quasi-plane discontinuous "cloud" of the amorphized areas of different sizes. Then, at a critical radiation dose, the part of the areas is combined, and a percolation cluster of the amorphized layer appears in the crystal. The cluster creates a long-range stress field. The model enables to explain the observed non-monotonicity in the dependences of the properties of the sample on the radiation dose, namely, with the increasing of the dose there is a loss of cohesiveness of the areas of the certain degree of disorder with others. As a result, they are replaced by a percolation cluster of more disordered areas. This process occurs many times under irradiation, which causes a fluctuation in the magnitude of mechanical stresses, manifested in the form of non-monotonic changes in the properties of the irradiated sample, in particular, in microhardness.

The above interpretations of the long-range action effect, as a rule, do not apply to the layer systems, while the problems of obtaining multiple-layer, multilayer and gradient structures by ion-beam and ion-plasma processing, including nanostructured topocomposites, are relevant [12].

2. Problem statement

Currently, nanostructured topocomposites are obtained by means of several stages of the ion-plasma action, which is accompanied by fragmentation and development of the highly defected structure of surface layers with the formation of nanocluster fragments on their surface [13]. The authors' approach, focused on getting topocomposite nanostructured coatings in terms of cross-cascade effect (CCE) [14], updates studying LRAE.

Of special interest is the study of the processes of evolution of surface structural-phase states arising in the conditions of CCE. It consists in the processing of materials simultaneously by three streams of ionized plasma under different angles relative to the surface of the sample. Its physical nature consists in overlapping cascades in the interaction of multidirectional flows of atoms, promoting thermal spikes and the transfer of the target of thermomechanical pulses. Previously, it was found [14] that in this case the conditions for the development and for the cascade overlapping of atom collisions localized in the boundary layer under the thermomechanical pulses initiating the processes of diffusion and segregation in the area of the interface are created. It was observed that it results in the formation of the transition area of the interface due to the mutual diffusion of the elements of the film and the base. However, there was no special study of the area of the possible impact of CCE.

Thus, the purpose of this work was theoretical and experimental study of the processes, defining the area of CCE impact and the study of the manifestation mechanisms of the long-range action effect in terms of CCE under the formation of nanostructured topocomposites.

3. Materials and methods

As a base material, hard alloys of the brand VK8 of the WC-Co system were used. The formation of nanostructured composites was carried out at the HHB-6.6 installation using a three-cathode system [15]. The ion-plasma effect was realized in several stages. At the first stage, the samples were cleaned

in the glow discharge. At the second stage, the films of Ti-Al-N composition with a thickness of about 30 nm were applied. The third stage of ion-plasma processing was carried out using three cathodes located under different angles relative to the processed surface. During the deposition of the coating on the substrate, the amplitude of the voltage pulses was about 5 kV, the pulse duration was about 50-60 µs, the frequency was 15 – 25 kHz at a constant negative voltage of 1000 V.
To implement the cross effect, high voltage pulses with an amplitude of about 20 kV, a duration of 10-20mks and a frequency of 10 – 15kHz at a constant negative voltage of 1000V were applied to the substrate. To obtain clusters of multicharged ions in the flow, a reflector of a special design was used. Nitrogen was used as the working substance. The pressure in the chamber was $7 \cdot 10^{-6}$ mm Hg. The modeling of the formation processes of the profile of embedded atoms was carried out using the computer program TRIM [16]. The profiles were calculated on a computer of the IBM-PC/AT type by processing 10000 trajectories. The initial energy of the incident ions was set within 35 – 60 keV. The determination of concentration dependences in the area of the interface was carried out by the method of secondary ion mass spectrometry on the mass spectrometer SAJW-0.5 SIMS. The microhardness tester PMT-3 with the Vickers diamond pyramid and nanoindenter “NANO G200” determines the microhardness (H) and the depth of indentation (h).

4. Results and discussion

The results of modeling of ion-induced processes in the two-layer system for the conditions of the incidence of the ions along the normal to the surface of the processed material are shown in Figures 1-3.

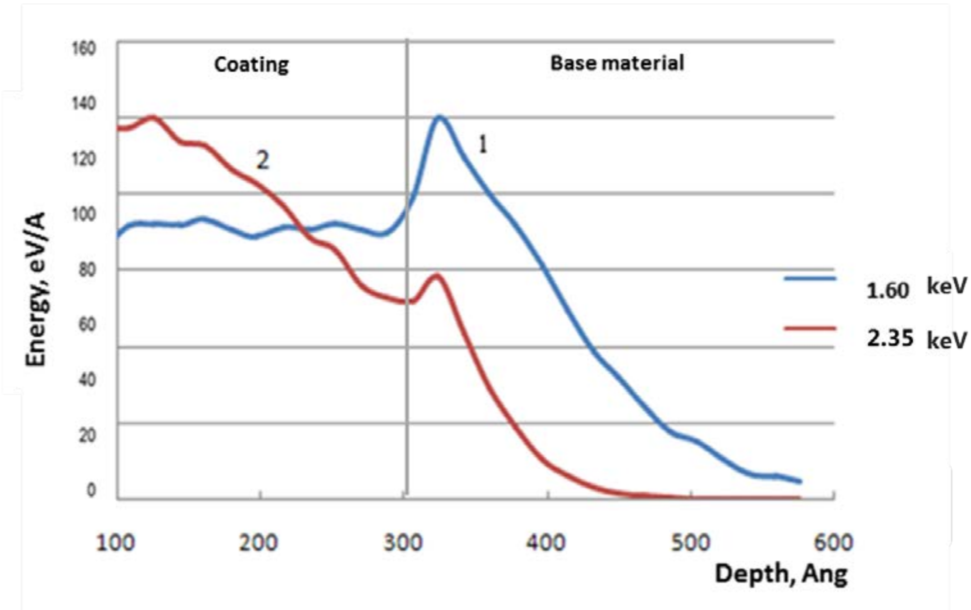


Figure 1. Distribution of the absorbed energy in the two-layer system "film-base" at different energies of incident ions at an angle $\alpha = 90^0$. Designation: 1 – ion energy E = 60 keV; 2 – ion energy E = 35 keV.

When you change the angle of incidence, the nature of the dependencies remains unchanged. The maxima of the distribution of the recoil atoms and the energy transferred to the recoil atoms are closer to the surface when the beam falls at an angle of 45 than under the normal incidence of the beam.

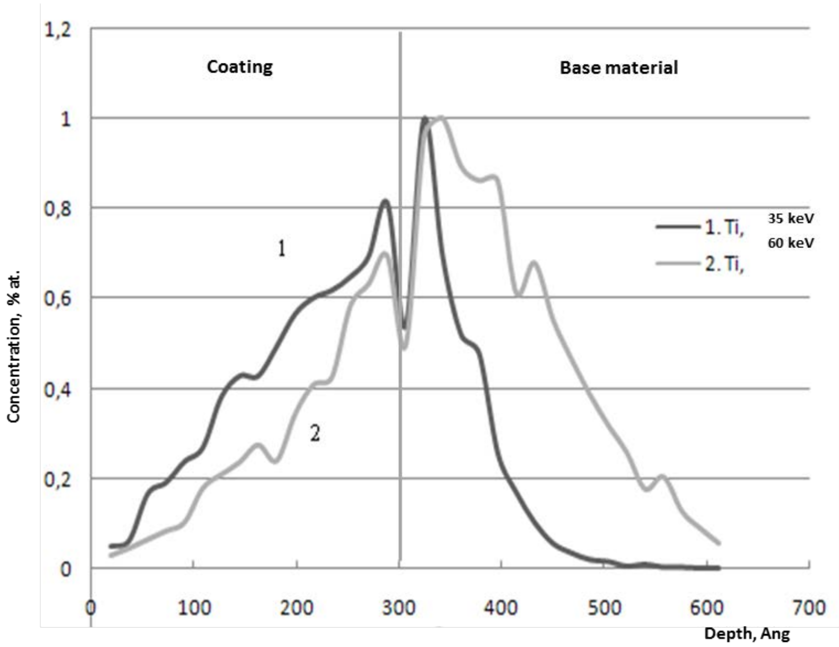


Figure 2. Distribution of titanium in the depth of the two-layer system "film-base" at different energies of incident ions at an angle α = 90^0. Designation: 1 – ion energy E = 35 keV; 2 – ion energy E = 60 keV.

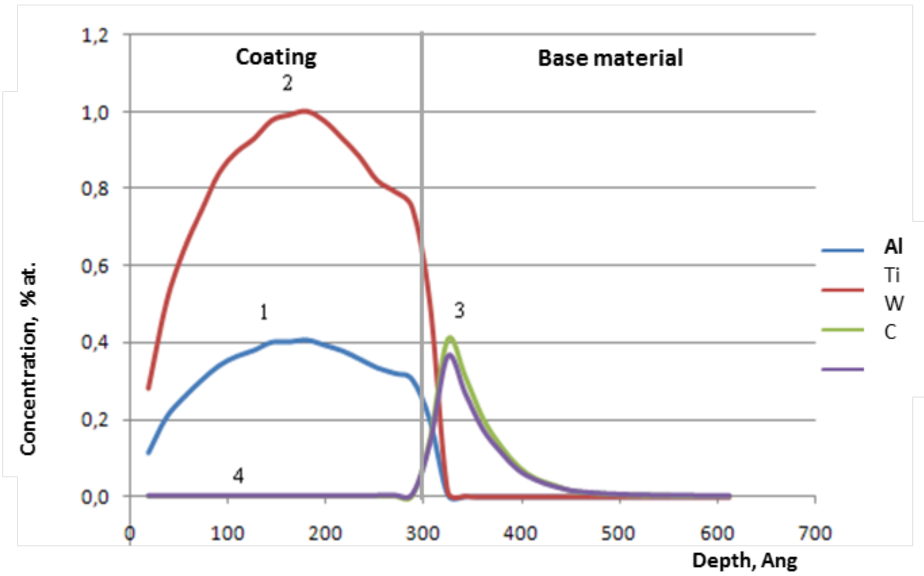


Figure 3. Depth distribution of recoil atoms in the two-layer "film-base" system at the energy of incident titanium ions E = 35 keV at an angle of incidence α = 90°.

The data obtained, according to the simulation results, allow us to note that the formation of concentration profiles shows a single pattern, consisting in the formation of pronounced maxima for the distribution of incident ions, recoil atoms and the energy transferred by the incident ion to recoil atoms at different distances from the surface. All other things being equal, the parameters are set for qualitative and quantitative changes in the nature of the distribution of the profile, namely, the position of the maxima is shifted deep with the increase in the energy of the incident ions both with the normal fall of the ion beam and at an angle < 90. Thus, both the impurity itself and the recoil atoms, together with the acquired energy, are unevenly localized in the depth of the target, depending on the modes of action.

The results of the model experiment are consistent with the results of the study of the elemental composition of the boundary layers of the two-layer system. On the concentration dependences of Ti and Al on depth distribution, maxima that are located at the distances from the surface are found, which are many times higher than the data of the model experiment (Fig. 4 a, b). At the same time, on the experimental dependences, the manifestation of local concentration inhomogeneities is noticeable, which gain in magnitude with the increase in the time of ion-plasma processing (Fig. 4 b).

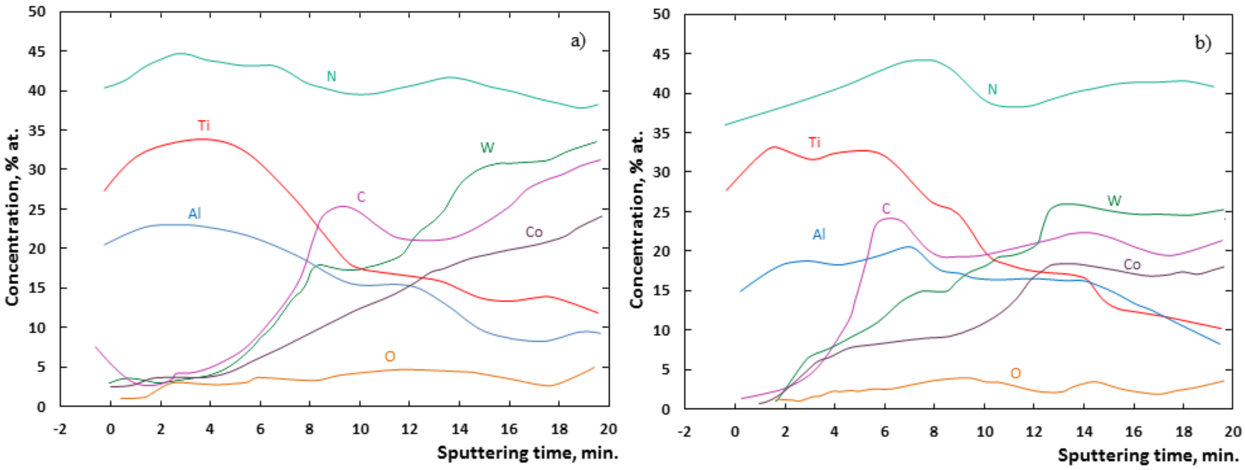


Figure 4. Concentration profiles of the elements distribution in the area of the interface of the "film-base" system.

The results of the microhardness change in depth are shown in Fig. 5. It can be seen that they also differ in the non-monotonic nature of the distribution with the pronounced maxima. These data suggest that in addition to ion-beam mixing, wave mechanisms of mass transfer contribute to the formation of these distribution profiles.

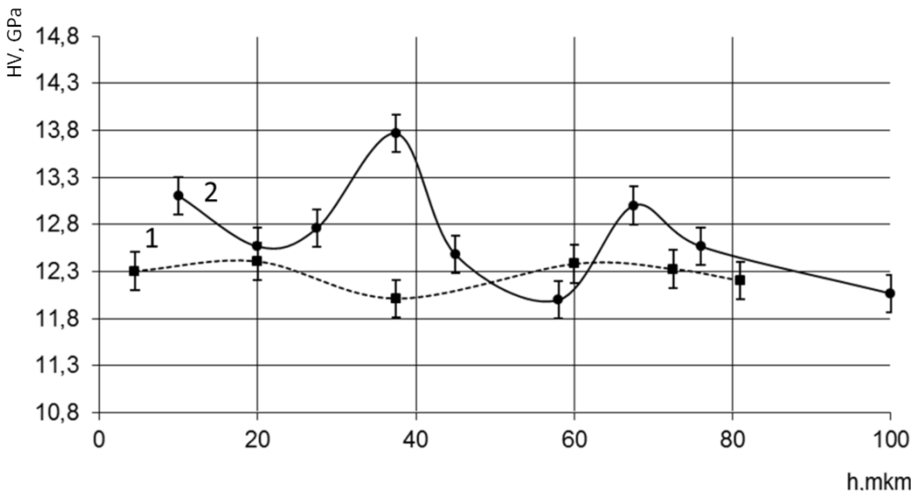


Figure 5. Change of microhardness in the depth of the film-base sample under ion-plasma action depending on the processing time. Designations: 1 – dependence of microhardness change after ion-plasma processing for 10 min; 2 – dependence of microhardness change after ion-plasma processing for 20 min.

The observed manifestations of the long-range action effect in the two-layer “film-base” system can be due to the structural sensitivity of the base material, in which a significant role in enhanced mass transfer belongs to the grain boundaries [17 - 20]. Since the configuration of grain boundaries and dislocations changes under the ion-plasma impact, the contribution of diffusion over extended defects can significantly increase.

Since the defective structure of solids strongly affects the processes of mass transfer [18, 19], the presence of inhomogeneities of hard alloys containing a wide range of different defects can significantly change the speed and sometimes the direction of intergranular diffusion developing in the field of elastic stresses of moving grain boundaries in the presence of the atmosphere of impurity atoms. As it was shown earlier, the observed inhomogeneities on the concentration profiles in the study of the processes of diffusion of impurity atoms along the grain boundaries may be due to the fact that "large" particles due to the elastic interaction with the boundary are decelerated by the latter, and "small" – are accelerated.

The dynamics of "deceleration - acceleration" processes of diffusion is well explained based on the known mathematical models of diffusion [21]. At the initial stage of ion-plasma processing, the density of extended defects is small. Migration of grain boundaries occurs in accordance with the kinetics of the type B. Diffusion of impurity atoms occurs on the low-defect volume of the material. The prevailing mechanisms of diffusion are volume diffusion and diffusion along isolated migrating grain boundaries [17, 19, 21], which determine the specificity of the distribution profile of impurity atoms. With the increase in the duration of the ion-plasma processing, the density of defects increases. In this case, there is an overlap of the volume diffusion fields due to individual dislocations and adjacent grain boundaries. As a result, the predominant diffusion mechanism is changed: the mechanism of the "type B kinetics" is changed to the mechanism of the "type A kinetics" [21].

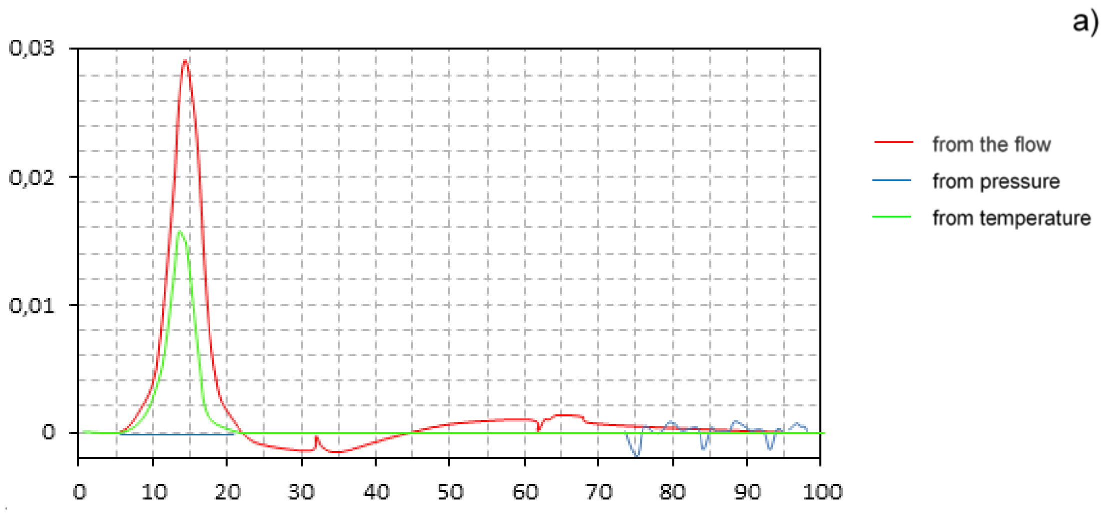
In the conditions of ion-plasma processing of the two-layer system with the use of CCE, which promotes intensive defect formation and development of diffusion phenomena, such processes become more pronounced and can lead to the formation of local boundaries separating the areas of compression and stretching at the micro level in addition to the boundary of the "film-base". It is the presence of these boundaries, in our opinion, that leads to the observed inhomogeneities located at depths significantly exceeding the calculated penetration depth of impurity atoms (Fig. 4).

To confirm this assumption based on the simulation model of mass transfer [14], a model experiment was conducted, which consists in studying the effect of radiation-stimulated mass transfer of temperature and pressure gradient on the nature of the distribution of concentration dependences. In the radiation-stimulated mass transfer model, the structural heterogeneity of the irradiated material is taken into account by varying the diffusion coefficient along the depth of the two-layer “film-base” system. When simulating the processes of multiple ion-plasma effects in the pulse mode, the initial concentration profile was taken as the initial distribution. This factor was taken into account by introducing a "moving" boundary. The current values of the coordinates of the surface were described by the expression:

$$w = \int_0^t u_g(\tau)\partial\tau$$

where $u_g(\tau)$ is the velocity of the boundary corresponding to the time τ.

On the moving boundary, w concentration values in this coordinate at the previous time were set. The contribution of the temperature and the pressure gradient to the change of the concentration profiles were evaluated by varying the time step *t*, the wave amplitude P_0, the period of occurrence of the pulse w_0, the number of pulses N and of the velocity u_g of the movement of the flow boundary. The results of the model experiment are shown in Figure 6.



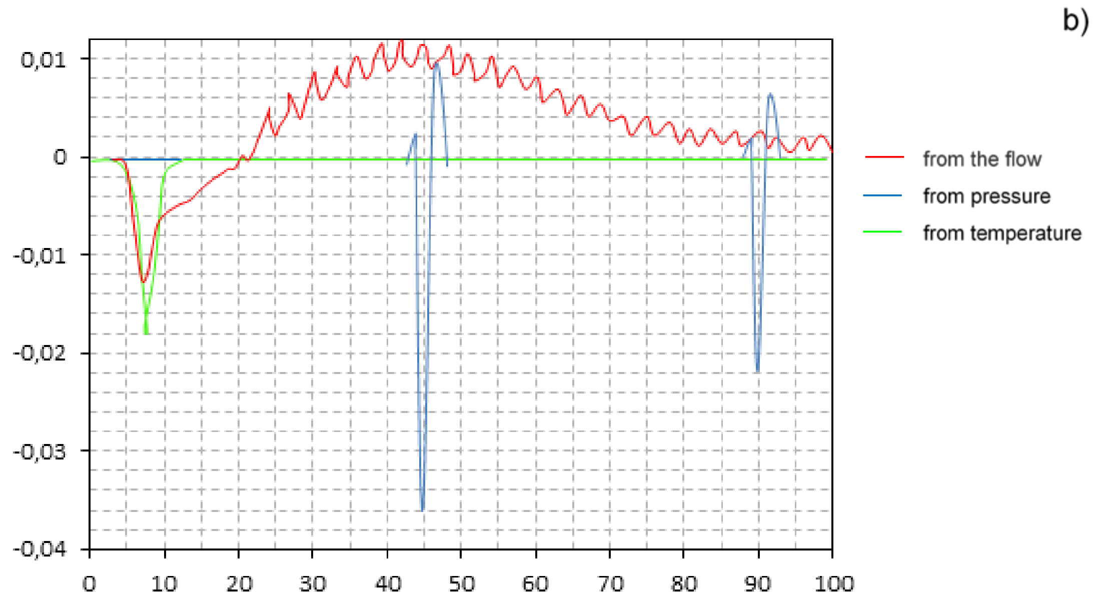


Figure 6. Change of concentration in the coordinates of space x and time t taking into account the contribution to the mass transfer of the temperature factor, the diffusion and the pressure gradient. Simulation modes: a) - the number of pulses N = 20; the pulse supply period F = 50; the pressure amplitude is 30; b) - the number of pulses N=60; the pulse supply period F = 50; the pressure amplitude is 30.

The analysis of the presented dependences allows us to note that, other things being equal, but fewer pulses, the contribution of temperature is noticeable (Fig. 6 a), while their increase in three times leads to a radical change in the nature of the distribution (Fig. 6 b). The dependences acquire a locally-wave character. The contribution of temperature is leveled, but the contribution of pressure becomes noticeable. It is not possible to explain such a character of concentration profiles within the existing models of the long-range action effect. However, judging by their character (Fig. 6 b), the transfer process was activated by additional sources formed in the process of the ion-plasma impact over time under the conditions of competing diffusion mechanisms caused by the changing nature of the structural sensitivity of the base material – hard alloy.

In the first approximation, this is due to the shift of the mechanisms of the grain boundary diffusion: there is a change in the "kinetics of the type B" on the "kinetics of the type A", and vice versa [21]. The number of sub-boundaries increases significantly over time. Consequently, the contribution of the mass transfer mechanism carried out by moving sub-boundaries is significantly increasing. In addition, relaxation mechanisms are practically leveled, apparently, because of increasing the time of ion-plasma action under CCE conditions, additional boundaries are formed, consisting of hardened sublayers with a high density of practically stationary extended defects stabilized by impurity atoms.
The observed in Fig. 6b sharp drops and subsequent jumps in the nominal values of the pressure parameter in a narrow range witness in favor of this statement. Thus, on the one hand, under certain modes of implementation of CCE, determined mainly, with other equal parameters of the impact to the processing time, there is the formation of insurmountable barriers because of the interaction of impurity atoms and defects formed during irradiation. On the other hand, when exceeding a certain threshold value of the defect concentration, depending on the time of impact, these layers begin to function as additional extended sources of defects, "injected" into the deep layers. Most likely, the process of "injection" is implemented with the participation of two mechanisms: the Coble mechanism, not directly related to the displacement of dislocations along the grain boundaries, and the Hall-Petch mechanism, characteristic of layers with structural (in the form of grain boundaries, phases, etc.) barriers. This can be confirmed by the results of a theoretical study conducted in [22], according to which the crawling of grain boundary dislocations during the relaxation period significantly accelerates the diffusion processes. In this case, the change in the average diffusion coefficient can increase by 4-5 orders of magnitude.

5. Conclusion

Conducted theoretical and experimental studies of the manifestation of long-range action effects, related to the formation of nanostructured topocomposites, revealed their characteristic features. In particular, it was found that the effect of combined ion-plasma flows intensifies the phenomena of diffusion mass transfer, including recoil atoms, as a result of which the penetration of impurity atoms to depths significantly exceeding the calculated values is detected. In addition, an increase in microhardness was recorded in the hard-alloy base, the distribution of values of which is characterized by the non-monotonic character and the presence of alternating highs and lows.
The study of the causes of the observed regularities made it possible to establish the factors and the mechanisms responsible for the anomalously deep penetration of impurity atoms and to reveal the relationship of non-monotonic dependences of microhardness with the change of prevailing mechanisms depending on the time of ion-plasma action on the two-layer "film-base" system. It was shown that the formation of hardened layers located at considerable depths is due to the specificity of the structural-phase composition of the hard-alloy base, which varies because of the change of diffusion kinetics mechanisms. In addition, when exceeding a certain threshold concentration of defects, depending on the time of impact, these layers can serve as the additional extended sources of defects, "injected" into the depth. The identified manifestations of the long-range action effect in the future will allow you to obtain new types of nanostructured topocomposites with the gradient-multilayered structure.

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Acknowledgments

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