Preferential sputtering of alloys by gas cluster ions

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Topography and composition of the surface of nickel-based alloys under irradiation with Ar_{2500}^+ cluster ions with the energy of 20 keV, and atomic Ar^+ ions with the energy of 3 keV have been studied. It has been experimentally found that the surface of the alloys is depleted by a component with a lower binding energy. It is shown that the change in the surface concentrations of the alloy components upon irradiation with cluster ions is an order of magnitude greater than upon sputtering with atomic ions. The degree of change in the surface composition is determined by the ratio of the sputtering yields of the alloy components.

Keywords: gas cluster ions, ion sputtering, XPS, preferential sputtering, surface topography.

Introduction

Interest in the processes of interaction of gas cluster ions with solids is due to the role that particle beams play in modern fundamental research and practical applications. Over the past two decades the gas cluster ions beams have been successfully used both for modification (ultra-precise polishing, implantation at ultra-low depths) [1–5], and for surface analysis by secondary ion mass spectrometry (SIMS) [6,7] or X-ray photoelectron spectroscopy (XPS) [8,9]. Numerical simulations of the processes occurring during such interaction are carried out by several scientific groups [10,11]. One of the key issues of these studies is the issue of preferential sputtering of one of the components during the irradiation of targets with a complex composition by cluster ions.

Thus, in [12] the components concentration profiles of the layer Ta_2O_5 grown on tantalum foil were studied using atomic ions Ar^+ and cluster ions Ar_{1000}^+. It was found that the preferential sputtering of oxygen caused by Ar_{1000}^+ ions with an energy of 6 keV was less than in the case of Ar^+ ions with an energy of 3 keV and 500 ev. Other authors studied the composition of the $SrTiO_3$ layer deposited on a silicon substrate using Ar_{300}^+ clusters with an energy of 8 keV, and Ar^+ ions with an energy of 500 eV [13]. When profiling with clusters, the ratio of the Sr concentration to the Ti concentration was much closer to the expected value 1 : 1, while in the case of profiling with atomic ions, this ratio reached 0.75 : 1. Moreover, in the work [14] it was shown that the damaged layer that appeared on the surface of PET (polyethylene terephthalate) and PTFE (polytetrafluoroethylene) polymers upon irradiation with Ar^+ ions with energy of 1 keV was removed using Ar_{1500}^+ cluster ions with energy of 10 keV. Thus, the authors found absence of selectivity during polymers sputtering by cluster ions.

However, in the same paper a significant depletion of the surface of the semiconductor compound $Cu(InGa)Se_2$ by selenium was found upon irradiation with Ar_{1500}^+ cluster ions with energy of 10 keV. A strong enrichment of the InP compound surface with indium was also observed upon bombardment with Ar_{300}^+ clusters with energy 8 keV [15].

Thus, it is clear that a complete understanding of the role of preferential sputtering during formation of the surface composition of multicomponent materials upon irradiation with cluster ions has not yet been achieved. For example, we recently studied the preferential sputtering of Pd from Ni_5Pd and NiPd alloys by argon cluster ions [16]. In the present paper, the influence of the concentrations of alloy components on the composition of its surface is studied in more details.

Besides, the study of the role of the ratio of the surface binding energies of the alloy components in the formation of a layer modified by irradiation represents interest. For this purpose, the effect of irradiation with cluster ions on the surface composition of the NiMoRe alloy was studied. Note that the lightest component (Ni) in this alloy, in contrast to Ni_xPd_y alloys, has the lowest surface binding energy.

1. Materials and methods

Polycrystalline samples of Ni_5Pd, Ni_3Pd, NiPd, $NiPd_3$ and $NiPd_5$ alloys, as well as NiMoRe (86−10.5−3.5 at.%)) purity 99.99 at.% were cut out in the form of rectangular plates with dimensions of 4×10 mm and 2 mm thick. The surface of the samples was mechanically polished and cleaned in organic solvents. The volume concentration was monitored using a scanning electron microscope (SEM) with an attachment for energy dispersive X-ray micro-analysis.

Experiments on the irradiation of samples with cluster ions and the study of the surface composition using XPS were carried out *in situ* on PHI 5000 Versa Probe II unit (company ULVAC-PHI) equipped with a source of gas cluster ions. Beams of cluster and atomic ions were directed at an angle of $55°$ from the perpendicular to the surface. The samples were irradiated with Ar_{2500}^{+} cluster ions with energy of $20\,keV$ and current of $80\,nA$ or Ar^{+} atomic argons with energy of $3\,keV$ and current of about $2.5\,\mu A$. The value of the residual pressure in the sample chamber before the start of the experiment and during XPS measurements was in the range of $10^{-8}\,Pa$, and during irradiation with cluster ions — in the range of $10^{-5}\,Pa$. Before the experiment the surface of the sample was cleaned with Ar_{2500}^{+} cluster ions with energy of $5\,keV$.

To determine the surface composition depending on the ion irradiation dose, the ion beam was turned off, and Ni $2p3$ and Pd $3d$ peaks were measured for the alloys Ni_xPd_y or Ni $2p3$, and Mo $3d$ and Re $4f$ peaks for NiMoRe alloy. The energy measurement ranges also included the first plasmon peaks. The atomic concentration of the components was determined based on PHI elemental sensitivity factors corrected for the instrument's transmission function. When determining the integral intensity of photo-electron lines (peak areas), the background was subtracted by the Shirley method. The size of the measurement region was set by the diameter of the monochromatized X-ray radiation Al K_α ($h\nu = 1486.6\,eV$) and was $200\,\mu m$. The measurements were carried out in the center of the rectangular region of the ion beams raster. In the case of cluster ions the size of the region was $1 \times 1\,mm$, in the case of atomic ions it was — $2 \times 2\,mm$.

The surface topography of the samples before and after irradiation was monitored using a Zeiss Ultra-55 SEM.

2. Results and discussion

2.1. Composition and topography of the surface of alloys Ni_xPd_y

Alloys Ni_5Pd, Ni_3Pd, $NiPd$, $NiPd_3$, and $NiPd_5$ were irradiated with a beam of Ar_{2500}^{+} cluster ions with energy of $20\,keV$, incident at an angle $55°$ from the perpendicular to the surface. For each alloy XPS recorded the surface composition vs. the ion irradiation dose. On Fig. 1, *a* „negative" dose corresponds to the nickel concentrations before the start of the experiment, „zero" dose — to the surface composition after cleaning. It can be seen that the cleaning almost did not change the ratio of nickel and palladium. Then the surface composition very quickly reaches the bulk value, and then the dependence of the nickel concentration on the irradiation dose is well approximated by an exponential function. The concentrations of the components determined after reaching the steady state are shown in Fig. 1, *b*. It also presents our experimental data on the surface composition of the NiPd alloy after irradiation with Ar^{+} atomic ions with energy of $3\,keV$, obtained using
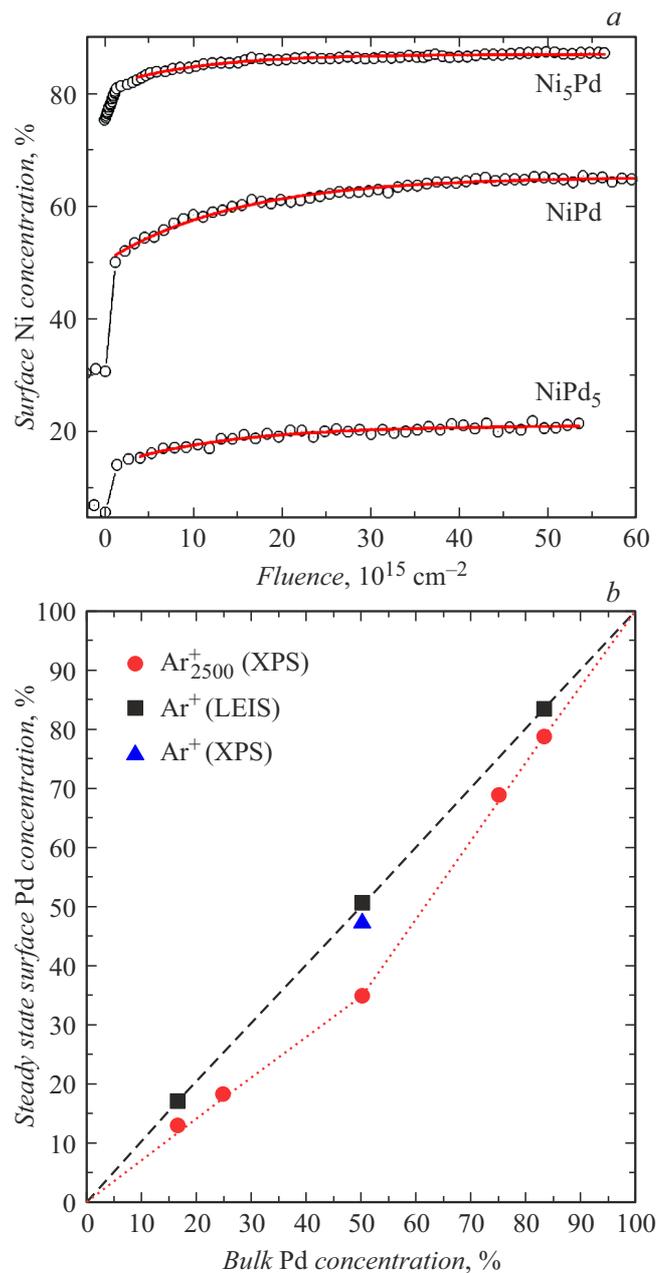
Figure 1. *a* — evolution of the nickel concentration on the surface under irradiation with cluster ions and its exponential approximation (solid lines); *b* — equilibrium concentration of palladium on the surface C_{Pd}^{s} vs. its volume concentration C_{Pd} for Ni_xPd_y alloys. Experimental statistical errors are within marker size. Low energy ion scattering (LEIS) data taken from [17].

XPS, as well as data on the surface composition of Ni_xPd_y alloys after irradiation with Ar^{+} atomic ions with energy of $3\,keV$ obtained using the low energy ion scattering (LEIS) method in [17].

Note that the diagonal shown in Fig. 1, *b* with a black dashed line corresponds to the absence of preferential sputtering. As can be seen from the Figure, for all the studied samples irradiation with cluster ions leads to a

much stronger depletion of the surface with palladium compared to irradiation with atomic ions. It is also clearly seen that with the volume concentration of palladium increasing in the initial sample, the deviation of the surface concentration of palladium on the irradiated sample from the volume concentration increases when going from Ni_5Pd to NiPd. The experimental data in this region are well approximated by the linear dependence (red dotted line (in the online version)). The strongest effect of preferential sputtering is observed in the case of an alloy with equiatomic composition: the palladium concentration on the surface decreases to 35 at.%. Further, as can be seen from Fig. 1, *b*, the degree of surface depletion with palladium as a result of irradiation decreases when going from NiPd to $NiPd_5$. In this region, the palladium concentration on the surface of the irradiated samples is also well approximated by a linear dependence, the slope of which differs from the approximation for $Ni_5Pd-NiPd$ alloys.

In order to understand the reasons for this behavior of the palladium concentration on the irradiated surface dependence on the initial composition of Ni_xPd_y alloy, the following experiments were carried out. First of all, the surface composition of the NiPd alloy was also determined for irradiation with Ar_{2500}^+ cluster ions along the perpendicular to the sample surface. Experiments shown that in this case the surface is also significantly depleted with the palladium, and the palladium concentration, as in the case of an oblique incidence of the ion flux, reaches a value of 34%.

Next, the topography of the alloys surface was studied after irradiation with argon cluster ions at an angle of 55°. The results of these studies for the NiPd sample are shown in Fig. 2, *a*.

SEM images showed that as a result of irradiation almost the same relief was formed on the surface of all samples of alloys of different composition. In this case of normal incidence of the ion beam, the surface roughness decreased in comparison with the initial value. Consequently, the dependences shown in Fig. 1, *b* cannot be explained by differences in relief.

It is known that two competing processes are responsible for the formation of a stationary surface composition upon irradiation with atomic ions: the preferential sputtering of one of the components as a result of the development of cascades of atomic collisions, on the one hand, and radiation-induced segregation, on the other hand. Our previous experiments [16] and the results shown in Fig. 1 demonstrate that the process of preferential sputtering of alloys under irradiation with cluster ions has much in common with the case of sputtering with atomic ions. The effect of preferential sputtering, i.e., the surface concentration of the components, depends on the irradiation dose. Moreover, palladium, whose atomic weight is higher than that of nickel, — component with lower binding energy on the surface — segregates to the surface and sputters predominantly.
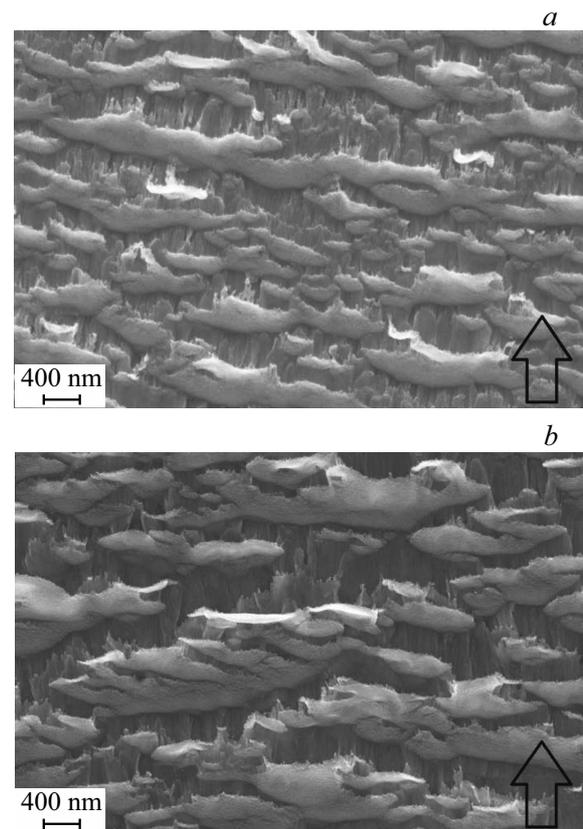
Figure 2. Topography of the NiPd (*a*) and NiMoRe (*b*) surfaces after irradiation with Ar_{2500}^+ cluster ions. The direction of incidence of the ion beam is indicated by the arrow.

To test these assumptions, we studied the dose dependence of the surface composition in the case of irradiation of the NiMoRe alloy, in which nickel has the lowest binding energy on the surface.

2.2. Surface composition of NiMoRe alloy

The surface concentration of the components of the NiMoRe alloy dependence on the ion dose, measured for a sample irradiated with Ar_{2500}^+ cluster ions is shown in Fig. 3. The flow of ions with energy 20 keV impinges at an angle 55° from the perpendicular to the sample surface.

It can be seen from Fig. 3 that the stationary sputtering mode is not achieved even at an irradiation dose of about 10^{17} ion/cm². Approximation of the dose dependences of the component concentrations by exponential functions shows that the irradiation dose of about $4 \cdot 10^{17}$ ion/cm² is required to reach the steady state.

Moreover, it can be seen from Fig. 3 that nickel, the lightest component of the alloy and the component with the lowest binding energy, is predominantly sputtered from the NiMoRe alloy. In the case of NiMoRe irradiation the changes in the surface concentration of the components are much more significant compared to the irradiation of Ni_xPd_y alloys: the nickel concentration decreased by
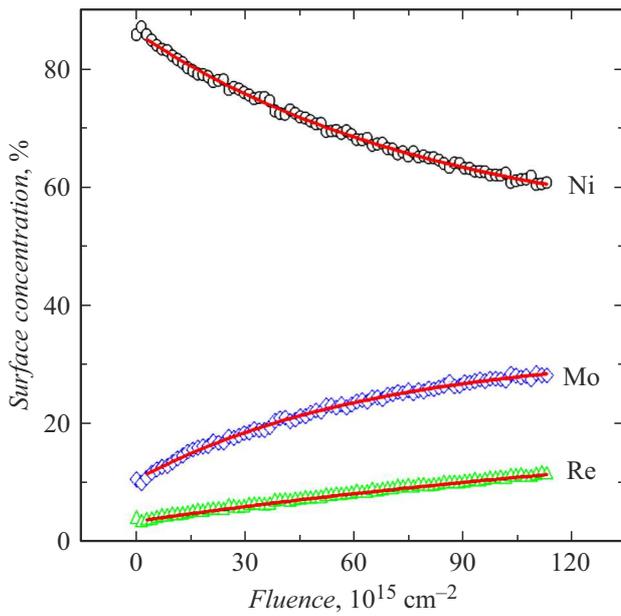
Figure 3. Surface concentrations of the NiMoRe alloy components vs. ion dose and their exponential approximations (solid lines).

Table 1. Surface composition of NiMoRe alloy

Component of alloy	Volumetric concentration, at.%	After irradiation with cluster ions, at.%	After irradiation with atomic ions, at.%
Ni	86	51.2	82
Mo	10.5	32.2	14
Re	3.5	23.4	4

Note. Stationary concentrations are obtained from exponential approximations of dose dependences. Data on irradiation with Ar^+ atomic ions with energy 4 keV are taken from [17].

about 35%, and the concentrations of molybdenum and rhenium increased by more than 2 times. (Table 1).

Thus, the experiments also showed that in the case of the NiMoRe alloy irradiation with cluster ions the surface composition changes more significantly than when irradiated with atomic ions.

2.3. Effect of preferential sputtering upon irradiation with cluster ions

When describing the experiment results, it was noted that the processes of the surface composition formation of alloy targets under the bombardment with atomic or cluster ions have both common features and significant differences. Before proceeding to a discussion of the results presented above, let us briefly review the ideas about preferential sputtering that were developed to date.

Preferential sputtering of Cu from the Cu_3Au alloy upon irradiation with low-energy Ar^+ ions was first observed by Gillam in 1959 [18]. He discovered that the preferential sputtering of Cu atoms leads to the formation of a near-surface changed layer, the composition of which differs from the composition of the bulk, and this layer thickness is comparable to the penetration depth of the bombarding ions.

However, only in the mid-1970s, when surface-sensitive methods of analysis began to be actively developed, the fundamental nature of the problem of sputtering of multi-component materials was realized, and extensive studies of the processes responsible for the formation of the modified layer began. It was found that the depth distributions of component concentrations of Ni-based alloys components formed under the action of low-energy ion bombardment at elevated temperatures are nonmonotonic [19–21]. For example, using Auger electron spectroscopy it was found that the uppermost surface layer of the CuNi alloy becomes enriched with Cu upon irradiation with Ar^+ ions with energy of 5 keV [19]. Since the Cu atoms were predominantly sputtered, the Gibbs segregation made up for the loss of Cu in the uppermost layer, leading to the depletion of the second and deeper subsurface layers. Thus, it was clearly demonstrated that Gibbs segregation, together with the preferential sputtering effect, is responsible for the composition formation of the changed layer.

At the same time, in experiments on the sputtering of AgAu and CuPt alloys in the linear cascade mode at target room temperature, when Gibbs segregation practically does not occur, it was found that the angular distributions of the sputtered components are nonstoichiometric by emission angles [22,23]. For example, in the case of CuPt alloy sputtering by Ar^+ ions with energies of 20 and 80 keV, platinum was predominantly sputtered along the perpendicular to the sample surface, while copper was sputtered at large emission angles. An attempt to explain these experimental data was made in [24]. In this paper, within the framework of the linear cascade theory it was shown that if there is a component concentration gradient in the upper layers of the target, then the angular distribution of the component that is depleted in the uppermost layer will be extended along the perpendicular to the surface, while the angular distribution of the other component enriched in the uppermost layer will be wider. And although the theory predicted an insignificant effect of preferential sputtering along the perpendicular to the surface, based on this theoretical consideration, a hypothesis was proposed in the paper [23] about the effect of radiation-induced Gibbs segregation (RIGS) on the surface composition. It was suggested that due to the linear cascade generation by ion irradiation in the region of collisions a sufficient atomic mobility is ensured for the implementation of Gibbs segregation at low target temperatures. In this case, it was assumed that the modified layer was depleted with Cu, but the uppermost layer of the target was enriched with Cu.

Along with this, the role of radiation-stimulated Gibbs segregation in the formation of the changed layer [25–28] was widely discussed. It was convincingly shown that

RIGS, together with sputtering, leads to the formation of a nonmonotonic distribution of component concentrations with depth. It was demonstrated that radiation-stimulated diffusion, mixing and knocking-on affect the formation of deep layers of the changed layer [29–31]. Note in this connection that, in the framework of the linear cascade theory, Sigmund [32] obtained a relation between the partial sputtering yield Y_i and Y_j of the components of the target consisting of elements i and j:

$$\frac{Y_i}{Y_j} = \frac{c_i}{c_j}\left(\frac{M_j}{M_i}\right)^{2m}\left(\frac{U_j}{U_i}\right)^{1-2m}, \qquad (1)$$

where c_i, M_i and U_i are concentration, mass and surface binding energy of the atom i respectively. For NiPd alloy gives $Y_{Pd}/Y_{Ni} = 0.87$, which means Ni preferential sputtering and surface enrichment with Pd. Such a discrepancy between the theory and experimental data, in particular, with our data on $Ni_x Pd_y$ alloys, is obviously due to the fact that expression (1) takes into account the kinematics of atomic collision cascades only and does not take into account RIGS. A number of other examples can be provided, indicating that there is still no complete understanding of the details of the process of preferential sputtering under the bombardment with atomic ions. But nevertheless, by now, a generally accepted scenario of preferential sputtering was developed, which consists in the following. At the initial moment of irradiation, for example, of a two-component keeped at room temperature and consisting of elements a and b, the component a will be sputtered predominantly if $Y_a > Y_b$, where Y_a and Y_b are partial sputtering yield of the corresponding components. This will lead to the fact that the component concentration in the upper surface layer will decrease with increasing of time (or dose) of irradiation. As a rule, the predominantly sputtered component is an element with a lower surface binding energy. At the same time, due to the development of a cascade of atomic collisions in the near-surface layer, the mobility of the target atoms will increase. This creates conditions for the Gibbs segregation implementation, i.e. the so-called hopping segregation, which will tend to compensate for the loss of a component in the upper layer due to sputtering. The depletion with a component formed in the second layer will be compensated by diffusion from deeper layers. Note that in the zone of action of the cascade of collisions, the diffusion coefficient can increase by several orders of magnitude [33,34]. In addition to radiation-induced diffusion, the profile of the depth distribution of concentrations can be influenced by such processes as predominant knocking-on and mixing. As a result of the joint action of these processes, at a certain radiation dose the equilibrium is established, i.e. a stationary mode, in which the changed layer is preserved with the radiation dose.

In contrast to the atomic ion interaction with the substance, when approaching the surface a large number of atoms constituting the cluster interact simultaneously with at least the same number of target atoms. In the initial stage of this interaction the atoms of the solid body are given an impulse directed deep into the target. As a result, an area of increased pressure appears in the surface layer. Estimates show that the cluster consisting of 1000 atoms and accelerated to energy of 10 keV creates a pressure of about 10 Mbar. It is obvious that the magnitude of the impulse transferred to the lattice atoms, and, consequently, the pressure value are determined by the ratio of the atom masses of the cluster and target. Under the action of this pressure the crystal lattice of the target is compressed, and a crater is formed, the front of which moves both deep into the target and in lateral directions. According to Hooke's law a restoring force arises that is proportional to the elasticity of the crystal and directed along the perpendicular to the front of movement of the crater walls. After the cluster collapse, relaxation of the crystal occurs. The processes of compression and relaxation of the crystal are clearly traced in our computer calculations-simulations of the cluster ions interaction with the target (see Fig. 3 in [35]). Simulations shown that along the surface of the crater formed during the cluster ion collision with the target, there is no sharp boundary between the solid body and vacuum: there is a certain layer formed by „excited" atoms in motion (see, for example, [36]). The results analysis of the computer simulation shows that the energy of atoms in this layer is by several orders of magnitude higher than the energy of thermal motion of atoms in the crystal, and the layer thickness is $2-3$ of interatomic distances.

Computer simulation of interaction of the Ar_{500}^+ ions bombarding the molybdenum target showed that the sputtering starts in 0.4 ps after the cluster atoms cross the boundary of the target surface. Note that during this time the lower boundary of the crater reaches its maximum. Our computer calculations show that the emission of sputtered particles continues for $2-4$ ps, while the energy of sputtered particles decreases with time.

Note a significant difference in the process of sputtering by atomic and cluster ions. During bombardment with atomic ions the sputtered surface is motionless. And in the case of irradiation with cluster ions the emission of sputtered particles occurs from the moving surface.

Thus, it is obvious that the sputtering model based on the consideration of linear cascades is not applicable for describing the cluster ions interaction with matter. Note that also in the case of multicomponent materials sputtering this theory does not adequately describe the process of preferential sputtering without the involvement of RIGS. In the published literature one can find a number of attempts to theoretically describe the cluster ions interaction with substance.

For example, as already mentioned in the Introduction, significant changes in the surface composition of the semiconductor compound $Cu(InGa)Se_2$ under the action of irradiation with Ar_{1500}^+ cluster ions with energy of 10 keV [14]. The selenium concentration decreased by approximately 12%. The authors of the paper, considering

the fact that the boiling point of selenium (958 K) is significantly lower than the boiling points of copper, indium and gallium (3200, 2345 and 2477 K, respectively), explained the preferential sputtering of selenium from the surface by the effect of local heating under the action of cluster bombardment. Such a model of thermal evaporation implies that the angular distribution of the sputtered particles must comply with the Knudsen law. However, experimental studies of the angular distributions of particles sputtered from NiPd and NiMoRe alloys shown that these distributions are far from cosine [37]. Besides, the boiling points of the NiPd alloy components are almost the same: 2940 K for Ni and 2900 K for Pd. Thus, temperature effects can hardly explain such a significant change in the surface composition upon irradiation with cluster ions.

In the paper [38] a model of sputtering due to a shock wave, which arises when a cluster collides with a solid target, is proposed. In the model the sputtering is considered as a result of the atom acceleration by a shock wave. As applied to the sputtering of the NiPd alloy, this means that since in the shock wave the atoms move at the same speed, the heavier atoms (Pd) receive higher energy and more easily overcome the surface potential barrier, and are sputtered predominantly. However, this mechanism does not work in the case of NiMoRe alloy sputtering.

Thus, it can be stated that, to date, there is no adequate theoretical description of the process of the cluster ions interaction with substance, and, in particular, of the effect of preferential sputtering. Therefore, now the most useful information is obtained from computer molecular dynamics simulation of the process.

Thus, despite the strong differences in the mechanisms of sputtering by atomic and cluster ions, both processes have common features. It is obvious that, as in the case of irradiation with atomic ions, the partial sputtering yields of the components due to atomic collisions in the near-surface layer during cluster bombardment differ. It is also most probable that in both cases, during the changed layer formation, the radiation-induced Gibbs segregation is present. Therefore, in this paper, an attempt was made to explain the experimental data on the cluster ions interaction with alloys using the approach that was successfully used in the case of multicomponent targets bombardment with atomic ions.

First of all, let us consider the dependence of the surface concentration of palladium in irradiated Ni_xPd_y alloys on its concentration in the initial sample (Fig. 1, *b*). Let's try to understand what changes during the transition from the Ni_5Pd alloy to the Ni_3Pd alloy.

Unfortunately, at present there are no data on the sputtering yield of each of the alloy components and the alloy itself upon irradiation with cluster ions. In the paper [39] the sputtering yield Y of various single-element targets are compared by cluster ions of argon and atomic ions Ar^+ with the same energies. It was shown that in the case of irradiation with cluster ions the dependence of Y on the atomic number of the target Z_2 has an oscillating

Table 2. Characteristics of components of targets used in the experiments

Target	Surface binding energy U_0, eV	Sputtering yield Y, at./ion
Pd	3.9	3.0
Ni	4.4	2.7
Mo	6.8	1.7
Re	8.1	—

Note. sputtering yield are taken from [43]. Reliable data on rhenium sputtering are unknown to us.

character, which repeats the analogous dependence for irradiation with atomic ions. The oscillating behavior of the dependence $Y(Z_2)$ reflects the fact that materials with a lower binding energy on the surface U_0 demonstrate a higher sputtering yield [32,40]. The values of the sputtering yield for atomic ions of argon with energy of 3 keV and the surface binding energies for the components of the used alloys in pure form are given in Table 2. Of course, the binding energy of nickel in the alloy differs from its binding energy in pure metal. Several models are known that allow one to calculate the binding energies of atoms on the surface of the alloy based on various considerations (see, for example, the discussion in [41,42]). However, in general, it can be assumed that the binding energies of the alloy components are related in the same way as the binding energies of pure substances, i.e., component with high binding energy in its pure form will also have high binding energy in the alloy composition. In this paper, we do not aim to give a complete quantitative description of the observed effects, so such a qualitative understanding of the regularities of binding energies will be sufficient for further reasoning. Besides, based on the results of paper [39], we will assume that the ratios of coefficients of alloy components sputtering by cluster ions are similar to those for atomic ions.

When going from Ni_5Pd to Ni_3Pd, the concentration of palladium in the sample increases. Since the palladium sputtering yield Y_{Pd} exceeds Y_{Ni}, the sputtering leads to the palladium concentration decreasing in the surface layer to a greater extent than for the Ni_5Pd alloy. Radiation-induced Gibbs segregation tends to compensate for the depletion of the surface layer with palladium, depleting the subsurface layer with palladium. As a result, the surface of the Ni_3Pd alloy is more depleted with palladium than surface of Ni_5Pd. A similar situation takes place in the transition from sputtering of Ni_3Pd alloy to sputtering of NiPd.

However, the situation changes upon irradiation of alloys in which the Pd concentration initially exceeds the Ni concentration. The Pd predominance in these alloys leads to its segregation increasing. The ratio between the predominant emission of Pd from the surface layer and the intensity of its radiation-induced segregation changes

reflecting the change in the slope of the dependence of the palladium concentration in the irradiated region on its concentration in the sample volume (Fig. 1, *b*).

As already noted, the formation of atomic collisions cascades initiated by atomic and cluster ions is fundamentally different. This circumstance probably determines the fact that the preferential sputtering effect is more pronounced in the case of cluster ions. At the same time, the ratio of the sputtering yield of the alloy components plays an important role in the formation of the surface composition. Indeed, the ratio $Y_{Pd}/Y_{Ni} = 1.16$, while $Y_{Ni}/Y_{Mo} = 1.6$ (Table 2). The highest nickel enrichment was found on NiPd alloy, with the nickel concentration on the surface exceeding its volume concentration by 32%. In this case, the concentration of the less sputtered components of the NiMoRe alloy (molybdenum and rhenium) after irradiation with cluster ions increased by almost three times.

For a more detailed analysis of the problems discussed in this paper, first of all, data on the depth distribution of components within the changed layer are needed. Experiments on the study of the layer modified by irradiation with cluster ions will form our further studies.

Conclusion

Experimental studies shown that, as a result of irradiation with cluster ions, a layer with a composition strongly different from the bulk composition is formed on the surface of nickel-based alloys. It was established that preferential sputtering with cluster ions leads to more significant changes in the surface composition of the alloys compared to irradiation with atomic ions. It was found that the surface of the alloy is enriched with component having higher binding energy. A model is proposed for the changed layer formation upon the alloys irradiation with cluster ions, assuming that the surface composition is formed mainly under the action of two opposing processes: collision mechanism, i. e., sputtering as a result of atomic collisions in the surface layer of the target, and radiation-induced Gibbs segregation. The effect of these mechanisms on the type of dependence of the palladium surface concentration in alloy irradiated with cluster ions on its bulk concentration is shown. On the other hand, it is shown that the ratio of the sputtering yields for the pure components that make up the alloy determines the magnitude of the preferential sputtering effect.

Conflict of interest

The authors declare that they have no conflict of interest.

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