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Preferential sputtering of NiTi alloy by atomic and gas cluster ions

© *A.E. Ieshkin*[1], *V.S. Chernysh*[1], *D.S. Kireev*[1], *B.R. Senatulin*[2], *E.A. Skryleva*[2]

[1] Moscow State University, Moscow, Russia
[2] National University of Science and Technology „MISiS“, Moscow, Russia
E-mail: ieshkin@physics.msu.ru

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X-ray photoelectron spectroscopy was used to study the evolution of the NiTi alloy surface composition under bombardment with atomic and cluster argon ions. A strong enrichment of the surface with nickel was found for both atomic and cluster ions, which is inconsistent with contemporary understanding of preferential sputtering. Possible reasons for this result are discussed.

Keywords: ion sputtering, cluster ions, preferential sputtering, XPS.

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Processes taking place during interaction between accelerated ion fluxes and solid surface are widely studied in state-of-the-art physics. This interest is caused by a great role of ion beams in fundamental research and technological applications. Emphasize that almost always multicomponent targets are considered in this context, since either the target is initially not a simple substance or the dopant is introduced by the ion flux itself due to ion implantation. However, regardless of a rather long history of investigation [1,2], we are still far from fully understanding the totality of processes occurring during such an interaction.

Among those processes, the most pronounced one is preferential sputtering of one of the material components. One of the factors initiating preferential sputtering is the difference in partial sputtering yields of the composite target components: the surface under bombardment will be enriched with the component having a higher sputtering yield. However, the target surface composition may vary not only due to collisional processes taking place under irradiation. In its turn, the emergence of the concentration gradient induces diffusion fluxes due to, among other factors, radiation-induced diffusion. In addition, segregation initiated by the ion irradiation can cause the enrichment of the upper atomic layer (relative to the second layer) with the segregating component.

A relatively new type of ions, which attracts a significant attention in the up-to-date research, is the type of gas cluster ions [3]. The mean kinetic energy per each of the cluster atoms is typically as low as a few electron-volts. Contrary to the conventional atomic ion, an accelerated cluster ion does not penetrate deep into matter, i.e. all its energy is released locally in the upper atomic layers of the target. As a result, in the interaction area there emerge extreme conditions, which can give rise to new physical phenomena. In this aspect, it is rather unobvious that processes taking place during interaction between cluster ions and surface of the composite target are similar to those proceeding during the atomic ions interaction with matter. In practice, specific features of interaction between gas cluster ions and matter are used for the surface relief modification, analysis of materials, and formation of coatings [3].

Earlier [4,5] we have reported on studying the surface composition and nanorelief which got formed under irradiation of the $\mathrm{Ni}_x\mathrm{Pd}_y$ and NiMoRe alloys with atomic and gas cluster ions. It was found out that, contrary to the case of bombarding with atomic ions, surface compositions of the studied alloys irradiated with cluster ions differ strongly from the bulk compositions. Therewith, variations in the surface composition could be predicted based on the analysis of the surface binding energy and sputtering yields of pure elements of the alloys. In this work, we have studied the dynamics of formation of the NiTi (nitinol) alloy surface composition under the action of atomic and cluster ions. We assumed that, because the ratios of parameters defining the near-surface processes differ from those of already studied alloys, it will be possible to make more general conclusions about the mechanisms for preferential sputtering of composite targets irradiated by atomic and cluster ions. Notice that, besides the fundamental interest, regularities of nitinol modification have been actively studied in last decades [6,7] because this material possesses shape memory and is widely used in biomedicine.

As the samples, rectangular nitinol plates $10 \times 8 \times 2.5$ mm in size were used; their composition was close to the equiatomic one: Ni — 49 at.%, Ti — 51 at.%. The sample surfaces were polished mechanically with silicon carbide powder and then rinsed in organic solvents. The pre-irradiation and post-irradiation topographies of the sample surfaces were controlled by Scanning Electron Microscopy (SEM).

Experiments on sample irradiation with ion fluxes were performed at setup PHI 5000 VersaProbeII (ULVAC-PHI, Japan) equipped with sources of atomic and cluster argon ions. Atomic ions were generated by electron-impact ionization of let-in atomic argon. The operating principle of the cluster ions source is based on formation of neutral

Table 1. Surface concentrations of the basic components prior to and after ion bombardment (lines used to determine the composition are indicated)

Experimental conditions	Concentration, at.% (±0.7)			
	C 1*s*	O 1*s*	Ti 2*p*	Ni $2p_{3/2}$
Initial surface	21.0	49.0	21.9	7.6
Ar^+, 300 eV, $3 \cdot 10^{16}$ ion/cm^2	11.4	30.2	20.5	26.6
Ar^+, 3 keV, $50 \cdot 10^{16}$ ion/cm^2	–	–	38.0	62.0
Ar^+_{2500}, 20 keV, $15 \cdot 10^{16}$ ion/cm^2	–	–	35.0	65.0

argon clusters during condensation of this gas due to adiabatic expansion through the supersonic nozzle with their following electron-impact ionization [3].

Energy of the atomic Ar^+ ions was 3 keV, the beam axis was directed at the angle of 55° to the surface normal (the setup standard geometry). According to the TRIM-code estimate, the mean ion projection range under these conditions is 2.2 nm. The ion current to the sample was 3.25 μA; the beam was scanned over the area of 2 × 2 mm. Ar^+_n cluster ions with the mean size of $n = 2500$ atoms had the energy of 20 keV and were directed normally to the surface since oblique incidence of the cluster ions in the standard setup geometry leads to very fast development of a pronounced surface relief. The cluster ion current to the sample was 85 nA. The beam was scanned over the area of 1.5 × 1.5 mm.

The surface composition was determined *in situ* by X-ray photoelectron spectroscopy (XPS). In this study, monochromatic AlK_α radiation (1486.6 eV) was used; diameter of the analysis area in the center of the irradiated region was 200 μm. The atomic concentration ratio Ni/Ti was determined based on the theoretical values of total ionization cross-section σ of levels Ni $2p_{3/2}$ and Ti 2*p* (14.6 and 7.9 in the cross-section units C 1*s*) [8], asymmetry parameter of the angular dependence of photoabsorption $\beta = 1.44$ and 1.36 for Ni $2p_{3/2}$ and Ti 2*p*, respectively [9], and also of mean free path λ (comparable with the analyzed layer thickness) of photoelectrons emitted from levels Ni $2p_{3/2}$ and Ti 2*p*, which was 1.27 and 1.81 nm, respectively, at the density of 6.6 g/cm^3 [10]. In the experiments, cycles of ion bombardment and analysis alternated, which allowed observing evolution of the surface composition in the process of irradiation. The chamber pressure was about 10^{-8} Pa during XPS spectra collection and 10^{-5} Pa in the process of the cluster-ion irradiation.

Table 1 presents concentrations of the main components of the alloy. Prior to starting the experiment, the surface was cleaned by low-energy (300 eV) argon ions with fluence of $3 \cdot 10^{16}$ ion/cm^2. Later, in the process of the experiment, post-cleaning residual carbon and oxygen were removed during the first cycles of etching.

The survey XPS spectrum measured after atomic ion irradiation, as well as the nickel and titanium lines obtained in the high-resolution mode, are given in Fig. 1.

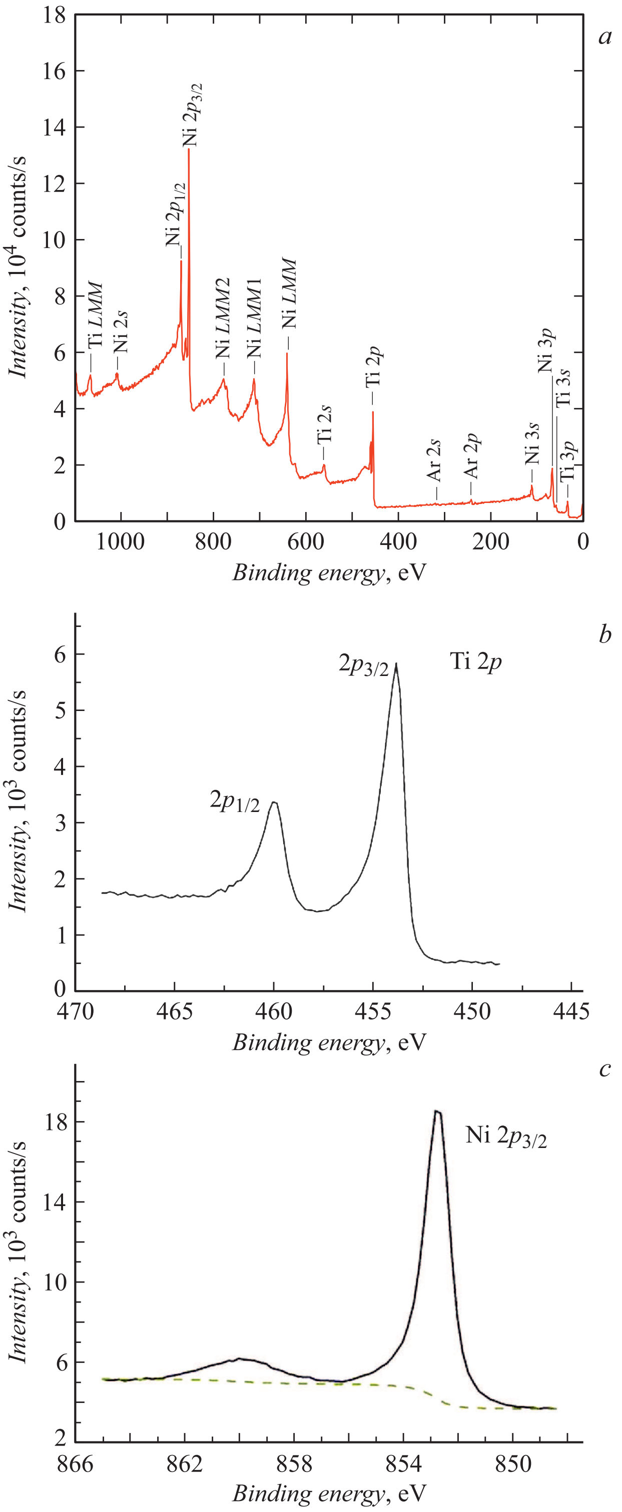

Figure 1. XPS spectra obtained after NiTi sputtering with atomic Ar^+ ions. *a* — survey spectrum; *b* — high-resolution Ti 2*p* spectrum (peaks at 453.8 and 460.0 eV); *c* — high-resolution Ni $2p_{3/2}$ spectrum (852.7 eV), the peak at about 860 eV is the plasmon peak characteristic of metallic nickel. The dashed line in panel *c* represents the background.

Fig. 2, *a* illustrates variations in the surface composition in the process of irradiation with atomic ions (3 keV) and cluster ions (20 keV). Fig. 2, *b* demonstrates the evolution of the nickel-to-titanium ratio with increasing ion radiation fluence. Under the atomic ion irradiation, the equilibrium concentration (Ti — 36 at.%, Ni — 64 at.%) gets reached at the fluence of about $3 \cdot 10^{16}$ ion/cm^2. This fluence corresponds to sputtering of a layer about 20 nm thick, that is, approximately ten mean projected ranges. Enrichment of the surface with nickel (Ti — 34 at.%, Ni — 66 at.%) is somewhat higher under the cluster-ion irradiation.

High-resolution XPS spectra obtained after irradiation with atomic and cluster ions corresponded to metallic nickel and titanium. The pre-irradiation and post-irradiation surface topography was controlled by SEM; no significant variations induced by ion bombardment were revealed.

Passing to the analysis of the results, let us emphasize that at present there is no model unambiguously predicting with what component the surface will be enriched (and to what extent) under bombardment with either atomic or cluster ions. It is believed that surface enrichment observed in metal alloys is generally consistent with the sputtering yields of pure materials, i. e. ion bombardment provides enrichment with the component having a lower sputtering yield in the case of a single-component target. In addition, some compounds, especially those which components have drastically different masses, exhibit enrichment with the component having a larger atomic mass [2]. Based on theoretical analysis of sputtering of equiatomic binary alloy in the linear-cascade mode, Sigmund obtained a formula describing the ratio of sputtering yields [11]:

$$\frac{Y_A^c}{Y_B^c} = \left(\frac{M_B}{M_A}\right)^{2m} \left(\frac{U_B}{U_A}\right)^{1-2m}, \qquad (1)$$

where M_i, U_i are the mass and surface binding energy of the i-th alloy component, $0 < m < 0.2$. The expression was derived in the low-fluence approximation.

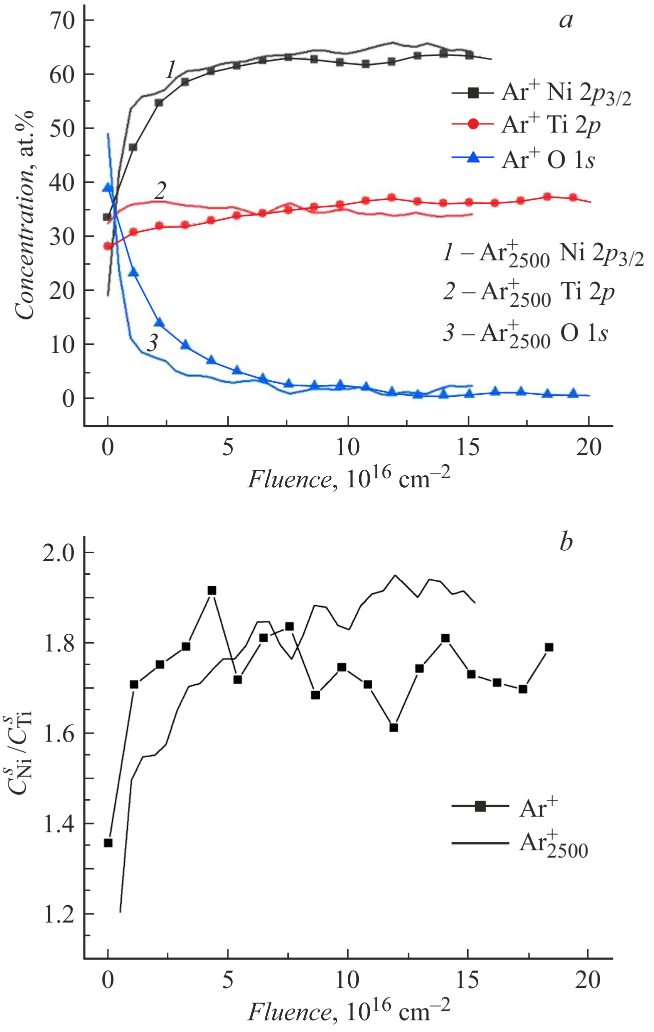

Figure 2. *a* — evolution of concentrations of the main surface components; *b* — the ratio between surface concentrations of nickel and titanium versus fluence.

Table 2. Parameters of chemical elements used in the experiments

Element	M, u	U, eV	Y, atoms/ion
Ni	59	4.46	2.7
Ti	48	4.89	1.2
Pd	106	3.91	3.8

The ratio between sputtering yields of pure Ni and Ti allows assuming the nitinol surface enrichment with titanium, while estimation according to (1) demonstrates a weak enrichment with nickel (Tables 2, 3). However, experiments showed an intense preferential sputtering of titanium, which is inconsistent with the above concerns. In addition, former investigations of angular distributions of matter [12,13] sputtered from this alloy demonstrated titanium segregation to the surface (while, typically, segregation of the component with a lower binding energy is observed for, e. g., NiPd [14,15]). Notice that for this alloy the experimental (determined by XPS) surface composition deviation from the 1:1 ratio (in this case, the XPS analysis depth was 1−2 nm) did not exceed the measurement error (Table 3). The results of [14] demonstrated the surface enrichment with nickel (having in the pure form a lower sputtering yield and a higher binding energy). Therewith, the estimate obtained from (1) shows enrichment with palladium due to a quite large difference in the component masses.

Earlier we showed [5] that irradiation with cluster ions induces in alloys NiPd and NiMoRe a strong preferential sputtering of the component having a lower binding energy independently of the ratio between the component masses. However, in this case the cluster ion irradiation of the NiTi alloy led to a great preferential sputtering of titanium, similarly to the case of atomic ion irradiation. To reach the equilibrium concentration, fluences were to be larger than in the case of irradiation with atomic ions, as it was in the case of NiPd sputtering.

Table 3. Ratios of atomic masses, surface binding energies and sputtering yields of pure components, and also ratios of stationary surface concentrations under irradiation with atomic and cluster ions and the estimate obtained via formula (1)

Elements	M_A/M_B	U_A/U_B	Y_A/Y_B	C_A^s/C_B^s		
				Experiment, Ar^+	Estimate (1)	Experiment, Ar_{2500}^+
Ni/Pd [4]	0.56	1.14	0.71	1.02	0.8	1.9
Ni/Ti	1.23	0.91	2.2	1.6	1.1	1.9

The observed effects may be explained by the fact that, contrary to the Ni–Pd system (which is a solid alloy, i.e. alloy permitting substitution of atoms of one type with atoms of another type over a wide range), Ni–Ti is not a solid alloy but an intermetallic compound containing a number of stable phases of different compositions. Processes induced by an energy impact on this material may be affected by thermodynamic effects associated with phase transitions. According to [16,17], formation of the Ni_3Ti phase is energetically more favorable than of the NiTi phase. Therefore, it is possible to assume the ion-irradiation-induced formation in the area of ion penetration, of the more energetically favorable phase with the predominant content of nickel; therewith, the excess titanium segregates to the surface and undergoes preferential sputtering. An attempt was undertaken to determine the surface phase composition by the method of electron backscatter diffraction (EBSD). However, almost all the surface (except for small regions exhibiting the cubic symmetry characteristic of NiTi) did not allow observing a diffraction pattern, which may be explained by excess titanium on the surface and absence of sufficiently large single-phase crystalline regions in deeper layers.

Finally, notice that, in view of NiTi application in biomedicine, formation on the alloy surface of layers enriched with nickel is undesirable, since it can diffuse into the human organism. However, this diffusion can be significantly reduced by the surface nanostructuring, namely, creation on it a nanoscale relief [18]. It is known that oblique incidence of cluster ions produce on the irradiated surface a pronounced undulating relief [5,19]. The effect of such a relief on the property of biocompatibility will be studied in our further research.

In summary, we have revealed a strong enrichment of the NiTi alloy surface with nickel as a result of irradiation with atomic and cluster argon ions. This result contradicts the contemporary concepts of the processes occurring in sputtering of multicomponent materials. To explain these discrepancies, this paper proposes a mechanism involving phase transitions in the irradiated target regions and release of excess titanium towards the surface followed by its sputtering. In addition, earlier we have revealed radiation-induced segregation of titanium despite its larger surface binding energy. Thus, comparison of the results of this study with our previous data leads to a conclusion that, in the case of a composite target irradiation, the element segregating to the surface undergoes preferential sputtering.

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Conflict of interests

The authors declare that they have no conflict of interests.

References

[1] N.Q. Lam, G.K. Leaf, H. Wiedersich, J. Nucl. Mater., **88**, 289 (1980). DOI: 10.1016/0022-3115(80)90285-8

[2] *Sputtering by particle bombardment II*, ed. by R. Behrish (Springer, Berlin–Heidelberg, 1983). DOI: 10.1007/3-540-12593-0.

[3] A.E. Ieshkin, A.B. Tolstoguzov, N.G. Korobeishchikov, V.O. Pelenovich, V.S. Chernysh, Phys. Usp., **65** (7), 677 (2022). DOI: 10.3367/UFNe.2021.06.038994.

[4] A.E. Ieshkin, D.S. Kireev, A.A. Tatarintsev, V.S. Chernysh, B.R. Senatulin, E.A. Skryleva, Surf. Sci., **700**, 121637 (2020). DOI: 10.1016/j.susc.2020.121637

[5] V.S. Chernysh, A.E. Ieshkin, D.S. Kireev, D.K. Minnebaev, E.A. Skryleva, B.R. Senatulin, Tech. Phys., **92** (12), 1694 (2022). DOI: 10.21883/TP.2022.12.55207.141-22.

[6] J. Zhu, Q. Zeng, T. Fu, Corros. Rev., **37**, 539 (2019). DOI: 10.1515/corrrev-2018-0104

[7] S. Shabalovskaya, J. Anderegg, J. Van Humbeeck, Acta Biomater., **4**, 447 (2008). DOI: 10.1016/j.actbio.2008.01.013

[8] J.H. Scofield, J. Electron Spectr. Relat. Phenom., **8**, 129 (1976). DOI: 10.1016/0368-2048(76)80015-1

[9] R.F. Reilman, A. Msezane, S.T. Manson, J. Electron Spectr. Relat. Phenom., **8**, 389 (1976). DOI: 10.1016/0368-2048(76)80025-4

[10] http://www.quases.com/products/quases-imfp-tpp2m

[11] *Sputtering by particle bombardment I*, ed. by R. Behrisch (Springer, Berlin–Heidelberg, 1981). DOI: 10.1007/3-540-10521-2.

[12] V.S. Chernysh, V.S. Tuboltsev, V.S. Kulikauskas, Nucl. Instrum. Meth. Phys. Res. B, **140**, 303 (1998). DOI: 10.1016/S0168-583X(98)00002-0

[13] K.K. Ho, K.P. Mohanchandra, G.P. Carman, Thin Solid Films, **413**, 1 (2002). DOI: 10.1016/S0040-6090(02)00339-5

[14] V.S. Chernysh, A.S. Patrakeev, Nucl. Instrum. Meth. Phys. Res. B, **270**, 50 (2012). DOI: 10.1016/j.nimb.2011.09.015

[15] P. Sigmund, A. Oliva, G. Falcone, Nucl. Instrum. Meth., **194**, 541 (1982). DOI: 10.1016/0029-554X(82)90578-X
[16] *Smithells metals reference book*, ed. by W.F. Gale, T.C. Totemeier, 8th ed. (Elsevier, 2004).
[17] T. Mousavi, M.H. Abbasi, F. Karimzadeh, Mater. Lett., **63**, 786 (2009). DOI: 10.1016/j.matlet.2009.01.017
[18] E.O. Nasakina, M.A. Sudarchikova, K.V. Sergienko, S.V. Konushkin, M.A. Sevost'yanov, Nanomaterials, **9**, 1569 (2019). DOI: 10.3390/nano9111569
[19] I.V. Nikolaev, N.G. Korobeishchikov, Appl. Nano., **2**, 25 (2021). DOI: 10.3390/applnano2010003

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