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Influence of irradiation by a particle beam on optical properties of metal mirrors

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The surface of copper and stainless steel mirrors near the area destroyed by electron beam has been characterized by means of ellipsometric diagnostics. The treatment did not result in any changes in the surface microrelief, independent on the treatment duration, although changes in the ellipsometric parameters have been observed. According to the XPS data, these changes are due to disordering in the about 2 nm thick surface layer resulting from Ar ion implantation.

По результатам эллипсометрической диагностики охарактеризована поверхность зеркал из меди и нержавеющей стали вблизи участка, разрушенного электронным пучком. Обработка не изменяла микрорельеф поверхностей независимо от времени обработки, хотя наблюдались изменения эллипсометрических параметров. По данным РФС, эти изменения обусловлены разупорядочением структуры поверхностного слоя толщиной около 2 нм вследствие имплантации ионов аргона.

The action of quasi-neutral plasma onto a material surface is defined by the parameters of its two components, namely, ion and electron subsystem. In the EH accelerator schemes, the generation of a quasi-neutral plasma beam causes an inevitable effect of its action onto the material surface due to a predominant role in the mass transport process being played by one of these two components. Constructively, it is possible to realize two main schemes of such a beam formation connected with reaching the equality of energy (1) or motion speeds (2) of such two components with opposite electric charge near the surface. In case (2), in accordance with ratio of electron and nucleus masses, the ion energy exceeds that of electrons by at least 2000 times. Then, an intermediate variance between two schemes mentioned above could be taken into account in the mass transport processes under action of quasi-neutral plasma. But in any case, the mass transport phenomenon at the surface and the mechanism of main interaction processes between the ion and electron subsystems of quasi-neutral plasma beam with the substance will be defined by characteristic parameters of this beam, namely, by the selected energy level E (both corresponding de Broglie wavelength and differential cross-section of elastic (inelastic) scattering, characteristic time of microparticle interaction with electron and lattice components of the substance) in each subsystem of these two ones, the irradiation dose, the treatment regime (continuous or pulse one defined by the pulse duration to the interpulse pause), the current density distribution within the beam cross-section, as well as by thermodynamic and structural parameters of the surface as such.

To solve that problem, it is necessary to consider the possible processes on the metals surfaces under irradiation by electrons and ions with various energies as well as to study the influence of neutron treatment on properties of the amorphous metal alloys. On the other hand, since some existing schemes of EH accelerators function in pulse (bunch) regime, it is necessary to con-

Table. The samples of materials and kinds of their treatment

Sample	Kind of treatment	Treatment parameters
Polycrystalline Cu	Electron irradiation	E = 0.5 MeV
Austenitic stainless steel ss 304 (Fe 70 % Cr 19 % Ni 9 % Mn 2 %, mass. %)	Ar+	E = 2 keV, during 5 and 15 min in pulsed mode with pulse duration 5 μs and the pause time 1 ms 0.2 Pa, current 0.1 mA
Amorphous metal alloys $Fe_{70}Cr_{15}B_{15}$ (at. %) quenched from melt at temperatures 1503–1523 and 1873 K	Neutrons from pulse source	E = 1 meV, irradiation during 12 h

sider the action of pulse treatment by ions on physicochemical state of metal surfaces.

The effects of electron and ion irradiation on the properties of metallic surfaces have been considered. The irradiation of polycrystalline metallic materials by electrons and ions in pulse mode has been carried out. To compare the effects of charged particles with effects of neutron irradiation, the latter treatment of amorphous metallic alloy Fe–Cr–B was performed. The samples and kinds of their treatment are presented in the Table.

Chemical analysis of the substrate layer of the stainless steel mirrors was carried out by XPS using the Mg Kα (E = 1253.6 eV) source without monochromator. Optical properties of the material were investigated using a home-made spectroscopic ellipsometer and a VASE one (λ = 250–1700 nm). The spectroscopic ellipsometry data were analyzed using the WVASE software, the sample surface microrelief was investigated prior to the optical studies by an atomic force microscope.

In the first approximation, the quasineutral plasma effect on the subsurface layer material could be considered basing on the additivity of contributions from two constituents of this beam to the mass transport process. The ion sputtering process is based on the Sigmund theory using Boltzmann equation under approach proposed by Thompson. It considers two-particle collisions in the hard spheres model. The elastic scattering of electrons takes place only if the incident electrons collide with the target nuclei. In the absence of screening, the scattering cross section is usually calculated using Rutherford equation. But in general case of schemes (1) and (2) even at low electron energies (~100 keV), both elastic and inelastic scattering of electrons is observed simultaneously in the course of interaction of the electron constituent of the bunch. Multiple scattering could also be possible (Williams theory, Berger method). Due to large difference in electron and proton mass, the energy of an electron from the bunch is transferred to several electrons of the atoms without energy exchange between the electrons and the crystalline lattice [1] (in metals, it is transferred to collective of electrons that are moving together when continuous electron energy loss is described by Bethe equation due to excitation of plasma oscillations). The peculiarity of the calculated space distributions of electron energy loss along the normal to surface (Spencer distribution [1]) consists in that the energy release maximum is situated at the distance of 1/4 Bethe radius (r_0 = 0.0104 cm) from the surface. In general case, the maximum depth δ (cm) of electron penetration into metal could be estimated using the Shonland equation [1]:

$$\delta = 2.35 \cdot 10^{-12} \frac{U^2}{\rho},$$

where U is the accelerating voltage in Volts (V); ρ ,the material density (g/cm^3). The calculations show that the surface temperature increases when penetration depth decreases. Even at the accelerating voltages near U = 20 kV, the metal surface is overheated considerably, that is why the surface evaporation intensity increases. As U increase, δ also increases, and during the 10^{-6}–10^{-5} s at specific power values $q_2 = 10^6$Wt/cm^2, the surface cannot be heated. However, explosive boiling of material is possible at certain depth of maximal energy release due to electron irradiation.

That is why it was important to study the copper mirror surface of 105 mm diameter in the area adjacent to the external border of the "crater" of a diameter not less than 20 mm (although a hollow of several square millimeters was formed around the

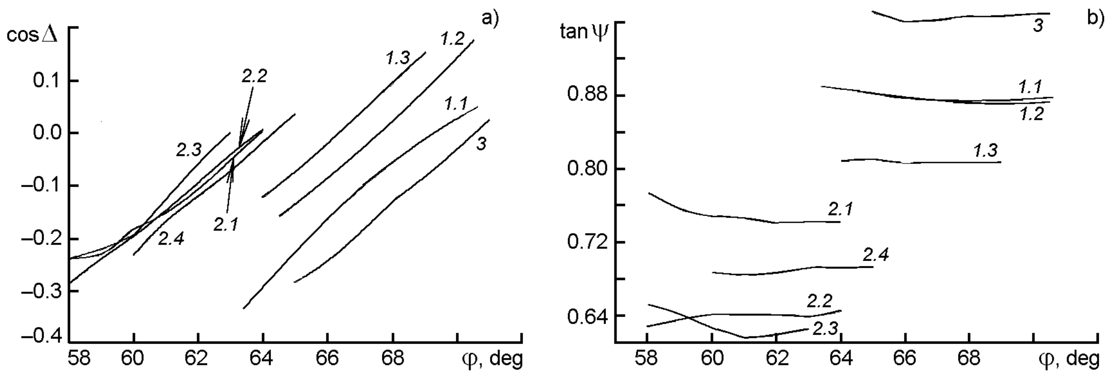

Fig. 1. Ellipsometric parameters Δ (a) and Ψ (b) dependences on the light incidence angle φ for two copper mirrors after their irradiation by electrons with energy 0.5 MeV (curves *1.1*, *1.2*, *1.3* (sample 1) and *2.1*, *2.2*, *2.3*, *2.4* (sample 2)) in comparison with unirradiated mirror (sample 3, curves 3) within bright A (curves *1.1*, *2.1*, *2.2*, *2.4*) and dark B areas (curves *1.2*, *1.3*, *2.3*) on *r* (curves *1.1*, *1.3*. *2.2*), *R* (curves *1.2*, *2.1*, *2.3*) and −*R* (curve *2.4*) distances from the "crater" center.

central area after the solidification of melted mirror material). Such a crater is formed after electron beam irradiation at voltage of 0.5 MV applied between copper anode (mirror) and copper cathode. At such conditions of the treatment, the crater edge contour acquired various shapes from a nearly circular (sample 1) to that similar to a rosette (sample 2). Dependences of ellipsometric parameters Δ and Ψ on the light incidence angle φ are shown in Fig. 1. In comparison with reference (unirradiated) sample 3, the principal angle of incidence φ_p and $\tan\psi_{min}$ are decreased from 1.5 to 4.0° and from 0.08 to 0.16 (sample 1) and from 6.0 to 7.5° and from 0.22 to 0.34 (sample 2), respectively. This means that after copper sputtering from the "crater" and further copper deposition onto undestroyed areas of surface in the vicinity of the "crater", the subsurface layer conductivity is deteriorated. It was found that at such Cu deposition on a mirror surface, the film of variable thickness over the radius is not formed because the same cosΔ corresponds to the areas A at *r* and R of sample 2. At the same time, for equidistant position from the "crater" center (bright A and dark B areas of sample 2), the ellipsometric parameters are slightly differ, perhaps due to various surface roughness resulting from the electron beam action within the "crater" cross-section. As to results of ellipsometric diagnostics and the solution of inverse ellipsometric problem, the parameters of the appropriate surface optical model (deposited layer (film) — substrate) in the vicinity of the mentioned "crater" were obtained. At a condition of energy selection for two components of the mentioned beam below the destruction threshold of subsurface layer, the usage of one of the components (e.g., electron) as a probe for physicochemical surface analysis becomes advantage of the experiment.

It is of interest to compare the action of the ion and electron beams similar in energy on the hardness within the subsurface layer data for α-Fe [3]. It has been obtained that only one hardness maximum after the action of 6–20 keV electron beam exists at the depth of 0.75 μm from the surface. At the same time, two microhardness maxima at the depth of 1 and 5 μm were observed after ion beam treatment of α-Fe. The result of joint action of electron and ion flows as constituents of the quasi-neutral plasma bunches in surface treatment due to the schemes (1) and (2) and the character of subsurface structure modification without the mirror surface destruction depends in this case on the selected energy level which should not exceed a certain threshold for a specific material. At this energy, for both bunch constituents, the advantage of the experiment is that one of the constituents (e.g. electron) could be used as a probe for physical and chemical analysis of the surface modification processes. It is enough to confine oneself to monoenergetic electron constituent and to apply the well known technique of electron spectroscopy.

At the same time, the optical characteristics of the Fe–Cr–B alloy quenched from the melt of the minimal temperature (1503–1523 K) after a long-time irradiation have become closer to those for the alloy

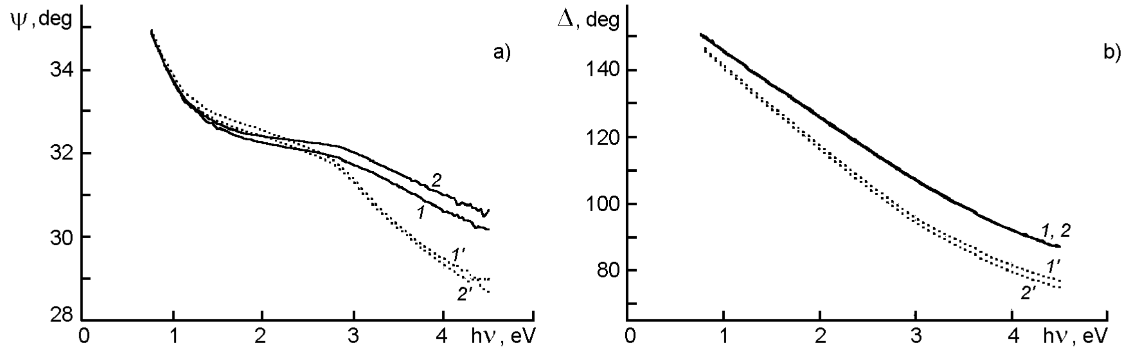

Fig. 2. Spectral dependences of the ellipsometric parameters Δ (a) and Ψ (b) for stainless steel 304 samples after pulsed treatment by Ar$^+$ ions ($E = 2$ keV) by plasma immersion ion implantation. Curves *1* and *2* correspond to the untreated stainless steel samples, curves *1'* and *2'* relate to ellipsometric parameters for these samples after irradiation during 5 (*1'*) and 15 min (*2'*).

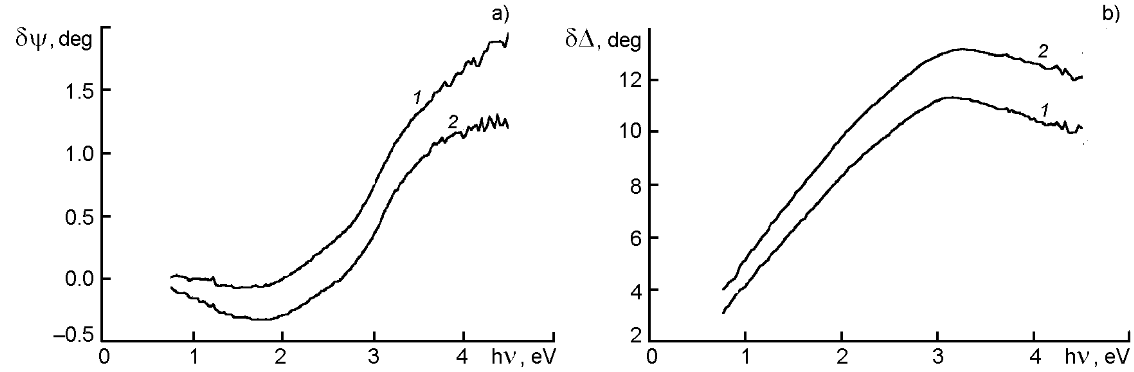

Fig. 3. Spectral dependences $\delta\Psi(h\nu)$ (a) and $\delta\Delta(h\nu)$ (b) determined as the difference between corresponding ellipsometric parameters for untreated surface and that irradiated by 2 keV Ar$^+$ ions for 5 (curves *1*) and 15 min (curves *2*).

quenched from the melt of the highest temperature (1873 K). Such changes of optical conductivity and the structure factor of this alloy may be associated with the structural relaxation of the amorphous metallic ribbon after a prolonged neutron irradiation. This process results in a partial intrinsic stress relaxation in the material without formation of crystalline regions. That is why a more homogeneous structure of amorphous metallic alloy (AMA) is formed. Hence, the proposed approaches and techniques permit us to control the consequences of the material irradiation, to estimate characteristics of space-time evolution of the temperature fields on the copper surface, changes of thermomechanical strains in metallic ribbons and level of the mass transport and surface erosion under the laser irradiation. All these consequences result from increased atom migration in condensed phase under high-energy irradiation.

The complex investigations of the stainless steel surfaces after ion implantation from the argon plasma were carried out. Before the investigations, the effect of Ar$^+$ ion treatment of $E = 2$ keV energy was evaluated by means of the software package SRIM2000 [5] with detail calculations of the cascade damages. It has been obtained that such processing results in formation of a layer with the damage maximum at the depth equal or less than 2.2 nm. Furthermore, the difference in the sputtering yield for Fe and other metal components of the stainless steel results in an enrichment of the steel surface in Fe atoms. The stainless steel surfaces were kept in air for several hours after irradiation and then were investigated by atomic force microscopy, spectral ellipsometry, and X-ray photoelectron spectroscopy. The surface microrelief was characterized by AFM prior to and after the irradiation. It has been determined that the ion treatment did not cause the surface

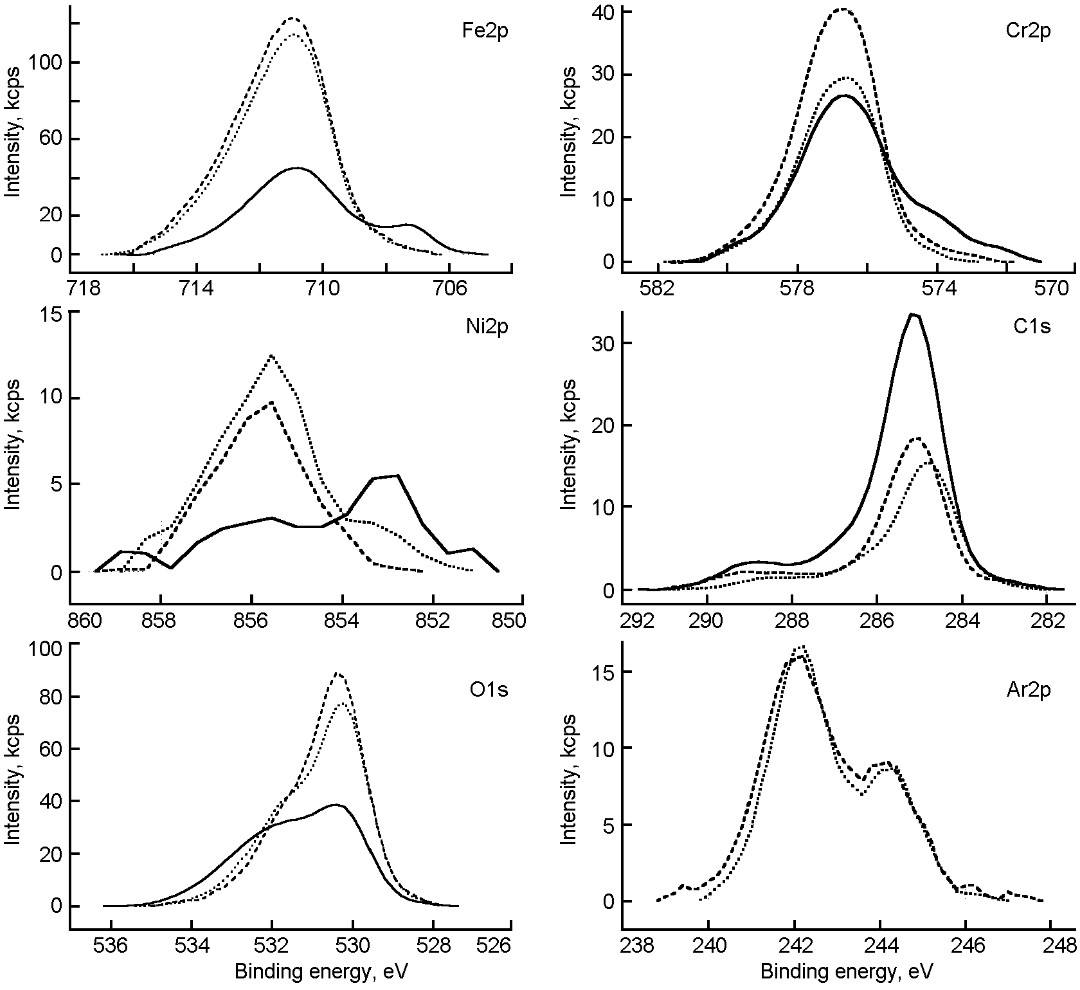

Fig. 4. XPS data for stainless steel surfaces before the irradiation (solid lines) and after Ar^+ ion bombardment during 5 min (dotted lines) and 15 min (dashed lines).

roughness parameters changes as it was obtained for the surface areas 1*1 μm^2 independently from the treatment duration.

The spectral dependences of ellipsometric parameters Δ and Ψ for the stainless steel samples are presented in Fig. 2. Using these dependences, the parameters $\delta\Delta = \Delta_0 - \Delta$ and $\delta\Psi = \Psi_0 - \Psi$ were calculated (where Δ_0 and Ψ_0 are the ellipsometric parameters for untreated stainless steel mirrors (curves *1* and *2*). Such calculations permit to evaluate quantitatively the effects of the pulse ion treatment on optical characteristics of the metallic mirror subsurface layer. The spectral dependences of the difference parameters $\delta\Delta(h\nu)$ and $\delta\Psi(h\nu)$ are presented in Fig. 3.

It was found that these differential parameters depend nonlinearly on the probing photon energy. This evidences a considerable absorption of light at the modified subsurface layer of the stainless steel mirrors. In accordance with the theoretical calculations using the SRIM-2000 software, the thickness d of the layer modified by ion bombardment is much smaller than the wavelength of incident light, λ. That is why to understand the effect of surface modification after the ion bombardment, the ellipsometric density D can be evaluated from the relationship [6]:

$$D = \ln\left(\frac{\rho_0}{\rho}\right) = \ln\left(\frac{\mathrm{tg}\Psi_0}{\mathrm{tg}\Psi}\right) + i(\Delta_0 - \Delta) = \qquad (1)$$

$$= i\frac{4\pi d}{\lambda}\frac{\varepsilon_s \sin(\varphi)\mathrm{tg}(\varphi)}{\varepsilon_s - (\mathrm{tg}(\varphi))^2}\frac{\varepsilon_f - \varepsilon_s}{1 - \varepsilon_s}\left(1 - \frac{1}{\varepsilon_f}\right),$$

where subscripts f and s relate to the film and substrate, respectively; φ is the angle of light incidence on the sample ($\varphi = 70°$ in the experimental data). The expression for

D (1) shows that the changes of ellipsometric parameters Δ and Ψ are directly related with the dielectric function of the film or modified subsurface layer ε_f.

Because the microrelief parameters of the stainless steel mirrors did not change after such treatment, the ellipsometric parameters modification can be caused by disordering of the subsurface layer due to ion implantation as well as modification of its stoichiometry. In order to determine what cause predominates, the XPS investigations were carried out. The Fe 2*p*, Cr 2*p*, Ni 2*p*, Ar 2*p*, C 1*s*, O 1*s*, N 1*s*, P 2*p* spectra have been obtained. The Fe 2*p*, Cr 2*p*, Ni 2*p*, Ar 2*p*, C 1*s*, O 1*s* XPS spectra for stainless steel are presented on Fig. 4. The N and P content is below the detection threshold of the XPS apparatus. The spectra for unirradiated stainless steel sample are shown by solid lines, those for the surfaces irradiated by Ar^+ ions during 5 min are presented by dotted lines, and those after 15 min irradiation are shown by dashed lines.

The XPS spectra of metals Fe 2*p*, Cr 2*p* and Ni 2*p*, which are main constituents of the unirradiated sample, demonstrate the peculiarities near 707, 574 and 853 eV. These peculiarities are due to contribution of Fe–Fe, Cr–Cr and Ni–Ni pairs respectively. Strong signals from metals bonded in oxides and hydroxides, respectively Fe_2O_3 (710.9 eV), FeOOH (711.6 eV), Cr_2O_3 (567.5 eV), $Cr(OH)_3$ (577.3 eV) and NiO (854.4 eV) are observed. It was obtained that the ion irradiation significantly changes the chemical binding structure on the stainless steel surface in such a way that the iron atoms enrich the subsurface layer and form chemical binding with atmosphere oxygen. It is confirmed by the increase of signal intensity from the oxides and hydroxides in the XPS spectra of irradiated stainless steel in comparison with these spectra for unirradiated samples. Furthermore, using XPS data it was obtained that even at such energies the Ar^+ implantation to the subsurface layer occurs. This is in agreement of the Ar2*p* signal appearance. Such ion treatment also diminishes the layer of carbon contamination on the surface.

Thus, the short-term (no more than 15 min) pulse irradiation of the stainless steel surfaces at the ion energy $E = 2$ keV, which is the imitation of one of the bunch mode, being one of the possible modes in the existing scheme of EH accelerators, results in substantial changes of the subsurface layer chemical composition due to argon implantation without changes in the surface microrelief parameters. The investigated films had the different thickness within 15 to 40 nm range. The film of a thickness $d > 50$ nm became almost opaque. The technique proposed permits to overlook the consequences of the irradiation of materials (copper, stainless steel) by ions and electrons, to estimate the characteristics of spatial and time evolution of temperature fields in copper mirror and the changes of thermomechanical stresses in amorphous metallic ribbons (Fe–Cr–B), the level of mass transport effects at the interface and the erosion of the surface under laser irradiation. All these consequences result from the action of the mechanisms of intensified atom migration in the condensed phase under high energy irradiation.

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Вплив опромінення потоками частинок на оптичні властивості металевих дзеркал

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За результатами еліпсометричної діагностики охарактеризовано поверхню дзеркал з міді та нержавіючої сталі поблизу зруйнованої електронним пучком ділянки. Обробка не змінювала мікрорельєф поверхонь незалежно від тривалості обробки, хоча спостерігалися зміни еліпсометричних параметрів. Ці зміни, за даними РФС, зумовлені розупорядкуванням структури прошарку завтовшки близько 2 нм внаслідок імплантації іонів аргону.