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IMPLANTATION-PLASMA NITRIDING

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Martensite steel 0.5Cr12Ni2MoMgMn and titanium alloy TiMo1Zr4.5Sn3 were nitrided by high intensity nitrogen plasma bombardment (current densities were $3\cdot10^{16}\,cm^{-2}\,s^{-1}$ and $1.2\cdot10^{17}\,cm^{-2}\,s^{-1}$ for martensite steel and titanium alloy correspondingly). Preliminary 30-keV N_2^+ ion implantation and subsequent plasma treatment essentially increases N penetration depth two orders of magnitude and surface hardness by a factor ~3. Approximately the same effect was received also at low energy (300 eV) and high intensity Ar^+ ion prebombardment and subsequent nitrogen plasma treatment. Near the surface a X-ray amorphous layer is created as a result of implantation-plasma treatment. High dose implanted atoms penetration is explained by their repulsive interaction and diffusion along dislocations.

Keywords: Implantation; Nitriding; Diffusion; Dislocation

1. INTRODUCTION

The advancement of ion implantation to the stage of wide practical applicability is often hindered by a small depth of ion penetration, at the energy of the ion used for doping equal to a few tens–hundreds keV. At the same time a long range effect [1–9] can result for some combination ion-metal in penetration of implanted atoms to the depth exceeding the corresponding ion ranges several orders of magnitude.

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An effective method of deep modification of various steels and alloys is a combination of ion implantation and plasma nitriding [4, 7, 9].

In this work an example of long range effect at combined ion implantation and plasma treatment is given.

2. EXPERIMENTAL TECHNIQUE

The experiments on N^+, N_2^+, Ar^+ ion implantation were done at separation-free ion plasma accelerator "VITA", which included a plasma accelerator [4], along with an ion source.

The ion-plasma accelerator VITA has the following characteristics: energy of high energy ions up to 40 keV, energy of low energy ions 250–400 eV, total current of high energy ions up to 30 mA, total current of low energy ions 1–2 A, high energy ions current density up to 200 μA/cm^2, low energy current density up to 25 mA/cm^2.

The steel 0.5Ch12Ni2Mo and the titanium alloy TiMo1Zr 4.5Nb1.5Sn3 were irradiated by 30-keV N_2^+ ions and by an intense low-energy (300 eV) Ar^+ and N_2^+ ion flux received from the plasma accelerator. The steel has very small modification after conventional implantation, the titanium alloy has a very broad application in aviation, medicine and so on. Therefore the chosen materials were of particular interest. The flux of the beam N_2^+ with 30-keV was $j = 3 \cdot 10^{14}\,cm^{-2}\,s^{-1}$ and dose was $10^{17}\,cm^{-2}$ for both steel and titanium alloy. The plasma nitriding has different regimes for these materials: the fluxes of nitrogen plasma were $3 \cdot 10^{16}\,cm^{-2}\,s^{-1}$ and $1.2 \cdot 10^{17}\,cm^{-2}\,s^{-1}$ and doses were $10^{19}\,cm^{-2}$ and $10^{20}\,cm^{-2}$ correspondingly.

The heating of a target was realized by the ion beam power released upon it and sustained at 300 C for steel and 550 C for titanium alloy. In order to activate the sorption processes at the surface and to study an effect of radiation defects under plasma nitriding a number of steel samples underwent the preliminary 30 keV Ar^+-ion bombardment. After processing the materials by high energy Ar^+ and N_2^+ ions and low energy nitrogen and argon plasma in different sequence the nitrogen distribution profiles in the steel and titanium alloy were studied by the Auger-electron analysis under subsequent layer etching and measurement of microhardness by Vickers technique at various loadings. The phase identification was performed by X-ray diffraction.

3. RESULTS AND DISCUSSION

3.1. Martensite Steel

In Figure 1 the nitrogen distributions in martensite steel are compared for the 4 cases: 1) irradiation with 300-eV N_2^- ions (dose $10^{19}\,cm^{-2}$), 2) implantation of 30-keV N_2^+ ions (dose $10^{17}\,cm^{-2}$) and subsequent irradiation by 300 eV N_2^+ ions (dose $10^{19}\,cm^{-2}$), 3) reverse to the case 2 sequence of irradiation, and 4) successive irradiation by 300 eV Ar^+ ions (dose $10^{19}\,cm^{-2}$) and then by 300 eV N_2^+ ions (dose $10^{19}\,cm^{-2}$).

The distribution of the nitrogen after plasma nitriding only at the duration of irradiation for 5.5 minutes by N_2^+ ions with the energy 300 eV at 300°C is close the table-like one, at the nitrogen concentration of about 5 at.% in the layer, 7 μm thick. The depth of nitrogen ion penetration is about 10 μm. The preliminary N_2^- ion implantation with

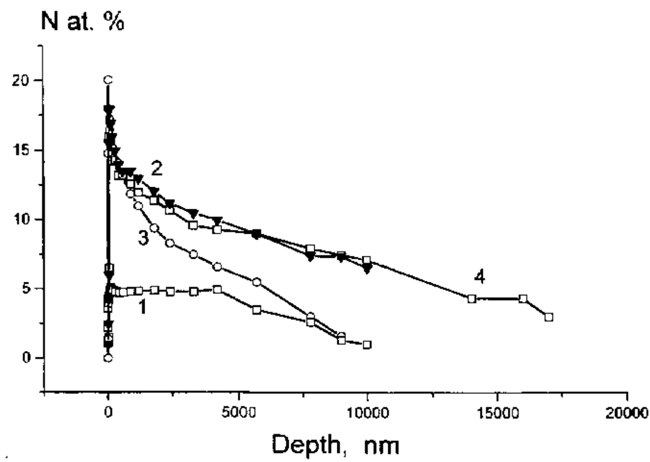

FIGURE 1 The depth distribution of nitrogen in martensite steel 0.5Cr12Ni2MoMn: (1) N_2^+ ions, energy 300 eV, dose $10^{19}\,cm^{-2}$; (2) N_2^+ ions, energy 30 keV, dose $10^{17}\,cm^{-2} + N_2^+$ ions, energy 300 eV, dose $10^{19}\,cm^{-2}$, current density 5 mA/cm^2; (3) N_2^+ ions, energy 300 eV + N_2^+ ions, energy 30 keV; (4) Ar^+ ions, energy 300 eV, dose $10^{19}\,cm^{-2}$, current density 5 mA/cm^2 + N_2^+ ions, energy 300 eV, dose $10^{19}\,cm^{-2}$, current density 5 mA/cm^2.

energy of 30 keV assists in an increase in the nitrogen ion penetration depth and in the concentration up to 18 at% near the surface. We believe that it is a result of near surface nitrides and radiation defects created at high energy N_2^- ion implantation.

The ion distribution in case of N_2^+-high-energy-ion implantation after plasma nitriding differs from that for the plasma nitriding by a rise in the nitrogen concentration up to 20 at.% in a subsurface layer.

The deep nitrogen penetration was also observed after steel surface treatment by Ar^+-ions-low-energy-flux before its bombardment by N_2^+-low-energy-ions (Curve 4). Such a strong effect by an intense (5 mA/cm^2) low energy Ar^+ ion bombardment on the diffusion of nitrogen point to an important role of the surface effects, along with the formation of radiation defects in a subsurface layer, related with the sorption processes which are activated by argon plasma. As a result of the preliminary low-energy-Ar^+-ion bombardment the nitrogen concentration under subsequent plasma nitriding rise a few times in the vicinity to the surface.

A positive effect of the joint implantation and plasma treatment was previously described in [7]. A difference of our technique is in that the deep penetration of the nitrogen ion penetration produced by the plasma accelerator is attained at an essentially lower temperature (−300 C instead of 450 C in glow discharge [7]).

The most perspective successive irradiation by 300 eV Ar^+ ions (dose 10^{19} cm^{-2}) and then by 300 eV N_2^+ ions (dose 10^{19} cm^{-2}) is presented here the first time [10].

The treatment of steel by 30-keV Ar^+-ions before its bombardment by 30-kev N_2^+ ions results in appearance of two peaks in the nitrogen depth distribution and a tail stretching for ~1 μm (Fig. 2).

Thus the implantation-plasma treatment of a steel surface by high energy and low energy nitrogen ions allows one to nitride the layer more than 10 μm thick and takes only 11 min radiation time. In this case no problem arise with the removal of the beam power released upon the target. It unavoidably arise under implantation of intense-high-energy-ion beams necessary for an increase in the depth of ion penetration into steel [11].

The results of studying an effect of various irradiation sequence for the steel by high energy N_2^+- or Ar^+-ions and by low energy ones on its microhardness by HV under various loading are given in Figure 3.

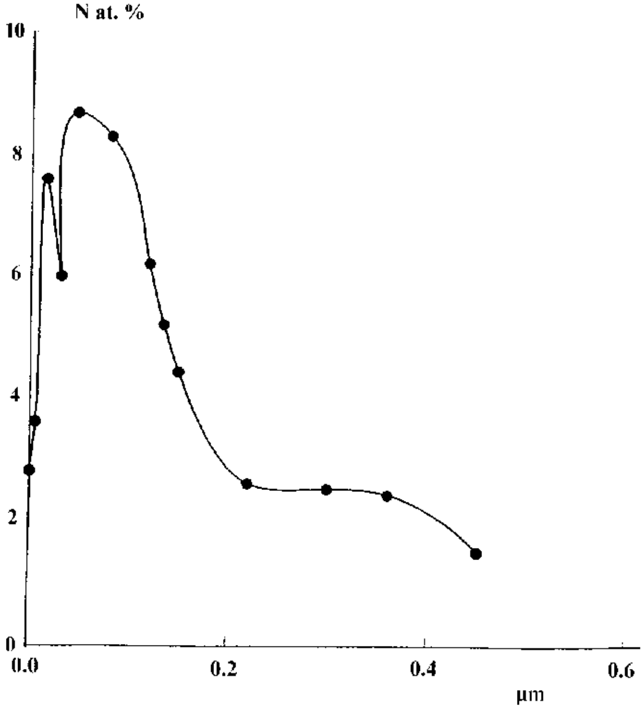

FIGURE 2 The depth distribution of nitrogen in martensite steel 0.5Cr12Ni2MoMn after successive irradiation by Ar^+ and N^+ ions with energy 30 keV (dose $10^{17}\,cm^{-2}$ for both ions).

An analysis of Figure 3 allows one to make the following conclusion:

1. N^+-ion implantation with the energy 30 keV is a low effective one for a given steel (Curve 1).
2. The plasma nitriding (Curve 2) 1.6 times increases microhardness in comparison with the N^+-high-energy-ion implantation with the energy of 30 keV.
3. The preliminary Ar^+-ions implantation (Curve 3) with the energy of 30 keV ($10^{17}\,cm^{-2}$ dose) introduces an essential contribution into the strengthening ($HV/HV_0 = 2.17$ at load 0.5 N) of a surface layer under subsequent plasma nitriding. It points to an effect of radiation defects on the strengthening of a surface layer under subsequent plasma nitriding.

4. The rise in microhardness ($HV/HV_0 \approx 3$ at load 0.5 N) and thickness of strengthening layer were higher after subsequent irradiation of the steel by 30-keV N_2^+-ions and high flux of 300-eV N_2^+ ions up to the dose of $10^{19}\,cm^{-2}$.
5. The maximal rise in microhardness ($HV/HV_0 = 3.7$) is attained under subsequent irradiation of the steel by Ar^+- and N_2^+-ions with the energy of 300 eV up to the dose of $10^{19}\,cm^{-2}$.

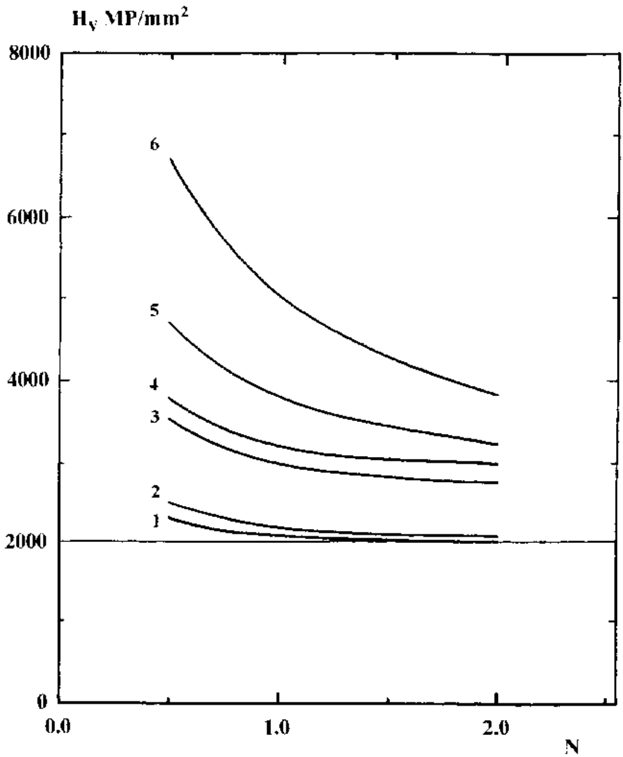

FIGURE 3 Vicker's microhardness of martensite steel as a function of loading at different regimes of irradiation by N^+ with energies 30 keV and 300 eV at 300 C. Curve 1 30 keV N_2^+ ions, dose $10^{17}\,cm^{-2}$; Curve 2 300 eV N_2^+ ions, dose $10^{19}\,cm^{-2}$; Curve 3 30 keV Ar^+ ions, dose $10^{17}\,cm^{-2} + N_2^+$, 300 eV, dose $10^{19}\,cm^{-2}$; Curve 4 30 keV N_2^+ ions, dose $10^{17}\,cm^{-2} + N_2^+$, 300 eV, dose $10^{19}\,cm^{-2}$; Curve 5 300 eV N_2^+ ions, dose $10^{19}\,cm^{-2} + N_2^+$, 30 keV, dose $10^{17}\,cm^{-2}$; Curve 6 300 eV Ar^+ ions, dose $10^{19}\,cm^{-2} + N_2^+$, 300 eV, dose $10^{19}\,cm^{-2}$.

Near the surface an X-ray amorphous layer is created as a result of implantation-plasma treatment. This essentially increases microhardness of the samples.

The similar effect of nitrogen ion penetration in depth from 6 μm to 15 μm and an essential increase in the surface microhardness under joint irradiation by high energy ($10^{17}\,cm^{-2}$ dose) N_2^+ ion beams and by low energy ones (dose is $\geq 10^{19}\,cm^{-2}$, current density is $\geq 5\,mA/cm^2$) we observed for a number of steels, independently of a crystalline lattice type and of the element composition.

3.2. Titanium Alloy VT-18U

Our previous investigation [9] shows that the effect of increase of nitrogen penetration depth and microhardness in titanium and its alloys is reached at higher flux of low energy N_2^-, higher dose and irradiation temperature than those for martensite steel. The regime of high energy N_2^+ ion implantation does not influence the mentioned parameters and was chosen the same as for martensite steel: $j = 50\,\mu A/cm^2$, $D = 10^{17}\,cm^2$.

The Figure 4 shows the depth distributions of nitrogen atoms in titanium alloy VT-18U: Curve 1 represents the depth distribution profile after plasma nitriding, Curve 2 gives that after implantation-plasma treatment. The sample temperature during 300-eV N_2^+ ion irradiation was determined by plasma flow power ($6\,W/cm^2$) and stayed at the level 550 C. The duration of plasma nitriding was determined by dose ($\geq 10^{20}\,cm^{-2}$), which can modify the phase composition of the surface layer, increase microhardness and penetration depth of nitrogen. This time in our experiment was 14 min.

The analysis of Figure 4 shows that the preliminary implantation of 30-keV N_2^+ ions increases the thickness of nitrided layer received at subsequent plasma nitriding. In that case a layer $\sim 3\,\mu m$ is uniformly saturated by nitrogen with concentration 40 – 50 at% (Curve 1), whereas at sole plasma nitriding it is only 0.7 μm (Curve 2). The thickness of total nitrided layer at implantation-plasma nitriding, measured by Auger analyzis with layer-by-layer etching, exceeds 6 μm.

It is of interest that the back side of the sample is also saturated by nitrogen after low energy N_2^+ ion bombardment (Fig. 4, Curves 1′

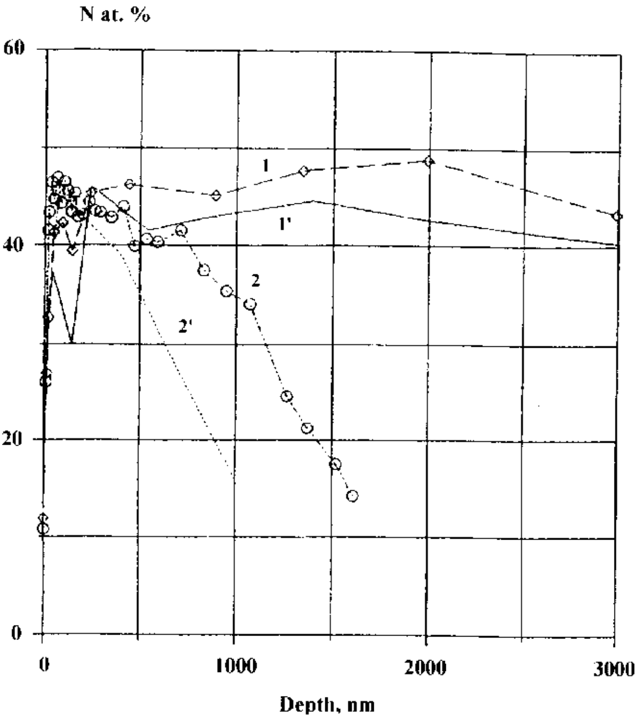

FIGURE 4 The depth distribution of nitrogen in the front (Curves 1 and 2) and back side (Curves 1′ and 2′) of titanium alloy VT-18U sample after irradiation by N_2^+ ions with energy 300 eV, dose 10^{19} cm^{-2} (Curves 1 and 1′) and after subsequent irradiation by N_2^+ ions with energy 30 KeV, dose 10^{17} cm^{-2} and 300 eV, dose 10^{20} cm^{-2}, current density 20 mA/cm^2 (Curves 2 and 2′). The temperature of irradiation was 550 C.

and 2′), without hiE post-bombardment. Rie and Lampe [12] have observed the same effect at nitriding of titanium and Ti-6A1-4V alloy in glow discharge at 700 – 1000 C.

X-ray analysis shows that after plasma nitriding the ε-phase of Ti_2–N is observed on the both sides of the titanium alloy sample. An additional implantation of 30-keV N_2^+ ions results in appearance of TiN δ-phase in the surface layer of the irradiated side, besides the sample obtains a yellow color which characterizes the stiochiometric titanium nitride. The preliminary high energy N_2^+ ion bombardment assists nitrogen atoms absorption and decreases their back diffusion from the sample at the bombardment with an incompletely ionized plasma.

The microhardness dependencies of the investigated alloys on the load after plasma nitriding and after implantation-plasma treatment are given in Figure 5. The plasma nitriding results in a microhardness increase at all loads. Near the surface microhardness increases more than twofold as compared with that of untreated samples. The preliminary high energy N_2^+ ion bombardment with subsequent low energy N_2^+ ions treatments results in a stronger increase of microhardness: near the surface it increases 3.3 times as compared with that of untreated samples.

The authors of Ref. [13] have investigated the influence of 100-keV N^+ ion implantation (dose was $5 \cdot 10^{17}\,cm^{-2}$, current density was

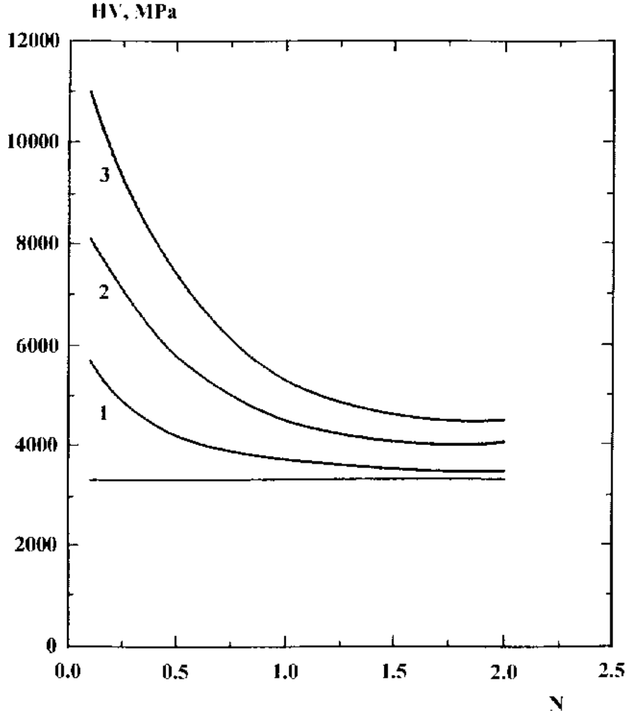

FIGURE 5 Vicker's microhardness of titanium alloy VT-18U as a function of loading after plasma nitriding at 300 eV, dose $10^{19}\,cm^{-2}$, current density $20\,\mu A/cm^2$ (Curve 1), successive irradiation by N_2^+ ions with energy 300 eV, dose $10^{19}\,cm^{-2}$ and then by N_2^+ ions with energy 30 KeV, dose $10^{17}\,cm^{-2}$ (Curve 2), and Curve 3 – irradiation sequence reverse to that for the case 2.

35 μA/cm^2) and nitriding at 400 – 700 C for one hour on wear. They have shown that nitriding at 600 C is more efficient than ion implantation. Our investigation have shown that the most efficient treatment of the titanium alloy is implantation-plasma nitriding, which the surface microhardness reach 12000 MPa, whereas the sole 40-keV N^+ ion implantation gives 6500 MPa [14] and the sole plasma nitriding gives 8200 MPa (see Fig. 5).

4. A MECHANISM OF ENHANCED DIFFUSION OF IMPLANTED ATOMS

Anomaly deep penetration of ion implanted additives is often observed at high doses and at high ion current of implantation. The conventional thermal diffusion of implanted atoms and radiation defects is not always sufficient to explain material modification at observed depth. Here a mechanism of enhanced diffusion which is possible at high concentration of implanted atoms is presented. In this case one need to take into account the interaction of implanted atoms. This interaction, being repulsive, results in pushing of additives towards the deeper layers.

This interaction changes the chemical potential μ of the matter. The addition to the chemical potential is [15]

$$\Delta\mu = \varepsilon \cdot c \tag{1}$$

c is the additive atoms concentration.

The gradient of chemical potential causes a force F acting on additive atom

$$F = -\frac{d(\Delta\mu)}{dx}. \tag{2}$$

The diffusion equation of additive atoms is as follows

$$\frac{\partial c}{\partial t} = D\frac{\partial^2 c}{\partial x^2} + B\frac{\partial}{\partial x}\left(c\frac{\partial c}{\partial x}\right), \quad B = D \cdot \varepsilon/T. \tag{3}$$

D is the diffusion coefficient of additive atoms. The second terms in (3) prevails at $Bc \gg D$ or at $c > T/\varepsilon \approx 1-3$ at.%. In this case the Eq. (3)

can be reduced to non-linear diffusion equation

$$\frac{\partial c}{\partial t} = B\frac{\partial}{\partial x}\left(c\frac{\partial c}{\partial x}\right). \tag{4}$$

At the boundary condition

$$Bc\frac{\partial c}{\partial x}\bigg|_{x=0} = -j. \tag{5}$$

this equation has a self-similar solution of a kind

$$c = \left(\frac{j^2 t}{B}\right)^{1/3} f\left(\frac{x}{x_m}\right), \quad x_m = (\varepsilon j^2 tD/T) \tag{6}$$

The function $f(\xi)$ can be well approximated by $f(\xi) = 0.9(1.5 - \xi)$. The penetration depth X_m increases if j increases.

For the boundary condition $c(0) = N_0$ we have another self-similar solution

$$c = N_0\left(1 - \frac{x}{\sqrt{2BN_0 t}}\right). \tag{7}$$

In that case the additive penetration depth grows with increased surface concentration N_0.

If the interaction of additive atom is an elastic interaction of rigid spheres, the interaction energy of such two atoms is [16]

$$U = 2\beta E_i(R/r)^6, \tag{8}$$

where E_i is the energy of additive atom introduction into the matter, R is the radius of additive atom, r is the distance between atoms, $\beta = 7.5(1-\sigma)(4-5\ \sigma)$, σ is the Poisson coefficient of the matter. Then

$$\Delta\mu = (4/3)\pi^{3/2}R^2 c(2\beta E_i T)^{1/2} \tag{9}$$

The estimation on the base of such interaction gives the penetration depth about an order of magnitude higher than that for conventional diffusion. However the other kinds of additive atom interactions are possible. This can explain a selective character of such deep penetration mechanism.

The other possible mechanism of implanted atoms deep penetration is diffusion along dislocations. A high density (up to $10^{10}\,cm^{-2}$) dislocation structure is formed under ion bombardment [16, 17]. Activation energy of an atom diffusion along a dislocation is expected to be about first Pieirls potential, usually $E_d \sim 0.1$ eV. Therefore the diffusion coefficient along a dislocation, D_d, is much higher than that in the bulk of material, D. At $T = 550°C$ D_d can be so high ($D_d \sim 10^{-3}\,cm^2/s$) that nitrogen atoms penetration through the whole sample is possible. The prebombardment by high energy Ar^+ or N_2^+ ions creates additional dislocations which assist in deep nitrogen penetration under subsequent plasma nitriding. But at high energy ion bombardment the maximum of created dislocation density is situated at the depth $1-20\,\mu m$, whereas at low energy Ar^+ bombardment one can expect creation of dislocation near the surface. Therefore low energy Ar^+ prebombardment can enhance the nitrogen penetration more effective then high energy ion bombardment.

5. CONCLUSION

1. Martensite steel 0.5Cr12Ni2MoMgMn and titanium alloy TiMo1Zr4.5Nb1.5Sn3 were nitrided up to the depth $\sim 10\,\mu m$ and $\sim 2\,\mu m$ correspondingly by high intensity nitrogen plasma bombardment. The nitriding for steel requires the heating of only to 250–300 C, and takes 5–6 min, and for titanium alloy the heating to 500–550 C takes 14 min.
2. The successive radiation of martensite steel and titanium alloy by high energy (30 keV) N_2^- ions and intensive low energy nitrogen plasma flux results in nitrogen penetration depth up to $> 12\,\mu m$ for steel, and $> 6\,\mu m$ for titanium alloy. It increases also the microhardness by factors 2 and 3 for steel and titanium alloy correspondingly as compared with that after 30–40 keV implantation only.
3. The preliminary irradiation of martensit steel surface by an intensive low energy flux of Ar^+ ions up to dose $10^{18}\,cm^{-2}$.
4. A theoretical model explaining deep penetration of implanted atoms at high dose, current density and preliminary irradiation with successive plasma treatment is proposed.

Acknowledgement

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References

[1] Guseva, M. I., "Investigation of sputtering and implantation of high energy ions in electromagnetic isotope separator", *Dissertation*, IAE, Moscow, 1962.

[2] Gabovich, M. D., Budennaya, L. D., Poriztkii, V. Ya. and Proztenko, I. M., "Vsaimideistvie atomnich chastizt s tveddum telom" (*Interaction of atomic particles with silids*, 1974), Kiev, **2**, 136 – 139.

[3] Pavlov, P. V., Zorin, E. I., Tetelbaum, D. I. *et al.* (1973). *Phys. Stat. Sol.*, **19**, 373.

[4] Guseva, M. I., Veselovzorov, A. N., Vladimirov, B. G. *et al.*, Authors certificate. N 1517371 Su1681681695, "*Method of metal and dielectric surface treatment*", Priority of discovery 17.08.1987.

[5] Guseva, M. I. (1982). *Poverkhnost. Fizika. Khimiya. Mekhanika.*, **4**, 27 – 51.

[6] Chmelevskaya, V. S., Solovyev, S. P. and Malynkin, V. G. (1990). *Itogi Nauki I Techniki. Puchki Zaryazhennych Chastizt I Tverdoe Telo.*, **2**, 151 – 193.

[7] Nunogaki, M., Suerawa, H., Kurotomi, Y. *et al.* (1991). *Nucl Instr. and Meth.*, **B39**, 591.

[8] Vladimirov, B. V., Gusev, V. M. and Ztiplenkov, V. S. (1979). *Atomnaya Energiya*, **47**, 50 – 53.

[9] Guseva, M. I., Atamanov, M. V., Veselovzorov, A. N. *et al.*, *Russian patent N 2039126*, 25.12.1992.

[10] Guseva, M. I., Atamanov, M. V., Veselovzorov, A. N. *et al.*, *Russian patent N 2070607*, 25.12.1992.

[11] Wei, R. *et al.* (1991). *Nucl. Instr. Meth. in Phys. Res.*, **B59 – 60**, 731.

[12] Rie, K. T. and Lampe, T. (1985). *Mat. Sci. Eng.*, p. 69.

[13] Martinella, R., Giovanardy, S. and Chevallard, G. (1985). *Mat. Sci. Eng.*, pp. 247 – 252.

[14] Guseva, M. I., Martynenko, Yu. V. and Smyslov, A. M., Deep modification of materials under implantation-plasma treatment. Experiment and theory. (*3rd International Workshop on Plasma-Based Ion Implantation*, Rossendorf, September, 1996).

[15] Landau, L. D. and Lifshizt, E. M., *Statistical Physics* (Technoko-Teoretichskaya literatura, Moscow-Leningrad, 1951), p. 43.

[16] Teodosiu, C., *Elastic Models of Crystal Defects* (Springer-Verlag, Berlin Heidelberg NewYork, 1982).

[17] Martynenko, Yu. V. and Moskovkin, P. G. (1994). *Rad. Eff. and Defects in Solids*, **129**, 193.