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INFLUENCE OF THE PLASMA STREAM IRRADIATION ON THE SURFACE MODIFICATION, STRUCTURE AND PROPERTIES OF MATERIALS

V.I.Lapshin, I.M.Neklyudov, V.I.Tereshin
National Scientific Center "Kharkov Institute of Physics and Technology"
61108 Kharkov, Ukraine

1. Introduction

Investigation of processes of intensive pulsed fluxes of particles and radiation influence on materials properties is now of great interest. This is due to two reasons at least. On the one hand, there is a necessity of investigations of fusion reactor materials behaviour under the irradiation by powerful pulsed plasma streams [1-4]. On the other hand, there was shown the possibility of material surfaces modification and hardening by pulsed plasma streams irradiation [5-10].

For forecasting the behavior of the fusion reactor materials irradiated by powerful plasma streams during many years there were used data obtained in investigations of materials behavior under their irradiation with steady-state high-energy ion beams of hydrogen and helium. In this case the influence of such parameters, as wide energy spectrum of particles, bombarding materials surfaces, and pulsed character of irradiation, that are essential for conditions of fusion reactor operation, was not taken into account.

As it was shown at the beginning of eightieth [11], due to the spread of particles by energy one of the most intensive factors of surface erosion, namely radiation helium blistering, can be suppressed. This was the reason for the verification of the conclusions about the possibility of a number of materials using in fusion reactor. As to the investigation of pulse surface loading, this is appeared to be of importance when there was shown that it is not possible to avoid such strong plasma instabilities as current disruption and others, followed by high power pulsed plasma flows (with power density 1-10 MW/cm^2) to the surfaces. The first experiments, carried out with pulsed plasma streams [1-3], have shown that such pulse plasma surface loading essentially influence the structure and mechanical properties of metals and constructional steels.

2. Experimental installation and diagnostics

All experiments, described here, were carried out in "Prosvet" device with the pulse plasma accelerator (PPA) as a plasma source [12]. Coaxial plasma accelerator with cathode 5 cm in diameter and 60 cm in length, and outer anode 12 cm in diameter generated plasma streams with the parameters as follows: plasma density (1-2)x10^{14} cm^{-3}, average ion energy up to 2 keV, pulse duration (3-5) μs, the repetition rate 1 shot per 3-5 min. Plasma energy density was varied in the range of (5-40) J/cm^2. PPA operated with different working gases. Hydrogen, nitrogen, helium, argon or their mixtures were used in those experiments.

The samples of different geometry and materials were used in these experiments. Among these there were samples of vanadium, niobium and nickel [1-3], copper and its alloys, stainless steels H16N15M3B and H18N10T [4, 10], as candidates for the first wall or inner elements of fusion reactor, as well as steels 40H, 12HN3A, ShH15, steel 45 and other steels and hard alloys VK8, VK20 [6, 8, 9, 11]. The geometry of samples was varied in dependence on type of experiment. For investigations of mechanical properties of materials samples of 200 μm in thickness with area of surface 10x3.5 mm were in use. The surfaces of annealed samples were chemically and electrolytically polished before irradiation. Those samples were placed in special supporting system providing good thermal contact with metal substrate. The temperature of sample surface was not controlled, but it could achieve the melting point. For analysis of surface modification the samples of (3-5) cm in diameter and 5 mm in thickness were utilized.

Magnetic and electric probes, local calorimeters, bolometers, spectroscopy and mass-energy analyzer were used for measurements of plasma parameters. As to the surface analysis, there were used microhardness-meter, profilograph, optical and electron microscopes, metallography, X-ray analysis and so on. Mechanical properties of samples were defined by deformation diagrams of sample tension.

3. Results of experiments and discussion

3.1. Vanadium and niobium

Vanadium and niobium samples were irradiated by plasma streams up to the dose of 2.4x10^{18} ion/cm^2 (around 400 shots). Analysis of sample surfaces with scanning electron microscope has shown that very deep cracks appeared at the boundary of grains of both materials as a result of irradiation (Fig. 1).

It was possible to expect that such a strong intergranular cracking between grains could influence the mechanical properties of the whole sample. Especially that under the irradiation the surface layer (about (1-3) μm) microhardness was increased by 3-6 times (Fig. 2). Nevertheless, tension test of the irradiated samples of vanadium and niobium had shown that their mechanical properties were not essentially changed.

As it was mentioned above, the temperature of the sample surface layer could be essentially increased under irradiation due to the high-energy deposition into the sample. Increasing the sample temperature provides drastic increase of the spread of hydrogen diffusion. As

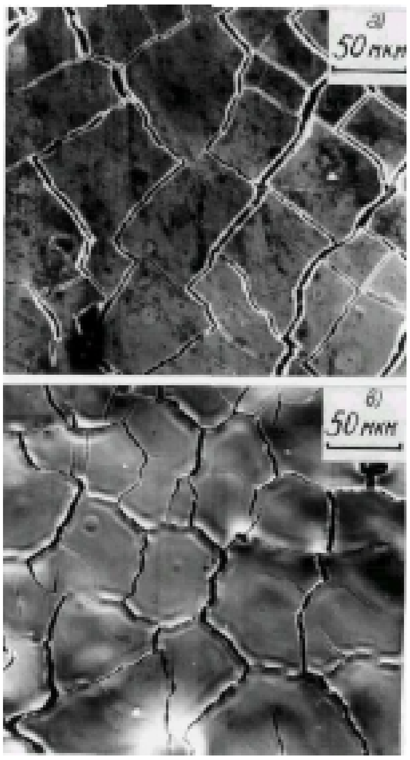


Fig.1. Microphotography of sample surfaces, irradiated by hydrogen plasma with fluence 1.8x10^{18} cm^{-2}: Up – niobium, down – vanadium; a – common view, b – details of structure

the result, one part of hydrogen abandons the material, but another one is accumulated in the region of inter-grains boundaries, forming the gas-filled microcavities and bubbles of high pressure. Besides, in the bulk of material there are formed rather stable complexes of hydrogen atoms with radiation-induced defects and atoms of impurities that provides hardening of the surface layer.

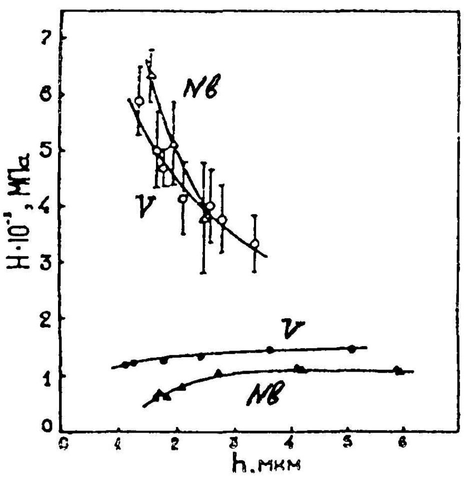


Fig.2. Dependencies of microhardness of vanadium surface (o, •) *and niobium one* (Δ,▲) *on the depth of indentor immersion in initial* (o, Δ) *and irradiated* (•, ▲) *states*

3.2. Copper and its alloys

Copper and its alloys are discussed as possible structural materials of fusion reactor. As far as in the case of FR copper materials should be influenced by hydrogen, there was a necessity to exclude such of copper alloys that have high "hydrogen brittleness". The most stable with respect to the "hydrogen brittleness" were found the following materials: copper produced by electron-beam melting (MVE) as well as types of copper alloys developed in the NSC KIPT - copper micro-alloyed by palladium (MVP), yttrium (MMVI), scandium (MMVS), and zirconium (MMVC).

The irradiation of samples of these materials was carried out under the plasma stream energy loading of 10 J/cm^2.pulse up to the dose 1.5x10^{18} cm^{-2}. Mechanical properties of samples, examined under the room temperature, are shown in Table 1.

One can see from this table that treatment of copper materials by plasma leads to the increasing of the yield point and to the ultimate strength as well as to the decreasing of their plasticity. One need to note that the maximum increase of yield point is observed for non-alloyed copper produced by electron-beam melting (about 270%). An increase of yield point of palladium-alloyed copper and alloys of copper micro-alloyed by chemically active dopants is around 90%.

3.3. Steels H18N10T and H16N15M3B

To avoid samples bending under the one side plasma irradiation, the samples treatments were carried out alternately on the front and back sides. Total dose of irradiation was (6-7).10^{17} ion/cm^2. Purely hydrogen and helium plasmas, as well as their mixture (50% H + 50% He) were used.

Table 1. Mechanical properties of copper and alloyed copper before and after treatment

Type of copper	Mechanical properties							
	Before plasma treatment				After plasma treatment			
	$\sigma_{0.2}$ KG/mm^2	σ_B kG/mm^2	δ, %	H_μ kG/mm^2	$\sigma_{0.2}$ kG/mm^2	σ_B kG/mm^2	δ, %	H_μ kG/mm^2
MVE	4.6	22	70	48	16.9	26	29	68
MVP	6.6	20	24	57	12.9	24	23	63
MMVI	4.4	22	72	51	8.2	23	46	67
MMVS	9.2	27	22	68	17.9	28	21	73
MMVC	7.0	20	38	61	12.0	20	32	72

Mechanical tests of as-received and being irradiated samples were done under the room temperature. The values of $\sigma_{0.2}$, σ_B, and δ measured under different experimental conditions are collected in Table 2.

Table 2. Mechanical properties of steels H18N10T and H16N15M3B

Irradiation conditions	Steel	$\sigma_{0.2}$, kG/mm^2	σ_B, kG/mm^2	δ, %
Before irradiation	H16N15M3B	205	526	42
	H18N10T	207	604	63
Hydrogen plasma	H16N15M3B	352	540	17
	H18N10T	357	632	27
Helium plasma	H16N15M3B	369	561	18
	H18N10T	394	564	23
Hydrogen-helium plasma	H16N15M3B	349	579	18
	H18N10T	336	617	23

One can see from the data of Table 2 and sample strain diagrams (Fig. 3) that mechanical properties of samples were essentially changed under their irradiation with pulsed plasma streams. As the result of irradiation, yield point of steels was increased by 1.7-1.8 times and the ultimate strength increased as much as 10 %. The significant variation was observed for the value of elongation. This value was decreased by 2 times for steel H16N15M3B and by 2.5 times for steel H18N10T. One need to note that even the high temperature annealing of samples dose not take off completely their hardened state. Etching from the both sides of sample surfaces of material layers with thickness up to 20 μm practically do not influenced the mechanical properties of materials gained due to their irradiation. This was the reason to conclude that achieved changing of the mechanical properties of thin steel samples is the result of structure-phase state variation in the whole sample volume.

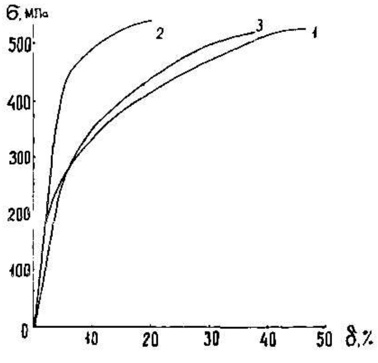
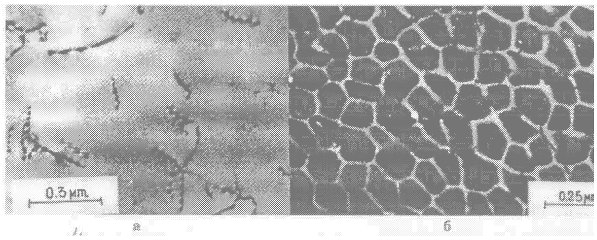


Fig.3. Diagram of H16N15M3B steel samples stretching for initial state (1), after irradiation (2) and after annealing of irradiated sample under 1050^0 C during 10 min

3.4. Electron-microscopic investigations of material structure

Electron-microscopic investigation of structure of stainless steel H16N15M3B samples had shown that it has monophase face-centered cubic lattice structure, equiaxial granes (with mean size of about 25 μm) with large-angle boundaries and small number of annealing twins. The second phase precipitates are presented by niobium carbonitrides with sizes within (0.1-1) μm and density ≈ 10^{12} cm^{-2}. The density of dislocations was ≈ 5x10^8 cm^{-2} (Fig. 4, a).



a **b**

Fig.4. Microstructure of H16N15M3B steel surfaces: a) – initial sample, b) – sample irradiated with helium plasma

The irradiation result is the essential changes of surface layer microstructure. One can see in Fig. 4, b that irradiation leads to shattering of grains by the blocks. The cell structure is formed with cell size of (0.15-0.25) μm. It was shown by electron diffractometry and dark-field electron microscopy that boundaries of blocks, seen at the surface of irradiated samples, are the amorphous phase inter-layers.

Step by step etching of the sample surface, and the electron microscopic analysis, had show that the cell structure, formed by blocks of grains, separated by the layers of quasi-amorphous phase, extended into a depth of up to 10 μm. With further increase of a depth this structure was gradually transformed into the cells, separated by dislocation network, the density of which was decreasing with the depth and disappeared at the depth of 25 μm (Fig. 5). At the depth of more than 25 μm the niobium carbonitrides appearance was indicated. Their absence at the upper layers of samples is the evidence of very high temperature of upper layers under the plasma irradiation.

The dislocation structure and shattering of grains by blocks, appeared under the plasma irradiation, is qualitatively similar to ones, appeared under the high temperature thermo-mechanical steel treatment [13]. Due to the creation of such structures one can to explain the variation of mechanical characteristics of austenite steels observed under their irradiation with powerful pulsed plasma streams.

3.5. Structural steels and alloys

One of the main aim of investigations of plasma streams influence on the properties of structural steels and alloys, widely used in different types of tools, is analysis of possibility to modify their surfaces to achieve their hardening. A number of materials were used in these experiments, such as steels H40, 12HN3A, H12, steel 45, steel 10, ShH15, 65G and so on. The samples of these materials were irradiated by pulsed streams of nitrogen, hydrogen, nitrogen-helium, nitrogen-hydrogen and others plasmas.

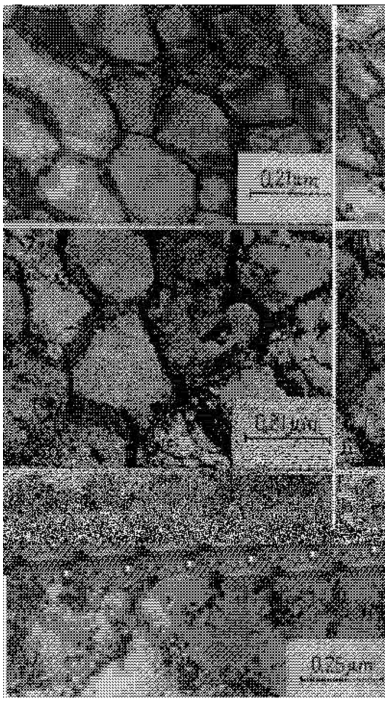


Fig.5. Cell boundaries structure changes in the irradiated steel in dependence on the depth from the surface: a – 1 µm, b – 5 µm, c – 25 µm. Magnification is $12x10^4$

Surface layer formation. Optical and electron microscopy were used for the analysis of structure of material cross-sections, prepared by diamond saw. As the result of surface irradiation by plasma streams with plasma energy loading within (10-40) J/cm^2, the melt layer was formed (Fig. 6). Its thickness was of an order 12 µm for energy load around 15 J/cm^2 and increased with energy loading increasing, achieving 30 µm for plasma energy density of 40 J/cm^2. The material structure changes were observed even in the bulk of steels up to the depth of an order 70 µm (the grain structure was changed and the number of bubbles was essentially decreased).

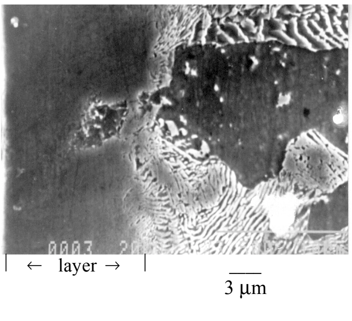


Fig.6. Cross-section of the H40 steel sample, irradiated with plasma, obtained by electron microscope

Phase-structure analysis. The results of X-ray surface analysis of H12 steel, both for irradiated and non-treated materials are shown in table 3. Similar results were obtained for other grades of steels.

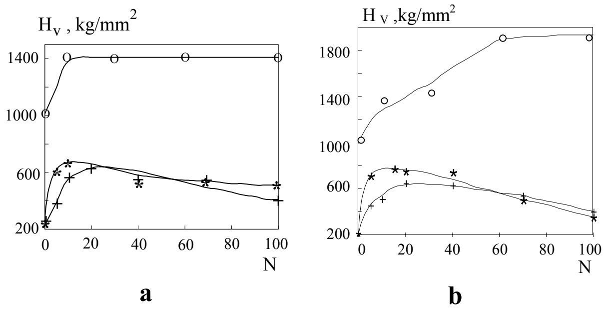
Table 3. Results of X-ray analysis of steel H12

#	2Θ°, CuK$_\alpha$	I, relative	d (Å)	Phase
1	22.00	Weak	4.04	Cr_2N
2	38.20	Weak	2.3559	Fe_2N
3	42.10	Weak	2.1462	Fe_4N
4	43.00	Middle	2.1034	Fe_2N
5	44.80	Middle	2.0230	α-Fe
6	50.30	Strong	1.8139	γ-Fe
7	73.70	Weak	1.2854	γ-Fe
8	89.80	Middle	1.0921	Fe_2N

One can see in this table, that the main phase at the surface of initial (non-treated steels) is α-Fe one. Besides the γ-Fe and Fe_3C (cementite) phases are seen. As the result of plasma irradiation (with the dose $1.5x10^{18}cm^{-2}$) the main phase at the surface appeared to be γ-Fe phase with preferred orientation in the direction [100]. The lattice spacing of γ-Fe phase for H12 steel irradiated with plasma was a=3.6256 Å that is essentially higher than the parameter of crystal lattice of common γ-Fe (a=3.5264 Å). One can assume that this increase of lattice parameter for γ-Fe was due to the effective nitrogen implantation into the crystal lattice. It was shown in [10] that under the similar conditions in the stainless steel H18N10T samples, a number of implanted nitrogen could achieve 5% of the total dose of irradiation.

Strong blurring of the diffraction reflections from the surface of steel 40H, observed after its irradiation with plasma, was the evidence of initial stage of surface layer amorphization.

Surface microhardness. The surface microhardness variation with increasing of the irradiation dose (number of pulses) is shown, as an example, in Fig. 7 for three kinds of steels and different plasmas.



a b

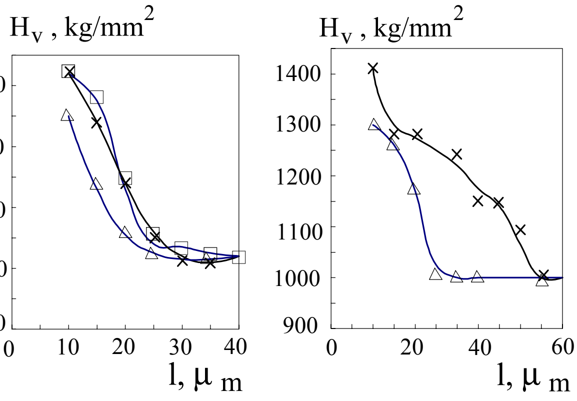
*Fig. 7. Dependence of microhardness on the number of plasma pulses: + - 12HN3A; * - 40H; o - VK-20. a - nitrogen plasma, b - hydrogen-nitrogen plasma*

These dependencies of microhardness on the total dose of samples treatment, in principal, are similar to all irradiated materials. The maximum value of microhardness was achieved for the exposure dose of $(5\text{-}10)\cdot10^{17}cm^{-2}$ (5-10 plasma shots). The relative increase of microhardness of irradiated samples as compare to the initial ones was varied in the region of (1.4 -4) times in dependence on grade of steel an its preliminary treatment. The absolute values of microhardness for different steels and alloys both for irradiated and not irradiated ones are shown in Table 4. One need to note that essential increase of microhardness was observed even for preliminary thermally quenched steels.

Table 4. Microhardness of materials processed by nitrogen plasma with energy density (15 - 20) J/cm^2

Material	H_V, kg/mm^2 Before processing	H_V, kg/mm^2 After processing
Steel 10	200	510
Steel 45	250	628
Steel 45, quenched	370	796
40H	252	751
40H,quenched	386	794
37O-S4	352	742
SAE 1040	264	527
65G	350	560
12HN3A	236	630
12HN3A, quenched	387	715
H12	312	510
H12, quenched	553	593
WCo20	1000	1400

The observed increase of microhardness of different steels and alloys is the result of phase-structure changing in the surface layers of materials due to mainly specific thermal influence and, only partly, due to the process of surface nitration. Confirmation of this conclusion follows from the practically identical dependencies of both microhardness on the number of pulses (Fig. 7) and microhardness distribution on the depth (Fig. 8) of irradiated materials for samples treated with the plasma streams of different gases.



a **b**

Fig. 8. Dependence of microhardness of different materials on the depth from the surface irradiated by nitrogen (×), hydrogen-helium ( ) and hydrogen-nitrogen (Δ) plasmas: a-12HN3A; b- WCo20

The depth of surface layer with increased microhardness was varied in dependence on plasma stream loading and achieved (20-30) μm for plasma energy density (30-40) J/cm^2 (for instance, Fig. 8).

One need to note that for all treated materials the depth of layers with increased microhardness (Fig.2 and Fig. 8) was essentially higher (more than 100 times) the mean free path of plasma ions in materials.

Effect of "long-ranging" (hardening into the high depth) takes place under the different types of solids irradiation, both steady state and pulse influence by high-energy beams of ions and neutrals, and has different physical nature. As to our case, the main reason for changing the structure and properties of materials under plasma irradiation is, naturally, due to the pulsed high temperature heating of the surfaces up to the temperatures exceeding the melt ones under the conditions of high shock pressure by plasma streams.

Wear resistance of steels irradiated by plasma streams. Investigations of variation of steel surface wear resistance under plasma streams irradiation was carried out for many grades of steels (40H, ShH15, steel 45 and so on) both non quenched and previously thermally quenched ones. The wear and tear of samples surfaces was measured by pin-on-disk method described in [9]. The speed of indentor sliding was 0.8 m/s under the normal load of 7 kG/mm^2. A friction path was varied in the range of (1-10) km. These tests followed by analysis of linear wear of sample surfaces, measured by profilograph-profilometer. Some results of such measurements are shown in diagram of Fig. 9 for friction path of 1 km.

It follows from these measurements that wear resistance of irradiated steels was increased up to 20 times (for 40H steel, 13 times for ShH15 steel and so on). It was increased up to 4 times even for preliminary quenched steels. Increase of friction path up to 20 km did not lead to essential increase of linear wear. This means that up to this friction path the wear and tear does not exceed the thickness of modified layer. Wear resistance tests carried out with using some other methods (flat-on-flat, abrasive, and cavitation methods) have shown also essential increase of wear resistance of steel samples irradiated by plasma.

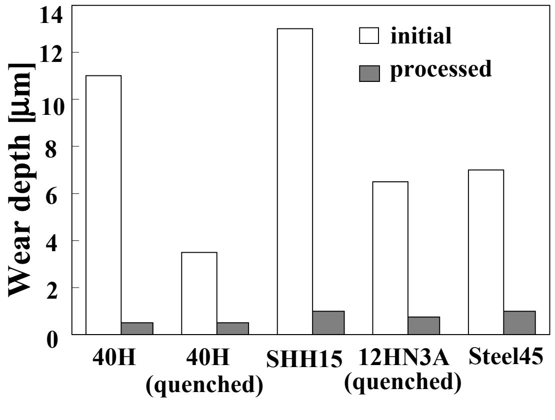


Fig.9. Linear wear of different steels for initial and irradiated samples

One need to note that plasma irradiation of samples leads to some increase of friction coefficient of their surfaces. This is especially true for surface irradiation by plasma with energy density more than 20 J/cm^2. In the latter case there was observed increase of surface roughness also. For energy load of about (12-15) J/cm^2 the roughness parameter R_A was of an order (0.4-0.7) μm. The latter result is good enough for many machinery tools.

Conclusions

The obtained experimental results have shown that irradiation of materials with powerful (1-10 MW/cm^2) pulsed plasma streams influence the properties of different metals and alloys in different way. For instance, in the case of pure vanadium and niobium such irradiation essentially changes the microstructure of their surfaces, but practically does not influence their mechanical characteristics. On the contrary, such irradiation of some austenite steels, H16N15M3B and H18N10T, leads to the deterioration of their mechanical properties. The most unfavorable factor of such plasma influence, from the point of view of their behavior in fusion reactor, is the drastic decrease of a plasticity of the mentioned above structural steels. Nevertheless, one need to note that experiments, described above, were carried out with steel samples of small thickness (200 μrn). For those samples the structure changes, that leads to changing of the sample mechanical characteristics, achieve the depths that are comparable with sample thickness. In the case of massive material samples effect of formation of structures, penetrating into the respectively small depth, can be insufficient for noticeable influence on the mechanical properties of steels. On the other hand, the conditions of our experiments were not adequate to fusion reactor conditions. In the latter case the pulses of plasma streams irradiating the material surfaces under current disruptions or other instabilities should be essentially longer that can essentially increase effects discussed above.

There was shown the possibility of essential surface modification of different steels and alloys under their irradiation by powerful pulsed nitrogen (or other gases) plasma streams. The thickness of modified layer with increased microhardness and wear resistance was increased with plasma energy loading and achieved 30 μm for plasma energy density of 40 J/cm^2. The wear resistance increase was as much as by 10-20 times (by pin-on-disk method of wear tests) and depended on the grade of material and plasma energy loading. Wear resistance was increased by several times even for preliminary thermally quenched steels. Due to the effects of long-range action the possibilities of essential hardening in depth of materials and tools are in a prospect.

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