Effects of low pressure radio frequency discharge on the physical and mechanical characteristics and chemical composition of diffusion coating on a surface of complex configuration details

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Abstract. The work deals with the influence of low-pressure radio frequency (RF) discharge on the surface properties of metals and their alloys. As objects of research to study the interaction of the jet low pressure RF discharge into the surface of the material the following materials were chosen: tungsten cobalt alloy, high speed steel, structural steel. In the presence of the materials energy parameters of low pressure RF discharge flows in the discharge chamber and the electrode gap were studied. A quantitative assessment of the gas composition inside the chamber to determine the characteristics of the plasma flow, making the major contribution to the modification of the surface was carried out. The influence of the input parameters of the plasma unit on the discharge characteristics was held. Identification of the main processes responsible for the modification of the surface of metals and alloys with the metal sample in the plasma jet and the effect of samples of products complex configuration on its properties is determined.
The results of studies of physical and mechanical characteristics and chemical composition of the surface layers of high-speed steels, alloys and steel before and after treatment by low pressure radio frequency discharges with the instrumental indentation methods and X-ray photo-electron spectroscopy. With the help of the quality control system of the inner surfaces tubular products were studied.

1. Introduction
For the set technological and operational properties of mechanical engineering products numerous technologies are widely used, allowing to modify the surface properties of materials.

Depending on the physical and chemical processes occurring during the modification of materials, hardening methods can be divided as follows: the methods of forming a coating or film on the surface of the product; methods that convert the chemical composition of the surface; methods of modifying microgeometry surface layer (surface roughness); methods that alter the structure and energy supply of the surface; methods that alter the structure of the material throughout.

There are several methods of modifying the surface by which the individual nanolayers properties can be changed, while other surface properties remain unchanged. One of such methods is a magnetic pulse treatment, which can be used to harden the layers of 3-10 nm thickness, however, the surface roughness of this layer does not change, fissured and embossed layers remain.

For surface cleaning and intensifying the process of chemical-thermal treatment various methods of electro physical effects are used: nitriding in an ultrasonic field at high pressures in a fluidized bed, ion nitriding in a glow discharge plasma, heating high-frequency currents, finishing treatment in a glow discharge ion bombardment, plasma-chemical treatment in active gas environment. However, the processes are very long, it takes time for at least one hour. At glow discharge plasma surface of the material is bombarded by charged particles. Plasma in an oxygen environment is effective for the cleaning of organic contaminants, since carbon is oxidized and removed in the form of CO and CO2 [1, 2].

Plasma phase condensation method in the conditions of ion bombardment is the most widely used in the domestic industry. As a result of erosion of material in the cathode spots, the burning at the cathode, which material corresponds to the composition of the coating material the plasma stream is generated. The anode is the body of the vacuum chamber. The pressure in the chamber while maintaining the discharge is 10-1 - 10-5 Pa [3]. Deposition of titanium nitride occurs by the evaporation of titanium cathode in nitrogen at pressures of 0.1 - 0.4 Pa [4]. Addition of methane or acetylene into the vacuum space or chamber leads to a condensation of carbide coating. To achieve high density of ion flux values directed to the surface plasma-specialized devices to control both the rate of plasma flow and its physical characteristics are used [5].

The ion-plasma methods are carried out by condensation of the plasma state of matter on the surface of a product [6,7]. These techniques are now widely used to produce heat-resistant and wear-resistant coatings of compounds such as carbides and nitrides of metals of IVa, Va and VIa groups of the Mendeleev periodic system, oxides of aluminum, silicon, beryllium. These methods permit to obtain coatings of not more than 0.1 mm thickness. Product temperature during the deposition process is 500 - 800 K, deposition rate - not more than 0.03 m / s. The hardness of the coating is more than 14 GPa, the roughness parameter degrades no more than 1 micron.

Plasma promotes chemical reactions between the atoms of the reactive gas and metal, formation of the gas ions, which affects the flow of the substrate, and also stimulates the neutral particles that are deposited on the substrate. Exposure to high-energy ion flux to the substrate influences the coating adhesion strength to a substrate, the coating structure, etc. By ion bombardment of the substrate the surface layer defects are formed, spraying, change of morphology and surface composition, crystallographic structure, the absorption of gas, heating the substrate are possible.

Based on the analysis of sources [8-11], there are many scientific papers among the PVD methods devoted to the studies of nanostructured materials with unique physical and mechanical properties, obtained by magnetron sputtering arc evaporation. Nanostructured carbide, nitride and boride coating (TiC, TiN, TiB2, Ti (C, N) etc.) are used in industry in many countries as a wear-resistant coatings on metal-working tool.

Electric spark alloying (ESA) based on the pre-emptive destruction of the anode material with the spark discharge in the gaseous environment and the subsequent products transfer to the cathode erosion [12]. On the surface of the cathode the layer with anti-corrosion properties, high values of hardness and wear resistance, change of thermodynamic state and phase composition is formed. Erosion of the alloying of the electrode depends on the processing conditions, material structure and other factors.

Efficiency of electric spark alloying process, the morphology and thickness of the coating depends on the phase composition of products of erosion, which in turn depends on the technology processing conditions: duration of doping, discharge energy, form of tool electrode movement. Phase and structural transformations are associated with the distribution of chemical elements in the surface layer, dependent on the duration of the treatment, discharge parameters, the properties of the electrode material and other factors.

The most important feature of the electric spark alloying process - the possibility of forming a coating on the working surfaces of parts with a wide range of physical, mechanical and chemical properties by varying the electrode material, electrical characteristics, transconductance environment. The formation of the hardened layer by doping parts improves their durability, which depends on the structure of the coating, the magnitude of residual stress and other factors. The electric spark alloying process disadvantages include limit thickness (50 micrometers), high roughness of the coating, the possibility of applying only to the conductive coatings.

The coatings obtained by different methods of deposition and sputtering, have a significant drawback - it is a problem of an adhesive strength, in order to achieve high levels of quality that requires pre-finishing and surface preparation. The main drawback of the method - the presence in the coating of microdroplet phase.

Using the method of ion-plasma processing of structural materials inner surface of the articles can be processed. A method of vacuum processing of the inner tube surface includes a coaxial arrangement of the discharge electrodes. As one of the electrodes of the workpiece is used, the initiation of the vacuum electrical discharge between the electrodes is created by the potential impact of bit-discharge plasma onto the inner surface of the product. The potential difference is created between the cathode -product and the anode made of non-magnetic material that is not shorter than the length of the workpiece. Exposure to plasma is carried out with applied to the discharge zone crossed electric magnetic fields, and the discharge current density is maintained at 15-20 mA / cm2, nitrogen pressure 25 Pa, and the magnetic flux density equal to 10-20 mT [13]. With this method the corrosion resistance of the inner surface of the tubular article is increased. The disadvantage of the method is the processing time. Vacuum ion-plasma method does not allow to speed up the process by increasing the density of the ion flow, since there is overheating of parts as a result surface hardness is reduced [14].

The above drawbacks are not observed in the modified nanodiffuzive nanolayers surface including coatings, which are obtained by ion implantation by exposure to RF discharges [15-18]. The method consists of gas saturation of the surface, gas atoms and molecules are introduced into the surface of the metal layer, reacting with the atoms of the material to form compounds of nitrides or carbides of the corresponding metal. Direction of nanodiffuzive layers creation on the surface of metals and alloys is poorly studied. These shortcomings have led to the development of long-term process, which combines the operations of the materials evaporation, directional particle flow formation and introduction of them to the treated surface, the ionization and excitation of atoms, cleaning and polishing of surfaces using radio frequency plasma torch operating at low pressures [19,20]. The advantages of this method for processing materials in order to form the directional properties of the surface are: short duration of treatment process, coating uniformity, the possibility of modifying the configuration of complex products and different materials, forming of a high-density flow of ions, the use of different types of electrodes, including electrolytic [21-27].

2. Experiment

For the processing of metals and their alloys by the flow of low pressure radio frequency (RF) plasma radio frequency capacitor installation with symmetric planar electrodes developed at the Department of “Plasma chemical and nanotechnologies high molecular materials” is used (Figure 1) [28,29]. RF voltage is applied from the radio frequency generator AECesar 1330. For the automatically matching of the generator with a load the matching device AEVarioMatch 5000 is used.

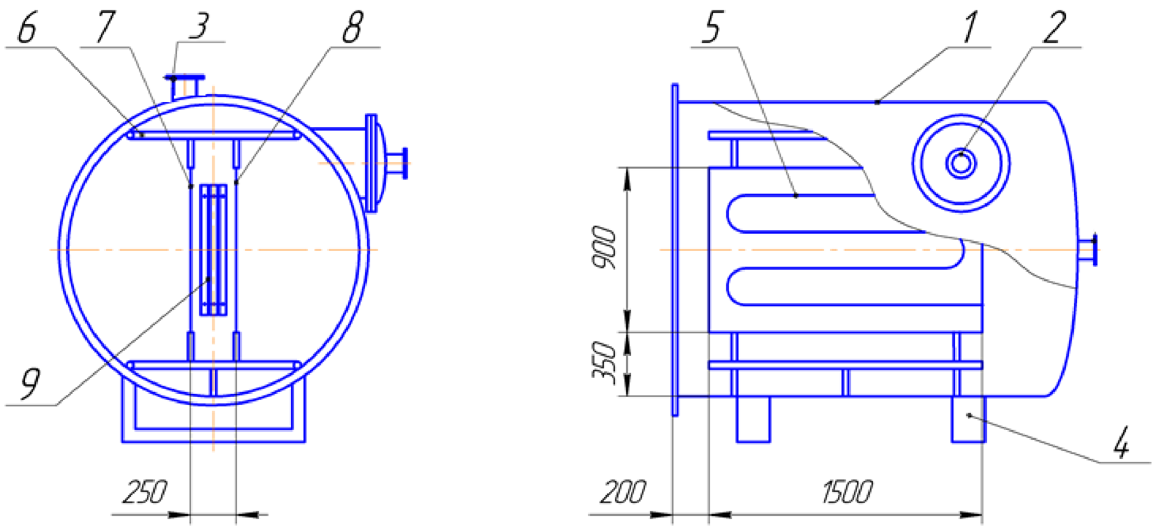

Figure 1 – RF plasma unit: 1 - vacuum chamber, 2 - flange vacuum system 3 - RF input, 4 - bearing, 5 - circuit cooling, 6 - dielectric rack 7 - RF electrode, 8 - ground electrode, 9 - workpiece.

The camera body is welded, made of stainless steel. The chamber walls are equipped with ribs. On the top radio frequency inputs, the unit of gas flow controllers, RF generator to the load matching system are placed. Hydraulic collectors of cooling systems are situated on the left side of the camera. There are nozzles for connecting the pumping system on the back wall of the chamber. is A collector system of process gases inlet is inside the discharge chamber in the door flange plane between the RF electrodes.

Vacuum pumping system is comprised of:

- Vacuum spool assembly;
- Vacuum double-rotor pumps;
- Vacuum pneumatic valve;
- Vacuum pneumatic valve;
- Gas flow regulator;
- Locking the gauge;
- Thermal sensor;

Spool vacuum pump AVZ-180 is designed to produce a pressure of 5000-6000 Pa depending on plasma gas flow rate or a mixture thereof (0.004 - 0.12 g / s) in a vacuum chamber and maintaining the pressure at the outlet the vacuum double-rotor pump DVN-500 during the operation of the first pump is contemplated. Pneumatic shutter is designed to prevent the ingress of atmospheric air into the vacuum chamber during emergency situations. Valves KVP-100 and KVP-63 are used for switching and bypass pumping foreline. Valve DPC-63 serves for air inlet after the manufacturing cycle.

Plasma torch with a flat electrodes for plasma discharge represents two water-cooling copper plates located at a distance of 40 cm. The electrodes are placed in a vacuum chamber with the special means for securing samples located between the electrodes.

Closed-circuit cooling system is designed to cool the unit AVZ-180 and RF electrode. System is based on the installation of refrigeration TDC-20.

Process parameters of RF capacitive discharge in a vacuum chamber with planar symmetrical electrodes are the following: gas pressure 20 - 25 Pa, the gas flow rate 0.01 - 0.1 g / s, the power delivered to the electrodes 1,5 - 1,8 kW. Products treated in pure argon plasma for 20 minutes are followed by 20 minutes in a mixture of argon and methane. Oscillator frequency - 13.56 MHz.

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Tungsten cobalt alloys, high-speed steel as the most common materials in the tool industry, intended for the manufacture of cutting tools and machining, and structural steel designed for the manufacture of hydraulic actuators used in mechanical engineering were chosen as objects of study for the researches.

Process parameters of the discharge of the tubular article inside are the following: gas pressure 20 - 25 Pa, gas flow 0.001 - 0.01 g / s, the power delivered to the electrodes 1,5 - 1,8 kW. Argon was used as the plasma gas in the processing of tubular products with the aim of pre-polishing and cleaning the surface from dirt, a mixture of argon and nitrogen in a ratio of 80:20 was used for carrying out the processes of hardening of the surface layers. The duration of treatment in the argon plasma was 20 minutes, then followed by 20 minutes in mixture of argon and nitrogen. Oscillator frequency - 13.56 MHz.

The workpiece is set and sealed between the upper and lower vacuum sealing flanges. The tubular product is part of the oscillating circuit and is analogous to inductance. RF power (13.56 MHz) of the radio frequency generator is supplied to the oscillation circuit. In the vicinity of the electrode vacuum tuning capacitor forming an oscillating circuit with electrode and allowing the best possible transmission of RF energy to produce accurate contour adjustment to the working frequency of the generator are arranged. Matching device is used for the automatically matching the generator with a load.

To equalize the temperature along the length of the product an additional supply of DC voltage is provided. Pumping equipment - vacuum unit ATS-150, consisting of a backing pump AVZ-20D and booster DVN-150. Vacuum gauges - membrane capacitive sensor MKS 627B. Working gas supply is held via the mass flow controller MKS 1179A.

The tubular product is isolated from the main body of the vacuum plant with quartz inserts. To the lower and upper parts of products electrical contacts are provided through which the product are fed with the RF voltage from the LC - circuit with a frequency of 13.56 MHz. Thus, the generated radio frequency electric fields are closed to the grounded to the portions tooling followed after insulators.

There is a potential difference between the electrodes that creates an electric pulling field within a tube channel that allows penetration of the plasma over the entire length of the workpiece for uniform processing.

Researches of the chemical composition of the surface layers of metals and alloys in plasma were carried out for the estimation of the impact effect of low pressure jet RF discharge on the details placed to the discharge chamber for the modifying processes. X-ray photo-electron spectroscopy (XPS) on SPECS electron spectrometer using A1Kα radiation (1486.6 eV) combined stratified surface etching of argon ions with an energy of 4 keV and a current density of 30 mA / cm2 (~ etching rate of 1 nm / min) was used.

Analyzes of the changes in the chemical bonds of the surface layers and the analysis of the depth of penetration of atoms of alloying elements into the metal was carried out by X-ray photoelectron spectroscopy. Experimental data are processed using the software package CasaXPS. The relative error in determining the concentration of elements was ± 0.5% of the measured value. The concentrations are calculated by the integral intensities of the respective spectra taking into account the element of sensitivity coefficients that reflect the photoionization cross section of the main electronic levels. Decomposition of multicomponent spectra of C1s and O1s were carried out using the software package CasaXPS. Some peaks are approximated by a mixed function of the Lorentz-Gauss. Their parameters are taken from reference spectra measured under identical conditions.

Mechanical properties were determined on the samples before and after treatment of the surface by low pressure RF plasma in methane by the indentation in an integrated measuring system NanoTest 600, which is designed to study the physical and mechanical properties of materials on the microscale measurements. The researches were performed according to the method of Oliver - Pharr [Oliver W., Pharr G. An Improved Technique for Detemining Hardness and Elastic Modulus Using Load and Displacement Sensing Indentation Experiments // J. Mater. Res. 1992. № 7 (6). P.1564-1583], using a Berkovich indenter (triangular diamond pyramid with an apex angle of 65.30 and a radius of curvature of about 200 nm). This technique consists of the selection of the parameters of the strength function which describes the experimental dependence of the immersion depth of the indenter and the contact area of the applied force, and calculating the hardness and elastic modulus from the data. In accordance with the procedure Oliver - Pharr plastic indentation depth is determined by the expression [30]:

$$h_c = h_{\max} - m*(C*F_{\max}) ,$$

where C – contact compliance, defined by the slope of the unloading curve at the point of application of maximum force. The value depends on the geometry of the indenter, which for a Berkovich indenter m = 0.75.

Herdness H is defined by the Vikkers method according to the maximum load $F_{\max}$ applied to the indenter contact area A with the sample: $H = F_{\max} / A$.

To determine the reduced Young's modulus it is necessary to determine the angle of unloading curve inclination in accordance with the ratio, which depends on the contact area

$$C = \sqrt{p} / \left(2E_r \sqrt{A}\right) .$$

Reduced Young's modulus is determined by the expression:

$$1/E_r = \left(1- n_S^2\right)\Big/E_S + \left(1- n_I^2\right)\Big/E_I ,$$

where n_S – Poisson's ratio of the sample material, n_I – indenter Poisson coefficient (0.07), E_S – Young's modulus of the sample, E_I – Young's modulus of the indenter (in the experiment E_I = 1141 GPa).

Measurement of the mechanical characteristics of the surface layers of the specimens were limited with depth and load forces, they were 150 and 1.53 mN. Lloading time and unloading point of the indentation was 20 seconds, the holding time at maximum stress – 10 seconds.

The distance between the points of the indentation corresponds to 40 microns, which was set automatically by software integrated measuring system NanoTest 600. After each introduction of the indenter in to the sample at the transition to the next point of the indenter measuring retracted from the surface to a distance of 20 mm to avoid contact with the surface.

The degree of roughness plays an important role in the measurements of physical and mechanical properties of the surface layers. In this regard, in order to increase reliability of the measurement results of the procedure was performed at least 30 times. After the measuring cycle, defined automatically, manually were deleted those data points that were in doubt.

The quality control system is intended for inner surfaces of the tubes for measuring surface roughness and hardness by non-destructive measurement of the inner surface of the 10 mm in diameter and 1,000 mm in length tubular product. Climatic performance is fullfilled according to GOST 15150-69.

Evaluation of surface changes, roughness, structure, research and measurement of geometrical parameters were carried out by means of confocal laser scanning microscopy OLYMPUS LEXT 4000 and OLYMPUS LEXT 4100. Relative measurement samples roughness error does not exceed 5%.

General increases range is in the frame from 50 to 17280 fold and depends on the lens that are used. The horizontal resolution is up to 120 nm, vertical up to 10 nm. Accuracy of measurement values are 0,2 + L / 100 mm, wherein L - value measured in microns. Microscope Olympus OLS LEXT 4000 has the functions of height measurement, area and volume, roughness parameters, automatic processing of the received images.

Analysis of samples crystal structure is performed by the X-ray diffraction at 0-9 diffractometer D8 Advance (BrukerAXS) using SuKα radiation. In order to identify the differences in the structural condition of the surface layers and a matrix (in volume) analysis was carried out in a moving beam geometry (fixed angle a = 0.5 °) and parallel beam geometries. A parabolic Gobel mirror (60 mm), horizontal Soller slit (0.12 °) and a semiconductor Si (Li) Sol-XE detector were used. The diameter of the goniometer is 500 mm. Shooting in the range of angles 2θ of 35^0 to 90^0 degrees, 0.02 degrees increments. Time at each point - 5 seconds.

The crystal structure was investigated by parallel beams circuit mode grazing incidence (angle of incidence = 3^0) at 2θ angles ranging from 30^0 to 55^0 0.02^0 increments and record time at each point is equal to 3 seconds with the help of multifunctional X-ray diffractometer Rigaku SmartLab. The slots of the incident beam: $5{,}0^0$ (Soller slit), 0.7 mm (a gap divergence). Diffracted beam slits: $5{,}0^0$ (Soller slit), 0.7 mm, anti-scatter slit 0.7 mm. Software processing of diffraction patterns was performed taking into account of the overlap Kα1 and Kα2 lines and without taking into account the instrumental function. Wave length CuKα1≈1.5406 Å.

Optimization of the process by scheduling a three-factor experiment with the following independent variables - the processing time, power level and pressure of the plasma gas – argon was carried out. The relative change in hardness as one of the defining physical and mechanical characteristics of the material is selected as a response function. Processing of the data was performed using STATISTICA 6.0 software package. Optimization results are shown in Fig. 2.

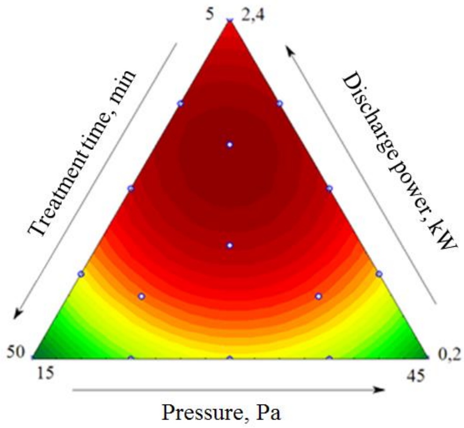


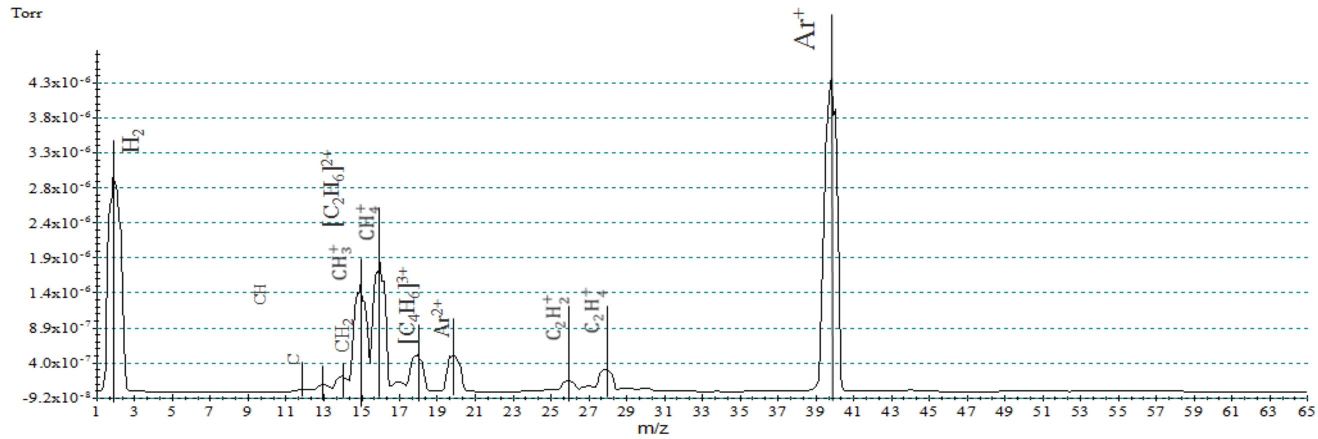
Figure 2 – Optimization of the process parameters of the hardening of metals and alloys in the low pressure RF discharge.

As seen it is seen in Fig. 2, the optimal conditions of the process of metals and their alloys hardening by a low pressure RF discharge are: processing time 20 minutes, the discharge power - 1.5-1.8 kW, argon gas pressure in the chamber - 25-28 Pa.

3. Results and discussion

The dynamic quadrupole mass spectrometer monitoring the gas composition was done in a vacuum chamber. Mass spectra of the plasma in a mixture of an inert (argon) and plasma chemical (methane, nitrogen) gases are given in Figures 3a and 3b.

The method is based on determining the mass to charge ratio of ions formed in the ionization of the gas supply during the generation of high-frequency jet low pressure discharge, it allows to make a quantitative assessment of the composition of the gas inside the chamber to determine the characteristics of the plasma flow, making the major contribution to the modification of the surface. In all cases in the chamber after evacuation, water is presented in an amount of 5-7% and a large amount of hydrogen - 23% in a mass spectrum by methane treatment. Ratio of argon and methane, argon and nitrogen from Figures 3a and 3b respectively corresponds to the flows of feed gases (GAr = 0,03g / c, GCH4 = 0,006g / c; GAr = 0,06g / c, GN2 = 0,009g / c) . Maximum decomposition of methane, which can be estimated from the amount of hydrogen in the chamber corresponds to the ratio of argon gas mixture with methane 80:20.



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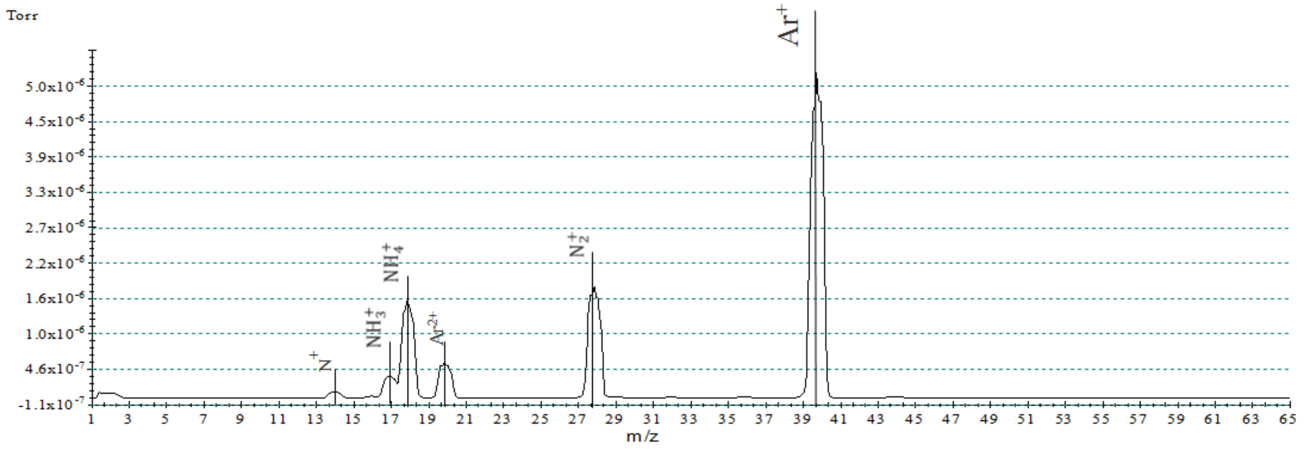


b

Figure 3 - Low pressure RF discharge mass spectra in the electrode gap in the vacuum chamber in a medium: a) Mixtures of reactive and inert gases (argon and methane in a ratio 80:20) b) Mixtures of inert and reactive gases (argon and nitrogen in a ratio of 80:20).

Figure 4 shows the X-ray photoelectron spectra of the untreated and treated high speed steels samples in methane. At the ion etching it is established that according the the depth of the sample the component 707 eV appears and grows corresponding unoxidized (metal) iron, but the iron oxide component (710 - 711 eV) is dominant. At the same time it is seen that in the treated sample unoxidized peak intensity of the iron is above compared with the untreated sample at the same depths. Apparently, there is a partial reduction of oxides in the processing in methane. Fe2p oxide component spectrum in its parameters corresponds Fe3O4 or complex oxide on its base with minor impurities of other alloying elements of the alloy. In the structure of the oxide present as two or three linkage ferric iron. In particular, the "shoulder" at 716 eV in the spectra Fe2p3/2 (sattelite) is associated with the presence of two linkage ferrous iron. The peak position of unoxidized iron is shifted by 0.3 eV towards higher binding energies relative to the position of pure (metal) iron, which may be due to the formation of carbide bonds Fe-C.

Carbon spectra are shown in Figure 5. One difference of C1s spectra of the treated and untreated samples is shoulder relative intensity spectrum in 288-290 eV field. In the sample without processing the spectra of the shoulder it is more pronounced because of the higher concentration of oxygen-containing compounds with carbon participation. After treatment with the methane low pressure RF discharge shoulder is substantially smaller or absent. In depth from the surface the iron unoxidized peak intensity increases in intensity in the spectrum of C1s 283.5 eV to appearance and growth synchronously, which corresponds to the C-Fe bonds. On the whole the integral spectrum of C1s peak is shifted from the position characteristic of the C-H (on the surface) in the direction of lower binding energies (C-C). The value of the binding energy for the reference graphite is 284,3-284,6 eV, the width of the standard graphite peak is ~ 1.4 eV. In the case of samples of high speed steel there are several non-equivalent chemical states of carbon in the sample layer that form a diffuse broad peak and are identified by the decomposition of the spectra into components.

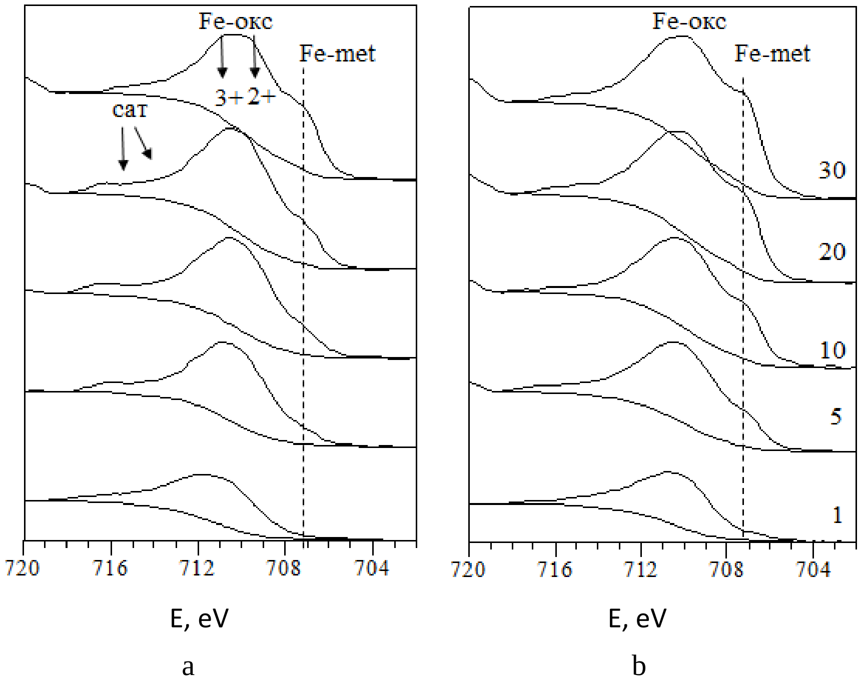


Figure 4 - Fe2p3/2 spectra of the treated (a) and untreated (b) high speed steel samples by the loew pressure radio frequency methane plasma. The numbers on the right - the depth in nm.

The spectra C1s component with Eb = 284.6-284,8 eV corresponds to the C-C bond. This peak is shifted slightly in the depth in the direction of the high-energy bonds. It is seen that in the treated sample relative intensity peak is significantly higher compared with the untreated sample, which may be due to the presence of a carbon or graphite structure. Accordingly, in the spectra of the treated sample peak intensity of hydrocarbon (C-H 285.6 eV) decreases. Processing in low pressure RF discharge leads to a decrease in the relative intensity of peaks in the field of energies Eb 287 eV, typical for carbon bonds with oxygen, which is consistent with a decrease in the oxygen concentration in the surface layers of the treated sample. At a depth of 30 nm in the spectra of the two samples a peak with Eb = 283.6 eV was revealed corresponding to carbon in an iron chemical. Thus, it can be argued that the treatment in methane leads to an increase in the proportion of carbon in the C-C bond (sp2-hybridized carbon).

Thus, according to the data obtained by XPS surface layers of high speed steel test samples contain high concentration of carbon. Carbon is chemically nonequivalent in several states, including chemical bonds C-C and C-Fe. The plasma treatment improves the carbon in methane concentration in the C-C bond, lowers the amount of C-H. According to the spectra characteristic losses, the surface layer structure, which includes carbon, forming C-C bond is characterized by a reference structure of graphite. The surface layers of both samples contain a significant amount of oxygen. Iron is oxidized throughout the analysis depth (not less than 30 nm). Processing in methane leads to partial reduction of iron oxides and oxygen concentrations decrease.

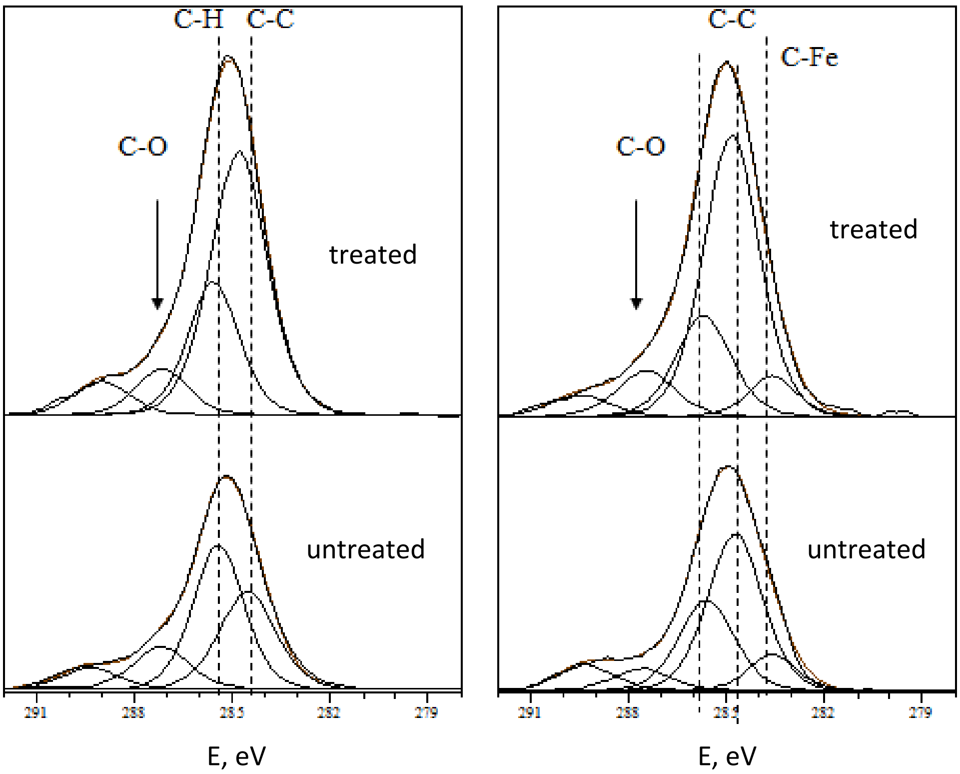


Figure 5 - Cls spectra of the treated and untreated samples at the 5 nm (a) and 30 nm (b) depth.

The concentrations of the elements in the surface layers of the tungsten cobalt alloy of untreated and treated samples are given in Tables 1 and 2 respectively. The absolute concentration of carbon in the treated sample is higher than in the sample without treatment. This - the same result as in the case of samples of high speed steel.

Structure analysis was carried out using the multi X-ray diffractometer Rigaku SmartLab. As a result of diffraction investigations revealed that the WC phase is present in both samples. Peak positions in the diffraction patterns are different - in untreated sample the interplanar distance is approximately 0,001-0,002 angstroms greater than in the treated sample, it can be assumed that changes were formed due to the introduction into the metal lattice structure of carbon ion because of the plasma chemical effect on the surface of the material.

Table 1 - The concentrations of elements in the surface layers of the tungsten and cobalt alloy sample without processing by low pressure radio frequency discharge.

Depth, nm	C	O	W	Co	Cu	Zn
1,0	61,5	23,8	0,8	1,9	5,7	6,3
3,0	43,3	31,2	1,4	3,4	9,8	10,8
5,0	40,3	30,0	1,7	4,3	10,9	12,7
10,0	37,2	29,2	2,1	4,8	13,0	13,7
20,0	30,5	26,6	3,0	4,9	20,3	14,6
30,0	25,5	22,6	3,9	4,4	29,2	14,4

Low pressure RF discharges processing in methane plasma chemical gas leads to the saturation of the surface layers by carbon and, simultaneously, to a partial recovery of cobalt and tungsten oxides and reduce the oxygen concentration.

Table 2 - The concentrations of elements in the surface layers of the tungsten and cobalt alloy sample after the low pressure radio frequency discharge processing.

Depth, nm	C	O	W	Co	Cu	Zn
0,5	74,2	19,0	0,5	1,0	1,5	3,7
1,0	73,0	15,4	0,5	1,0	5,6	4,5
3,0	69,7	15,1	0,8	1,5	7,2	5,7
5,0	61,5	21,4	0,9	2,1	7,6	6,6
10,0	58,0	18,2	1,8	3,5	10,4	8,1
15,0	54,3	19,2	2,4	3,8	12,2	8,1
20,0	50,8	17,9	2,8	4,0	16,3	8,3
30,0	44,0	18,0	3,5	4,1	20,7	9,7
40,0	36,1	15,4	4,4	3,9	29,9	10,4
50,0	32,1	12,4	5,2	4,2	34,8	11,2

Fig. 6 shows the spectra N1s nitrogen after background subtraction of inelastically scattered secondary electrons. Maximum nitrogen has a binding energy spectra in the 397-398 eV, which corresponds to its chemical interaction with metals.

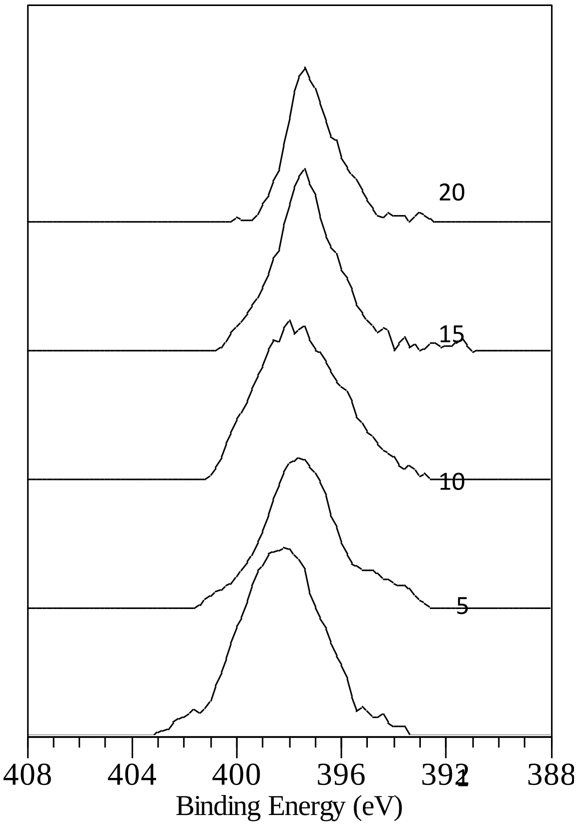
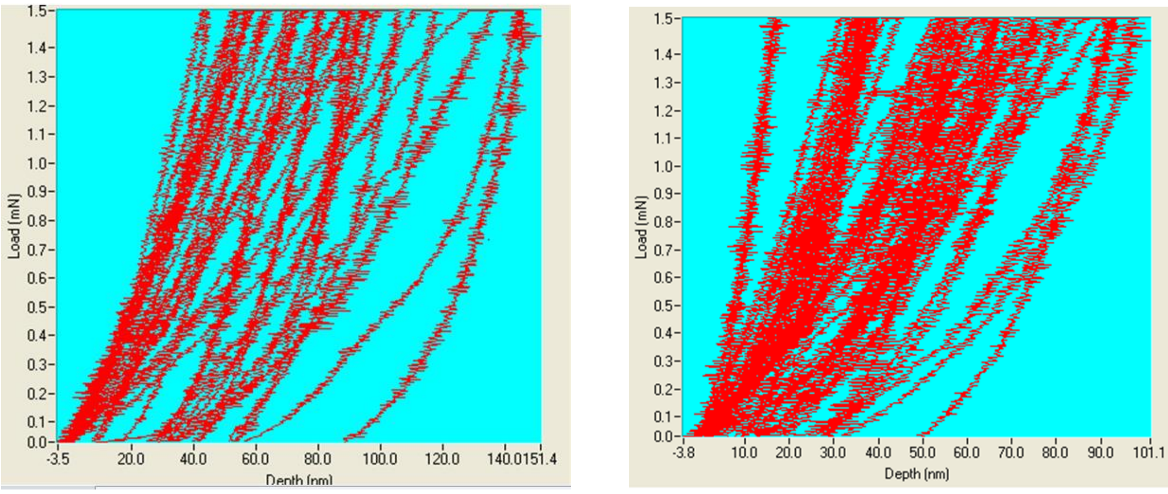


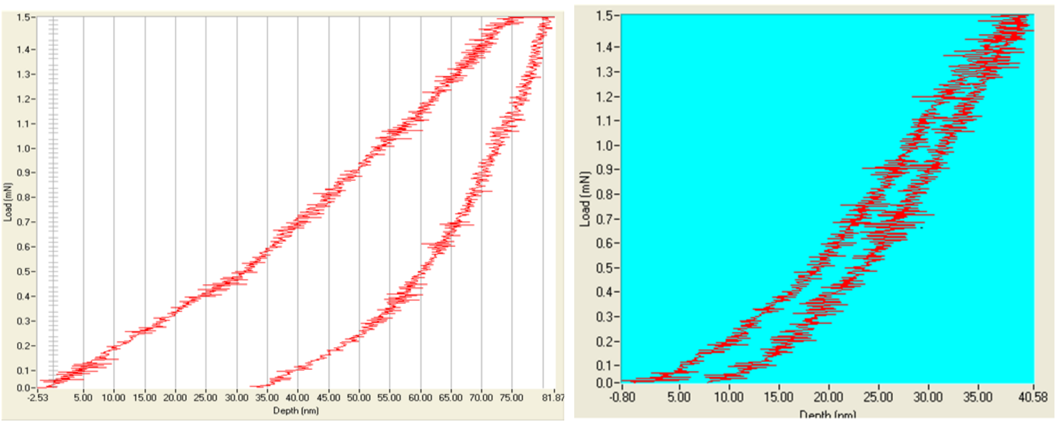
Figure 6 - N1s spectrum of the surface layers of steel 30HN2MFA after plasma treatment in nitrogen.

Characteristic diagrams "loading - unloading," which were included in the estimates for the high speed steel samples to determine the physical and mechanical characteristics of the surface layer before and after treatment by low pressure radio frequency discharges are shown in Fig. 7. Dependence of the applied force F, mN the penetration depth of the indenter h, nm in samples of high speed steel are shown in Fig. 8 (chart loading - unloading, for the forces of 1,53 nH).



a b

Figure 7 - Typical diagrams "load - unload" - according to the applied force F, mN penetration depth of the indenter h, nm. High speed steel samples before (a) and after (b) treatment of the surface by low pressure radio frequency plasma. The strength Fmax 1,53 nH.



a b

Figure 8 - The dependence of the applied force F, mN on the penetration depth of the indenter h, nm in high speed steel samples (chart loading - unloading) for strength Fmax 1,53 nH. Sample pre-treatment (a, 16 sample points indentation) and after treatment after treatment of the surface by low pressure radio frequency plasma (b, 20 sample points indentation).

The results of the studies are summarized in Table 3. Analysis of the table shows that after treatment of the high speed steel samples surface by low pressure RF plasma there is an increase in microhardness of 30-40%, thereby the modulus of elasticity also increases, as a result reduced plastic depth hc and maximum indentation depth hmax decrease. The differences are fixed by limiting the maximum load Fmax 1.53 mN at a depth of 60-80 nm.

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Table 3 – Physical and mechanical properties of high speed steel surface layers before and after low pressure radio frequency plasma treatment.

Physical and mechanical characteristics	High speed steel	
	Before treatment	After treatment
Maximum depth h_{max}, nm	90,06	60,75
Maximum load F_{max}, mN	1,53	
Plastic identation depth h_c, nm	67,04	40,18
Microhardness H , GPa	2,30	3,66
Reduced Young's modulus of elasticity E_r , GPa	55,20	84,91
Young's modulus of elasticity E_S	0,42	0,61

4. Conclusions

Complex studies of influence of effective parameters of the low pressure radio frequency discharges processing on the chemical composition and physical and mechanical properties of the surface layers of high speed steels, tungsten cobalt alloys and steels made by X-ray photoelectron microscopy and mechanical tests using instrumental indentation and scanning probe microscopy have allowed the following conclusions:

- It is found that the RF treatment in the jet discharge at low pressure causes a change in the chemical composition of the surface layers of metals and their alloys. Surface modification of metal is possible in the RF discharge generated between the symmetrical parallel plate electrodes. The effect of low pressure RF discharge on the properties of metals and their alloys depends on the plasma parameters, and the structure of the material.
- It is experimentally found that alteration of the chemical properties of high speed steel and alloys following after the exposure of tungsten cobalt alloys and steels by low pressure RF jet plasma occurs with a change of the crystal lattice parameters and increase of the physical and mechanical properties of the material. Diffusion Nano layers formation on the metal surface increases the wear resistance of the final product, increase operating characteristics of equipment.
- Studies have shown that the use of an ionized gas stream as a processing tool (plasma) allows the modification of the surface of cutting tools, parts of complex configuration. Gas saturation occurs with surface layers of metals and alloys at a depth of 500 nm for the processing time to 40 minutes, resulting in an increase in strength properties, durability, and product service life.

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References

[1] Saifutdinov A.I. Dynamics contraction of DC glow discharge in argon /A.I. Saifutdinov, A.A. Saifutdinova, N.F. Kashapov, SA. Fadeev //(2016) Journal of Physics: Conference Series, 669 (1). – art. no. 012045.
[2] Lopatin I.V. Independent glow discharge of low pressure hollow cathode at a current of tens of amperes /I.V. Lopatin P.M. Schanin, Y.K. Akhmadeev, S.S. Kowalski, N.N. Koval // Plasma physics.-2012.-№7.-V.38.-P. 639-643.
[3] Zhang, C.S. Experimental and theoretical study on interaction between lanthanum and nitrogen during plasma rare earth nitriding/C.S. Zhang, M.F. YanZ. Sun//Applied Surface Science1.–2013. –v.287.–№15.–p.381–388.
[4] Semenov, A.P. Wear-resistant coatings applied by vacuum ion-plasma methods / A.P. Semenov, A.I. Grigoriev // Technology of mechanical engineering. -1973.-№7.-P. 15-20.
[5] Patent. 110088 RU. A device for vacuum coating / I.I. Vasiliev; the applicant and the patentee "Kazan National Research Technological University" .- Application №2011113754; application date 08.04.2011;publishing date 10.11.2011.
[6] Brzhozovskii, B. Composite ion-plasma coatings with nanodisperse reinforced phase: scientific and practical aspects of synthesis / B Brzhozovskii, V Martynov, E Zinina and M Brovkova // IOP Conference Series: Materials Science and Engineering. – 2016. – V. 116. – 01022007.
[7] Smallman, R.E. Oxidation, Corrosion and Surface Engineering/R.E. Smallman//Modern Physical Metallurgy.–2014.–v.8.–p.617–657.
[8] Marin, E. Diffusive thermal treatments combined with PVD coatings for tribological protection of titanium alloys / E. Marin, R. Offoiach, M. Regis, S. Fusi, A. Lanzutti, L. Fedrizzi//Materials & Design.–2016.–v.89.–p.314–322.
[9] Catalogue of Vacuum technology NPF "Alan Practitioner» PVD vacuum coating application methods. Website URL: http://www.elanpraktik.ru/technology/pdf/pvd_%20metody.pdf (reference date 03/10/2014)

[10] German S Fox-Rabinovicha Hierarchical adaptive nanostructured PVD coatings for extreme tribological applications: the quest for nonequilibrium states and emergent behavior /German S Fox-Rabinovicha, Kenji Yamamotob,Ben D Beakec,Iosif S Gershmand,Anatoly I Kovaleve,Stephen C Veldhuisa,Myriam H. Aguirref, Goulnara Dosbaevaa, Jose L Endrinog//Science and technology of advanced materials.–2016.–V.13.–№4.

[11] Pelletier, J. Plasma-based ion implantation and deposition: A review of physics, technology and applications /J. Pelletier, A. Anders//IEEE Transactions on Plasma Science.–2005.–v.33.–№ 6.–p.1944–1959.

[12] Belyakov A.V. The technology of electric spark for the rotor blades of steam turbines and equipment for its realization resource improvement / A.V. Belyakov, V.V. Sarantsev, A.N. Gorbachev, F.I. Panteleenko, E.L. Azarenka, B.F. Reutov // Electrical staitions.-2016.- №1.

[13] Patent. The method of the vacuum tube inner surface processing, RU 2039845.

[14] Calanda, N.A. Magnetic and magnetoresistive properties of nanoheterostructures Al2O3-Sr2FeMoO6-δ-Al2O3 / N.A. Calanda, G.G. Peas, M.V. Yarmolich, A.A. Lozovenko, E.J. Buzzards // Physics of solid substance.-2016.-№2.-V.58.-P. 341-348

[15] Frederico Augusto Pires Fernandes Microstructure of nitrided and nitrocarburized layers produced on a superaustenitic stainless steel/Frederico Augusto Pires Fernandes, Luiz Carlos Casteletti, Juno Gallego//Journal of Materials Research and Technology.–2013.–v.2.–p.158–164.

[16] Abdullin, I.Sh. Surface Layers Modification of Tungsten-Cobalt Alloy by Low Pressure RF Plasmas/I.Sh. Abdullin, V.S. Zheltukhin, I.R. Sagbiev, R.F. Sharafeev//Proc. of 61st annual gaseous electronics conference, Oct. 13-17, 2008.–Dallas, Texas, USA./Abstract: FTP1.00021.

[17] Rosiana Boniatti The influence of surface microstructure and chemical composition on corrosion behaviour in fuel-grade bio-ethanol of low-alloy steel modified by plasma nitro-carburizing and post-oxidizing/Rosiana Boniatti, Aline L. Bandeira, Ângela E. Crespi, Cesar Aguzzoli, Israel J.R. Baumvol, Carlos A. Figueroa//Applied Surface Science.–2013.–v. 280.–p.156–163.

[18] Zheltukhin, V.S. Low Pressure Radio-Frequency Plasmas in the Nanolayers Formation on the Surface of Construction Materials/V.S. Zheltukhin, I.Sh. Abdullin, I.R. Sagbiev, R.F. Sharafeev//Proceedings of International Conference «Micro- and Nanoelectronics-2007».–Moscow-Zvenigorod, Russia.–2007.–P. 32–39.

[19] Kashapov N.F. Hardening of the surface plasma jet high-frequency induction discharge of low pressure /N.F. Kashapov and S.N. Sharifullin //IOP Conference Series: Materials Science and Engineering. – 2015. – V. 86. doi:10.1088/1757-899X/86/1/012021.

[20] Sharifullin S.N. Plasma method of increasing the roughness class and hardening surfaces of products /S.N. Sharifullin, N.R. Adigamov, S.V. Slavnina // Bulletin of Samara Scientific Center of the Russian Academy of Sciences. Special. Issue "Actual problems of mechanical engineering", 2009. - P. 15 - 18.

[21] Makhotkina , L.Yu. Design of special purpose products made of nanomodified leather / L.Yu. Makhotkina, V.I. Khristoliubova, L.R. Khannanova-Fakhrutdinova // IEJME – Mathematics education. – 2016. – V. 11, № 6. – P. 1495-1503.

[22] Sagbiev, I.R. Low pressure radio frequency Jet discharge in the process of surface modification of structural materials nanolayers: Dis. Doctor. Sciences /I.R.. Sagbiev.- Kazan, 2009.-332p.
[23] Sharafeev, R.F. The flow of low pressure radio frequency plasma in the processes of interaction with the surface materials: Abstract. Ph.D. Dis. / R.F. Sharafiev.- Kazan, 2010.- 20 p.
[24] Shaehov, M.F. Physics of low pressure radio frequency discharge in the processing of capillary-porous and fibrous materials: Abstract. Doctor. Science Dis. / M.F. Shaehov.-Moscow, 2006.-32 p.
[25] Gaysin, Al.F. Features of the transition of low-current radio frequency capacitive discharge with an electrolytic electrode to the high-current discharge / Al.F. Gaysin // High temperature. -2015.-№1.-V.53.-P. 18-22.
[26] Markov, A.V. Heating of a gas and a polymeric material in low-temperature plasma of a high-frequency discharge//A.V. Markov, Y.P. Yulenets//High Temperature.–2015.–№2.–T.53.–C.167–170.
[27] Makhotkina, L.Yu. Design of special purpose products made of nanomodified collagen-containing materials with radio-frequency discharge / L.Yu. Makhotkina, S.N. Sharifullin // IOP Conference Series: Materials Science and Engineering. – 2016. – V. 134. – 012020.
[28] Abdullin, I. Formation of diffusive nanostructured layers on a surface of metals and their alloys/I. Abdullin, A. Khubatkhuzin, V. Khristoliubova// State-of-the-art Trends of Scientific Research of Artificial and Natural Nanoobjects: abstracts for 4th International Scientific conference, 22-25 April 2014. –Saint-Petersburg. –P. 161–163.
[29] Khristoliubova, V.I. Gas and plasma dynamics of RF discharge jet of low pressure in a vacuum chamber with flat electrodes and inside tube, influence of RF discharge on the steel surface parameters / V.I. Khristoliubova, N.F. Kashapov, M.F. Shaekhov // IOP Conference Series: Materials Science and Engineering. – 2016. – V. 134. – 012017.
[30] Oliver, W.C. An improved technique for determining hardness and elastic modulus using load and displacement sensing indentation experiments / W.C. Oliver, G.M. Pharr // J. Mater Res.-1992, V. 7.- no. 6.- pp. 1564–1580.