New technology of ion-plasma modification of the contact surfaces of reed switches in oscillatory discharge

2012 J. Phys.: Conf. Ser. 345 012003

(http://iopscience.iop.org/1742-6596/345/1/012003)

NEW TECHNOLOGY OF ION-PLASMA MODIFICATION OF THE CONTACT SURFACES OF REED SWITCHES IN OSCILLATORY DISCHARGE

K A Arushanov, I A Zeltser[1], S M Karabanov, R M Maizels, and Y N Moos

Ryazan Metal Ceramics Instrumentation Plant Joint Stock Company, Novaya St. 51V, Ryazan, 390027, Russia.

[1]E-Mail: zeltseria@rmcip.ru

Abstract: The iron-nickel contact surfaces of reed switches after ion-induced modification have been studied using methods of Auger-electron spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy, and optical microscopy. It was demonstrated that the corrosion stability and erosion resistance of the modified contacts is associated with the features of surface topography as well as with a formation of nitride layers. Experimental grounds for a production possibility of reed switches with the modified contact surface instead of electroplating based on the precious metals are given.

Key words: reed switch, ion, plasma, nitriding, coating, modification, contact, nitride, Auger-electron spectroscopy, X-ray photoelectron spectroscopy, atomic force microscopy.

1. Introduction

One of the main technological problems of reed switch production is the deposition of special (corrosion- and erosion-resistant) coatings on the contact surfaces of permalloy springs. To deposit a coating, the electroplating technique is generally used and noble and precious metals (gold, palladium, rhodium, ruthenium, etc.) are employed as materials [1].

However, this technological approach is characterized by large electro- and material capacity, high prices of the equipment, low ecological level, and difficulty of the alloy deposition with the required chemical and phase composition and structure when forming thin nonporous or thick films having low internal stresses and high adhesion to the material of a contact piece.

It’s known that one of the most promising methods for increase of corrosion and erosion resistance of metal surface is ion nitriding in pulsating plasma of glow discharge [2, 3].

The idea of usage of this method for producing of contact surfaces, that are alternative to electrodeposits based on precious metals, has found it’s experimental verification for the first time in the work [4]. It was developed further in series of works [5-25].

The present paper is a follow-up of these works. The aim if this article is studying of influence of ion-plasma treatment parameters, switching regimes on properties of nickel-iron contact surfaces and creation of a new technology of reed switch modification with usage of nitriding and reactive cathode sputtering in oscillatory discharge.

2. Materials and Methods

2.1.Samples

The samples were reed switches MKA-14108 [1] structurally made on base of off-the-shelf devices MKA-14103 [1] (**Figure 1**). The special feature of design of such reed switches in comparison with the off-the-shelf devices consists in lack of any special coatings on permalloy contacts.

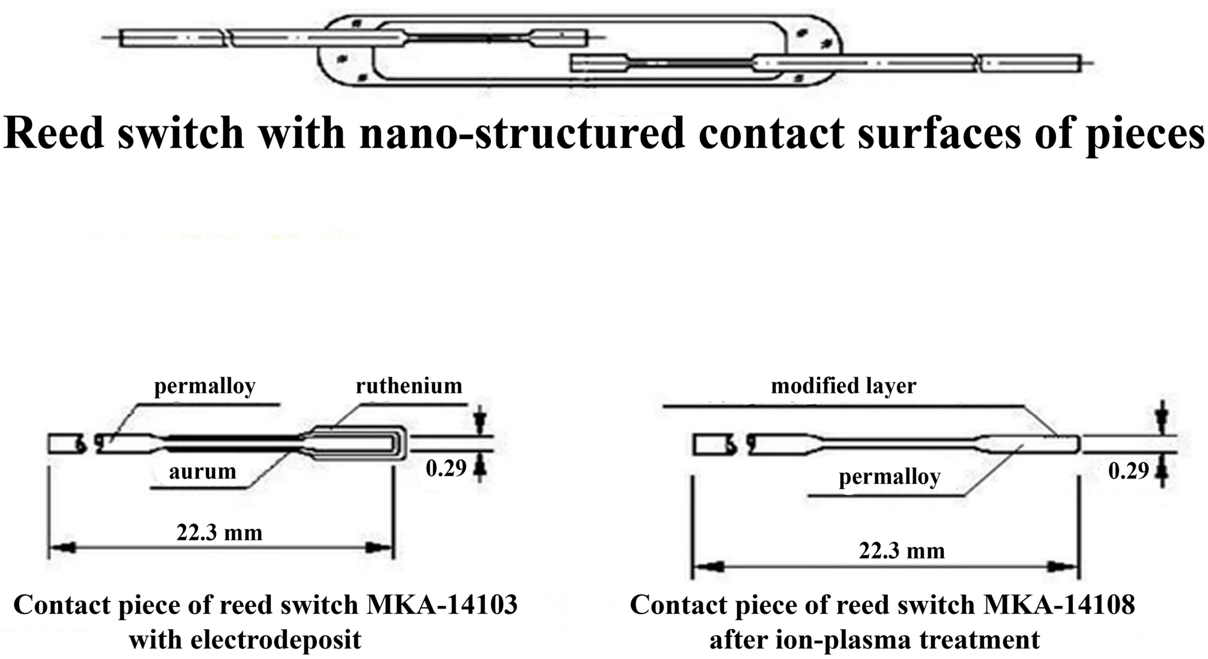


Figure 1. Reed switch design.

2.2. Technology

The processing route for production of reed switches MKA-14108 is shown in **Figure 2**, and the primary processes – in **Figure 3**. The specificity thereof as compared with the typical flow layout [1] consists in replacement of the operation “Plating“ by the operation “Ion-Plasma Treatment“ (“IPT“).

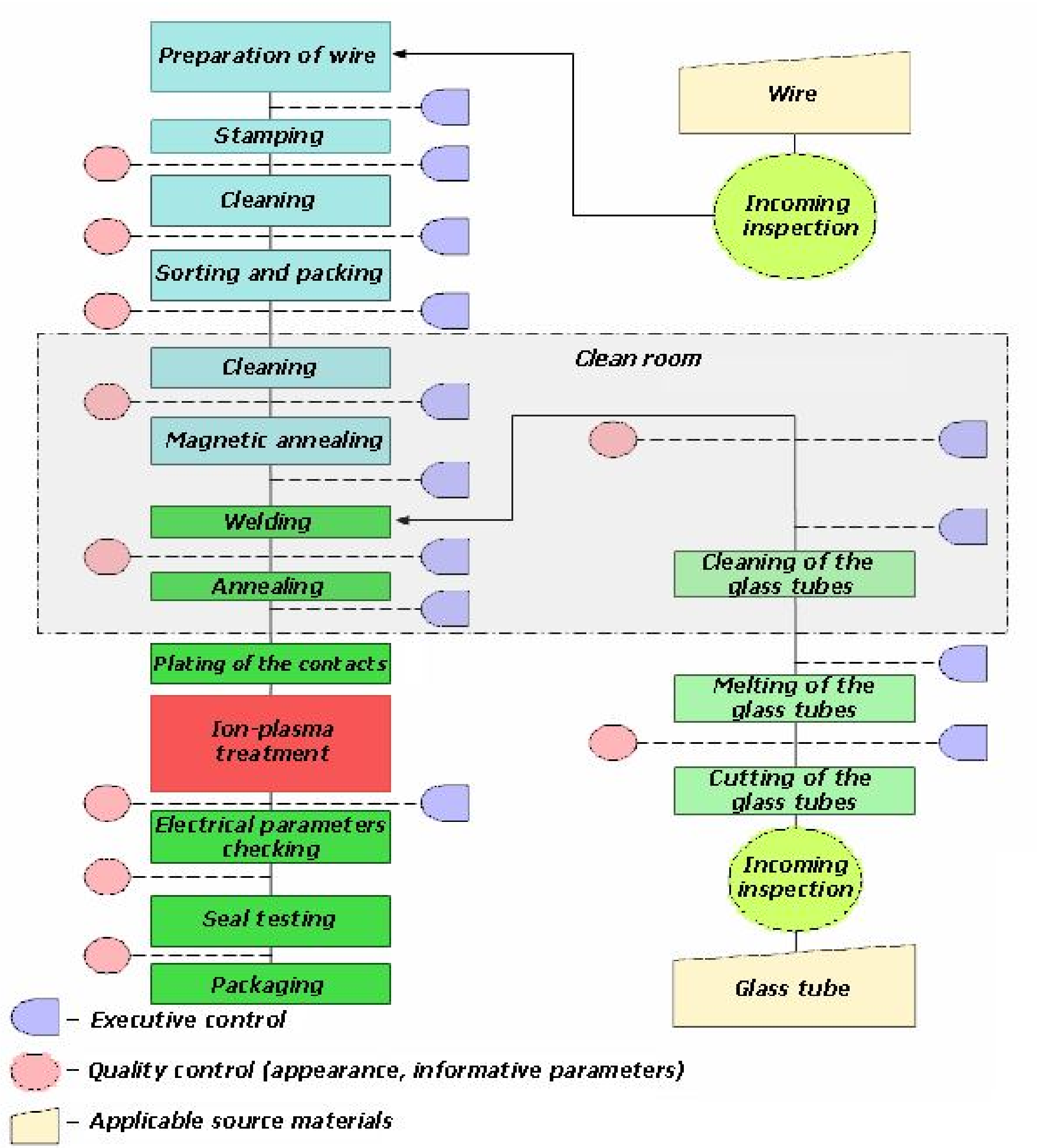


Figure 2. Processing route for reed switches MKA-14108 with the modified contact surface (instead of electroplating).

Contact springs were pressed from Permalloy Dilaton wire, degreased and subjected to hydrogen annealing. The wire was stretched from vacuum-melt Permalloy (52% Ni, 48% Fe). Spectrally pure (99.999 %) nitrogen with the pressure in the envelope of reed switch in the value of $33 \cdot 10^3 - 40 \cdot 10^3$ Pa was used as gas filling when sealing.

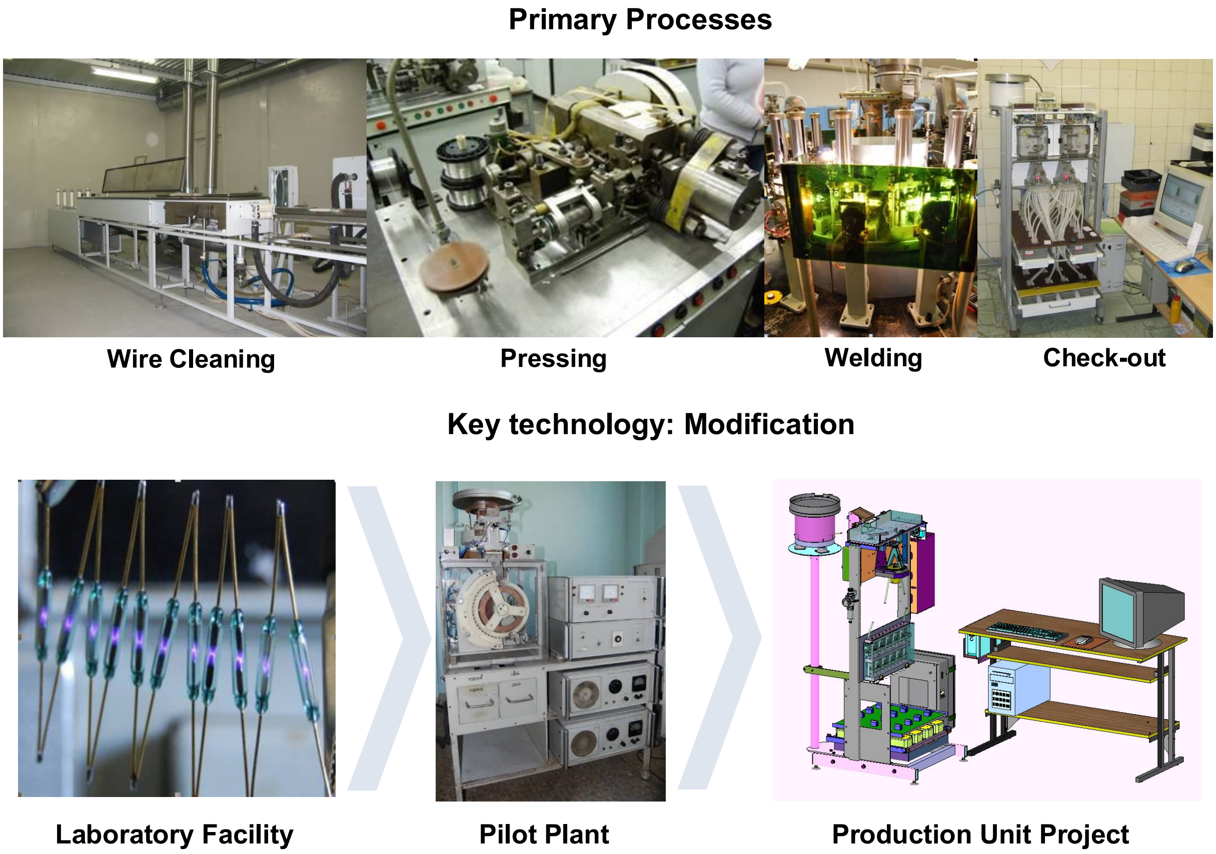


Figure 3. Technology.

2.3. Ion-Plasma Treatment

Ion-plasma treatment (IPT) of the contact surfaces was carried out by high-voltage pulsed discharges which were initiated on the open contacts (with a gap d = 27–30 µm) by means of a specially developed device [5, 7] (**Figure 3**).

Two modes of IPT characterized by the electrophysical conditions of discharge, and as a consequence, - by a heating degree of the substrate, were used. The first IPT mode is the mode of ion nitriding, providing the diffusion saturation of near-surface layers of contacts in the region of overlap by nitrogen atoms, formation on the treated parts of nitride layer with the prescribed contact properties. Properties of the hardenable surface, corrosion- erosion resistance and electroconductivity are optimized due to the necessary combination of nitride and diffusion layers which grow into a base material. Depending on a chemical composition, the nitride layer is either γ'- phase (Fe_4N) or ε-phase ($Fe_{2\text{-}3}N$). The second mode is the mode of reactive cathode sputtering. During this process, a film comprising iron and nickel nitrides is sputtered onto the surface of contacts. Like ion-nitrided layers, this coating also meets the modern requirements for the contact surfaces of reed switches. Duration of a single IPT in both modes was 30 sec.

The distinctive feature of the ion nitriding and reactive cathode sputtering of reed switches is that in contrast to the conventional technologies [2, 3, 26], the saturation of near-surface layers of contacts by nitrogen and sputtering of contact coatings is carried out not in nitrogen-containing vacuum (p = 150-1000 Pa), but at rather high pressure ($p = 33\cdot 10^3 – 40\cdot10^3$ Pa) of nitrogen. By this it's not necessary to apply the special vacuum equipment for ion nitriding of near-surface layers and forming of coatings by methods of reactive cathode sputtering [2, 26]. Nitriding and sputtering processes are performed direct in the reed switch. The glass envelope functions as a working chamber, and contact pieces serve as anode and cathode alternately.

2.4. Research technique

The samples after treatments by high-voltage discharges and the samples without treatments were put to the switching tests. Resistance tests, breakdown voltage measurements and switching reliability tests of reed switches were performed with the help of the special-purpose equipment [1] according to methods presented in [1].

About the state of modified surface it was judged by the results of Auger-electron spectroscopy (AES), X-ray photoelectron spectroscopy (XPS), atomic-force microscopy (AFM) and optical microscopy (OM). Gas composition and pressure were controlled by means of a magnetic mass-spectrometer. The findings were matched with the measured results of a number of characteristics, particularly, of breakdown voltage and transient contact resistance.

3. Results and Discussion

3.1. Ion-Nitrided Layers

Analysis of topography of contact surface (before and after treatment thereof) was performed in air with the help of atomic-force microscope (by probe nanolaboratory (PNL) NTEGRA manufactured by NT-MDT Company, Zelenograd, Moscow, Russia). For optical researches of the working surfaces of contacts of reed switches, the metallurgical microscope MMP-4 with a computer system of image visualization was used. Si cantilevers of NSG10/W_2C type, with a hard conducting coating of W_2C 30 nm thick, with work function $e\varphi_p$ = 4.902 eV were used.

The contact surface of reed switch after IPT according to the first mode (ion nitriding) may be divided into three areas, typical by surface topography, which are revealed on images of contact pieces, obtained in optical (**Figure 4**) and atomic-force (**Figure 5**) microscopes.

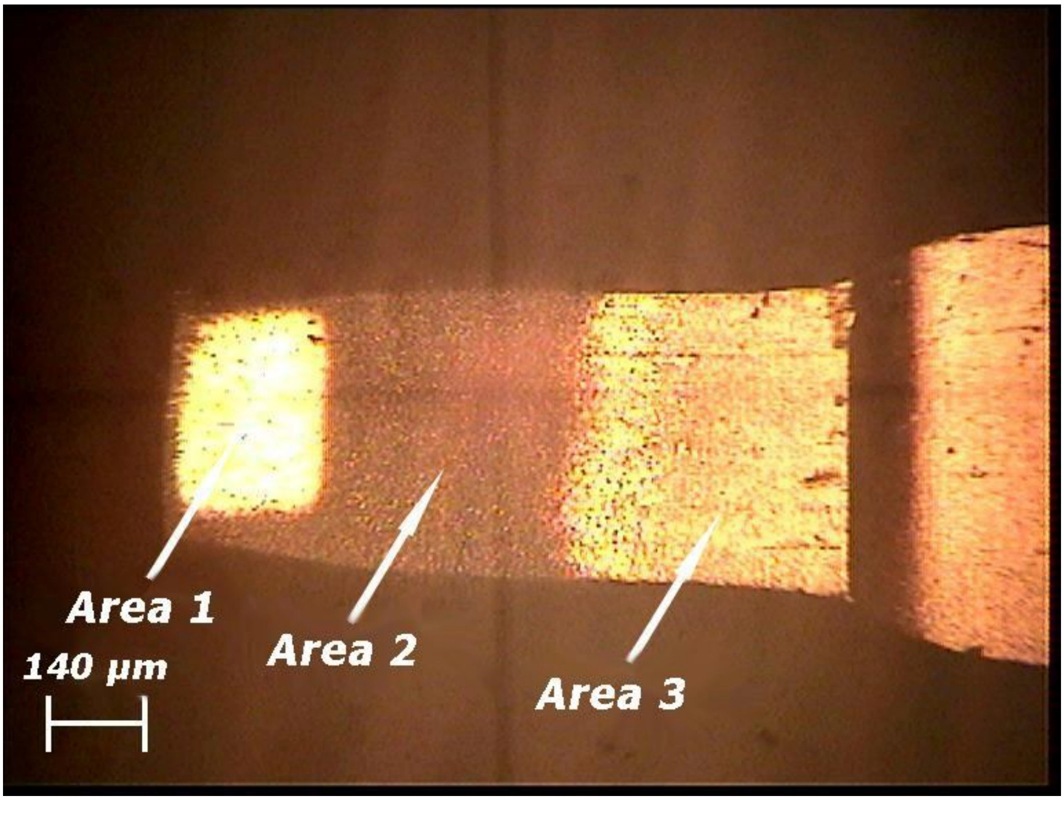


Figure 4. Contact piece of the reed switch after the hundred-fold ion-plasma treatment.

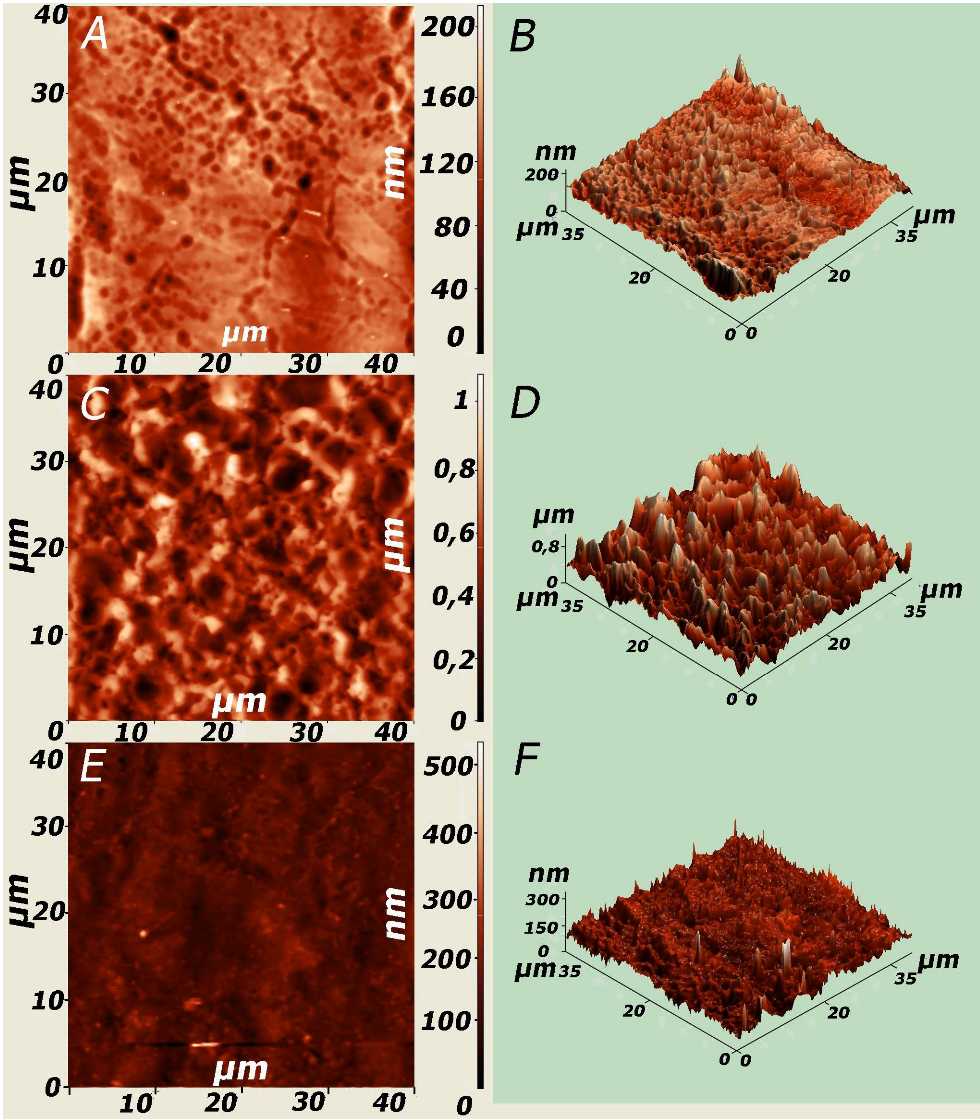


Figure 5. AFM-image of the contact surface of reed switch after 100-fold IPT: **(A)** and **(B)** -2D- and 3D-image of area 1; **(C)** and **(D)** - 2D- and 3D-image of area 2; **(E)** and **(F)** - 2D- and 3D-image of area 3.

Area 1 (**Figures 4, 5a,b**) is a working area (contact overlap area), where gas discharge is ignited when voltage is supplied on the open contacts of reed switch. As a result of reactive cathode sputtering, the nitrides (FeN and NiN) are formed in gas phase of overlap area, the part of which is deposited on the contact surface in area 1, where under ion bombardment nitriding of surface is performed according to Kelbel mechanism [26].
Reactions which determine the ion nitriding process (the first IPT mode) in conditions of the glow discharge according Kelbel mechanism are shown in **Figure 6,** and Figure 6b shows reactions determining the sputtering process of contact coatings by method of the cathode sputtering.
When accelerating in the area of cathode drop of the potential, the nitrogen ions bombard the target – cathode. At that, the majority of ion energy (about 90 %) is expended on the target heating, and the rest – on the electron emission, ion implantation and sputtering of atoms (Fe, Ni, C, O) located on the target surface. As a result of reactive cathode sputtering, in the gas phase, iron and nickel nitrides are

formed which are deposited on the contacts and glass envelope of the reed switch. When metal gets to the surface at the temperature of 300-500˚ C, the molecules of metal nitrides MeN (Fe, Ni) of permalloy dissociate and form low-order nitrides Me_2N, Me_3N, Me_4N. Nitrogen escaped in this case is diffused partially into the target and partially is vaporized into plasma.

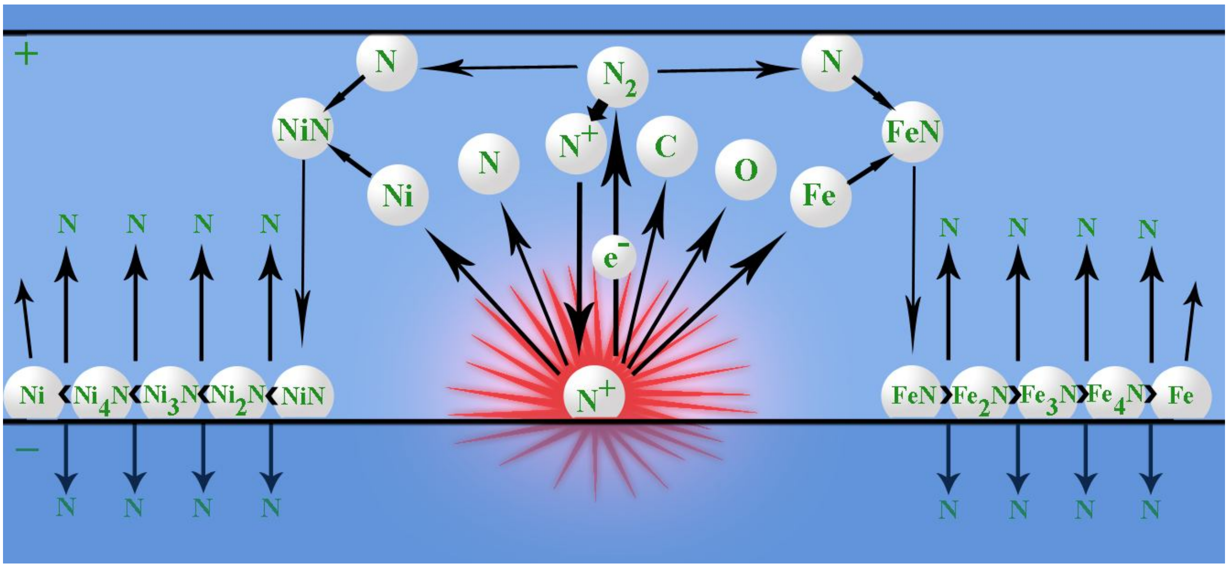


Figure 6. Ion nitriding.

As a result of diffusion, a part of FeN and NiN molecules will be deposited on the surface of contacts, in area 2 adjacent to the area 1 (**Figures 4, 5 c, d**). Area 3, after estimating in accordance to optical (**Figure 4**) and atomic-force (**Figure 5 e, f**) images should not contain nitrides or contains it in very small quantity. The surface of area 1 is heated as a result of ionic bombardment, and of areas 2 and 3 - in consequence of heat exchange with the areas 1 and 2, respectively. Therefore, because of low-grade heating, dissociation of FeN and NiN molecules, and, consequently, the ion nitriding of surfaces of areas 2 and 3 is unlikely. On the surface of contacts in area 2 (**Figure 4**) and on the inner surface of glass envelope, located near to the region of overlap, reactive cathode sputtering products form a black coating (**Figure 7**). The same coating can be formed in area 1, if, due to low ion energy (or current density), the temperature threshold of dissociation of FeN and NiN molecules will not be overpassed. It’s possible that during the diffusion a small amount of cathode sputtering products comes to the reverse sides of reed switch contacts.

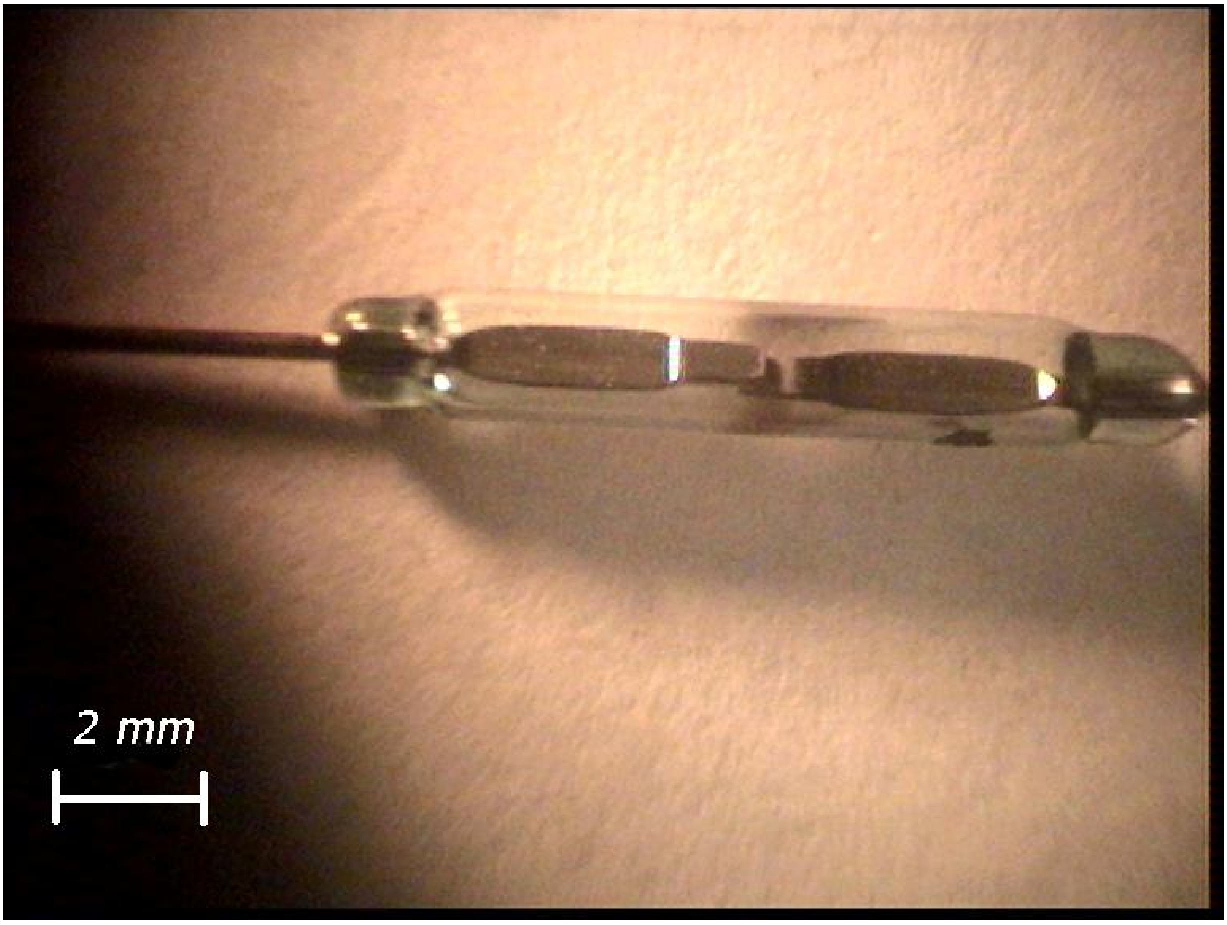


Figure 7. Reed switch after a hundred-fold ion-plasma treatment.

3.1.1.Auger- and AFM-Investigations
Elemental composition analysis of the surface of contacts (before and after treatment) was carried out using Auger electron spectrometer [27]. The device is equipped with the cylindrical mirror electron energy analyzer (resolution of 0.25 %) with an integrated electron gun having a beam current up to 1 μA if diameter of the beam is 100 μm. To clean the surface of contact pieces of reed switches and for layer-by-layer Auger analysis, an ion gun with a differential pumping of the working gas (Ar) and ion current density up to 3.5 mA/cm2 was used. All measurements were conducted in vacuum 2×10^{-7} Pa to eliminate effects of electron-stimulated adsorption of molecules of residual gases on the investigated surfaces.

Conductive nano-asperities

The received Auger profile of phase distribution in depth together with an indication of nitrogen concentration in stoichiometric compounds (Fig. 8) as well as images of nanostructured contact 50 nm asperities (Fig. 9) on a new heterogeneous Fe_3N (30 nm) and Fe_4N (40 nm) base are evidence of formation of the nanostructured surface contact layer.

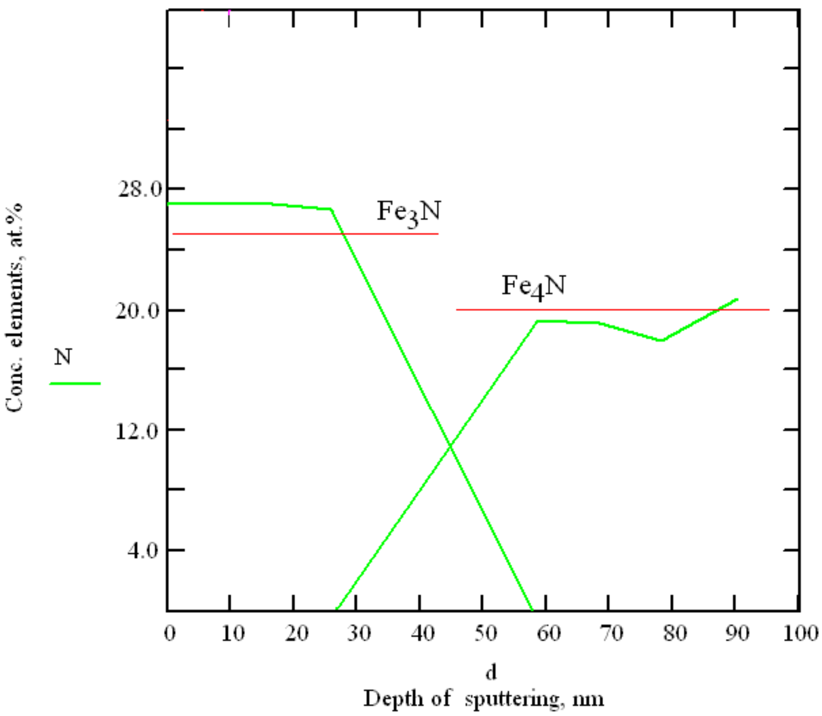


Figure 8. Restored phase distribution depth profile with an indication of nitrogen concentration in stoichiometric compounds of Fe_3N and Fe_4N. Single treatment (duration 30 s).

The surface nanostructure (nano-relief with the conductive nano-asperities) provides realization of the higher reliability principle – a multilevel echelon protection of contacts from erosion, corrosion and mechanical damages, improves the noise immunity from foreign particles, and as the final result, solves cardinally a quality problem of reed switches, what substantially reduces a failure number while in operation.

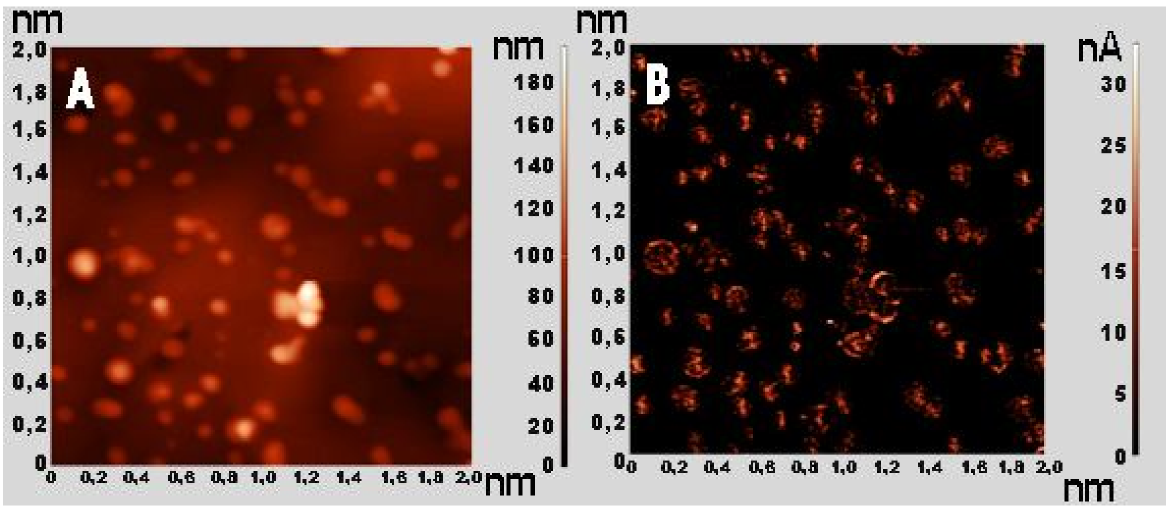


Figure. 9. AFM-image of nitrated surface area of contact spring of reed switch: **(A)** – constant actuating force method; **(B)** – spreading resistance imaging method. Single treatment.

Surface pores and cones.

Effects of ion-plasma fluxes on the surface can change its energy state, and that is showed by the relief evolution, for example, heterogeneous etching and reveal of the polycrystalline structure of the solid body. In addition, relief changes reveal ion-induced voltages, processes of recrystallization, compositional change of the near-surface layers and change of the dislocation mobility.

Ion-plasma fluxes initiate a formation of the surface stresses, diffusion activation, change of the dislocation structure, phase state. The development of these processes usually leads to the relief modifications. It is also necessary to take into account a result from the interaction of all processes of the forming relief indicated above with the processes of sputtering, ion-stimulated segregation, desorption, etc.

In the consequence of ion bombardment, the surface pores are formed in area 1 on the surface of contact pieces (**Figures 5a, b, 11**). The concentration thereof, as is evident from **Figures 5 a, b, 11,** grows with increase of duration of IPT.

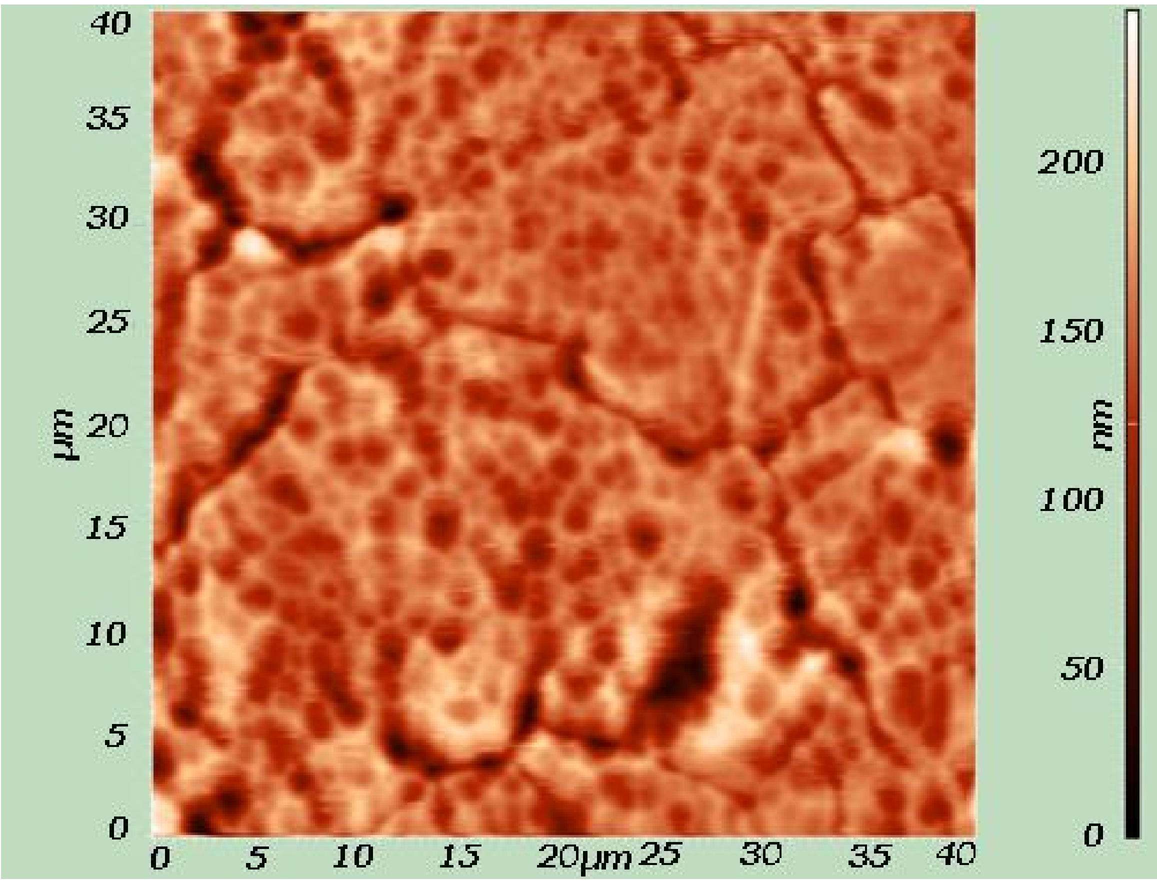


Figure 11. 2D AFM-image of area 1 of the contact surface of reed switch after 200-fold IPT. On the certain stage of development, the conical asperities start to grow on the bottom of pores (Figure 12 a, b).

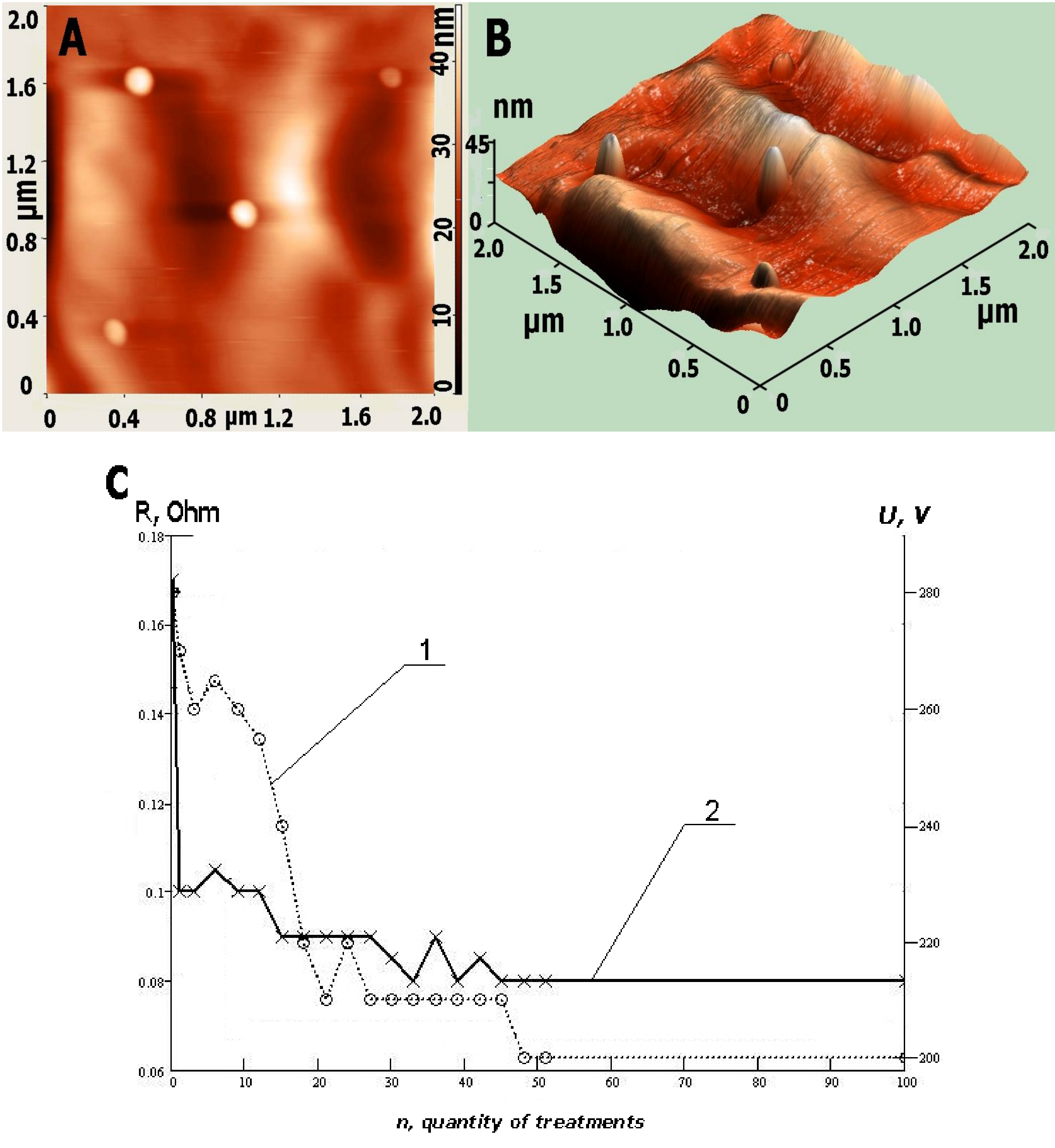


Figure 12. 2D **(A)** and 3D **(B)** AFM – image of area 1 of contact surface of a reed switch after 100-fold IPT; **(C)** dependences of resistance R (curve 2), breakdown voltage Uп (curve 1) of reed switch MKA-14108 median direction on quantity of treatments n. The quantity of reed switches in a lot is 100 pcs.

The conditions of appearance and mechanism of development of surface pores and cones on the solid surface treated by ions are considered in the paper [28]. On the author’s opinion the main reason of their formation are processes caused by ion-induced voltages and connected with atom movement in the surface layer. It is conditionaled on ion-enhanced diffusion, dislocation displacement and recrystallization. Pores formation must arise from supersaturation of surface with interstitial atoms and filling of microscopic vesicles of lattice with it is the result of ion-stimulated diffusion and recombinational processes in the near-surface layers. Yield of this formations to the surface in the field of ion-induced voltages leads to creation of open pores that at first have annular shape with gradual increase of slope of sidewalls. Pore development is completed with the growth of cone ledges on their bottom.

At ion bombardment redeposition of atoms from pore slopes to its bottom leads to formation of areas with lower voltage level and consequently to formation of cones on pore bottom on account of local diffusion sink. Meanwhile cone formations lower voltage level on the bottom, material flow from pore to the surface becomes slower, as a result the pore decreases and then disperses [28].

Surfaces with such relief (**Figure 12**) can possess reduced yield of sputtering and secondary electron emission. They reflects ion flows in a less degree, are characterized by selectivity of optical properties, high field-emission parameters. The structure of cones can change catalytic, corrosion and emission properties of reed switch contact surface. As follows from experimentally obtained dependence of breakdown voltage on quantity of treatments (**Figure 12 c**) stabilization of cone surface structure comes after 30 (thirty) IPT.

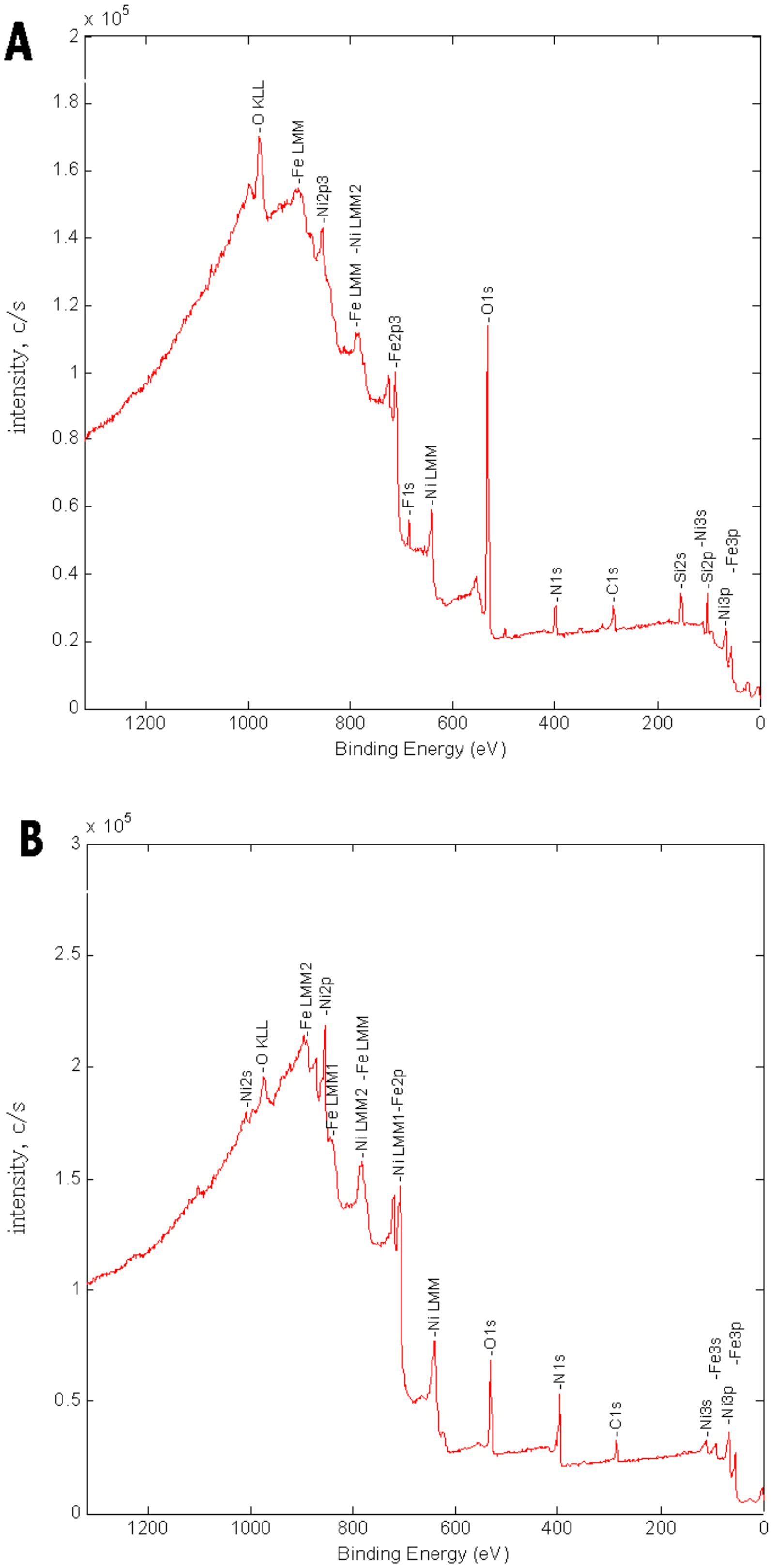
3.1.2. XPS and AFM-researches

Analysis of elemental and chemical composition of contact surface (before and after treatment, switching) is realized on scanning X-ray photoemissive microprobe PHI Quantera SMX (made by Physical Electronics, Inc., USA-Japan).

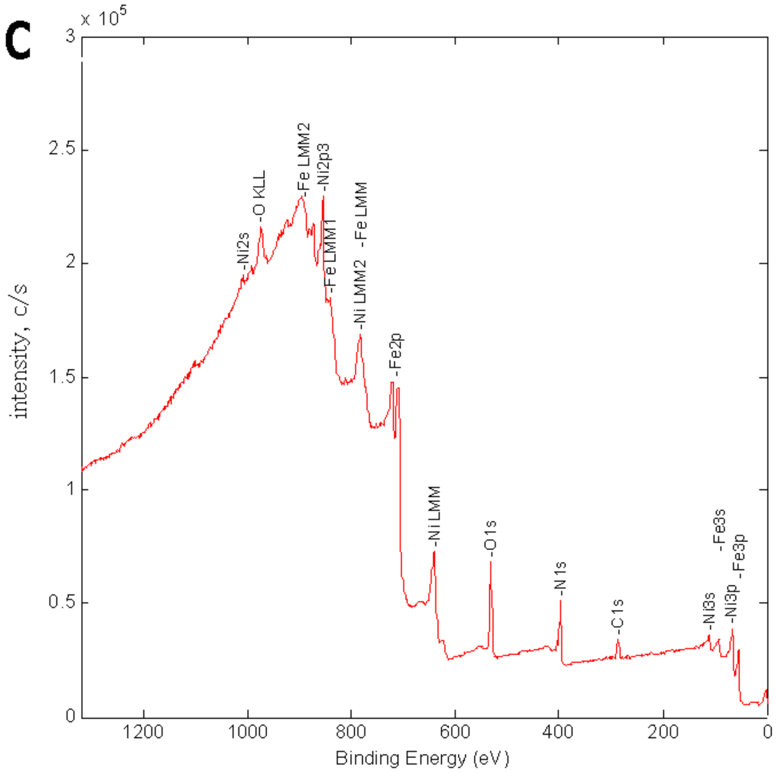
All measurements were carried out in vacuum 1×10^{-8} Pa for removal of effect of electron-stimulated adsorption of residual gas molecules on the surfaces under analysis. Sputtered cleaning was not carried out. Surface sensing was carried out in the overlap area of contact-pieces by X-ray beam of about 7 μm diameter.

Emission from aluminum anode Al Kα 1486.6 eV was used. Measurements of resistance, breakdown voltage of reed switches and reliability tests (in regimes 30 V - 0.5 A - $1.25\cdot10^6$ operations at temperature 155 ºC - $1.25\cdot10^6$ operation in normal conditions (n.c.) and 50 mV – 5 μA - 10^8 operation in n.c.) were carried out with the help of special-purpose equipment [1] in methods, represented in [1].

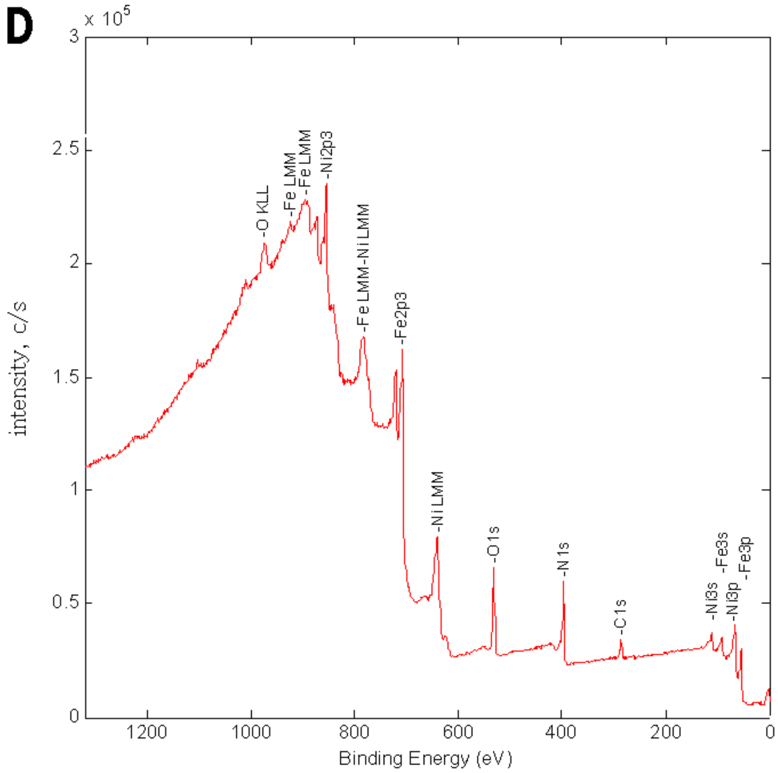
There are obtained review XPS – spectra (**Figure 13**) and photoelectron spectra of lines C 1s, O 1s, Ni 2p, Fe 2p, N 1s, Si 2p (**Figure 14**).


A
x 10^5
intensity, c/s
Binding Energy (eV)
-O KLL
-Fe LMM
-Ni2p3
-Ni LMM2
-Fe LMM
-Fe2p3
-O1s
-F1s
-Ni LMM
-N1s
-C1s
-Si2s
-Ni3s
-Si2p
-Ni3p
-Fe3p
B
x 10^5
intensity, c/s
Binding Energy (eV)
-Ni2s
-O KLL
-Fe LMM2
-Ni2p
-Fe LMM1
-Ni LMM2
-Fe LMM
-Ni LMM1
-Fe2p
-Ni LMM
-O1s
-N1s
-C1s
-Ni3s
-Fe3s
-Ni3p
-Fe3p

C


x 10^5
intensity, c/s
Binding Energy (eV)
-Ni2s
-O KLL
-Fe LMM2
-Ni2p3
-Fe LMM1
-Ni LMM2
-Fe LMM
-Fe2p
-Ni LMM
-O1s
-N1s
-C1s
-Ni3s
-Ni3p
-Fe3s
-Fe3p

D


x 10^5
intensity, c/s
Binding Energy (eV)
-O KLL
-Fe LMM
-Fe LMM
-Ni2p3
-Fe LMM-Ni LMM
-Fe2p3
-Ni LMM
-O1s
-N1s
-C1s
-Ni3s
-Ni3p
-Fe3s
-Fe3p

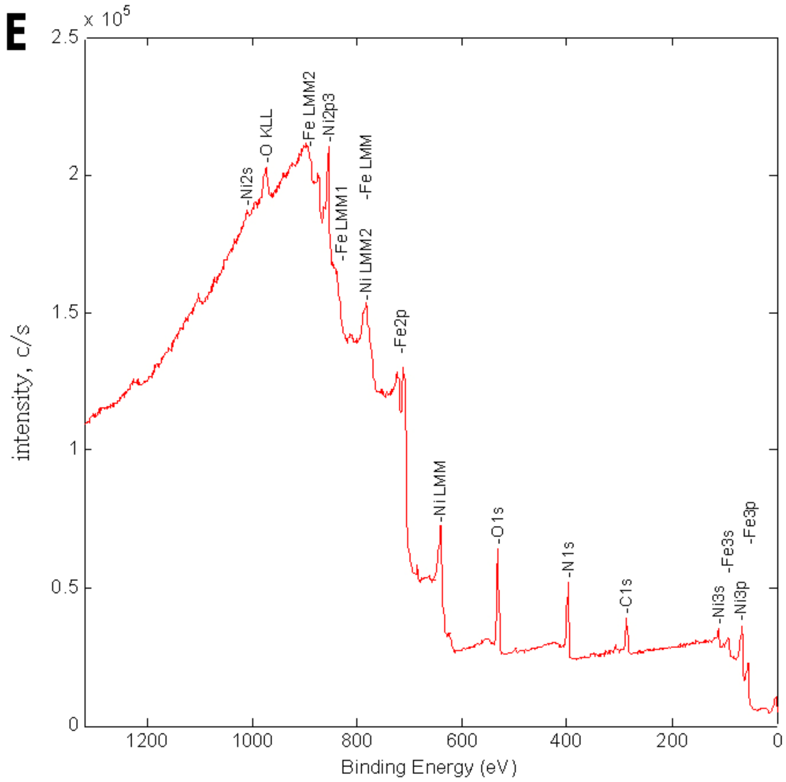
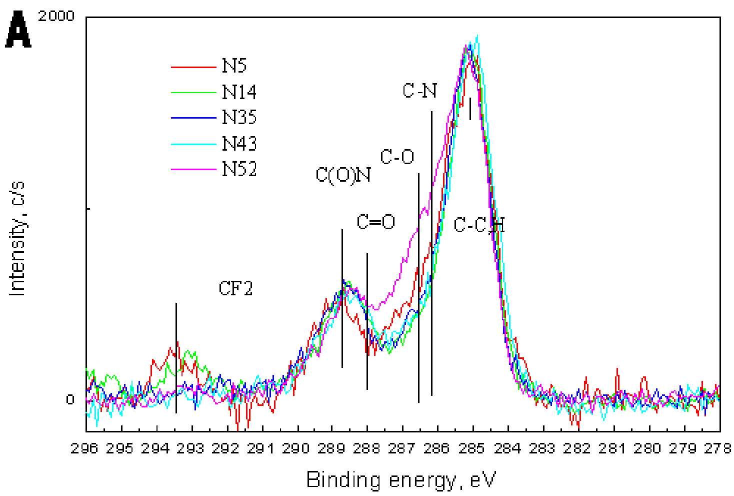
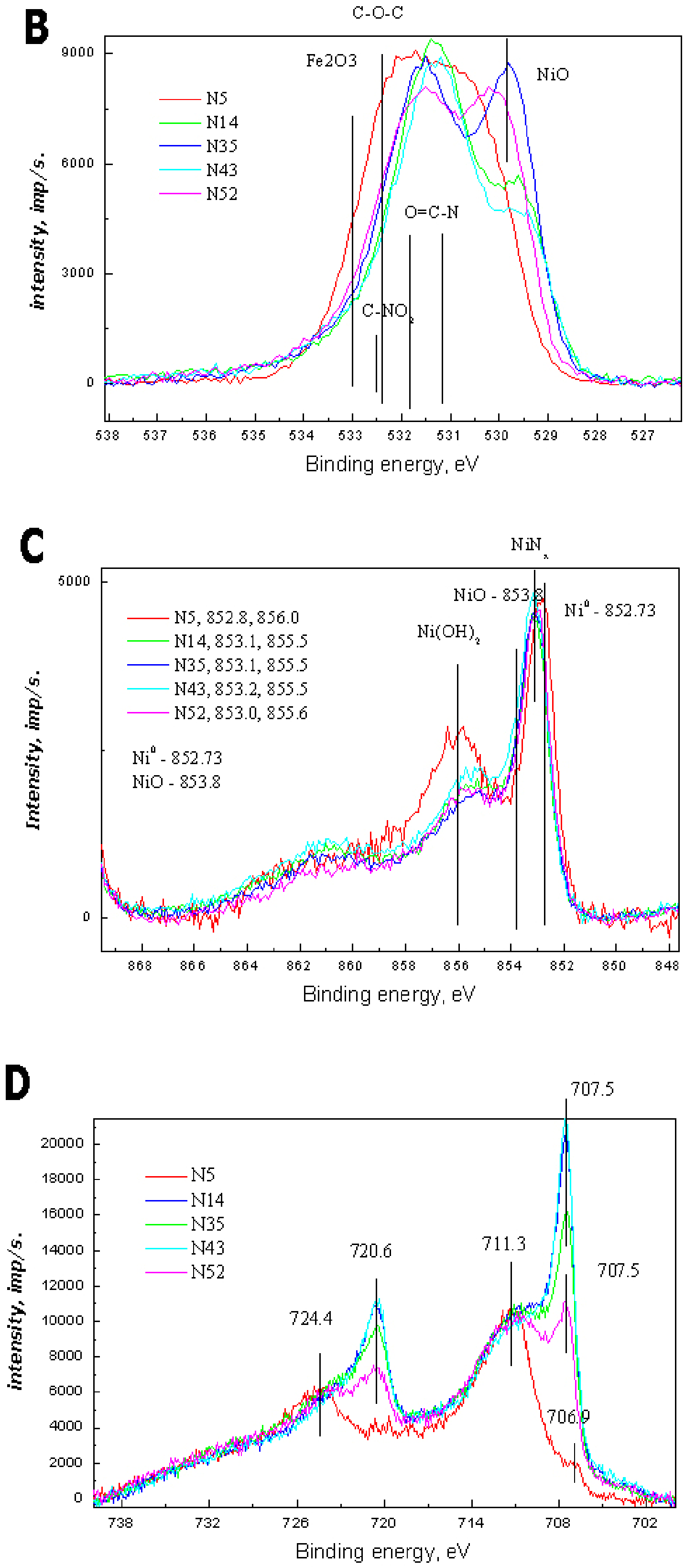
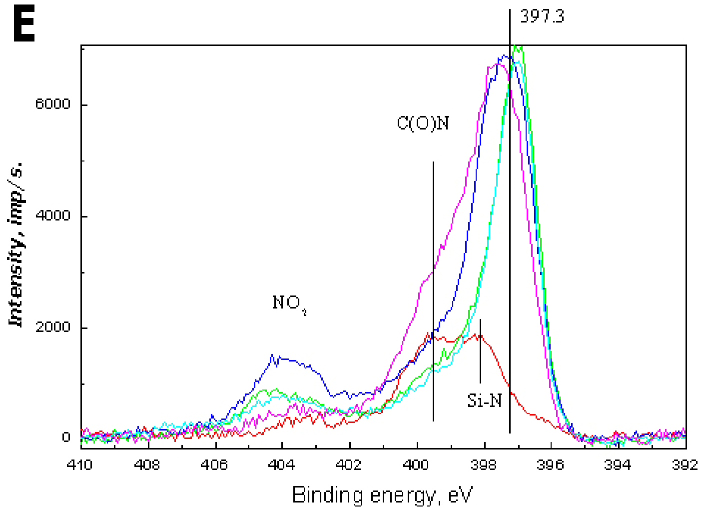


Figure 13. Review XPS-spectra: **(A)-** reed switch 5, **(B)-** reed switch 14, **(C)-** reed switch 35, **(D)-** reed switch 43, **(E)-** reed switch 52.




B
C-O-C
Fe2O3
NiO
N5
N14
N35
N43
N52
O=C-N
C-NO2
intensity, imp/s.
Binding energy, eV
C
NiNx
NiO - 853.8
Ni0 - 852.73
Ni(OH)2
N5, 852.8, 856.0
N14, 853.1, 855.5
N35, 853.1, 855.5
N43, 853.2, 855.5
N52, 853.0, 855.6
Ni0 - 852.73
NiO - 853.8
Intensity, imp/s.
Binding energy, eV
D
707.5
N5
N14
N35
N43
N52
720.6
711.3
707.5
724.4
706.9
intensity, imp/s.
Binding energy, eV



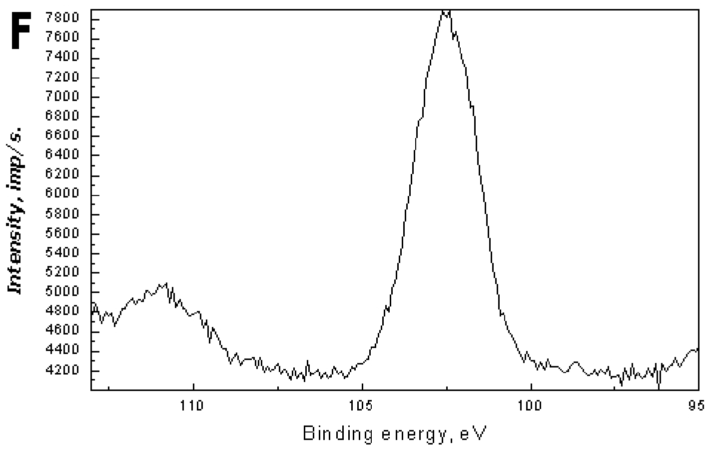


Figure 14. Photoelectron spectra **(A)-** C 1s, **(B)-** O 1s, **(C)-** Ni 2p, **(D)-** Fe 2p, **(E)-** N 1s, **(F)-** Si 2p.

The results of processing of review XPS-spectra of contact surfaces and reed switch resistance and breakdown voltage measurements are given in **Table 1** [14, 21].

Welding

In the review photoelectron spectrum taken in the overlap area of contact pieces of reed switch №5 (**Figure 13a**, **Table 1**) after welding, except of iron and nickel lines, lines of oxygen, carbon, silicon, fluorine and nitrogen are present. XPS-spectra of lines O 1s, Ni 2p, Fe 2p (**Figures 14 b, c, d**) indicate that in the virgin sample Fe and Ni are in oxidized state. Spectrum C 1s (**Figure 14 a**) denotes the presence of different carbonaceous groups on the contact surface. The position of the main peak in spectrum C 1s (285.0 eV) denotes good conductivity and small thickness of surface contamination layer. Photoelectron spectra N 1s (**Figure 14 e**) give states N in test samples. The main peak with energy of about 397.3 eV corresponds to nitride state. It is seen that in the virgin sample (№ 5) Si_3N_4 is present, that also follows from binding energy of the peak Si 2p (102.5 eV) **(Figure 14 f)**.
So we can suggest that the growth of reed switch resistance after welding is connected with oxidation of contact surface, nanodrops of glass and other products of thermal decomposition of glass and remains of technological environment (for example remains of hydrofluoric acid HF, used for glass envelope manufacturing), adsorption of oil vapor in the air with the further formation of polymer films.

Table 1. Regimes of IPT and switching, reed switch resistance R, breakdown voltage U, element concentration on contact surfaces of samples № 5, 43, 35, 14, 52.

№ of a sample	IPT regime	Switching regime	R, Ohm	U, V	C1s, at. %	N1s, at. %	O1s, at. %	Fe2p, at. %	Ni2p, at. %	F1s, at. %	Si2p, at. %
35	200 V - 30 s - 100 tr.	Without switching	0.08	210	13.5	29.2	27.6	17.8	11.9	-	-
43	200 V - 30 s - 30 tr.	Without switching	0.09	200	13.4	31.6	22.4	18.5	14.1	-	-
52	200 V - 30 s - 30 tr.	30 V – 0.5 A - $1.25 \cdot 10^6$operat. at 155 ºC - $1.25 \cdot 10^6$operat. in n.c.	0.09	250	22.4	27.6	26.0	13.9	10.1	-	-
14	200 V - 30 s - 30 tr.	50 mV - 5 μA - 10^8 operat. in n.c.	0.09	220	14.5	30.5	24.7	16.8	13.5	-	-
5	Non-IPO	Without switching	0.22	290	9.3	8.7	53.5	8.3	4.6	3.3	12.5

Ion-plasma nitriding

After 30 treatments by high-voltage pulsed discharges resistance of reed switches MKA-14108 reduced and became to correspond to resistance of off-the-shelf devices MKA 14103 **(Table 1)**.

In the review XPS-spectrum taken from the reed switch after 30-fold IPT (sample № 43) (**Figure 13 d)**, as on the spectrum from untreated in gas discharge contact surface of sample №5 **(Figure 13 a)**, lines of iron, nickel, oxygen, carbon and nitrogen are observed. However after IPT the situation has greatly changed. The lines of silicon, fluorine are absent, intensity of oxygen line decreased, and lines of iron, nickel, carbon and nitrogen became more intensive. Observed in practice change of surface structure, reduction of resistance and breakdown voltage after IPT is directly connected with sputtering by nitrogen ions of polymer films and spurious coatings (from silicon oxide, ferric and nickel oxide) that improves red switch resistance and also with nitriding and gasabsorbtion processes.

In the photoelectron spectrum Ni 2p (**Figure 14 c)** the shift of the main peak to the side of high binding energy denotes the formation of connection with N. The presence of NiO in the first place follows from spectrum O 1s (**Figure 14 b)**. The formation of oxynitride phase is possible. The state with energy 707.5 eV in photoelectron spectrum Fe 2p (**Figure 14 d)**, as in the case with Ni should be considered as connection with N. The main peak with energy about 397.3 eV in photoelectron spectrum N 1s (**Figure 14 e)** also corresponds to nitride state of surface of reed switch № 43.

After 100-fold treatment by high-voltage pulsed discharges the resistance of reed switches MKA-14108 median-direction matches with the resistance of off-the-shelf devices MKA 14103.

In the review XPS-spectrum taken from reed switch № 35 after its 100-fold IPT (**Figure 13 c)**, as in the spectrum of sample № 43 after 30-fold IPT (**Figure 13 d)**, lines of iron, nickel, oxygen, carbon and nitrogen are observed. In the spectrum it is seen that after 100-fold IPT the situation has not considerably changed. The lines of silicon, fluorine are also absent, the intensity of carbon and oxygen lines has a little bit increased (C by 0.1 at. %, O by 5.2 at. %), and intensity of lines of iron, nickel, nitrogen has on the contrary reduced (Fe by 0.7 at. %, Ni by 2.2 at. %, N by 2.4 at. %).

Switching

At comparison of XPS-spectra of samples № 43, 14 and 52 taken before and after reliability tests (**Figures 13 b, d, e)** the same tendency if found as at hundred-fold treatment. After tests in microregime (50 mV - 5 μA - 10^8 operations in n.c.) intensity of carbon and oxygen lines increased (C by 1.1 at. %, O by 2.3 at. %), and intensity of iron, nickel, nitrogen lines on the contrary decreased (Fe by 1.6 at. %, Ni by 0.7 at. %, N by 2.4 at. %). In the power regime (30 V - 0.5 A -$1.25{\cdot}10^6$ operations at 155 ºC - $1.25{\cdot}10^6$ operations in n.c.) this tendency is more obvious. The intensity of carbon and oxygen lines has considerably increased (C by 9 at. %, O by 3.6 at. %), and intensity of iron, nickel, nitrogen lines on the contrary has considerably decreased (Fe by 4.6 at. %, Ni by 4.0 at. %, N by 4 at. %).

It is connected with that in the power regime plasma arc of opening appears [1]. Because of arc thermal effect in contact microspots surface heating higher than boiling temperature occurs, that leads to intensive metal vaporization [1]. As a result, as it is seen from AFM-images (**Figure 15**) cone-shaped craters (sphalerite formations) of about 2000 nm diameter and about 120 nm depth are formed on the surface of contact pieces.

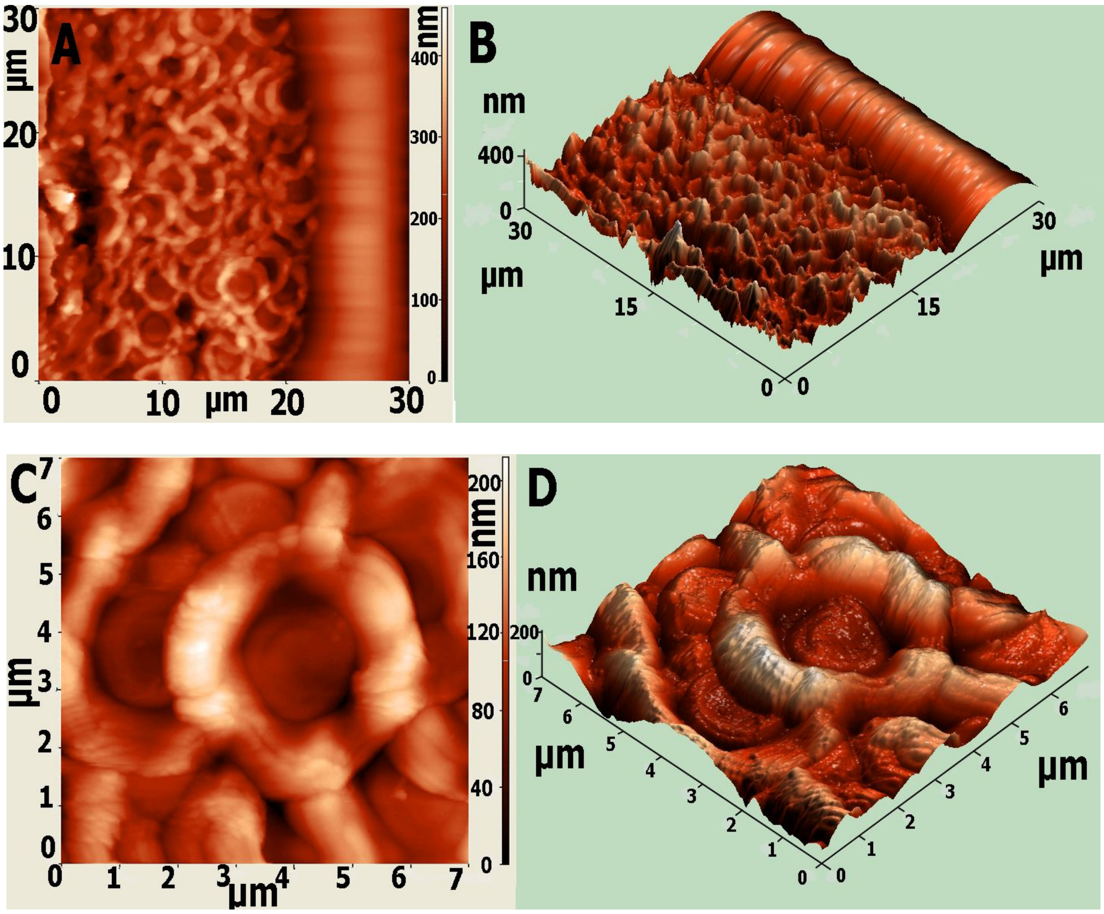


Figure 15. AFM – image of contact surface of sample № 52 (after IPT and switching in regime: 30 V – 0.5 A -$1.25{\cdot}10^6$operat. at 155 ºC -$1.25{\cdot}10^6$operat.in n.c.): **(A), (B)** – 30 x 30 μm; **(C), (D),** - 7 x 7 μm.

Simultaneously diffusion carry-over of carbon and oxygen to the surface with the formation of carbon dioxide according to the data of mass spectrometric analysis [18, 22]. On account of arc thermal effect in contact microspots decomposition of nitrides occurs with nitrogen release. Meanwhile reed switch breakdown voltage increases by 50 V. This growth is connected with gas pressure growth in reed switch, because the product (pd) for contact gap of reed switch corresponds to the right branch of Paschen [18], (**Figure 16**).

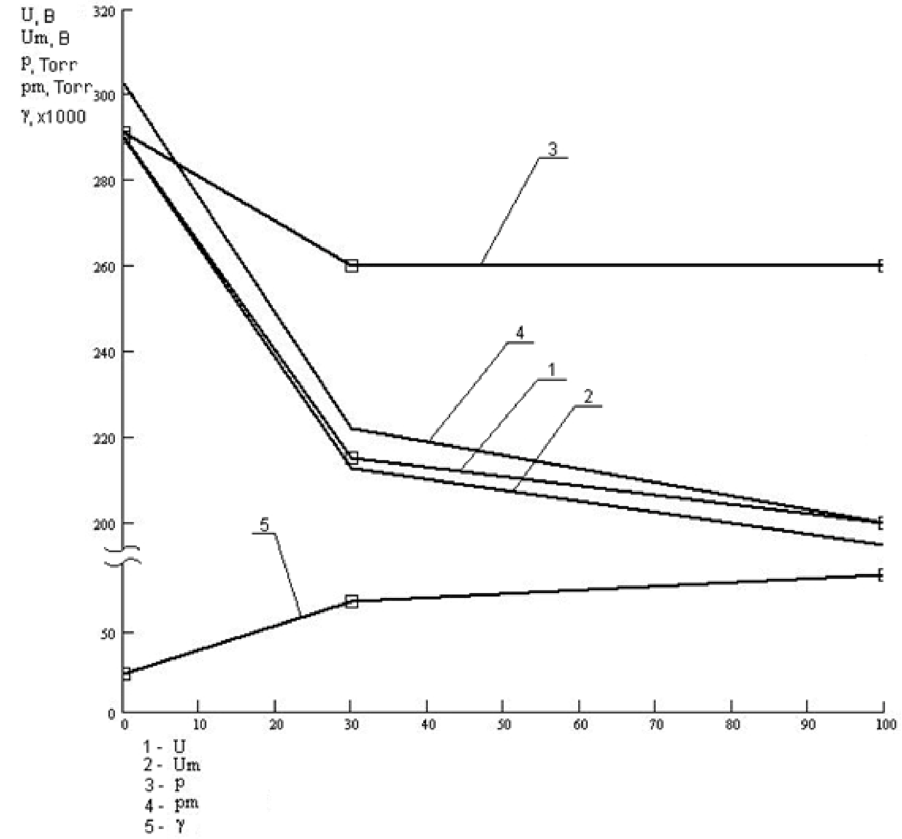


Figure 16. Dependences of breakdown voltage U -1, gas filling pressure P - 3, coordinate of minimum of Paschen curve U_m - 2, p_m - 4, cumulative rate of secondary electron emission γ - 5 of reed switch MKA-14108 median-direction on quantity of treatments n.

However in spite of partial destruction (to a lesser degree – microregime or father – power regime) of near-surface nitride layers by switching, failures of the samples under test were not observed.

3.2. The coatings obtained by reactive cathode sputtering method

Sputtering
The surface of contact piece after IPT according to the second regime (of reactive cathode sputtering) can be divided for convenience by images of contact piece surfaces, taken with the help of optical (**Figure 17**) and atomic-force (**Figure 18**) microscopes in two areas of distinctive topography.

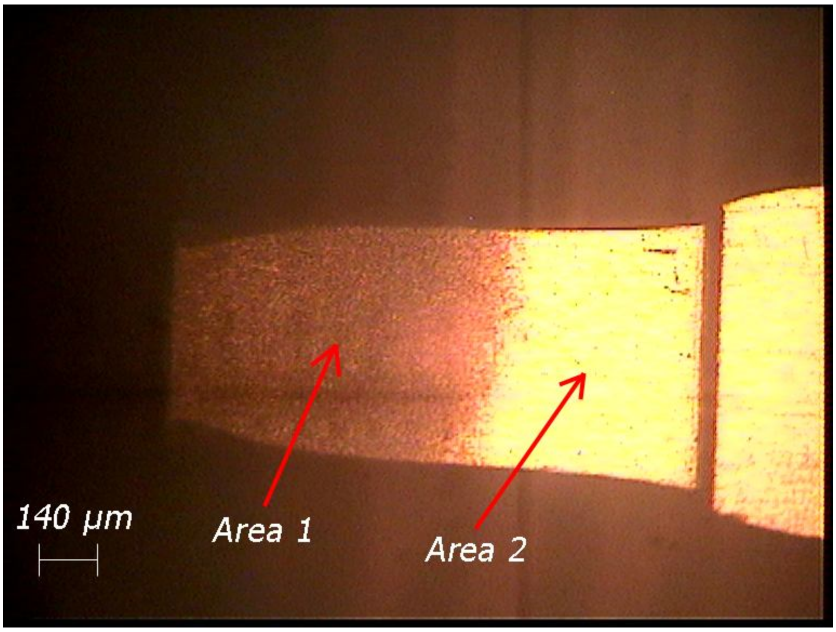


Figure 17. Reed switch contact-piece after 30-fold ion-plasma treatment (reactive cathode sputtering mode).

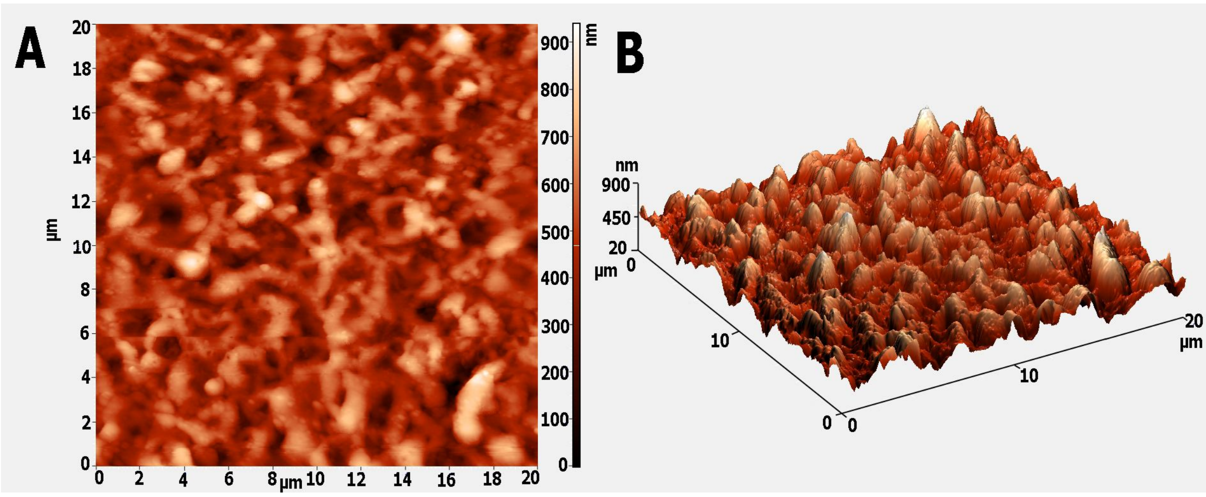


Figure 18. AFM-image of reed switch contact surface after 30-fold ion-plasma treatment (reactive cathode sputtering mode): **(A)** and **(B)** -2D and 3D image of area 1.

Area 1 (**Figures 17, 18a, b**) is a working area (contact-pieces overlapping area) where, in fact, a gas discharge is allowed with the voltage supply to the opened reed switch contacts. As a result of the reactive cathode sputtering, nitrides (FeN and NiN) the most part thereof is deposited on the contacts surface in area 1 are formed in the gas phase of the overlapping area.
Figure 19 demonstrates the reactions determining the process of the contact plating deposition by the reactive cathode sputtering method. Nitrogen ions accelerating in the area of the potential cathode loss

bombard the target – cathode. Thereby, the most part of ion energy (about 90%) is consumed for the target heating, and the rest part – for the electron emission, ion implantation, and atom sputtering (Fe, Ni, C, O) located on the target surface. As a result of the reactive cathode sputtering, iron and nickel nitrides which thereafter are deposited on the reed switch contact-pieces and glass envelope are formed in the gas phase. With the deposition on the contact surface in area 1 (with temperature less than 400-500˚ C) molecules of metals MeN (Fe, Ni) nitrides of permalloy do not dissociate as in case of ion nitriding but form a black-colored film (**Figure 17**). The coating thickness, according to the data of metallographic investigations, was (after 30-fold IPT) about 400 μm.

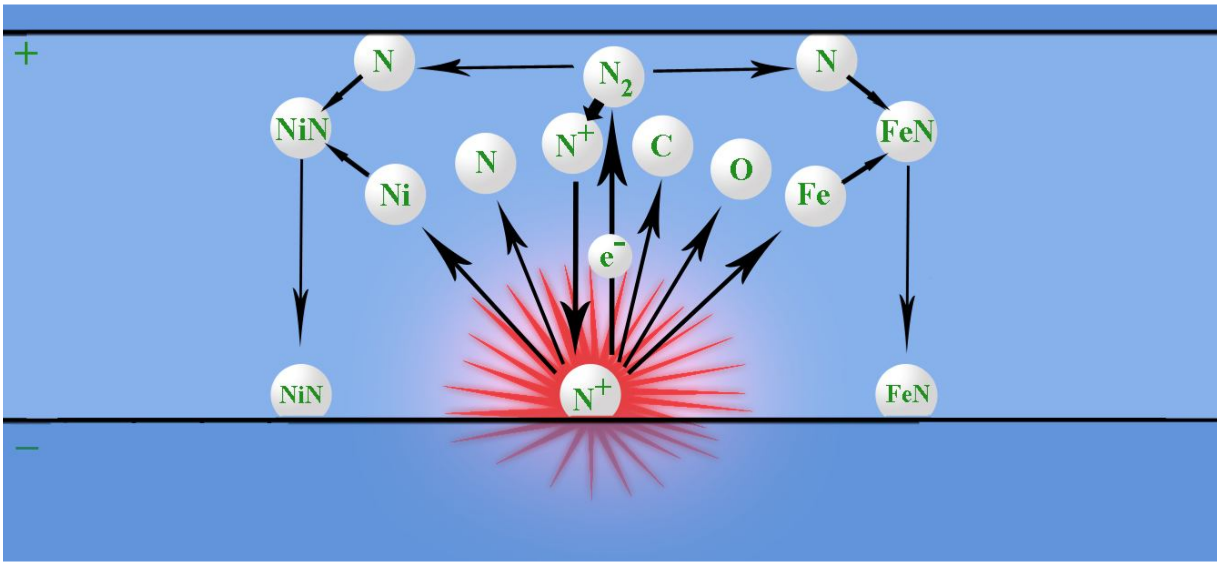


Figure 19. Coating deposition by reactive cathode sputtering method.

As a result of diffusion, a part of FeN and NiN molecules will be deposited on the contacts surface in area 2 neighboring with area 1 (**Figures 17, 18 c, d**) and the inner surface of the envelope, located near the overlapping area (**Figure 7**). A small number of the products of cathode sputtering also gets on the reverse sides of the reed switch contact-pieces.

Switching tests

It is known [1] that the basic effect of the corrosion, erosion and contaminations impact on the electrical contacts lies in the conductivity trouble therefore the contacts resistance to these processes can be characterized by a number of closures, whereby the conduction changes tragically. The contacts erosion resistance can be characterized by a number of closures whereby the contacts conduction trouble or the contacts non-breaking occurs.

Experimental prototypes of the reed switches after high-discharge treatments in the reactive cathode sputtering mode (the second mode of IPT) and without such were under comparative switching tests as per the technique developed earlier in the paper [25] for MKA-14108 reed switches with ion- nitrided contact surfaces. The tests were conducted for the active load and in the idling mode (without load). It allowed optimizing the modes of the contact spring surface modification and studying physical processes occurring on all stages of the reed switch treatment and operation.

Comparative switching tests of MKA-14108 pilot reed switches and MKA 14103 off-the-shelf devices showed that MKA-14108 pilot reed switch operation time, pretreated by high-voltage pulsed discharges in the reactive cathode sputtering mode, meets the requirements specified for the durability of MKA 14103 off-the-shelf devices (**Table 2**).

Table 2. Results of comparative switching tests.

Switching tests mode	Reed switch type	Without failures, %	Rmax Before tests, Ohm	Rmax After tests, Ohm
50 mV - 5 mkA, 100 Hz, 10^6 operations	MKA-14103	100	0.1	0.1
	MKA-14108, without treatment	21	0.25	10
	MKA14108, with treatment	100	0.08	0.09
5 V - 10 mA, 100 Hz, 10^6 operations	MKA-14103	100	0.17	0.11
	MKA14108, without treatment	27	0.35	22.7
	MKA14108, with treatment	100	0.07	0.08
20 V - 0.5 A, 50 Hz, $5{\cdot}10^6$ operations	MKA-14103	38	0.16	40
	MKA14108, without treatment	47	0.31	0.11
	MKA14108, with treatment	100	0.09	0.10
24 V - 400 mA, 50 Hz, $5{\cdot}10^5$ operations	MKA-14103	100	0.13	0.5
	MKA14108, without treatment	100	0.29	0.11
	MKA14108, with treatment	100	0.07	0.01
36 V - 15 mA, 50 Hz, $5{\cdot}10^6$ operations	MKA-14103	25	0.2	8.7
	MKA14108, without treatment	53	0.49	0.34
	MKA14108, with treatment	100	0.07	0.09
50 V - 50 mA, 50 Hz, $5{\cdot}10^5$ operations	MKA-14103	100	0.14	0.22
	MKA14108, without treatment	100	0.38	0.25
	MKA14108, with treatment	100	0.07	0.08
100 V -100 mA, 50 Hz, $5{\cdot}10^5$ operations	MKA-14103	2	0.17	0.19
	MKA14108, without treatment	100	0.27	0.23
	MKA14108, with treatment	100	0.08	0.09

For the treatment mode optimization and identification the tests of MKA-14108 reed switch pilot samples before and after treatment without load (in idling mode) were conducted. The switching number changed step-by-step from 0 to 107 collisions. R was measured on each stage of the reed switch testing (**Figure 20**).

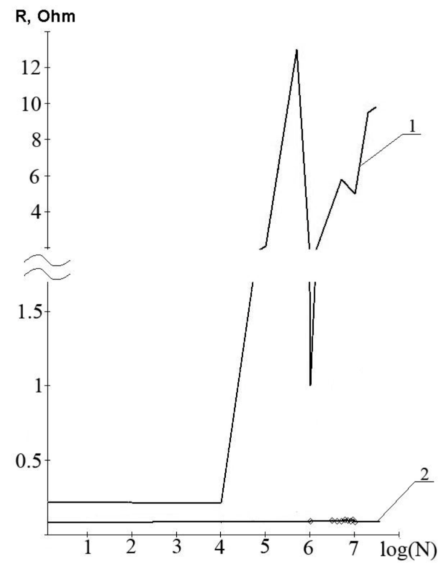


Figure 20. Dependence of resistance R of MKA14108 reed switch along the median upon the number of operations N in dry circuit (1 – untreated contact-pieces, 2 - contact-pieces after IPT in the reactive cathode sputtering mode). Reed switch batch quantity is 100 pcs.

Moreover, the pilot samples were tested for the reliability with an active load as per the combined mode (**Figure 21**).

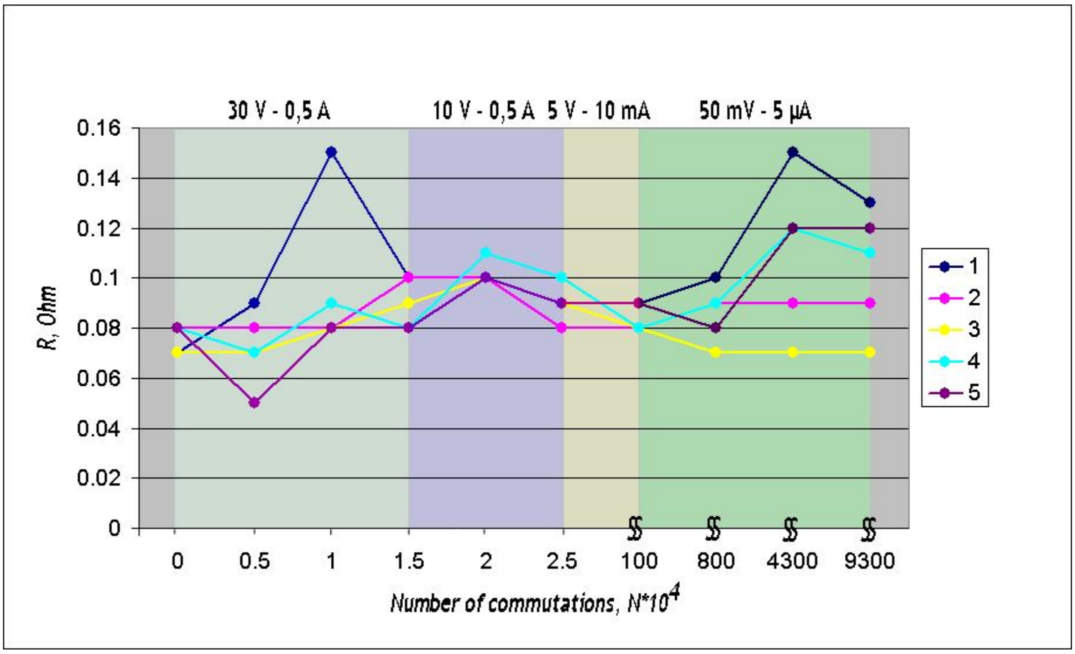


Figure 21. Dependence of resistance R of MKA14108 reed switches (5 pcs.) upon a number of operations N in the combined mode.

AFM-image of the contact surface, obtained by the reactive cathode sputtering method, before and after switching are shown in **Figures 18** and **22**.

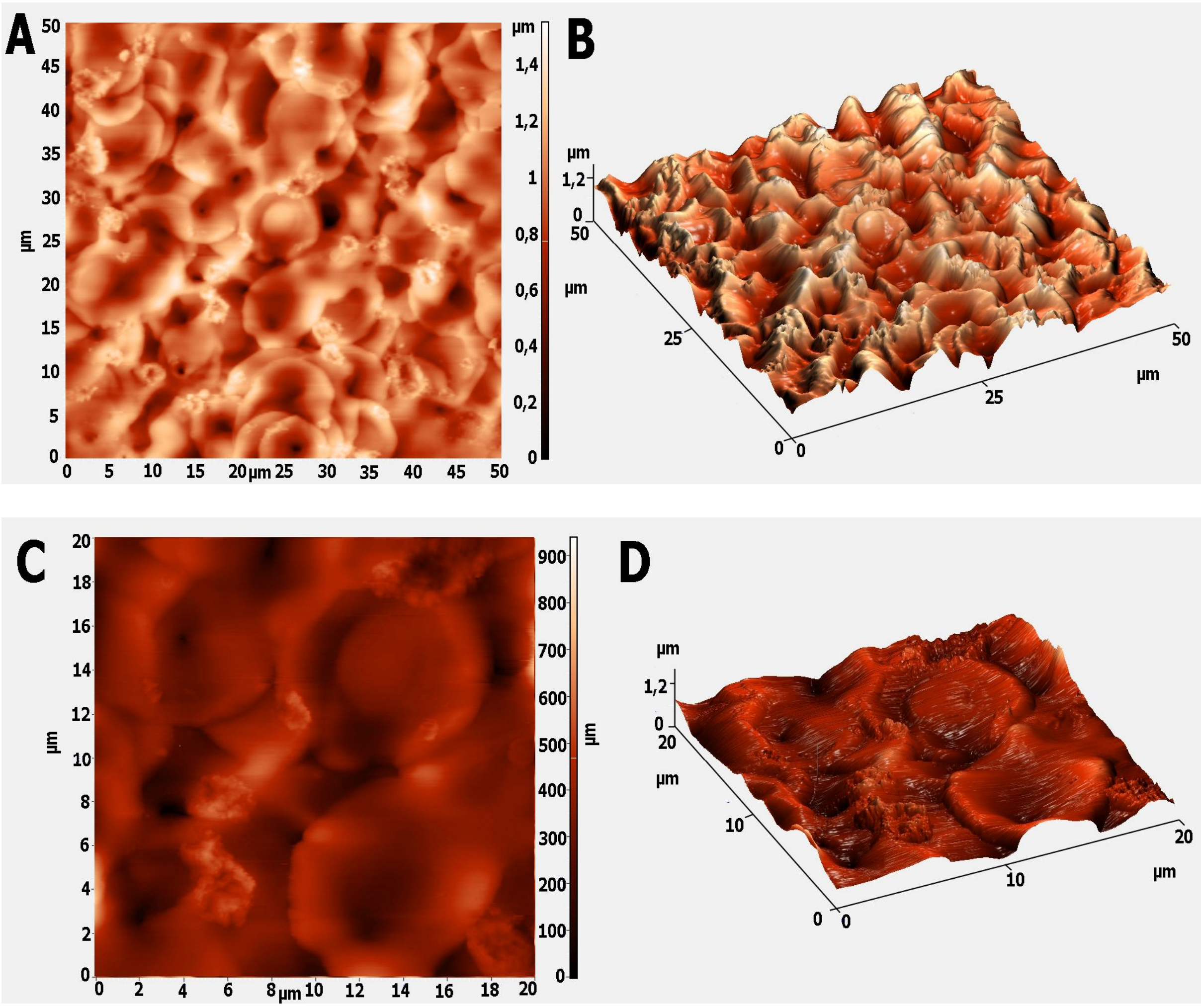


Figure 22. 2D and 3D AFM – image of the contact surface of MKA-14108 reed switch (after IPT in the reactive cathode sputtering mode and following switching in the combined mode: **(A), (B)** – 50 x 50 µm; **(C), (D),** - 20 x 20 µm.

Due to the heating effect of the breaking arc [1] occurring in the range of 0 – $2.5 \cdot 10^4$ operations (**Figure 21**), the surface heating over the boiling temperature occurs in the contact micro-spots. It leads to the intensive metals evaporation. As a result, AFM-images show (**Figure 22**) that the cone-shaped craters of about 8000 µm in diameter and about 100 µm in depth are formed on the surface of the contact-pieces.

Considering the experimental curves delineated in **Figures 20, 21,** one can make a conclusion about a full compliance of the deposited coatings to the requirements [1] for reliability, resistance value and stability, specified to the coatings of stock-produced MKA-14103 reed switches.

Therefore, switching reliability tests for the reed switch with the contact coatings fabricated by the reactive cathode sputtering method showed a positive result. They confirmed a high film adhesion to the substrate material. Apparently, the adhesion bonds strength is stipulated by an additional activation of the surface by plasma operation.

4. Conclusion

A principally new technological process of the magnetically operated contacts (MC) contacting surfaces modification (MK) when after the contact springs sealing within the glass enveloped fulfilled with nitrogen through MCs being opened, they pass current pulses which cause forming micro-nanosized layers with the specified contact properties in the surficial area of MCs, was developed.

As a result of the implemented investigations it was managed to provide such electrophysical discharge conditions under which in the surficial area and on the surface of the permalloy reed switch contacts, corrosion- and erosion-resistant nitride layers with a high electrical conduction are formed by the methods of ion nitriding or reactive cathode sputtering, that allows refusing electroplating application made of precious metals.

Therefore, the obtained results denote the viability of ion nitriding and reactive cathode sputtering methods application for the reed switch production.

Reference

[1] Karabanov S.M.; Maizels R.M.; Shoffa V.N. *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Intellect”: Dolgoprudny, Russia, 2011).

[2] Arzamasov B.N.; Bratukhin A.G.; Eliseev Y.S.; Panayoti T.A. *Ion chemicothermal treatment of alloys in gas medium*; (Publishing house “MSTU named after Bauman N.E.”: Moscow, Russia, 1999).

[3] Lyaschenko B.A.; Mironenko V.I.; Radko O.V.; Bobyr S.A. *Features of 30ХГСА steel nitriding in pulsating discharge*; (Published in VCNU, Cherkassy, Ukraine, 2007; pp. 107-110); (in Russian).

[4] Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N.; Sablin V.A. Modifications of sealed magnetically operated permalloy contacts surface by pulsed discharges. In the collected papers of the second international theoretical and practical conference *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Poligraph”: Ryazan, Russia, 2009; pp. 174-177); (http://www.rmcip.ru – in Russain).

[5] Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Sablin V.A. Investigation and development of modification methods of hermetically sealed magnetically operated contacts surface. In the collected papers of the second international theoretical and practical conference *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Poligraph”: Ryazan, Russia, 2009; pp. 184-207); (http://www.rmcip.ru – in Russain).

[6] Zeltser I.A.; Karabanov S.M.; Kuznetsov A.A.; Maizels R.M.; Sablin V.A.; Chernyak E.Y. Investigation of ion-plasma modification of iron-nickel sealed magnetically operated contacts by Auger spectroscopy. In the collected papers of the Second International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Poligraph”: Ryazan, Russia, 2009; pp. 178-183); (http://www.rmcip.ru – in Russain).

[7] Karpov A.S.; Maizels R.M.; Shishkina L.V.; Shkutenko L.N. Plant for automatic ion-plasma treatment of reed switches. In the collected papers of the second international theoretical and practical conference *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Poligraph”: Ryazan, Russia, 2009; pp. 169-173); (http://www.rmcip.ru – in Russain).

[8] Kuznetsov A.A.; Vasilyev E.V.; Zeltser I.A.; Chernyak E.Y. Analysis of elemental and chemical composition of reed switch contact zones by Auger spectroscopy. In the collected papers of the Second International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*; (Publishing house “Poligraph”: Ryazan, Russia, 2009; pp. 84-87); (http://www.rmcip.ru – in Russain).

[9] Arushanov K.A.; Zeltser I.A. Instrument and technological aspects of reed switch with nanostructured contact surfaces creation. (Vestnik RSURE, 2009, 3, pp. 93-98); (in Russian).

[10] Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N.; Sablin V.A. Modification of sealed magnetically operated iron-nickel contacts surface. In reports theses of X International Workshop *Structural fundamentals of materials modification by methods of non-traditional technologies*, (MHT-X; Obninsk, Russia, 2009; pp. 58-59); (in Russian).

[11] Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N.; Sablin V.A. Nanostructure

Modificated Contact Surface. In *Abstract Book of International Conference "Information and Structure in Nanoworld"*; (Saint-Petersburg, Russia, 1-3 July, 2009; p. 83).
[12] RF Patent No.2391733. Magnetically operated sealed contact. / Karabanov S.M., Zeltser I.A., Maizels R.M., Trunin E.B.
[13] RF Patent No.2393570. Method of reed switch with nitrided contact-pieces production. / Karabanov S.M., Maizels R.M., Arushanov K.A., Zeltser I.A., Provotorov V.S.
[14] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maslakov K.I.; Naumkin A.V. Investigation of plasma modification of magnetically operated contacts by methods of X-ray photoelectron spectroscopy and atomic force microscopy. In materials of 7 International Theoretical and Practical Conference *Recent developments of the European science, Volume. 36. Chemistry and chemical technologies. Physics*; (Sofia, Bulgary, 2011; pp. 56 – 61); (in Russian).
[15] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N. New method of reed switch contact surfaces modification. In materials of 7 International Theoretical and Practical Conference *Recent developments of the European science, Volume. 36. Chemistry and chemical technologies. Physics*; (Sofia, Bulgary, 2011; pp. 52–55); (in Russian).
[16] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N. Nanorelief formation of contact surfaces. In XI International Workshop *Structural fundamentals of materials modification* (MHT-XI) Reports theses; (Institute of Atomic Energy of Scientific Research Nuclear University of Moscow Engineering and Physical Institute, Obninsk, Russia, 2011; pp. 20-22).
[17] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N. Ion-induced modification of contact surfaces. In materials of XX International Conference *Ion interaction with surface*, VIM-2011; (Zvenigorod, Russia, 25-29 of August 2011; pp. 206-209).
[18] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Trunin E.B. Diffusion nitrogen saturation of surficial layers of reed switch contacts in pulsating plasma. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 31-38).
[19] Avachev A.P.; Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Konobeev V.A. Investigation of plasma modification of magnetically operated contacts surface by methods of atomic force and optical microscopy. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 47-53).
[20] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maizels R.M.; Moos E.N. New method of magnetically operated contacts modification. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 54-60).
[21] Arushanov K.A.; Zeltser I.A.; Karabanov S.M.; Maslakov K.I.; Naumkin A.V. Investigation of ion-plasma modification of iron-nickel magnetically operated contacts surface by X-ray photoelectron spectroscopy. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 39-46).
[22] Zhuravlev S.A.; Zeltser I.A.; Maizels R.M.; Polyakov A.S.; Chernyak E.Y. Analysis of chemical gas composition inside reed switches. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 68-69).
[23] Arushanov A.K.; Zeltser I.A.; Kuznetsov A.A.; Chernyak E.Y. Application of Auger spectroscopy for investigation of plasma modification of magnetically operated contacts. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based thereof*, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 61-67).
[24] Drozdov M.N.; Zeltser I.A.; Karabanov S.M.; Teodoru O.M.N.D. Application of mass-spectrometry of secondary ions for investigation of ion-plasma modification. In 3 International Theoretical and Practical Conference *Magnetically operated contacts (reed switches) and units based*

thereof, reports theses; (Ryazan, Russia, 28-30 of September 2011; pp. 129-133).
[25] Karabanov S.M.; Zeltser I.A.; Maizels R.M.; Moos E.N.; Arushanov K.A., Creation of Principally New Generation of Switching Technique Elements (Reed Switches) with Nanostructured Contact Surfaces. *Journal of Physics: Conference Series*, 2011, V. 291, No.01 2020, pp. 1-17.
[26] Chatterjee – Fischer R.; Eysell F. – W. *Nitriding and carbonitriding*; Editted by Supov A.V.; (Publishing house “Metallurgy”: Moscow, Russia, 1990; p. 280).
[27] Kuznetsov A.A.; Abramova S.Yu.; Potapova T.E.; Protopopov O.D. *Journ. of Electron Spectr. and Rel. Phenom* 1994, V. 68, pp. 407-412; (in Russian).
[28] Begrambekov L.B.. Modification of solid bodies surface with ion and plasma impacts; (Moscow Engineering and Physical Institute, Moscow, Russia, 2001).