https://doi.org/10.15407/ujpe67.4.292

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PROPERTIES OF STEEL MODIFIED BY SURFACE ION IMPLANTATION WITH Mo, Ti, AND Al

Modification of metals by a surface treatment is one of the first problems of modern materials science. The use of ion-plasma technologies for a modification of initial specimens, in particular, by ion implantation, for this purpose can be considered a promising solution. We study the microstructure, phase and elemental compositions, wetting forces, and electrical properties of steel with implanted ions of titanium, aluminum, and molybdenum. The results obtained by means of XRD, XPS, optical microscopy, and laboratory experiments show significant differences between the treated and untreated specimens. The modification of metal by ion implantation causes changes in the wettability and electrical characteristics and indicates the prospects of this technology for mechanical engineering, chemical, food, pharmaceutical industries, for the construction of structures and vehicles, including their work under severe atmospheric conditions.

K e y w o r d s: XPS, XRD, nanoscale surface modification, ion implantation, wetting force.

1. Introduction

Nowadays, more and more scientists and industrialists focuse their efforts on the finding of new materials and modification of existing ones. Many studies considered the physical and chemical characteristics of metals, since the topic of a change in surface properties is very relevant in our time. In this case, varios methods of surface modification are widely used. One of these methods is the ion implantation which offers not the application of an additional layer, but the introduction of ions directly into the surface layer [1–5]. In particular, it was shown in [1] that the implantation of molybdenum into ball-bearing steel leads to a decrease in the coefficient of friction. Wear on steels with implanted nitrogen and titanium is reduced. In this direction, the use of ion-plasma technologies can be considered as promising. In [2–4], results on changes in the surface microrelief of metals and alloys are presented. This occurs due to the bombardment of them with ions of nitrogen, molybdenum, *etc.* and leads to a change in mechanical characteristics. In addition, the author of work [3] recommended an implantation fluence close to 10^{18} cm^{-2} for the optimal modification of the material.

According to studies [4], the implantation with a fluence of about 10^{18} cm^{-2} not only changes the surface microgeometry of steels, but also increases their microhardness by several times. Implantation of nitrogen with a fluence of the order of 10^{17} cm^{-2} improves the chemical stability of titanium in liquid media [5].

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Hereby, the ion implantation allows one to change the surface structure, its roughness and elemental composition, which has a significant influence on the physical and chemical properties of the surface and bulk of the material. An important advantage is that the ion implantation permits one to change substantially physical and chemical properties without affecting the shape and size of the structural element.

Protection of metal structures, cars, and people from lightning strikes is an urgent problem today, because the existing protection systems cannot provide the absolute protection against lightning. Lightning rods often work under conditions of high humidity and in the direct contact with water. Therefore, it is important to study the properties of lightning rod materials under conditions of their wetting as such. A number of works, in which this problem was studied [6–10], confirm its relevance. However, there are practically no articles with the results of the studies of physical and chemical characteristics such as the wetting of implanted specimens. Therefore, the present work is devoted to studying the properties of specimens treated by the ion implantation in the aspect of their use as atmospheric materials.

2. Method of Synthesis of Speccimens

The specimens were synthesized by ion implantation using the technology of the introduction of ions into the surface of a material due to the acceleration in the electric field.

The generation of ions occurs at the source by crossed electric and magnetic fields. The ion implantation installation (Fig. 1) consists of a vacuum chamber, an ion source, a vacuum unit, a vacuum pump, a high-voltage source, a control panel, a cooling system, a discharge stabilization system, cylinders with a working gas, vacuum meters and valves.

The accepted doping dose was $4\div5\times10^{17}$ ions/cm^2. It is achieved by the processing for an hour at an operating voltage of about 20 kV. The preliminary preparation of the specimens was performed in an ultrasonic cleaning device.

The process takes place in a vacuum; so, the material does not undergo a thermal deformation. Nitrogen is used as the working gas to generate the target ions.

Therefore, as a result of the processing, the steel specimens (foil of steel 12Cr18Ni10Ti, briefly SS),

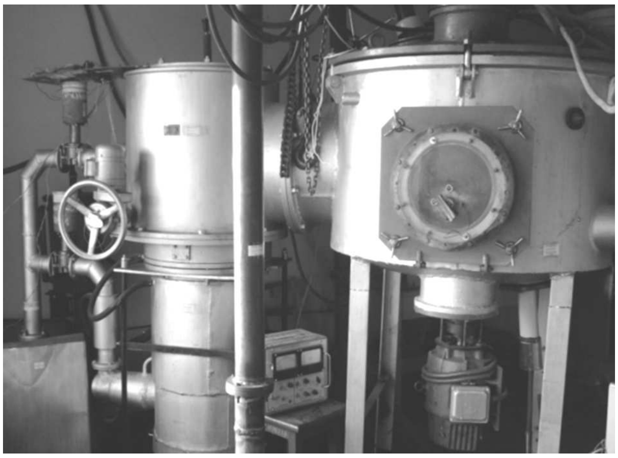


Fig. 1. Appearance of the research installation

which contained base ions, nitrogen and target ions (Mo, Ti, and Al, respectively briefly Mo/SS, Ti/SS, and Al/SS) are synthesized. The expected depth of the modified nanoscale layer does not exceed 1 μm [11], and it does not significantly affect the weight and size of the specimens.

3. Research Methodology and Results of the Processing

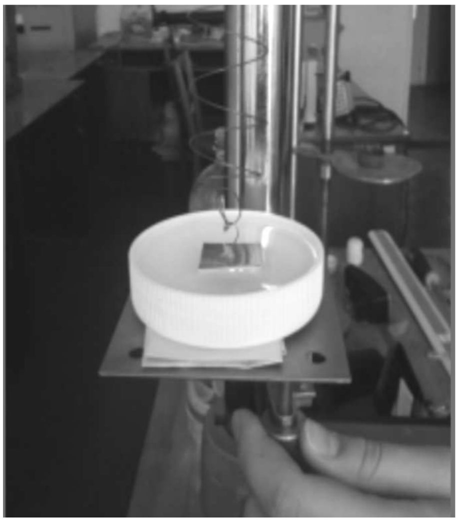
The ion implantation affects the topography and surface composition. That's why the morphology and elemental composition are studied.

To analyze the surface phase composition for the specimens treated by the ion implantation, the method of low-angle X-ray scattering with 2D X-ray Rigaku was used. The incident radiation was recorded at an angle of 5°, with an exposure of 10 min.

An instrumental microscope and the Gwyddion program are used to study the morphology of the specimens [12].

The investigation of the elemental composition of the surface of specimens by X-ray photoelectron spectroscopy is performed on a spectrometer equipped with a hemispherical analyzer (SES R 4000, Gammadata Scienta) and calibrated according to ISO 15472: 2001. The spectra are calibrated along the line of C 1s electrons with an electron binding energy of 285 eV.

The wetting ability of the four specimens (initial stainless steel and specimens treated by the ion implantation with Mo, Ti, and Al ions) are tested using a spring device that determines the force of separa-



a

b

Fig. 2. Appearance of a research installation for studying the wetting by a separation force (*a*) and the gravimetric method (*b*)

tion from the liquid (Fig. 2, *a*) and the gravimetric method with a multifunctional digital Scale DP – 01 (Fig. 2, *b*).

4. Results and Discussion

The XRD-results of studying the phase structure of the surface layer showed the presence of the austenitic phase only in both the initial specimen and specimens treated by the ion implantation. This may indicate the absence of pronounced crystalline structures (amorphous layer) in the upper layer of the material formed by implanted ions (Fig. 4, *a, b*), as confirmed by data from works [13–15].

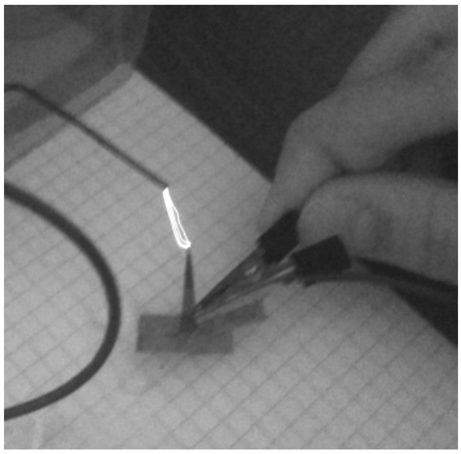


Fig. 3. Sample connected to the device during the test 2θ

Despite the impossibility to identify implanted ions using XRD-analysis, the optical studies showed significant changes in the microstructure of the steel surface (Fig. 5).

From micrographs (Fig. 5, *a*), it is seen that the original steel has a pronounced roughness. This roughness is noticeably smoothed out for the specimen treated with aluminum ions (Fig. 5, *c*). The specimens treated by the ion implantation with molybdenum and titanium have a smooth surface, but also have distinctive large cavities. Moreover, in the Mo/SS specimens, this effect is most pronounced (Fig. 5, *b, d*).

The determination of the changes in the elemental composition of the surface layer was performed by the XPS analysis. The XPS results show that, in the original (raw) steel, all components are present in the form of pure elements and their oxides. A similar situation is observed for Mo/SS, where the surface layer contains MoO_3. At the same time, the specimens treated by the ion implantation with lighter impurity ions (Al and Ti) represent a higher scientific interest (Fig. 6). Based on the bond energies and the splitting constant values [16], nitrides and oxynitrides are formed in metals in addition to oxides in the indicated specimens. The presence of nitrogen in the compounds can be explained by its presence in the plasma, with the help of which the ion flow is generated.

Thus, the ion implantation leads to changes in the microstructure and elemental composition of the thin (nanoscale) surface layer, which should af-

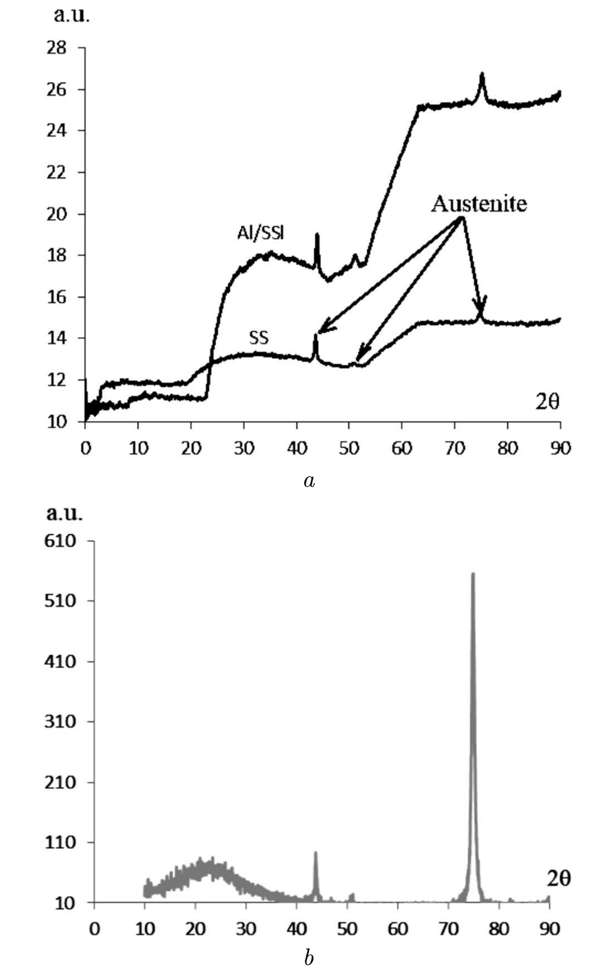


Fig. 4. The XRD-data of: initial specimens and Al/SS (*a*), Mo/SS (*b*)

Table 1. **Wetting force**

Speci-mens	Elastic force, mN	Specimen weight, mN	The wetting force, mN	Specimen area, mm^2	Specific wetting force, N/m^2
SS	12.437	1.668	10.769	291.4	36.9
Ti/SS	13.473	0.981	12.492	230.6	54.2
Al/SS	14.510	3.139	11.371	414.6	27.4
Mo/SS	9.557	1.274	8.283	107.2	65.4

fect the physical and chemical properties of the treated metals.

The study of physical and chemical properties, namely the wetting, showed that the properties of the

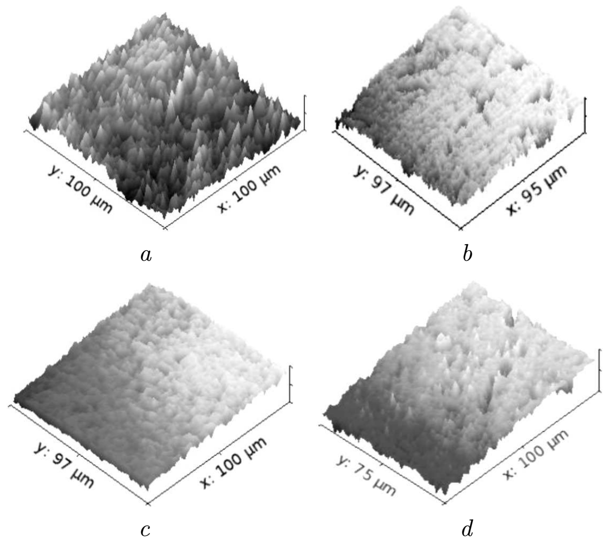


Fig. 5. The morphology of: SS (*a*), Ti/SS (*b*), Al/SS (*c*), Mo/SS (*d*)

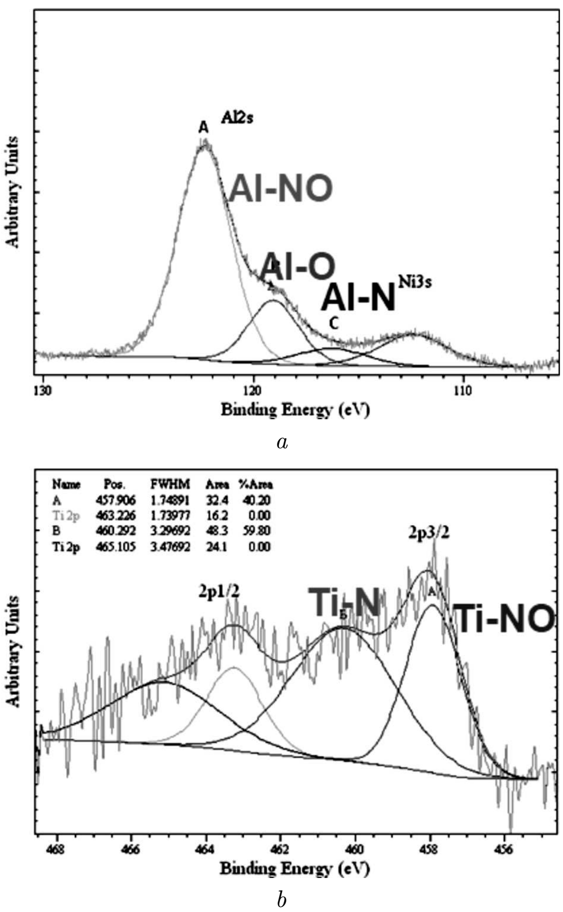


Fig. 6. The XPS-data of: Al/SS (*a*), Ti/SS (*b*)

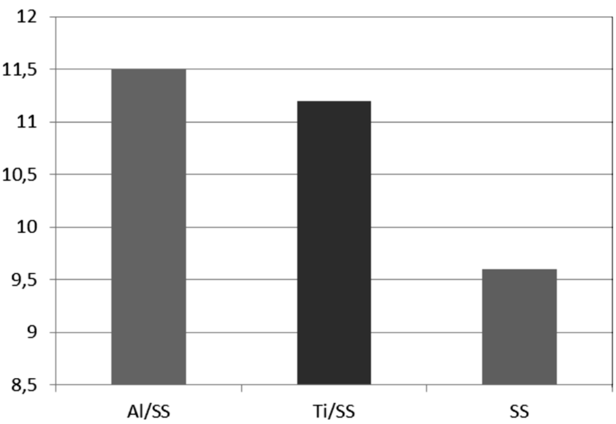


Fig. 7. Maximum distance of discharges for SS, Al/SS and Ti/SS, mm

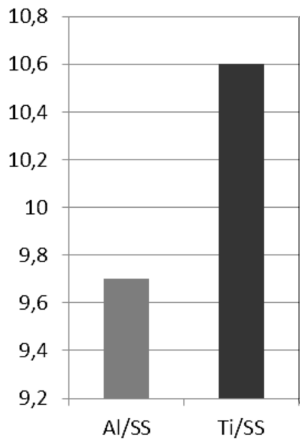


Fig. 8. Distance of equal effects of wetted specimens

Table 2. **Discharge frequency**

Speci-mens	Distance (mm)		
	9	10	11
Al/SS	Continuous lightning	Continuous lightning	53
Ti/SS	Continuous lightning	33	2
SS	22 discharges	0	0

specimens treated by the ion implantation and those of the initial steel are significantly different.

At first, it is established that the wetting forces for the treated and untreated steels are different (Table 1).

As was predicted previously, Mo/SS and Ti/SS are close in properties.

However, Al/SS has the opposite effect, while Mo and Ti show a better wetting (greater wetting force than the original steel), and Al/SS is wetted worse.

Moreover, considering that the electrical properties depend also on the distribution of charges (ions) in the surface layer, the breakdown was studied for Al/SS and Ti/SS.

It is found that the specimens with aluminum ions continue to work at a greater distance from the spark gap than the specimens with titanium ions (Fig. 7).

This may be due to a higher concentration of charges on the Al/SS surface, which is confirmed by the determination of the generation distance for the first (initial, channel-forming) discharge (noise effects). We note that, in the specimens with Al, the crackling begins at a greater distance.

The specimens treated by the ion implantation also show a greater efficiency than the initial specimen by depending on the frequency of discharges (Table 2).

With the simultaneous inclusion of two specimens treated by the ion implantation after the water supply, the first discharge occurred on Al/SS. Then the intense beats were observed for both specimens. But after some time, the more powerful bits occurred only on Ti/SS. Only one lightning was observed on Al/SS.

Probably, such changes in the behavior are associated with the evaporation of water on the specimens. On Al/SS, water is much more effective than on Ti/SS. But after the evaporation, the discharges almost completely switch to the titanium-implanted surface.

This hypothesis is confirmed by the determination of the distance at which the wetted specimens work identically (Fig. 8).

In these experiments, the active discharges occurred within 1.5 min. It is worth noting that the results hold during repeated repetitions and inspections. Breakdowns on the treated steel occurred much more often than on the untreated one. Titanium yields to aluminum during the tests with maximum distance. But, with the simultaneous connection, lightning strikes it more often than Al/SS, even at a greater distance from the arrester.

5. Conclusions

We have synthesized the specimens with ions of aluminum, molybdenum, and titanium that are based on stainless steel. It is shown that the ion implantation significantly changes the state (microstructure and composition) of the surface layers of the specimens. The microrelief is smoothed, and the compounds of target ions with nitrogen are formed in the surface layer. The wetting force is determined and compared for treated and untreated steels. It is found that the wetting force acting on the surface layer of the treated specimens significantly exceeds that for the original ones. It is shown that the specimens with Mo, Ti, and Al ions differ by their electrical properties and have significant advantages over the untreated steel. The breakdown frequency, force, and discharge time for the specimens with titanium and aluminum ions are found to be higher than for those from the untreated steel. It is practically established that the wettability of specimens affects their behavior under discharge conditions.

Considering that ion treatment, according to literature data, improves the mechanical (hardness, wear resistance, friction coefficient, *etc.*), chemical (corrosion resistance, adhesion) and geometric (roughness, number of surface defects, microrelief shape) characteristics of materials and directly, as is shown in this work, affects the wettability and electrophysical properties. The above results indicate the promising use of the ion implantation as a finishing treatment, when creating materials for electrical devices which operate in chemically active media, for example, for the lightning protection devices. Such advantages of the ion implantation as the possibility of any target-substrate combinations, small quantity of consumables, low temperature, and controllability of the process make it competitive in comparison with other technologies used for a modification of materials. Varying the processing mode makes it possible to predict properties of the material for the use in shipbuilding, mechanical engineering, *etc.* and creates prospects for a further research.

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Received 09.01.20

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ДОСЛІДЖЕННЯ ХАРАКТЕРИСТИК НАНОРОЗМІРНИХ ШАРІВ ІМПЛАНТАТУ У СТАЛІ

Модифікація металів поверхневою обробкою – одна з перших проблем сучасного матеріалознавства. Використання іонно-плазмових технологій, зокрема іонної імплантації, для цієї мети можна вважати перспективним рішенням. Проведено дослідження мікроструктури, фазового та елементарного складу, сил змочування та електричних властивостей сталі з імплантованими іонами титану, алюмінію та молібдену. Результати XRD, XPS, оптичної мікроскопії та лабораторних експериментів показали значні відмінності між обробленими та необробленими зразками. Модифікація металу шляхом іонної імплантації та, як наслідок, зміни змочуваності та електричних характеристик свідчать про перспективи цієї технології в машинобудуванні, хімічній, харчовій, фармацевтичній промисловості, для будівництва конструкцій і транспортних засобів, у тому числі для роботи в складних атмосферних умовах.

Ключові слова: XPS, XRD, імплантат, модифікація нанорозмірних поверхонь, іонна імплантація, сила змочування.