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Досліджено вплив різних комбінацій «мішень – сталева підкладка» на механічні та хімічні властивості захисних покриттів, отриманих за допомогою іонно-плазмової обробки. Широке застосування іонно-плазмових технологій для зміцнення виробів стримується недосконалістю обладнання, відсутністю достатніх теоретичних і експериментальних досліджень з контролю і регулювання фізичних властивостей і технічних параметрів процесу обробки. Зняття цих проблем можливе на підставі подальших досліджень і нових рішень в області технології зміцнення. Для досліджень в цьому напрямку використовувався експериментальна іонно-плазмова установка з програмним забезпеченням для регулювання і контролю енергії, дози, концентрації імплантованих іонів, тиску робочого газу, товщини покриття. Застосована ефективна методика підвищення якості робочої поверхні сталевого інструменту, яка дозволила здійснити масоперенос легуючих елементів поверхневою іонно-плазмовою обробкою. За рахунок регульованої низькотемпературної двохстадійної іонізації атомів азоту і легуючих елементів в реакційному обсязі відбувалося насичення кристалічної решітки заліза імплантованими іонами і утворення карбонітридних фаз легуючих елементів, відповідальних за підвищення твердості, зносо- і корозійної стійкості. Виявлено оптимальні параметри процесу імплантації ($U_p=25$ кВ, $I_p=35$ мА, $D=4,01 \cdot 10^{17}$ см⁻² за 1 год.), які дозволили досягти поліпшення поверхневих властивостей конструкційної вуглецевої, конструкційної легованої, інструментальної сталей. Встановлено взаємозв'язок між терміном служби виробів і властивостями отриманої після імплантації поверхні. Показано збільшення терміну служби виробів з покриттям TiN (в 1,5–3 рази), CrN (в 1,9–6 разів) і ZrN (в 3–12 разів) в порівнянні з виробами без покриття. Проведено аналіз і визначено найбільш ефективні варіанти комбінацій «мішень – сталева підкладка» для практичного застосування захисних покриттів. Оскільки застосування порівняно недорогих сталевих виробів з підвищеними характеристиками міцності має економічні вигоди для виробника і є однією з тенденцій сучасного виробництва

Ключові слова: іонна імплантація, захисне покриття, сталева підкладка, зносостійкість, термін служби

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ANALYSIS AND COMPARISON OF MECHANICAL AND CHEMICAL PROPERTIES OF PROTECTIVE COATINGS OBTAINED AT DIFFERENT COMBINATIONS OF "TARGET – SUBSTRATE"

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1. Introduction

Wear-resistant steels and hard alloys are widely used in various sectors of the national economy. The stamps of such steels and alloys are distinguished by high resistance to surface abrasion and contact deprecation and are widely used in the automotive industry, metallurgy, the woodworking industry, medicine, electronics, etc. [1].

Ensuring the improvement of product quality is important to the consumer and contributes to the growth of the manufacturer prestige, but often leads to an increase in the

cost of products due to the complexity of technology production, as well as the associated energy and resource costs.

With the development and improvement of various technologies, it has become possible to obtain protective coatings that have good mechanical and chemical properties. However, the use of ion-plasma technology to harden the surface is hampered by imperfect equipment, the lack of sufficient theoretical and experimental research to control and regulate the physical properties and technical parameters of the process.

The use of coatings with high protective properties on the working surfaces of products from cheaper materials is

characterized by economic benefits for the manufacturer, reduced costs for the products purchase, increased productivity, reduced time for auxiliary operations. But at the same time, there are difficulties associated with the selection of “target – steel substrate” combinations and the identification of the different combinations effect on the mechanical and chemical properties of protective coatings. Similar difficulties are again associated with insufficient knowledge of the processes occurring during plasma processing, and the ability to control these processes to change the properties of the surface. In addition, scientific studies conducted in [2, 3] are aimed at improving the surface properties of steels and alloys, which initially had good strength characteristics. The fact that in [4, 5] the effect of the alloying element is mainly studied only on the mechanical or chemical properties of the surface also does not provide complete information about the possibilities of using plasma processing methods to obtain high-quality materials.

It is a relevant task to undertake further research in this field.

2. Literature review and problem statement

The need to replace expensive materials with cheaper, but not inferior in their protective properties, materials predetermined the development of many different methods of surface treatment: plasma, electronic, light, etc. [6, 7]. One of the methods developing in this direction is ion implantation. The authors highlight the possibilities of the method for enhancing the properties of materials protecting against depreciation and corrosion [8–12].

For example, the analysis carried out in [8] confirms the effectiveness and availability of this method for improving the tribological and physicochemical characteristics of parts made of titanium alloys. It is assumed that by varying the dose of ions and the possibility of their introduction into the irradiated material, both sequentially and in parallel, it becomes possible to expand the field of materials application. However, to confirm this hypothesis, the corresponding research results are not given.

Studies of the corrosion wear of thin-walled elements modified by carbon atoms by ion implantation have established the effect of implantation and its effect on corrosion resistance [9]. However, it should be noted that in this work, attention was mainly focused on the study of the mechanism of corrosion. This means that it is not determined how this method affects the physical-mechanical characteristics of elements for their wide use in various industries. Paper [10] came closer to solving this problem [10]. The composition and structure of the carbon-implanted layer were analyzed using X-ray photoelectron spectroscopy, Auger-electron spectroscopy and X-ray diffraction. It is shown that due to the occurrence of vacancies and dislocations, the enrichment of alloying elements, a decrease in the number of free electrons in the field of carbon implantation, it becomes possible to improve the corrosion resistance. However, according to authors in [11], the formation of surface nitrides and their concentration, rather than supersaturated surface defects, affects the corrosion properties. Obviously, this may be due to the difference in the methods of implantation and materials in the combinations “alloying element – substrate”.

The knowledge obtained in [8–11] represents great interest for use in aggressive environments, but cannot be fully

used when conditions change. This involves that the effect of implantation on mechanical properties has not been studied and the relationship between all surface properties after modification has not been adequately determined.

In [12], the authors established the effect of implantation and double implantation of molybdenum and tungsten ions on the structural phase transformations of titanium alloys. It is shown that due to an increase in the implantation dose, an increase in hardness and friction wear resistance occurs. Despite the practical significance of such results, the effect of processing parameters on the chemical properties of the surface has not been considered. According to the authors of this work, the physical picture of the observed phenomena is still far from their full understanding, which additionally confirms the importance and perspective of systematic theoretical and experimental research in this direction.

The results of studies conducted in [13] show that the ion implantation method is a very good tool for controlled changes in the mechanical properties of steel and can be used to process various machine parts. The feasibility of such an application is confirmed by x-ray measurements, measurement of roughness and hardness of samples. However, it should be noted that a significant effect was observed after the implantation of nitrogen ions and subsequent annealing. This circumstance makes it impossible to apply the methodology used for thin-walled and small-sized products due to the presence of high temperatures, leading to distortion and defects in products.

The feasibility of using ion implantation to improve the hardness and tribological characteristics of bearing steels is confirmed by the results of studies in [14]. Authors established the interrelation between physical and mechanical properties after alternate surface implantation with titanium and nitrogen ions. It should be noted that the authors have not confirmed the effectiveness of this technology for steels of various classes and purposes, which is of interest from a practical point of view.

Therefore, there is a reason to believe that with the subsequent development of new technologies, interest in the method of ion implantation and the problems involved in the work will increase. In this regard, it becomes necessary to further accumulation of theoretical and experimental information. The replenishment of the array of knowledge will allow a better understanding of the processes occurring during surface treatment, to manage these processes in the right direction. This will make it possible to determine different combinations of “target-substrate” for further use in the technology of manufacturing new high-quality materials.

3. The aim and objectives of the study

The aim of this study is to identify the effect of various “target – substrate” combinations on the mechanical and chemical properties of protective coatings. This will make it possible to improve the surface quality of relatively inexpensive steel products under conditions of low-temperature implantation and to expand the limits of application of the method presented.

To accomplish the aim, the following tasks have been set:

- based on a comprehensive analysis to determine the materials in the combinations “target – substrate”;
- process samples by ion implantation;

- to identify the optimal parameters for improving the protective properties of the surface;
- to explore the properties of the treated surface;
- to establish the relationship between the properties of the surface obtained after ion implantation and the service life of the processed products.

4. Materials, equipment for ion-plasma processing and research methods for the mechanical and chemical properties of protective coatings

The target materials were ductile, corrosion-resistant titanium (Ti), chromium (Cr) and zirconium (Zr). The substrate materials were selected carbon structural steel of the ordinary quality VSt3sp type, alloyed construction steel of the 40H grade and tool steel of the HVG and R18 grades, as one of the most common steels in the manufacture of tools, machine parts and mechanisms. To obtain target nitrides on the steel substrate, nitrogen was used as the working gas. The areas of application of nitrides are very diverse due to the fact that they give products hardness, thermal and corrosion resistance [15–20].

Samples were processed in an experimental ion-plasma unit (Fig. 1) with an information-recording program for regulating and controlling the implantation process.



Fig. 1. Physical appearance of the experimental setup

Giving the plasma necessary energy parameters is owing to various physical effects that explain the diversity of ion sources [21–25]. In this work, the ion source of the installation provided a two-stage ionization of the nitrogen atoms and the target at the working gas pressure $p_g=3.32 \cdot 10^{-2}$ Pa. Due to ionization, their low-temperature implantation into the surface layer of superficial substrate.

After the ion-plasma treatment using standard methods, the following was carried out:

- semi-quantitative and qualitative analysis of all chemical elements of solids in the near-surface region using the JAMP-10S Auger spectrometer from JEOL (Japan);
- X-ray analysis to determine the various phases in the surface layer of the processed samples on the x-ray unit DRON-4 in CuK_α radiation and DRON-4-13 in FeK_α radiation;
- optical research to study the structure of samples at the vertical microscope MIM-7 and the horizontal microscope MIM-8;

- measurement of the coatings thickness in the study of the cross section of the system “substrate – coating” at the metallographic microscope MIM-8. To implement this measurement, the sample in a frame filled with epoxy resin was ground, polished to a mirror surface and etched. Etching was carried out with a solution of 4 % HNO_3 in ethanol (from 3 minutes to 20 minutes, depending on the substrate material);
- measurement of the coating thicknesses using the device PMT-3;
- sclerometric tests and high-quality measurement of the adhesive-cohesive bond on the PMT-3 device;
- quantitative assessment of surface roughness parameters in a contactless manner using an MII-4 micro-interferometer;
- tests of wear resistance of coatings at AE-5 friction machine built on the principle of samples surface friction on the flat side of a reference brass disk with lubricant feed from an aqueous emulsion (sample load – 1 kg disk rotation speed – 100 rpm);
- determination of the rate of samples corrosion in the environment of an aqueous emulsion.

5. Results of studying the protective coatings mechanical and chemical properties obtained at different combinations of “target – substrate”

The optimal implantation parameters using titanium, chromium and zirconium targets are given in Table 1. As one can see from Table 1, to achieve the highest efficiency of obtaining high-quality surfaces at low discharge currents ($I_d \sim 0.3\text{--}0.5$ A) in an environment of low temperatures, the optimum voltage and current applied to the steel substrate was $U_s=25$ kV and $I_s=35$ mA.

Fig. 2 shows the spectrum of Auger electrons in a differentiated form. This spectrum was obtained from the sample surface of structural carbon steel after 120 min of treatment using a titanium target. The results of spectrometry were determined peaks, which confirm the presence in the surface layer of iron, titanium, nitrogen, carbon and oxygen. You should be pay attention to the fact that these peaks were observed on the surface before and after two etching of the sample with an ion gun to a depth of 300 Å.

Table 1

Optimal ion implantation parameters

The name of an implantation parameter	Target		
	Ti	Cr	Zr
Discharge voltage U_d , V	400	430	410
Discharge current I_d , A	0.5	0.35	0.3
Voltage applied to target U_t , B	2.0	1.2	2.1
Target Current I_t , mA	50	60	40
Voltage applied to substrate U_s , V	25	25	25
Current supplied to substrate I_s , mA	35	35	35
Implantable ion dose D , cm^{-2}	$2.0 \cdot 10^{16}$ – $8.03 \cdot 10^{17}$	$6.69 \cdot 10^{16}$ – $6.02 \cdot 10^{17}$	$6.69 \cdot 10^{16}$ – $6.02 \cdot 10^{17}$

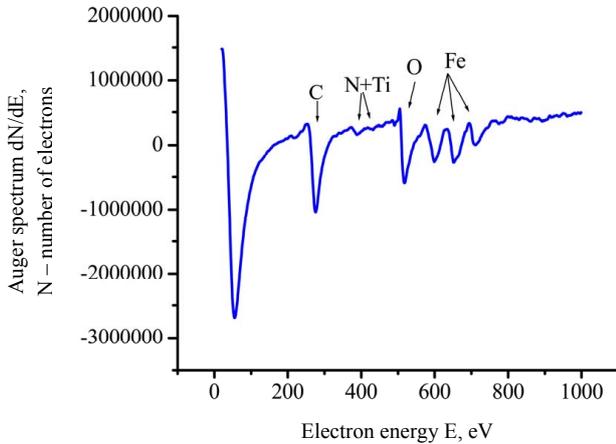


Fig. 2. Spectrogram of the VSt3sp steel surface after 120 min implantation of Ti ions and N

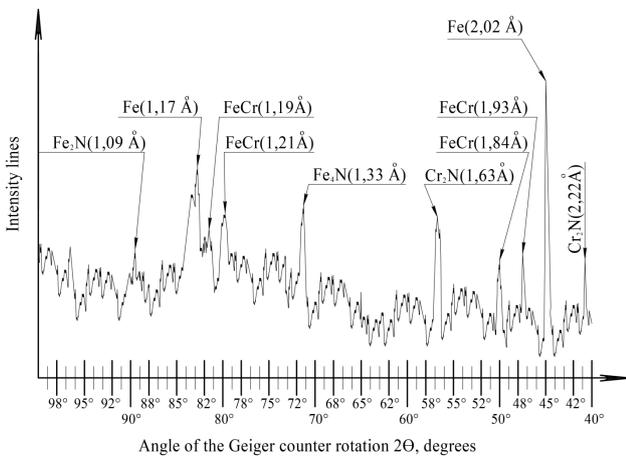


Fig. 3. Diffractogram of the coating obtained in $\text{CuK}\alpha$ radiation on a 40X steel substrate with 50 min implantation of Cr and N ions

Various phases were identified in the surface layer of steel samples, the implantation time of which ranged from 3 to 120 minutes. The results of the X-ray analysis of the coating obtained on the substrate of structural alloyed steel at 50 min implantation using a chromium target are shown in Fig. 3. As can be seen from Fig. 3, besides iron lines, intense lines of Fe_3N , Fe_4N , CrN , Cr_2N , and FeCr phases are observed. I would especially like to note the fact that, against the background of weakly shifted iron lines on the diffractogram, the lines of Fe_3N nitrides are weakened, but the lines of the CrN and Cr_2N phases, whose presence contributes to more intensive hardening of the surface layer, become stronger.

The results of optical studies of the high-speed samples surface steel P18 after implantation using a zirconium target showed a decrease in grain size at the initial processing times. Zirconium ions, having a 2 times higher atomic mass in comparison with chromium and titanium ions, penetrate the steel substrate with 2 times more kinetic energy. It should be noted that from 50 minutes to 90 minutes of modification a grain growth of the newly formed phase is observed (Fig. 4, 5).

Fig. 6 shows the results of the thickness dependence studies of the coating obtained on a substrate of structural alloyed steel using a zirconium target, on the time of implan-

tation. As can be seen from Fig. 6, at longer implantation times, the surface layer grows due to the mass transfer of nitrogen and zirconium ions into the substrate. Optical images of the cross sections examined are shown in Fig. 7, 8, illustrate an increase in coating thickness from 0.63 μm to 1.16 μm at 20 min and 40 min of implantation, respectively. It should be noted that the formation of a CrN phase contributes to an increase in the coating thickness in addition to the ZrN phase.



Fig. 4. Structure of steel R18 before implantation $\times 1,320$

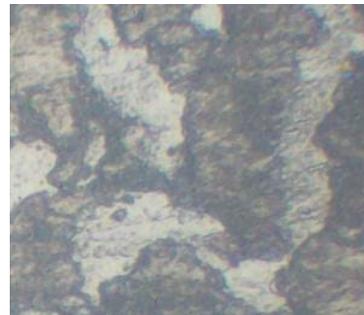


Fig. 5. Structure of P18 steel after 90 min implantation of Zr and N ions $\times 1,320$

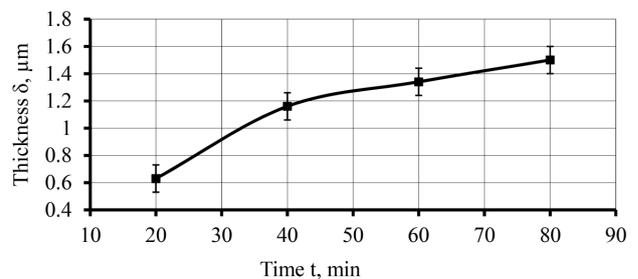


Fig. 6. Chart of the modified coating thickness on a 40X steel substrate versus the time of implantation of Zr and N ions

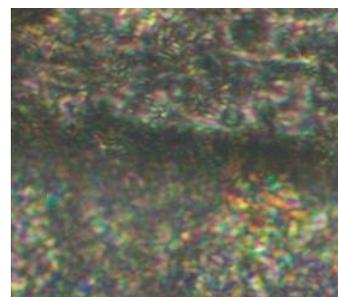


Fig. 7. Optical image of the modified coating cross section on the 40X steel substrate after 20 min implantation of Zr and N ions $\times 1,950$

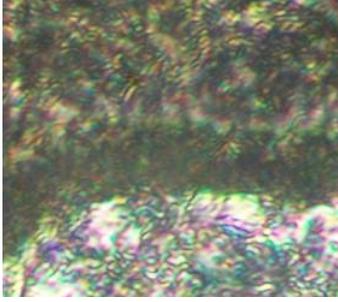


Fig. 8. Optical image of the transverse section of the modified coating on the 40X steel substrate after 40 min implantation of Zr ions and $N \times 1,950$

Fig. 9 shows the results of the hardness dependence studies of a modified coating of structural carbon steel on the time of implantation using a chromium target. It should be noted that the increase in hardness up to 50 minutes of implantation is due to the intensive formation of iron nitrides, and after 50 minutes – the CrN phase, which has a greater hardness than the chemical compound iron FeN.

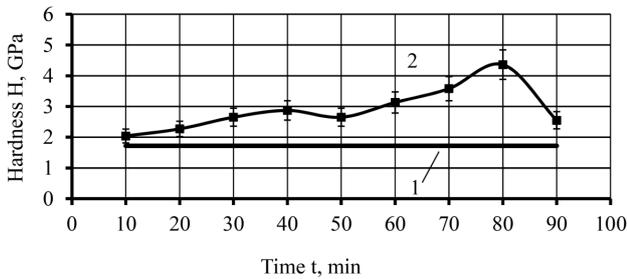


Fig. 9. Chart of hardness of the modified VSt3sp steel coating depending on the time of implantation of Cr and N ions; 1 – substrate hardness; 2 – hardness of the “coating-substrate” composition”

The results of sclerometric studies of the structural carbon steel surface are presented in Fig. 10, 11. As can be seen, as the processing time increases, the groove width narrows, which, in turn, indicates an increase in the adhesive-cohesive bond of the coating with the substrate. It should be stressed that the strong adhesion of atoms to the base is caused not only by the formation of the CrN phase, but also by the deep mass transfer of implanted ions.

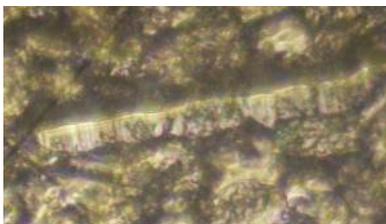


Fig. 10. Results of sclerometric studies of coatings on VSt3sp steel with a load of 15 g on the indenter after 60 min implantation of Cr and N ions $\times 800$

The results of wear resistance studies showed that among all coatings, the smallest value and wear rate are observed for samples obtained after implantation using a zirconium target (Fig. 12). According to the research results, the mass wear of the sample was determined and the

wear resistance was evaluated. As can be seen from Fig. 12, the wear values for surfaces of structural alloyed steel with coatings reduced by 2.6 to 6.7 times in comparison with surfaces without coating.



Fig. 11. Results of sclerometric studies of coatings on VSt3sp steel with a load of 15 g on the indenter after 80 min implantation of Cr and N ions $\times 800$

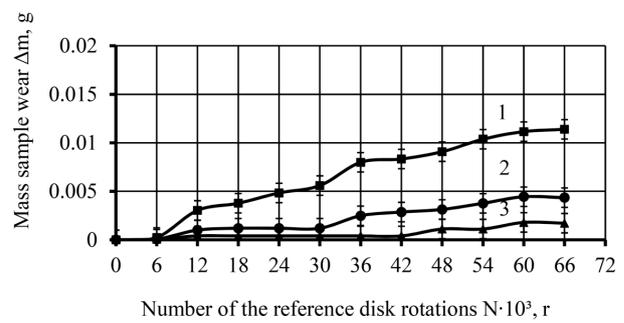


Fig. 12. The results of steel surface wear resistance studies 40X: 1 – without coating; 2 – 20 min; 3 – 80 min implantation of Zr and N ions

Fig. 13 shows the results of a samples surface corrosion resistance studies of structural carbon steel before and after implantation using titanium, chromium and zirconium targets. The dependences shown in Fig. 6, illustrate that the corrosion resistance of coated samples increases from 3.9 to 5.4 times in comparison with uncoated samples. It should be noted that this difference is caused by the different porosity of the coatings.

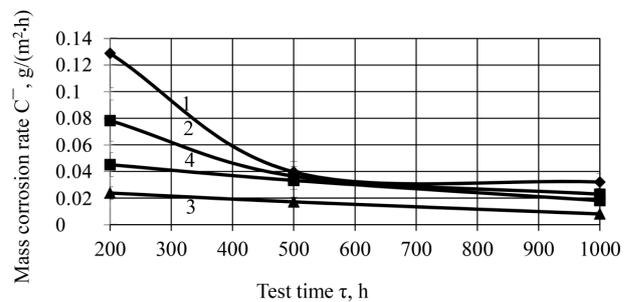


Fig. 13. Results of the VSt3sp steel surface corrosion testing: 1 – uncoated; 2 – with TiN coating; 3 – with CrN coating; 4 – with ZrN coating

For clarity, the results of experimental studies are summarized in Table 2.

To confirm the obtained results of the experiment, technological tests were carried out on a drawing tool – dies used in broaching brass wire used to produce strings of musical instruments, knives and knitting disks and sewing equipment (Fig. 14–17).

Table 2

Comparison of mechanical and chemical properties of protective coatings obtained by ion-plasma processing, with an indication of their thickness

No.	Properties	Carbon steel			Structural alloy steel			Tool steels		
		Ti	Cr	Zr	Ti	Cr	Zr	Ti	Cr	Zr
1	Microhardness, GPa	3.271	4.355	3.755	3.583	5.407	3.422	8.45	5.407	3.422
2	Magnitude of adhesive-cohesive bond, GPa	2.156	1.935	5.772	4.850	3.104	14.253	5.772	2.156	10.913
3	Corrosion resistance, %	40	82	65	20	81	29	49	24	10
4	Roughness Ra, μm	0.02	0.022	0.018	0.018	0.018	0.016	0.024	0.026	0.022
5	Wear resistance, %	46	52	92	50	60	85	45	60	70
6	Thickness, μm	0.85	0.76	1.02	0.63	0.89	1.51	0.63	0.94	0.82



Fig. 14. Spinneret of 40X steel with CrN coating



Fig. 15. Knitting equipment knives with ZrN coating



Fig. 16. Knives with ZrN coated sewing equipment



Fig. 17. Knitting equipment with ZrN coated wheels

The histogram of the coated steel spinnerets working zones operational durability obtained using a zirconium target is shown in Fig. 18. It should be noted that the histogram shows the efficiency of using all the spinnerets after ion-plasma treatment in comparison with the spinnerets without processing. Special attention should be placed on the same operating time of dies made of structural alloy steel and tool steel, since the cost of structural alloy steel is 2.5 times lower than that of tool steel.

The histogram of the P18 disks working surface increase in wear, depending on the coating obtained using the targets

of titanium, chromium and zirconium, is shown in Fig. 19. It should be noted that the histogram illustrates the effectiveness of the application of all investigated coatings, since the operating time of the processed disks increases from 1.5 to 3 times in comparison with disks without coating.

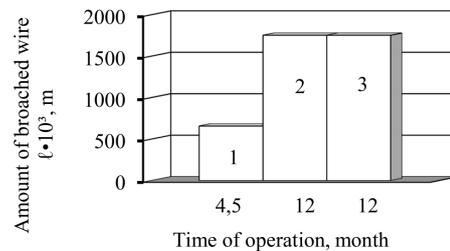


Fig. 18. Histogram of ZrN coated spinnerets operational durability: 1 – VSt3sp steel; 2 – 40 X steel; 3 – P18 steel

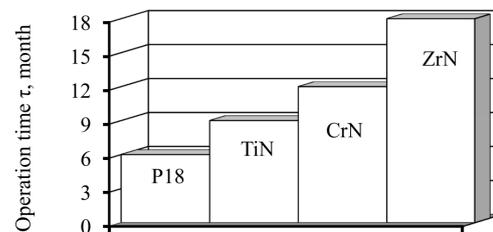


Fig. 19. Histogram of the working surface of the disc increase in wear from the coating

Based on the obtained results, it can be stated that the selected methods for studying the modified surface make it possible to establish the relationship between the parameters of ion-plasma treatment, the properties of the hardened surface and the tool life.

6. Discussion of results of studying different combinations of “target – substrate” on the mechanical and chemical properties of protective coatings

Based on the analysis of the whole complex of experimental studies conducted in the work, the optimal parameters of ion-plasma treatment were found (Table 1). It is worth noting that the solution for optimizing the technological parameters of processing allows the analysis of surface properties to determine various combinations of “target – substrate” for their use in the technology of obtaining new quality materials.

As a result of the Auger-electron-spectroscopic analysis of the sample surface after implantation on the experimental

setup, the formation of a modified coating was confirmed. Its presence is evidenced by peaks of Auger electrons spectra in a differentiated form, obtained from the surface of steel samples (Fig. 2). After such confirmation, it is of interest to study the phase composition and structure of nitride coatings.

X-ray analysis showed that on all steel substrates the obtained coatings are multiphase (Fig. 3). With an increase in processing time, the phases of the target materials nitrides grow. Alloyed alloying additives (CrN, W₂N), alloying additive phases and target materials (W₂Zr, Fe₂Ti) are also formed on alloyed steels. Obviously, the formation of these phases, each of which has its own structure, and the presence of additives (chromium, vanadium, manganese) in the composition of the steels influence the difference in the external pictures of the substrate surfaces. The formation of titanium, chromium and zirconium carbonitride phases, which are responsible for improving the mechanical properties on the surface of the steel, is also confirmed by the diffractometric studies of samples in FeK_α radiation.

Optical studies of the surface after implantation with nitrogen ions using a titanium target showed that the structure of all investigated steels becomes more fine-grained. With the use of a chromium target, the structure becomes fine-grained only on the surface of structural steel and practically does not change with tool steels. Grain enlargement was observed only after 20 minutes of 40X surface modification structural alloyed steel with chromium nitride and after 50 minutes of all steel substrates with zirconium nitride modifications (Fig. 4, 5).

The presence of fine-grained structure leads to an increase in hardness, and the enlargement of grain – to the growth of nitride phases, adhesion of the coating thickness. To confirm these assumptions, experimental thicknesses were carried out. Overall, steel substrates, the thickness of the coatings increased over time of implantation (Fig. 6), but in most cases the coatings with a coarse-grained structure differed most ($\delta_{\max}=1.51 \mu\text{m}$ – ZrN coating) (Fig. 7, 8).

The time dependence of the microhardness of nitride coatings obtained using a titanium target on various steel substrates had a non-uniform character, in contrast to chromium nitride and zirconium coatings. A more equitable dependence was observed on these coatings due to the homogeneity of the phase composition and the formation of stable nitride phases of Cr and Zr. The maximum increase in hardness (2.5 times) on steel substrates was obtained by implantation of chromium nitride (Fig. 9). Similar values of the coatings hardness – substrate composition are in agreement with the results in [26] and were observed by the authors in [27]. This indicates that during plasma hardening, the main contribution to the increase in the microhardness of the coating-substrate composition is applied by the applied coating. However, the obtained results are somewhat lower compared with those given in [27], which may be caused by a lower process temperature.

In most cases, after 60 minutes of implantation, a decrease in hardness occurred due to the appearance of internal stresses and defects from the penetration of ions into the grating. However, along with this increased value of adhesion. The maximum adhesion value of 14.253 GPa was obtained on a substrate of structural alloyed steel at an implantation time of 60–90 min using a zirconium target, the atoms of which more deeply penetrate the substrate and enhance the adhesion properties of the resulting coating.

Sclerometric studies have shown that at any time of ion-plasma treatment on all samples of the coating are not completely separated from the substrate (Fig. 10, 11). This indicates good plasticity properties of materials. Usually increasing hardness leads to brittleness and reduced tools service life. With increasing surface hardness, the material remains ductile, which prolongs the life of the product.

In addition, the operational durability of tools, machine parts is greatly influenced by the quality of working surfaces. A comparison of the samples roughness parameters before and after the implantation of titanium, chromium and zirconium nitrides revealed their decrease after plasma treatment by 1.7–2 times (that is, improvement by 1 class), which will increase the wear resistance.

The results of wear resistance measurements of steel samples were analyzed before and after modification with Ti, Cr and Zr nitrides. There were two stages in the dependences: burn-in and stable wear. The main difference was observed at the run-in stage. Over here, the wear rate decreased and there was a decrease in the amount of wear after modification from 2 to 12 times. The best wear resistance was possessed by steel substrates coated with ZrN (Fig. 12).

The results of wear resistance studies are in line with work [28, 29] and indicate that not only the implantation duration, but also the type of implanted ions affects the magnitude and wear rate of steel samples. However, in contrast to the results of studies published in [28, 29], the data obtained suggest that wear-resistant coatings can be obtained under conditions of low-temperature implantation. Such processing is finish, does not cause uneven heating or warping of the product.

When studying the samples surfaces corrosion resistance before and after ion implantation, the modified samples proved to be more resistant to corrosion, but the anticorrosive properties of the steel with nitride-coated chromium showed the best of all (Fig. 13). Their corrosion resistance is 3.4–5.4 times higher than that of uncoated steel. This does not differ from the practical data, well known from [24, 28], and also suggests the possibility of a significant improvement in the physicochemical properties of the surface layers of structural and tool materials using ion implantation.

Analyzing the results of the conducted research (Table 2), it was found that the greatest increase in hardness and corrosion resistance in the work was obtained on substrates of VSt3sp steel and 40X during the implantation of Cr nitride. ZrN coatings on 40X and P18 steel substrates are distinguished by the maximum adhesive-cohesive bond and wear resistance. Improving the quality of products is directly related to increasing their durability; therefore, zirconium nitride coating is most effective for solving this issue. According to the results of research, 40H structural alloyed steel with a modified zirconium nitride coating has not only good mechanical and physicochemical properties, but also is more economical than tool steels (~2.5 times cheaper).

During technological tests, dies made of VSt3sp, 40X, R18 and HVG steels, the working surfaces of which were modified with titanium, chromium and zirconium nitrides, confirmed the results of experimental studies. For a long time dies made of structural alloyed and tool steels coated with zirconium nitride (Fig. 14) have worked.

The working surfaces of parts for knitting and sewing equipment made of high-speed steel R18 were also modified with nitrides of titanium, chromium and zirconium

(Fig. 15–17). In all that time of the surface coated with zirconium nitride showed greater resistance (Fig. 18, 19).

From a theoretical point of view, the conducted studies are interesting, since they make it possible to assert that an effective method has been obtained for improving the mechanical and chemical properties of protective coatings, which is an advantage of these studies. From a practical point of view, the effect of hardening of inexpensive steel materials has been discovered, which makes it possible to determine various combinations of the target – substrate for use in the technology of manufacturing new high-quality materials.

7. Conclusions

1. Based on a comprehensive analysis for the production of protective coatings, the materials in the combinations “target – substrate” were determined. The target materials were ductile, corrosion-resistant titanium, chromium and zirconium. The selected substrate materials were carbon steel of ordinary quality of the VSt3sp grade, alloyed 40X structural steel and tool steel of the HVG and R18 grades, as one of the most common steels in the tools manufacture, machine parts and mechanisms. To obtain target nitrides on the steel substrate, nitrogen was used as a working gas, since nitrides impart hardness, thermal and corrosion resistance to the products.

2. The surface treatment was performed using low-temperature ion implantation to improve the protective properties of the steel surface. The efficiency of the method for increasing the surface properties has been established, which consists in the mass transfer of alloying elements due to controlled two-stage ionization of atoms in the reaction volume.

3. The optimization of the implantation process modes ($U_s=25$ kV, $I_s=35$ mA, $D=4.01\cdot 10^{17}$ cm⁻² for 1 h) was revealed, which makes it possible to obtain high-quality protective coatings.

4. This research has established the effect of implantation parameters, target material, working gas on the properties of the treated steel surface. Due to this effect, the processes occurring during surface treatment make it possible to obtain a coating thickness of 0.24–1.51 μm, to increase hardness by 2.5 times, corrosion resistance by 5.4 times, wear resistance by 12 times.

5. The analysis and comparison of the coatings obtained with different combinations of “target – substrate” was carried out. It was found that to improve the quality of the working surfaces of steel tools, machine parts and mechanisms, zirconium nitride coatings on substrates of 40X, HVG, R18 alloyed steels are most suitable. The statement was confirmed by technological research: plasma treatment increases the service life of steel tools with TiN coating (1.5–3 times), CrN (1.9–6 times), and ZrN (3–12 times) compared to uncoated products. It is economically more profitable to use products from cheaper steel 40X with ZrN coating.

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