Problems of Tribology, V. 27, No 3/105-2022,89-95

Problems of Tribology
Website: http://tribology.khnu.km.ua/index.php/ProbTrib
E-mail: tribosenator@gmail.com

DOI: https://doi.org/10.31891/2079-1372-2022-105-3-89-95

Microstructure and wear resistance of modified surfaces obtained by ion-plasma nitriding of 40XH2MA steel

I.V. Smyrnov[1], A.V. Chornyi[1], V.V. Lysak[1], O.S. Drobot[2], P.V. Kaplun[2*], M.M. Poberezhnyi[2], A.V. Rutkovskyi[3]

[1]*National Technical University of Ukraine "Igor Sikorsky, Polytechnic Institute", Ukraine*
[2]*Khmelnitskyi National University, Ukraine*
[3]*G. S. Pisarenko. Institute for Problems of Strength of the National Academy of Sciences of Ukraine*
**E-mail:kaplunpavel@gmail.com*

Received: 27 July 2022: Revised:03 Septembert 2022: Accept:18 September 2022

Abstract

The article is devoted to the analysis of wear resistance of diffusion coatings, which were applied by ionic nitriding on steel 40XH2MA. There is a comparison of the technological efficiency of the results. The parameters of technological modes used in the process of application are presented, with the list of equipment and stages. The authors conduct the comparative analysis of chemical composition, microstructure, metallographic and tribological studies. They study the wear kinetics of 40XH2MA steel with nitrided coatings as well as provide practical recommendations on the use of hardened samples in dry friction conditions.

Key words: structural steels, physical and mechanical properties, ionic nitriding, technology, diffusion coatings, wear.

Problem statement

In recent years, many industries have established a tendency to use ion nitriding as an energy- efficient, environmentally friendly method of chemical-thermal hardeningof machine parts, cutting and stamping tools.To a large extent, this is facilitated by the creation of modern high-tech automated equipment, which made it possible to get rid of significant disadvantages of gas nitriding, such as duration, labor intensity of the process, instability of the results, low strength properties of the nitrided layer, etc.

Nitriding refers to surface modification processes that increase the local concentration of nitrogen in the metal structure. Many metals and alloys have shown the capacity for nitriding, that is, ability to increase hardness and wear resistance as a result of saturation with nitrogen in the amount from 5 to 50 atomic percent.

The most effective technological process of surface hardening is the method of ion nitriding in hydrogen-free media, which is well studied and is widely used for modification of metal materials. Unlike nitriding in hydrogen-containing media, in this case, there is no weakening of the base caused by the harmful effects of hydrogen on the metal, electricity and gas consumption is reduced, nitriding time is shortened, the absence of toxic ammonia makes this method environmentally friendly.

Literature review

Many scientific papers and monographs of both Ukrainian and foreign scientists are devoted to the processes and technologies of ion-plasma nitriding [1-5]. Of particular interest are publications from the countries where these technologies are highly developed and the production of industrial equipment is established, these are the Austrian company "RÜBIG", the German companies "ELTROPULS" and "PLATEG-PULSPLASMA", the Bulgarian company "IONITECH", the Brazilian company "NINRION" and others.

In the Institute for Problems of Strength named after H.S. Pysarenko, the technology of modification of the surface of structural elements of general engineering was developed by the method of vacuum ion-plasma gas-thermocyclic nitriding, which is based on the theory of thermal fatigue, abnormal mass transfer under mechanical load and the effect of discrete energy input. This technology has a number of advantages: only the surface layer of the part is heated by glow discharge energy; cyclic heating and cooling cause thermal stress in the surface layer, which accelerates diffusion processes and, consequently, reduces processing time; discrete energy input and heating only the surface layer reduce energy consumption by up to 10 times [6].

A promising direction of controlling the structure and service properties of working surfaces is the use of pulsed plasma technologies. The National Technical University of Ukraine "Ihor Sikorsky Kyiv Polytechnic Institute" conducts research on ion-pulse high-frequency nitriding. This approach is based on a combination of a pulsed discharge for creating a plasma flow of diffuser elements and a pulsed biasing of the substrate potential for ion implantation or modification of a surface with the transition to the batch pulsed excitation mode of induction discharge.The pulsed modulation (periodic interruption) of gas discharge current or voltage of substrate negative biasreduces the average power of the thermal load on electrodes (cathode, anode, electrodes of separators, screens, etc.). This mode significantly reduces the operating temperature and makes it possible to modify surfaces and/or apply coatings on heat-sensitive substrates, such as hardened steels without the risk of overheating [7].

Thus, further study of surface modification by ion-plasma nitriding for improving its functional properties is relevant and appropriate in the case of specific implementation.

The aim of the work is to analyze and study the microstructures of modified surfaces using different technologies of ion-plasma nitriding for enhancing the wear resistance of parts and structural elements made of 40XH2MA steel.

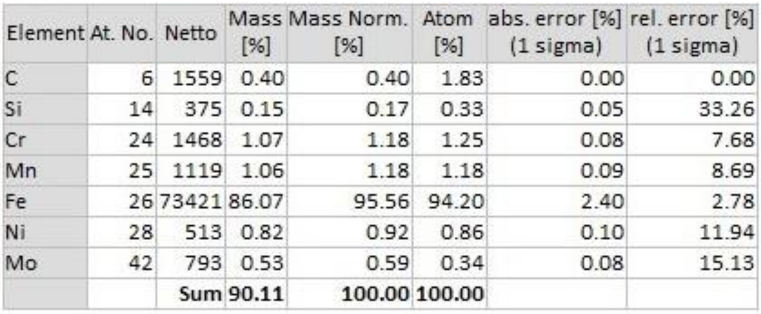
Materials and methods

In the work, to study nitriding processes, structural alloyed high-quality steel 40XH2MA (ДСТУ 7806:2015) was used, which is used for the manufacture of heavily loaded critical parts – disks, cam clutches, gears, connecting rods, valves, crankshafts, etc.

According to the quality certificate, this steel has the following composition: 0,41%C, 0,31%Si; 0,57%Mn; 0,003%S; 0,017%P; 0,8%Cr; 1,37%Ni; 0,07%W; 0,01%V; 0,21%Mo, 0,18%Cu; 0,001%Ti; 0,016%Al; 0,009%N. The actual composition of the steel was determined during the study of microstructures, and it is slightly different from the data on the certificate, which may be due to the elimination of elements in the sample content, the results are shown in Table 1.

Table 1

The actual composition of the steel



Element	At. No.	Netto	Mass [%]	Mass Norm. [%]	Atom [%]	abs. error [%] (1 sigma)	rel. error [%] (1 sigma)
C	6	1559	0.40	0.40	1.83	0.00	0.00
Si	14	375	0.15	0.17	0.33	0.05	33.26
Cr	24	1468	1.07	1.18	1.25	0.08	7.68
Mn	25	1119	1.06	1.18	1.18	0.09	8.69
Fe	26	73421	86.07	95.56	94.20	2.40	2.78
Ni	28	513	0.82	0.92	0.86	0.10	11.94
Mo	42	793	0.53	0.59	0.34	0.08	15.13
		Sum	**90.11**	**100.00**	**100.00**		

Before nitriding, all samples were subjected to normalization with heating to 850±10°C for 15 min followed by cooling in air.

The study of microstructure, chemical composition was carried out using a scanning electron microscope VEGA3 manufactured by TESCAN; optical images of the microstructure were taken using a microscope manufactured by CARL ZEISS, JENA. The microhardness of the nitrided surface was measured by a PMT-3 microhardness tester with a load on the indenter of 20 g. Wear resistance of the samples testedby the method of friction plane on plane in conditions of dry friction metal on metal, with the sample reciprocating movement according to the scheme shown in figure 1. The friction samples were in the shape of bars with the following dimensions: length – 20 mm, width – 10 mm, thickness – 6 mm;the samples were cut from the original round samples with a diameter of 33 mm before and after nitriding.

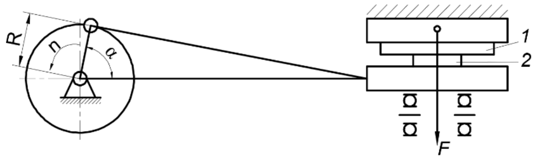


Fig. 1. Kinematic diagram of the friction unit 1 - counterbody, 2 - test sample

The hardened steel U13 with hardness of 70 HRC served as the counter body, the pressure in the contact zone of the counter body on the sample was 10 kPa. Friction of each sample was carried out for 6 hours, graphs were built based on the dependence of mass loss on the distance covered and time.

Results

In accordance with the set goal, the surfaces of samples with nitrided layers, which were obtained by three technologies of ionic nitriding, were studied in the work.

By the first technology, nitriding was applied using an experimental nitriding unit U1 designed by Podilskyi Scientific Physics and Technology Center of the Khmelnytskyi National University in the following modes: T = 560°C; P = 160 Pa; τ = 300 min; 75%N_2+25%Ar . The part was placed in a sealed chamber on a special device to which the negative pole of the power supply was connected, and the walls of the chamber were connected to the positive pole. Air was pumped out of the chamber to a pressure of 1.33 Pa, then the chamber was filled with pure Ar to a pressure of 1330 Pa, pumped out again to 1.33 Pa, and a constant voltage was applied to the electrodes using a special power supply to excite the glow discharge. The ion cleaning process was started at the voltage up to 1200 V for 30...60 minutes. Then the voltage was reduced to 500...1200 V, and the pressure was increased to operating pressure.

The process was carried out in the mode of anomalous glow discharge, where the surface of the part participates in the discharge as a cathode electrode and is covered with a layer of plasma. The density of current supplied to the part is up to 20 mA/cm^2. The temperature of the sample during nitriding was regulated by changing the parameters of the power supply mode and did not exceed 560 ° C, the control was carried out using a pyrometer F.08196.Ar purity at the initial stage was 99.993%.

By the second technology, nitriding was applied using the VIPA-1 unit designed by the H.S. Pysarenko Institute for Problems of Strength of the National Academy of Sciences of Ukraine. The technological process is as follows. The part is placed in a sealed container and connected to the negative pole of the current source, and the container walls are connected to the positive pole. Air is pumped out of the container to a pressure of 1.33 Pa, the container is purged with working gas for 5...15 minutes at a pressure of 1330 Pa, then it is pumped out again to a pressure of 1.33 Pa, a pulsating voltage of 1100...1400 V is applied to the electrodes using a special power supply and a glow discharge is excited. At this stage, cathodic spraying is carried out for 5...60 minutes, during which the part is cleaned. Then the voltage is reduced to operating voltage and the pressure is increased to 25...250 Pa. At these parameters, the actual process of diffusion saturation with nitrogen is carried out, and the voltage of 1000...1200 V is pulsating with a current pulse duration t = 10...20 ms and a pulse period T = 40 ms. Meanwhile, the filling factor Q, which is equal to the ratio of the value of the pulse period T to the duration t of a single pulse, is in the range of 2...4 because at $Q < 2$ arc discharges which cause damage to the surface of the workpiece may occur and at $Q > 4$ the efficiency of ion treatment decreases.

In the process of diffusion saturation, there is a cyclic termination of the reaction gas supply to the vacuum chamber in the ratio of 80%Ar + 20%N_2 with a half-cycle duration of 15...30 min, while the temperature of nitrogen saturation and denitration (resorption) is different – higher or lower than the eutectoid transformation temperature (591ºC) [8].

The process of nitriding by the third technology was carried out on an experimental vacuum unit, which was additionally equipped with a special source of the regulated constant voltage, a high-frequency generator and a pulse modulator made on vacuum electronic devices GU-81M. Due to the properties of their characteristics, these devices automatically limit the current to the load to a specified value and interrupt the arcing process, which is accompanied by explosive local destruction of the cathode surface.

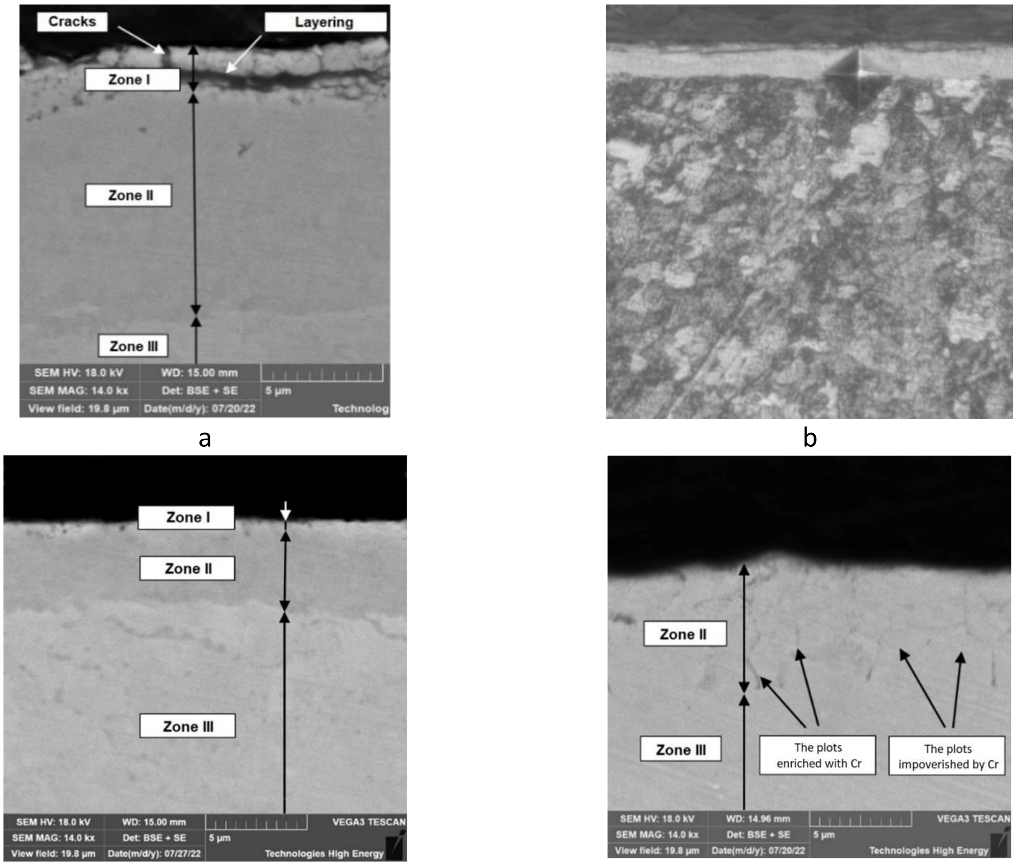
The process was carried out in the mode of anomalous glow discharge, under which the entire surface of the cathode electrode (in our case, the part) participates in the discharge and is covered with plasma glow (Fig.2). The voltage for such discharge is hundreds of volts, and the current density on the part is up to 10 mA/cm^2. The operating parameters were set in the following range: voltage – 0.8-1.0 kV, pulse frequency – 10 Hz; pulse ratio– 1.5-2; working gas pressure in the chamber – 250-350 Pa, process length – 5-6 hours. The sample temperature during nitriding was regulated by changing the parameters of the pulse power supply mode and did not exceed 580°C. A mixture of 75%N_2 and 25%Ar was used as working gas, and pure Ar was used to clean the surface at the initial stage.

The use of pulse mode with a frequency of 10kHz ensures the stability of the process of diffusion saturation of the surface without electrical breakdowns and arcing, thus, in accordance with the volt-ampere characteristic of the electric discharge, the mode of anomalous glow discharge is realized. An important role in this process, as well as in the second technology, is played by the pulse density, the decrease in which leads to the localization of the amount of plasma, which can be compensated by increasing the voltage, but it causes overheating on the sample surface, which can lead to undesirable structural transformations.

Thus, the glow discharge burning occurred uniformly around the perimeter of the samples (Fig. 2), which provided the uniform thickness of the diffusion layer.

Fig. 2. Burning process of anomalous glow discharge in pulse mode. 1 - anode, 2 - cathode (part), 3 - anode glow, 4 - cathode glow.

Figure 3 shows electron pictures of sample surfaces after nitriding under the modes corresponding to the three described technologies. Table 2 shows the results of chemical analysis of sample surfaces in different zones formed during the nitriding process.



a b

c d

Fig. 3. Electronic pictures of the sample surface after nitriding: a, b - sample №1 by the first technology, c - sample №2 by the second technology, d - sample №3 by the third technology

Table 2

The results of chemical analysis of sample surfaces

Sample №	Analysis zone	Composition of elements, mas. %						
		N	Si	Cr	Mn	Fe	Ni	Mo
1	Zone I	6,13	0,63	1,58	–	90,8	0,86	–
	Zone II	4,76	0,19	1,12	–	93,02	0,91	–
	Zone III	1,71	0,4	2,83	–	94,09	0,74	–
2	Zone II	5,55	0,3	1,02	1,03	89,28	1,19	–
	Zone III	2,20	0,15	1,03	1,11	93,83	1,00	0,28
3	Zone II	5,9	0,32	0,58	0,63	90,75	1,42	–
	Zone III	3,27	0,25	0,52	1,07	93,4	0,99	0,1

Analysis of the results of determining the chemical composition of the nitrided layer showed that the structure is layered and consists of two zones: nitride, where the γ′- phase was formed, and nitrogenous ferrite. Alloying elements chromium and nickel dissolve in ferrite, increase the solubility of nitrogen in the α-phase forming special nitrides. Being released in a finely dispersed state, these nitrides contribute to enhancing the hardness of the nitrided layer, mainly in the lower layer of the saturated zone. Chromium, as a transition element, actively interacts with nitrogen and increases the solubility of nitrogen in the α-phase. Zone I with γ′-phase is very thin and brittle, microcracks and delamination are found (Fig.3 a).

After nitriding on the surface of sample No. 1 in zone I, the nitrogen concentration reaches 6.13 wt.%, respectively 18.05 atm% (Table 2). According to the iron-nitrogen diagram (Fig. 4), at a nitrogen concentration of about 20 atm%, iron nitride Fe4N will be formed, which causes the maximum hardness of the surface at the level of 805 MPa.

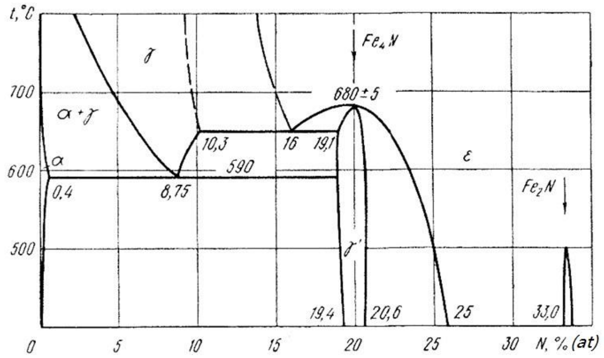


Fig. 4. Iron-nitrogen diagram

The amount of chromium in zone I increased to 1.58 mas.%, respectively to 1.25 atm% in comparison with its average amount in steel before nitriding of 1.18 mas.% (Table 1), and nickel, on the contrary, decreased from 0.92 mas. %, respectively from 0.86 atm %, in the initial state (Table 1) to 0.86 mas. %, respectively to 0.61 atm % after nitriding.

In zone II, the chemical composition of the nitrided surface differs from both the initial and the nitrided one: the nitrogen amount reaches 4.76 mas.% (16.6 atm %), and the alloying elements chromium and nickel show different activity. The amount of chromium decreased to 1.12 mas.% (1.05 atm %), and the amount of nickel decreased to 0.91 mas.% (0.76 atm %) (Table 2). Zone III, where the nitrided layer was formed, also underwent changes in the chemical composition: the amount of nitrogen decreased to 1.71 mas. % (6.47 atm %), and the amount of chromium increased to 2.83 mas. % (2.88 atm%). The amount of nickel remained at 0.74 mas.% (0.67 atm %), which is less than the average amount of nickel in steel before nitriding of 0.92 mas.% (Table 2). Thus, the microanalysis data indicate that the chemical composition of the saturated layer did not change in a uniform manner. Nitrogen has the highest concentration at a distance of 6-7 mcm from the surface (Fig. 5), chromium is more actively involved in the formation of the surface layer, where its concentration increased to 1.58 mas.% (1.25), and nickel remained in the deeper layers of the samples.

The surface nitrided layer reaches 200 mcm, and the hardened zone reaches 300 mcm. In the case of the indenter pyramid hitting the boundary between the white nitrided layer and the base with a load on the indenter of 100 g, the microcracks and delamination are not found (Fig. 3, b).

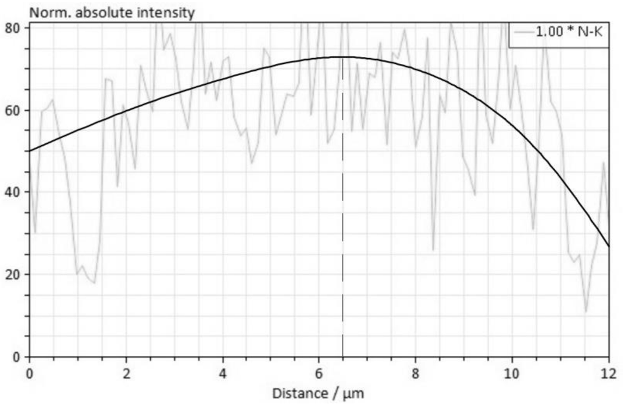


Fig. 5. Change of nitrogen concentration inwards from the surface of sample №1

The analysis of nitrogen distribution in sample No. 2 shows a slight increase in concentration to 5.55 mas. %, respectively to 18.77 atm% in zone II and to 2.20 mas. % (8.13 atm%) in zone III (Table 2). However, there is a significant decrease in the nitride zone I and the transition zone II from 10 mcm to 5 mcm (Fig.3, c), a small amount of molybdenum of 0.28 mas.% is observed, which may be due to the chemical heterogeneity of the steel bar from which the samples were cut. The distribution of nitrogen in sample No. 3 is similar to sample No. 2 in zone II in the amount of 5.9mas.%, respectively of 18.8 atm% and 3.27 mas.% (11.69 atm%) in zone III, there is also a small amount of molybdenum which is 0.1 mas.%. At the same time, zone I is absent, which can be explained by the absence of γ′-phase formations. The sample is different from the previous samples due to uneven redistribution of chromium (Fig. 6), with enrichment at the grain boundaries in the amount of 2.44 mas.% respectively of 2.13 atm and depletion in the grains to 0.52 mas.% respectively to 0.5 atm (Table 2, Fig. 3, d).

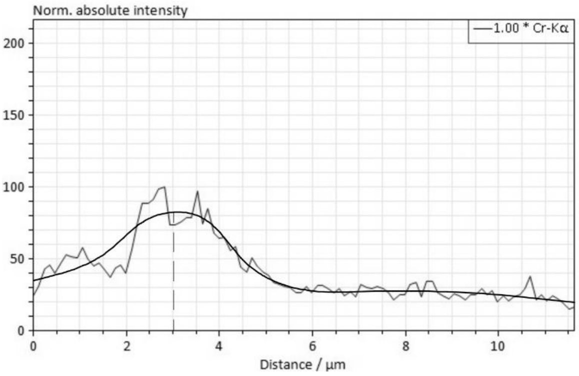


Fig. 6. Change of chromium concentration inwards from the surface of sample№3

The results of the analysis show the difference of microstructures and chemical composition in the surface zones of the nitrided surface of the samples treated by different technologies.The size, presence or absence of the nitride zone I with high nitrogen concentration and, accordingly, the maximum hardness on the surface are of particular importance; the redistribution of chromium in near-surface layers is also important, which in turn is reflected in the wear results shown in figure 7.

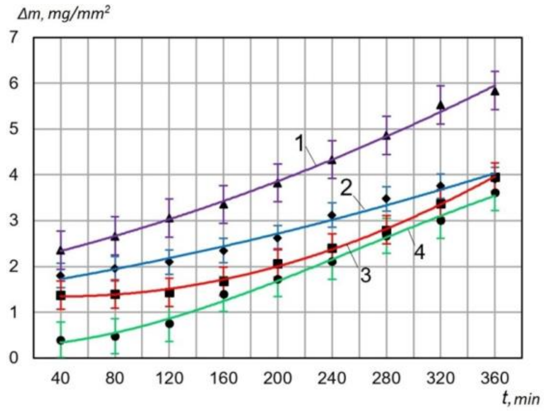


Fig. 7. Wear kinetics of samples from 40XH2MA steel in the initial state and after ionic nitriding.
1 – virgin sample; 2 – nitrided sample №3; 3 – nitrided sample №2; 4 – nitrided sample №1.

Based on the graphs shown in figure 7, it can be concluded that sample №1 nitrided by the first technology has the highest wear resistance, which is particularly apparent in the first minutes of friction, after wear of the nitride zone with maximum hardness, the mass loss of the sample increases uniformly. Sample No. 3 has almost the same wear at the beginning and at the end of the tests compared to sample No. 2, however, the wear changes uniformly with time as in the case of the non-nitrided sample, which can be explained by the more homogeneous structure of the nitrided layer. In general, after 360 minutes of testing, the wear resistance of all nitrided samples is 50-70% higher than that of the virgin non-nitrided sample.

Conclusion

The microstructural studies of the modified surfaces of 40XH2MA steel samples showed the difference in the structure and chemical composition of nitrided layers obtained by different ion-plasma nitriding technologies.

The size and presence on the surface of nitride zone with the formation of γ′-phase at the nitrogen concentration of 18-20 atm%, which along with high hardness has defects such asmicrocracks and delaminations, is of particular importance. Reduction of this zone, up to its complete elimination, is facilitated by the use of gas-thermocyclic and pulsed high-frequency ion-plasma nitriding technologies.

Tests under conditions of metal on metal dry friction showed that the wear resistance of all nitrided samples processed by the above technologies is 50-70% higher than that of the virgin non-nitrided sample.

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Смирнов І.В., Чорний А.В., Лисак В.В., Дробот О.С., Каплун П.В., Побережний М.М., Рутковський А.В. Мікроструктура та зносостійкість модифікованих поверхонь отриманих іонно-плазмовим азотуванням сталі 40ХН2МА

Стаття присвячена аналізу зносостійкості дифузійних покриттів,що були нанесенні іонним азотуванням на сталь 40ХН2МА. Проведено порівняння технологічної ефективності результатів. Приведені параметри технологічних режимів, що використовувались в процесі нанесення, вказаний перелік обладнання та етапи. Проведено порівняльний аналіз хімічного складу, мікроструктури, металографічних та трибологічних досліджень. Вивчена кінетика зношування сталі 40ХН2МА з азотованими покриттями, що були нанесені. Надані практичні рекомендації щодо використання зміцнених зразків в умовах сухого тертя.

Ключові слова: конструкційні сталі, фізико-механічні властивості, іонне азотування, технологія, дифузійні покриття, знос.