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Improvement of Strength and Wear Resistance of Metal Products with Ion-Plasma Nitride Coatings by Pulse Technique Implementation*

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Повышение прочности и износостойкости металлических изделий с помощью импульсной методики нанесения ионно-плазменных нитридных покрытий

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Рассматривается инновационная технология, разработанная в Институте проблем прочности им. Г. С. Писаренко НАН Украины, а именно: импульсная технология нанесения ионно-плазменных покрытий, использование которой позволяет получить диффузионные слои с необходимой структурой путем управления процессом диффузионного насыщения и его оптимизацией в зависимости от конкретных технических требований. При этом диффузионные слои с азотированными и неазотированными фазами могут быть получены путем регулирования состава ионизированных газов и интенсивности тлеющего разряда. Предлагаемая инновационная методика, запатентованная на национальном уровне в 2013 году, в настоящее время используется для промышленного внедрения на отечественных авто- и авиаремонтных заводах. Краткий обзор современных промышленных разработок в этой области показывает, что предложенная методика может быть использована в современных коммерческих приложениях/комплексах для нанесения PVD-покрытий. Представленные результаты экспериментальных исследований статической и усталостной прочности, а также износостойкости в агрессивных средах образцов из стали 40Х13 с нанесенными покрытиями по импульсной технологии подтверждают ее положительный эффект.

Ключевые слова: термоциклические ионно-плазменные покрытия, термоциклическое ионное азотирование, физическое осаждение паров, тлеющий разряд, усталость, износ.

Introduction. The process of vacuum ion-plasma nitriding (VIPN) of materials was invented over 60 years ago, but is still treated as quite exotic for the majority of the enterprises of mechanical engineering in Ukraine. However, complexities related to implementation of this method, such as high cost of equipment, necessity of ensuring strict vacuum standards are fully compensated by high quality of the treated products, drastic cost reduction, and high ecological safety [1–3].

In comparison with widely used expedients of strengthening chemical-thermal processing of steel parts, such as cementation, nitrocementation, carbonitriding cyanidation and gas nitriding in furnaces, the VIPN method has the following basic advantages: higher superficial hardness of the nitrated parts, lack of deformation of parts after processing, increased endurance limit and improved wear resistance of treated parts, possibility of processing blind and through holes, invariable hardness of the nitrated layer after heating to 600–650°C, possibility of producing layers of the required composition, possibility of

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processing large and complex-shaped products; absence of environmental contamination, essential treatment cost reduction, as well as lower treatment temperature, which excludes structural transformations [4–8].

At the Pisarenko Institute of Problems of Strength of the National Academy of Sciences of Ukraine a new ionic-plasma thermocyclic nitriding (IPTN) technology was developed, which is based on academic developments such as the theory of thermal fatigue, abnormal mass transfer under mechanical loading conditions, and the effect of discrete energy input. This technology, which is protected by the patent of Ukraine [9], has the following advantages:

(i) only surface layers of treated article are heated without warming its core. Heating is provided by the glow discharge energy, so no furnace is required for heating;

(ii) cyclic heating and cooling of treated article induce thermal stresses in the surface layer, which enhances diffusion processes by 2–3 times with respective treatment time reduction;

(iii) since the shape, dimensions, and surface roughness of treated article remain unchanged, no finishing treatment is further required;

(iv) short-term treatment duration, cyclic nature of high-speed discrete energy input, and heat localization in the the surface layer strongly reduces energy consumption costs.

Preliminary industrial tests confirmed the possibility of replacing the processes of gas nitriding and cementation by the IPTN in the environment of nitrogen and argon mixture.

This technique is currently used for small-scale industrial implementation in domestic aircraft and machinery repair shop-and-plants, and is can be utilized in the available commercial applications for physical vapor deposition (PVD) of coatings, including NNV 6.6. I4 unit produced by VNIIINSTRUMENT (Russia) [10], the division of ion-plasma coatings of Saturn (Rybinsk, Russia) [11], Ionitech (Bulgary) [12], and PLATIT p-80 Ion-Plasma Unit (Platit Co., Switzerland) [13]. Analysis of these potentials is not detailed here for brevity, but noteworthy is the appearance of a competing alternative technique of pulsed-DC plasma assisted chemical vapor deposition of ion-plasma coatings recently proposed and verified on H13 hot work tool steel by authors [14]. In this article, we'll focus on the effects of the proposed IPTN treatment on the mechanical properties, static strength, fatigue strength and wear resistance of the industrial stainless steel 40Kh13.

Material. Chemical composition and mechanical properties of 40Kh13 steel are given in Tables 1 and 2, respectively.

T a b l e 1

Chemical Composition (in vol.%) of 40Kh13 Steel

C	Si	Mn	Ni	S	P	Cr	Fe
0.35–0.44	up to 0.6	up to 0.6	up to 0.6	up to 0.025	up to 0.03	12–14	84

T a b l e 2

Mechanical Properties of 40Kh13 Steel

σ_u, MPa	$\sigma_{0.2}$, MPa	δ_5, %	ψ, %
950	725	14.0	41.5

The material was obtained after the standard heat treatment (quenching from 1050°C in air, tempering at 650°C) with hardness of 277–286 HB. In the tempered condition, 40Kh13 steel microstructure consists of martensite, carbides, and insignificant quantity of residual austenite. According to earlier studies of this steel [1], after heating above temperature 860–880°C its structure consists of austenite and carbides of chrome. Starting from quenching temperature of 1050°C and higher, hardness of this steel exhibits a decreasing trend, which may be attributed to increased content of residual austenite. Tempering of quenched 40Kh13 steel results in decomposition of martensite into ferritic-carbide mix and in reduced hardness. However, within the tempering temperature range of 450–550°C, the secondary hardening effect is observed due to segregation of dispersed carbides.

Two types of specimens of steel 40Kh13 are used: plane specimens with dimensions $36.0 \times 7.5 \times 1.0$ mm for static and cyclic loading, and rectangular specimens with dimensions 30×30 mm and 10 mm thickness for wear resistance tests.

IPTN Experimental Setup. For the formation of diffusion layers by vacuum ion-plasma nitriding pulse technique (IPTN), a universal VIPA-1 experimental set-up developed at the Pisarenko Institute of Problems of Strength was used (Fig. 1). Technological parameters of the formation of hardened layers are: temperature is 550°C, pressure is 25–150 Pa, treatment time is 10 h, ratio of reacting gases is 80% Ar + 20% N_2. The general view of VIPA-1 experimental set-up with vacuum chamber for IPTN coating deposition is shown in Fig. 1. Details on this equipment and technology can be found elsewhere [2, 9]. The shape of IPTN pulses is depicted in Fig. 2. Hardening of specimen surfaces occurs uniformly along the perimeter, which provides a uniform thickness of the diffusion layer. For reference, several specimens were treated by isothermal ion-plasma nitriding method as depicted in Fig. 3.

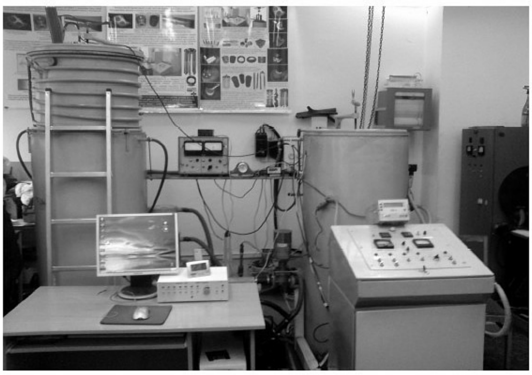


Fig. 1. General view of VIPA-1 experimental set-up with vacuum chamber for IPTN pulse nitriding technology.

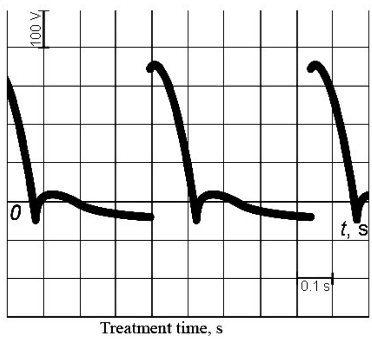


Fig. 2. Shape of IPTN pulses.

Visualization of ion-plasma processes occuring during IPTN treatment of test specimens and industrial applications (in particular, a gearwheel) of 40Kh13 steel is given in Fig. 4. As it was mentioned in the introduction, identical conditions for ion-plasma nitride coating deposition are ensured for small- and large-scale articles.

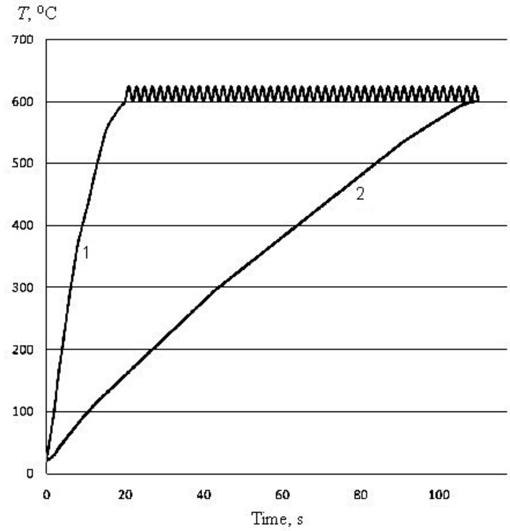
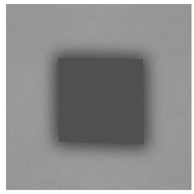
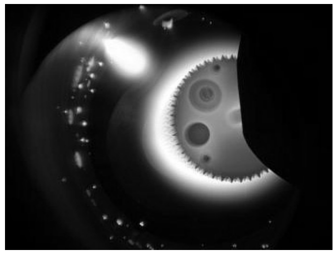


Fig. 3



a



b

Fig. 4

Fig. 3. Heating rate of specimens by the method of ion-plasma thermocyclic nitriding isothermal (*1*) and IPTN pulsing (*2*) modes.
Fig. 4. 40Kh13 steel specimen (a) and industrial gearwheel (b) in VIPA-1 vacuum chamber subjected to IPTN treatment.

Using the IPTN technique, specimens were heated to $T = 500°$ C and treated by different modes of thermal cycles: ± 20, ± 50, and ± 100. After treatment, the diffusion layer depth values were measured by the standard technique, which included preparation of microsections, etching and measurements via electron microscopy, as well as indirect verification via layer-by-layer microhardness measurements (microindentation). As shown in Fig. 5, the nitriding duration effect on diffusion layer depth is the most pronounced for IPTN treatment with ± 50 cycles, the least is for isothermal nitriding. This can be related to the above-mentioned specifics of the tempering temperature range of 450–550°C, where the secondary hardening effect due to segregation of dispersed carbides in the core material occurs parallel to the nitriding treatment of the surface layers.

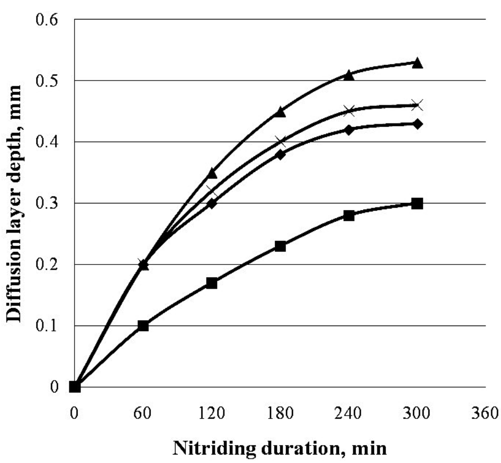


Fig. 5. Nitriding duration vs diffusion layer depth: isothermal (■), ± 25°C (◆), ± 50°C (▲), and ± 100°C (×).

Static Tensile Tests. Untreated specimens and those treated with IPTN cycle of $\pm 50^\circ$ C with working portion dimensions of $36.0 \times 7.5 \times 1.0$ mm were subjected to static loading on a servohydraulic Instron test machine to produce the stress–strain diagram (Fig. 6).

The comparative analysis of plots in Fig. 6 implies that IPTN treatment did not deteriorate the characteristics of static strength of steel 40Kh13, but even improved them by 7%.

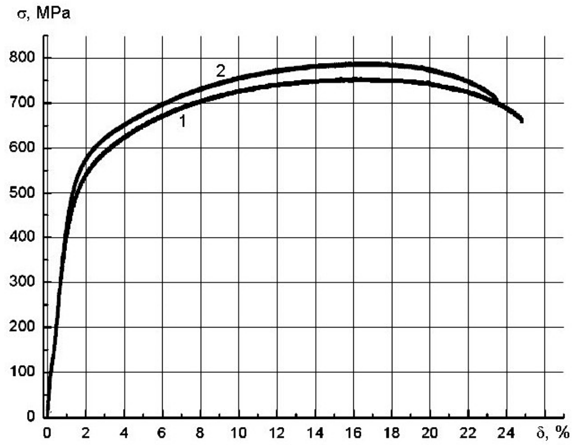


Fig. 6. Stress–strain diagrams of 40Kh13 steel specimens: untreated (*1*) and subjected to IPTN treatment with IPTN cycle of ± 50°C (*2*).

Fatigue Tests. High-cycle fatigue strength tests were carried out via a magnetostrictive setup, the operating principle of which is based on the magnetostriction phenomenon, i.e., the ability of some materials and alloys to change their linear dimensions under the influence of an alternating magnetic field [16]. Thus, by adjusting the vibration amplitude of the magnetostrictor, fatigue tests of 40Kh13 steel specimens were conducted*.

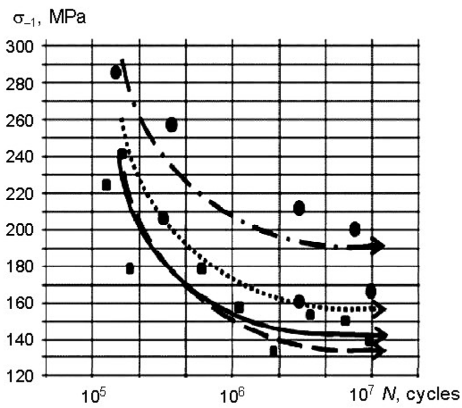


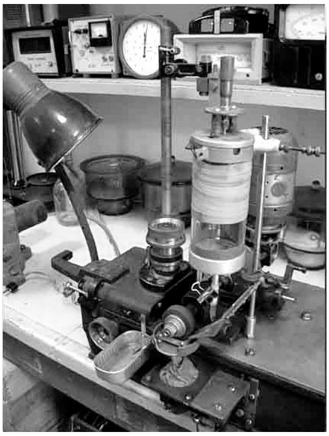
Fig. 7. Fatigue curves of 40Kh13 steel specimens at frequency 10 kHz subjected to IPTN treatment with different thermal cycle ranges: untreated (■, solid line), ± 20°C (dashed line), ± 50°C (●, dash-and-dot line), and ± 100°C (●, dotted line).

The results of experimental studies are depicted in Fig. 7. Their analysis implies that 40Kh13 steel specimens subjected to IPTN treatment with thermal cycle $\pm 50^\circ$ C have the best fatigue strength characteristics, as compared to untreated specimens, their high-cycle

* Tests were conducted by Ph.D. A. G. Trapezon.

fatigue strength increased by 20%, while IPTN treatments with thermal cycles ± 20 and $\pm 100^{\circ}$ C resulted, respectively, in fatigue strength deterioration by 5% and improvement by 5%. This trend is attributed to generation of residual stresses in the surface layers of treated specimens, and is similar to those observed by other researchers for steel specimens with ion-plasma coatings [15–19].

Wear Resistance Tests. Wear resistance tests of IPTN-deposited coatings are conducted on an experimental unit [20] according to GOST 23.208-79 (Fig. 8). The friction process is effected with a free abrasive, which is consistent with ASTM C 6568. Test equipment is depicted and schematically shown in Fig. 8.



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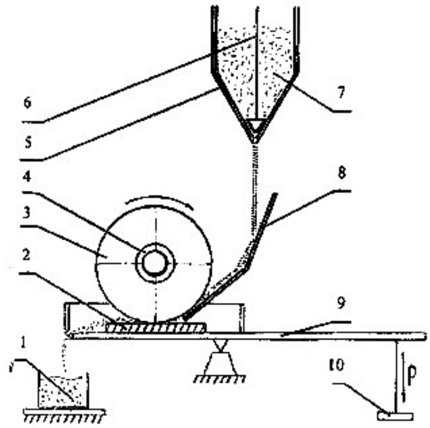


b

Fig. 8. Photo (a) and schematic diagram (b) of a unit for wear tests: (*1*) abrasive debris collector, (*2*) specimen, (*3*) rubber roller, (*4*) roller core, (*5*) free abrasive feeder, (*6*) abrasive feeder velocity controller, (*7*) free abrasive, (*8*) abrasive feeder shute, (*9*) load lever, and (*10*) load.

As seen in Fig. 8b, specimen *2* is worn with free abrasive *7*, which is fed by rubber roller *3* to the friction surface. Quartz sand (SiO_2) with grain sizes of 200–250 μm was used as an abrasive. Prior to wear tests, an abrasive was dried (humidity did not exceed 0.16%). The wear level was measured by the weight method with accuracy up to 0.0001 g on analytical scales ADB-200. Prior to tests, specimens were washed in ethyl alcohol, dried and weighted. Wear tests were conducted at a 0.158-m/s sliding velocity, a 200-N load (with a 272-mm lever) and a 50-m friction length.

In additon, wear studies were conducted in the following environments: water + quartz sand, damp salt + quartz sand. Grain sizes of quartz sand and experimental conditions were the same as above. For comparative analysis of wear resistance characteristics, 40Kh13 steel rectangular specimens (both untreated and IPTN-treated ones) were used as shown in Fig. 9. As aggressive environments we used: (1) quartz sand, (2) water + sand, and (3) damp salt + sand. The respective results on weight loss by wear are given in Fig. 10.

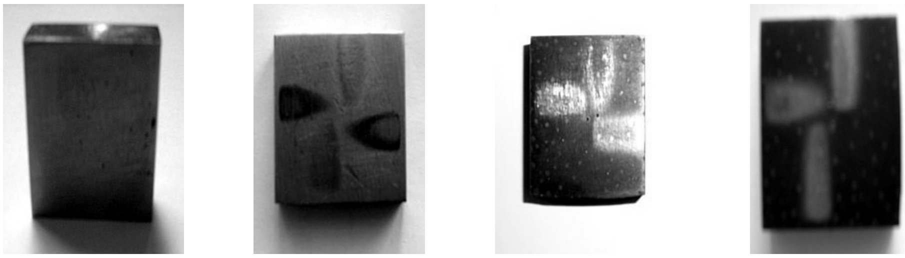
The experimental staudies have revealed the following trends:

1. The maximal wear intensity is observed for untreated 40Kh13 steel specimens.

2. IPTN technique enhances wear resistance 40Kh13 steel specimens: in sand – by 3 times; in water + sand – by 3.5 times, in salt + sand – by 2.5 times.

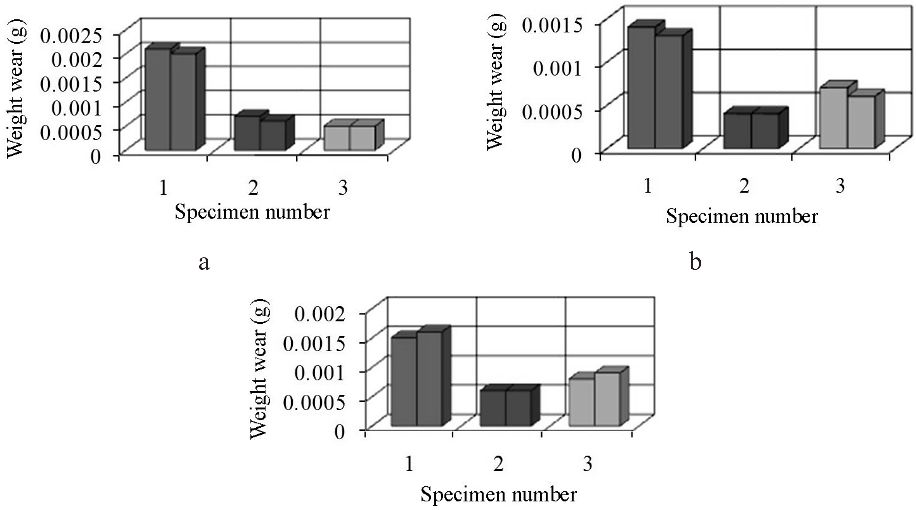
3. The isothermal nitriding technique enhances wear resistance 40Kh13 steel specimens: in sand – by 4 times, in water + sand – by 2 times, in salt + sand – by 1.7 times.

4. The IPTN technique is superior to the isothermal one for water + sand and salt + sand environments.



a b c d

Fig. 9. 40Kh13 specimens before (a) and after (b) wear tests in sand, water + sand (c), and damp salt + sand (d).



c

Fig. 10. Weight loss of 40Kh13 steel specimens: in sand (a), water + sand (b), and damp salt + sand (c): (*1*) untreated specimens, (*2*) after thermocyclic IPTN mode of nitriding, and (*3*) after isothermal mode of nitriding.

Conclusions. The proposed ion-plasma coating deposition pulse technique offers a considerable opportunity for producing diffusion layers with good wear resistance, fatigue resistance and static strength. The results of the respective experimental studies on 40Kh13 steel specimens treated by the proposed pulse technique confirm its positive effect.

Р е з ю м е

Розглядається інноваційна технологія, розроблена в Інституті проблем міцності ім. Г. С. Писаренка НАН України, а саме: імпульсна технологія нанесення іонно-плазмових покриттів, що дозволяє отримати дифузійні шари з необхідною структурою шляхом управління процесом дифузійного насичення і його оптимізацією в залежності від конкретних технічних вимог. При цьому дифузійні шари з азотованими та неазотованими фазами можуть бути отримані шляхом регулювання складу іонізованих газів і інтенсивності тліючого розряду. Запропонована інноваційна методика, що була запатентована на національному рівні в 2013 році, в даний час використовується для промислового впровадження на вітчизняних авто- та авіаремонтних

заводах. Стислий огляд сучасних промислових розробок у цій області показує, що запропонована методика може бути використана в сучасних комерційних прикладаннях/комплексах для нанесення PVD покриттів. Представлені результати експериментальних досліджень статичної й втомної міцності та зносостійкості в агресивних середовищах зразків зі сталі 40Х13 із нанесеними покриттями з використанням імпульсної технології підтверджують її позитивний ефект.

1. V. V. Kharchenko (Ed.), B. A. Lyashenko, E. K. Solovykh, et al., *Optimization of the Coating Technology According to Strength Criteria* [in Russian], Pisarenko Institute of Problems of Strength, National Academy of Sciences of Ukraine, Kiev (2010).
2. B. A. Lyashenko, A. G. Trapezon, and A. V. Rutkovskii, "Vacuum-plasma deposited coatings as a provision for enhancing the fatigue strength of materials," *Vibr. Tekhn. Tekhnol.*, No. 5 (21), 76–79 (2001).
3. A. G. Trapezon, B. A. Lyashenko, and N. V. Lipinskaya, "Fatigue of VT20 titanium alloy with vacuum plasma coatings at high temperatures," *Strength Mater.*, **41**, No. 4, 417–422 (2009).
4. V. V. Kudinov and V. M. Ivanov, *Plasma Deposition of Refractory Coatings* [in Russian], Mashinostroenie, Moscow (1981).
5. V. V. Kostikov and Yu. A. Shesterin, *Plasma Coatings* [in Russian], Metallurgiya, Moscow (1978).
6. A. I. Grigorov and O. A. Elizarov, *Ion-Assisted Vacuum Deposited Wear-Resistant Coatings* [in Russian], Naukova Dumka, Kiev (1979).
7. A. Alsaran, I. Kaymaz, A. Celik, et al., "A repair process for fatigue damage using plasma nitriding," *Surf. Coat. Technol.*, **186**, No. 3, 333–338 (2004).
8. G. V. Klevtsov, N. A. Klevtsova, L. L. Il'ichev, et al., "Influence of plasma ion assisted deposition coatings," *Vestn. Orenburg. Gos. Univer.*, No. 10, 171–175 (2007).
9. V. V. Kharchenko, B. A. Lyashenko, A. V. Rutkovskii, et al., *Technique of Surface Hardening of Steel Machine Parts by Ion-Plasma Nitriding in a Pulsed Glow Discharge* [in Ukrainian], Ukraine Patent on Useful Model No. 78071 C23C 8/06 (2006.01), Published 11.03.2013, Bull. No. 5.
10. Official Site of VNIIINSTRUMENT (Russia), www.vniiinstrument.ru.
11. *Technologies of Protective Coatings by Division of Ion-Plasma Coatings of Saturn* (Rybinsk, Russia), http://npo-saturn.ru/?sat=32.
12. *Plasma/Ion Nitriding Technology for Best Coating*, Official Site of Ionitech (Bulgary), http://www.ionitech.com/.
13. Official Site of Platit Co. (Switzerland), http://platit.com/coating-equipment/p80?page=0%2C1.
14. M. Azadi and A. Sabour Rouhaghdam, "Nanomechanical properties of TiN/TiC multilayer coatings," *Strength Mater.*, **46**, No. 1, 121–131 (2014).
15. A. G. Trapezon, "Methodological problems in the investigation of thin hardening films," *Strength Mater.*, **39**, No. 2, 178–188 (2007).
16. A. G. Trapezon, "To the method of accelerated evaluation of fatigue of metals with hardening coatings," *Strength Mater.*, **41**, No. 2, 174–182 (2009).
17. S. Y. Sirin, K. Sirin, and E. Kaluc, "Effect of the ion nitriding surface hardening process on fatigue behavior of AISI 4340," *Mater. Charact.*, **59**, No. 4, 351–358 (2008).

18. J. Qian and A. Fatemi, "Cyclic deformation and fatigue behaviour of ionitrided steel," *Int. J. Fatigue*, **17**, No. 1, 15–24 (1995).

19. S. Fukui, H. Nakayama, and T. Tanaka, "Effects of TiN thin films prepared by ion beam and vapor deposition method on fatigue strength of high strength martensitic stainless steels," *Trans. Jap. Soc. Mech. Eng. A*, **64**, No. 622, 1455–1462 (1998).

20. A. V. Rutkovskii and A. Yu. Kumurzhi, "Investigation of diffusion layers of steel 40Kh13 obtained by thermocyclic ion-plasma nitriding of friction in corrosive environments," in: *Friction and Wear Problems* [in Ukrainian], NAU-Druk, Kiev (2011), pp. 240–230.

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