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MATHEMATICAL MODELING OF OBTAINING WEAR-RESISTANT COATINGS USING SELF-PROPAGATING HIGH-TEMPERATURE SYNTHESIS TECHNOLOGY

The paper considers methods for obtaining chromoaluminized coatings and presents a new technology for the formation of protective layers on steels under conditions of self-propagating high-temperature synthesis. With the use of mathematical modeling methods, when obtaining wear-resistant coatings on machine parts under conditions of self-propagating high-temperature synthesis, optimal compositions of SHS mixtures have been developed. The study of the wear resistance of chromoaluminized layers on steels 50 and U80A alloyed with boron and silicon allows us to speak about an increase in the wear resistance of machine parts and mechanisms by 2—3 times.

Keywords*: mathematical modeling, wear resistance, synthesis, SHS charge, temperature.*

В роботі розглянуті методи отримання хромоалітованих покриттів та представлена нова технологія формування захисних шарів на сталях в умовах високорозповсюджуваного високотемпературного синтезу. Із застосуванням методів математичного моделювання, при отриманні зносостійких покриттів на деталях машин в умовах високорозповсюджуваного високотемпературного синтезу, розроблено оптимальні склади СВС сумішей. Дослідження зносостійкості хромоалытованих шарів, на сталях 50 та У8А, легованих бором та кремнієм дозволяє говорити про збільшення зносостійкості деталей машин та механізмів у 2—3 рази.

Ключові слова*: математичне моделювання, зносостійкість, синтез, СВС-шихта, температура.*

Problem’s Formulation

The efficiency of the final result depends to a large extent on the correct choice of the surface hardness of machine parts — their long-term performance at minimal cost. Test algorithms should form the technology in such a way as to determine what and how should be applied in the technology of obtaining protective coatings. The technology should provide for a range of different modes of chemical-thermal treatment, control and diagnostic devices — from manual to automated execution, with their rational use in the processes of production, testing and operation of machine parts. It should have a wide range of algorithms and programs that are applied to specific parts, operations and tasks of improving the wear resistance of steel parts operating under sliding friction conditions. The use of a new technology for the formation of wear-resistant coatings under the conditions of self-propagating high-temperature synthesis requires its thorough study and research.

There are many methods for hardening the surface of steels, some of them are used in several versions. They are divided into two large groups [1]:

– processes of formation of protective coatings, which include: application of electrolytic coatings, galvanization, deposition of coatings from the gas phase by PVD and CVD methods, laser deposition, etc;

– processes associated with the modification of the material of existing surfaces. The most advanced techniques in this area include surface hardening using laser technology, electron beams, ion implantation, etc., as well as classical methods of chemical-thermal surface treatment (nitriding, boriding).

Methods for obtaining protective coatings on metal products differ in the technology of coating, and the main purpose of creation is good adhesion to the substrate, as well as obtaining a continuous, non-porous and resistant protective layer in this environment. Currently, the main methods of applying a protective coating are: galvanic precipitation during electrolysis, thermal spraying or metallization, thermal diffusion saturation in powder, immersion in molten metal, cladding. According to the type of connection of the protective layer with the substrate, adhesive and diffusion metal coatings are distinguished.

Surface saturation of steel with aluminum, chromium, zinc and other elements is called diffusion saturation with metals [2]. The product, the surface of which is enriched with these elements, acquires valuable properties, which include high heat resistance, corrosion resistance, increased wear resistance and hardness.

In this regard, it is important to use technologies that allow obtaining coatings with a limited or minimal time of their formation. One of such technologies is the method of self-propagating high-temperature synthesis [3—4].

Analysis of recent research and publications

Many scientists are engaged in the issues of increasing the wear resistance of machine parts. Recently, the use of chromium-alloyed coatings has become widespread. Chromium aluminizing — simultaneous or sequential saturation of metals and alloys with chromium and aluminum — is used mainly to increase wear, heat and corrosion resistance of parts. The main methods of chromoaluminizing include: solid, vapor phase, gas and liquid. In turn, saturation from the vapor phase is divided into contact and non-contact, gas — simultaneous and sequential, solid — simultaneous and slip [7—9].

The solid method includes saturation in powder media. This method consists in the fact that the part on which the coating is created is placed in a container and covered with a powder mixture. The mixture usually contains: metal or alloy powder, which is the coating itself, an activator, which is most often used as halogen salts, and a neutral substance, the powder of which is introduced into the mixture to prevent sintering of the metal component. The peculiarity of the method is that the mixture contains an activator, and as a result of its interaction with the metal, a gaseous compound is formed.

Alloying of chromoaluminized coatings with titanium, silicon and boron makes it possible to sharply increase the operational characteristics and, along with high corrosion and heat resistance, to obtain more universal layers with high surface hardness, scale resistance and corrosion resistance due to the formation of additional silicon and titanium oxides.

Chromium aluminizing can be carried out in a sequential manner, chrome plated and then aluminized. Diffusion chromium plating is one of the progressive technological processes of chemical-thermal treatment, which makes it possible to obtain material with special physical and mechanical properties and at the same time reduce the cost of expensive and hard-to-machine steels through the use of more economical carbon steels. With an increase in the aluminum content in the layer, the diffusion rate of chromium increases, and the concentration decreases. The sequential method of iron saturation makes it possible to obtain a layer with a higher concentration of chromium and aluminum. Simultaneous saturation in powder mixtures with the use of high-frequency heating sharply accelerates the process of chromoaluminizing in the absence of a brittle FeAl phase in the surface layer [10—11].

Formulation of the study purpose

The purpose of the work is the search for optimal SHS powder mixtures that allow the formation of intermetallic protective layers on steel 50 and U8A under conditions of self-propagating high-temperature synthesis, the study of the structure of protective layers and their wear resistance under sliding friction.

Presenting main material

In the work, steels 50 and U8A were used for coating. Chemical-thermal treatment was carried out in an open-type reactor ($P = 105$ Pa) in the temperature range of 900—1050 °C and the total duration of isothermal holding up to 60 min. As a saturating medium, a mixture of powders with a dispersion of 100—400 μm of the following materials was used:

1. Cr_2O_3 — chromium (III) oxide — a source of chromium in the coating.
2. Al_2O_3 — aluminum oxide (III) — inert additive.
3. Al — aluminum grade ASD1— oxide reducer, source of aluminum in the coating.
4. B — technical boron — a source of boron in the coating.
5. Si — silicon grade Kr1 — a source of silicon in the coating.
6. I_2— metallic iodine — activator of the saturation process.
7. NH_4Cl — ammonium chloride — activator of the saturation process.

In order to find compositions of SHS powder mixtures that provide high wear resistance, a full factorial experiment was used.

The choice of the optimal composition of the mixture for carrying out SHS processes under conditions of thermal self-ignition was carried out on the basis of the results of studies of the thermal picture of the SHS process and the physical and mechanical properties of protective coatings, in particular wear resistance, ΔG (test on the SMT-1 thorn machine, τ test — 5 h) [5—6, 12].

Optimization options:

Y_1 — wear resistance indicators, $\Delta G\ \tau_{исп}$ 5h, for system B alloyed with boron;

Y_2 — wear resistance indicators, $\Delta G\ \tau_{исп.}$5h, for a system alloyed with silicon Si.

The following were chosen as independent variables: the content of the chromium component, silicon, boron and aluminum in the SHS mixture. Steel 50 was chosen as the starting material. The process activators are I_2 and NH_4F for all systems.

The calculated levels of variation intervals, the nature of their changes and coding schemes are presented in Tabl. 1 and 2. The introduction of more than 5 % of the gas transport agent into the mixture leads to a strong etching of the sample surface, less than 1 % does not activate all gas transport reactions.

To obtain a 100 % composition of SHS powder mixtures, Al_2O_3 was used as the final product.

Table 1. Investigated factors for the chromium-aluminum-boron system

Characteristic	Факторы		
	Al %, wt.	B %, wt.	XC %, wt.
The code	X_1	X_2	X_3
Main level	10	10	20
Variation interval	5	5	5
Lower level	5	5	15
Upper level	15	15	25

Table 2. Investigated factors for the chromium-aluminum-silicon system

Characteristic	Факторы		
	Al %, wt.	Si %, wt.	XC %, wt.
The code	X_1	X_2	X_3
Main level	10	12	20
Variation interval	5	5	5
Lower level	5	7	15
Upper level	15	17	25

As a result of the regression analysis, a number of equations were obtained showing the dependence of the wear resistance of protective coatings on the mode of thermal self-ignition and the content of alloying elements.

As a result of calculations, the following equations were obtained

$$Y_1 = 77{,}444 - 0{,}9X_1 + 1X_2 - 3{,}1X_3 - 0{,}0556X_1^2 + 3{,}4444X_2^2 + 1{,}9444X_3^2 + 0{,}125X_1X_2 - 0{,}125X_1X_3 - 1{,}875X_2X_3; \tag{1}$$

$$Y_2 = 107{,}04 - 0{,}3X_1 + 3{,}8X_2 - 3X_3 - 0{,}0556X_1^2 + 1{,}4444X_2^2 + 6{,}4444X_3^2 + 0{,}125X_1X_2 - 0{,}375X_1X_3 - 1{,}875X_2X_3. \tag{2}$$

The numerical values of the regression coefficients and their significance, determined taking into account the difference in variances for each response function, as well as the significance test by the Student's criterion and the evaluation of the adequacy of the model by the Fisher criterion are presented in Tabl. 3.

Table 3. Results of regression analysis of experimental data

Parameter	Response Function	
	Y_1	Y_2
b_0	77,444	107,04
b_1	-0,9	-0,3
b_2	1	3,8
b_3	-3,1	-3
b_4	-0,0556	-0,0556
b_5	3,4444	1,4444
b_6	1,9444	6,4444
b_7	0,125	0,125
b_8	-0,125	-0,375
b_9	-1,875	1,875
Δb	2,028	5,58
t-criterion	2,78	2,78
F-criterion	1,51<6,59	5,61<7,70

Checking the adequacy of the models shows that they can be used to predict the values of the response functions for any values of the factors that are between the upper and lower levels. To do this, it is advisable to switch to natural variables using the translation formula presented in the following form

$$X_{ij}^{k} = \frac{X_{ij}^{n} - X_{ij}^{o}}{\Delta_i}, \tag{3}$$

where X_{ij}^{k} — coded value of the studied *i*-th factor in the *j*-th equation; X_{ij}^{n} — natural value of the studied *i*-th factor in the *j*-th equation; X_{ij}^{o} — value of the studied *i*-th factor in the *j*-th equation at the main level; Δ_i — value of the variation interval of the studied *i*-th factor.

If we replace the variables X_i in equations (1—2) with the right side of equation (3) and then reduce similar ones, we get natural equations that describe the effects of the thermal self-ignition mode and the content of alloying elements on the wear resistance of protective coatings:

$$Y_1 = 77{,}444 - 0{,}9Al + 1B - 3{,}1XC - 0{,}0556Al^2 + 3{,}4444B^2 + 1{,}9444XC^2 + 0{,}125\,AlB - 0{,}125AlXC - 1{,}875BXC; \tag{4}$$

$$Y_2 = 107{,}04 - 0{,}3\,Al + 3{,}8\,Si - 3\,XC - 0{,}0556\,Al^2 + 1{,}4444\,Al^2 + 6{,}4444\,XC^2 + 0{,}125\,AlSi - 0{,}375\,AlXC - 1{,}875\,SiXC. \tag{5}$$

To assess the adequacy of the equations, a calculation was carried out using the obtained regression equations for the optimal mode of thermal self-ignition. The calculation results were compared with experimental studies. As can be seen from Tabl. 4, the error between the calculated and experimental values of the response function does not exceed 5.

Table 4. Ratio of calculated and experimental data

Indicator	Calculated value	Experimental	Error
ΔG(B)	84,903	85	0,09
ΔG(Si)	105,4	105	0,4

In order to determine the mode and SHS compositions that provide optimal indicators of wear resistance of coatings, three-dimensional graphical dependencies were built (Fig. 1—2).

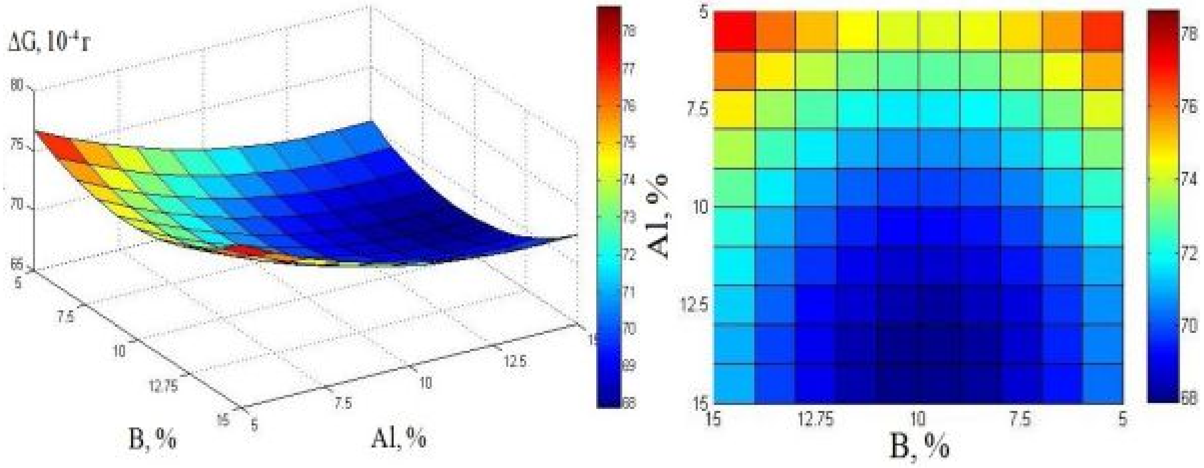

Fig. 1. Optimization of the wear resistance of the surface layer for the Cr-Al-B system: the effect of boron and aluminum content on the wear resistance of steel 50 with a protective intermetallic coating

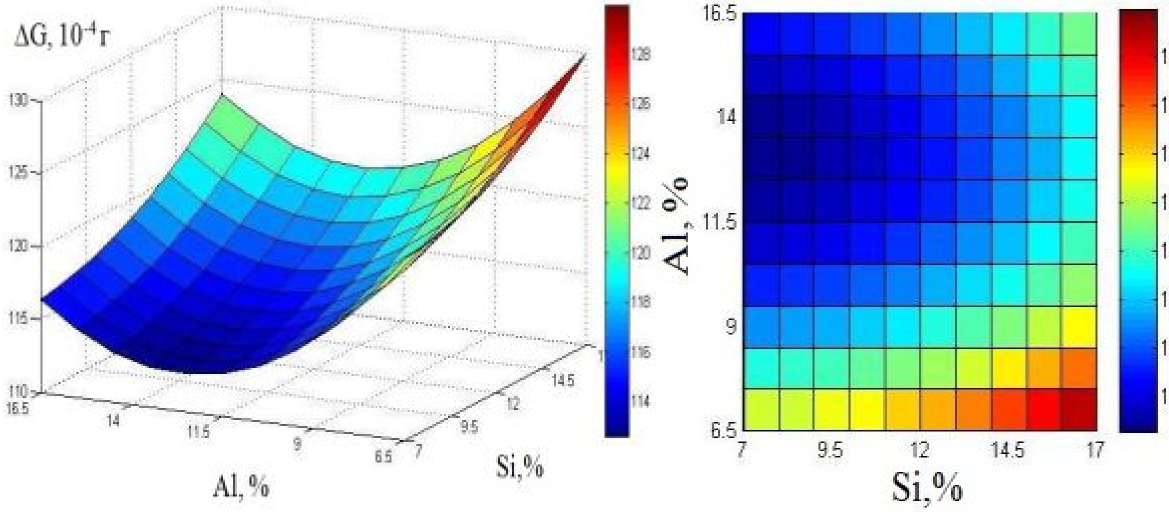

Fig. 2. Optimization of the wear resistance of the surface layer for the Cr-Al-Si system: the effect of boron and chromium content on the wear resistance of steel 50 with a protective intermetallic coating

Research results and discussion. An analysis of the reactions occurring during the SHS process, as well as the results of experiments and metallographic studies, made it possible to obtain a scheme for the formation of protective coatings. The process of formation of protective coatings in the mode of thermal self-ignition can be conditionally divided into five stages — inert heating of the SHS mixture to the temperature of self-ignition, thermal self-ignition, heating of parts, isothermal exposure and cooling.

At the initial stage (stage 1), inert heating of the mixture occurs. When a diffusing element, boron or silicon, is used as a supplier, the formation of a borated or siliconized layer is observed.

At stage 2 — the stage of thermal self-ignition, the self-ignition temperature rises at a rate of 200—400 °C/s to a maximum value. At this stage, along with the formation of active boron and silicon atoms, reactions occur for the formation of elemental chromium and their combination with carriers (fluorine, chlorine and iodine), with the formation of volatile halides. If the activation energy of the interaction of the elements of the charge with the carrier is less than the activation energy of the main reduction process, then the formation of volatile halides will proceed quasi-stationary as the main reaction proceeds. If the self-ignition temperature is lower than the temperature at which the volatile halide begins to form intensively, then for this case, the formation of halides occurs only at the stage of unsteady temperature growth. When the maximum temperature is reached, which converts the pyrolysis temperature of chromium diiodide, silicon, its rapid decay occurs.

At stage 3 — the stage of heating products, the temperature drops to the process temperature Tp due to the reception of the released heat by the products. Active atoms begin to diffuse into the substrate and the carbide phases are alloyed with boron and silicon. Doped boride and silicide phases begin to form.

At stage 4 — the stage of isothermal exposure, a constant diffusion flow of formed active atoms of chromium, aluminum, silicon and boron is formed. The diffusion layer increases and the chromium aluminized layers are doped with boron and silicon. With an increase in isothermal exposure, an increase in the layer thickness occurs. The growth of the layer obeys a parabolic law.

At the 5th stage — the stage of cooling, a diffusion layer is formed with a lower intensity due to a decrease in the diffusion coefficient of silicon and boron due to a drop in temperature. The layer consists of two phases: the outer one, which is chromium borides and silicides, and the inner one, the carbide phase.

Studies have shown that such a high rate of coating formation can be explained by the fact that austenite formed during high-speed heating due to the stage of self-ignition is characterized by a high structure defect and fine grain size, which sharply increases its diffusion susceptibility to saturable elements. Thus, it is possible to control both the layer growth rate and their phase composition and structure. The main factors influencing the kinetics of the formation of protective layers are the composition of the SHS charge, the amount of the chromium component, the time of isothermal holding, the composition of the treated steel, and the type of SHS process taking place in the combustion mode or in the thermal self-ignition mode. On fig. 3 shows the microstructures of chromium-alloyed coatings alloyed with boron, titanium and silicon, obtained in the mode of thermal self-ignition in optimal mixtures. According to the results of a metallographic study, on a Neophot-21 microscope, and X-ray diffraction analysis, it was found that chromium-alloyed coatings doped with boron, silicon, and titanium contain in their composition, in addition to the main phase (Fe_3Al, $(FeCr)_{23}C_6$, $(FeCr)_7C_3$, $(FeCr)_3C$, Cr_3C; Fe_2Al_5, When applying chromium-aluminated layers doped with boron, the coating consists of single-phase doped layers of the type $(FeCrAl)_2B$.

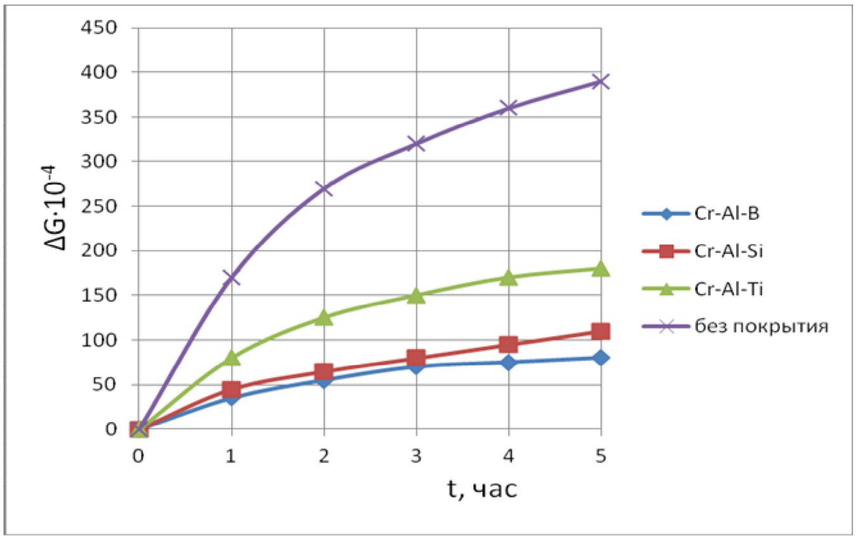

Fig. 3. Effect of test time on the wear resistance of intermetallic coatings on steel 50 when tested on a friction machine SMT-1

When applying chromium-alloyed layers doped with silicon, a layer is formed on the surface $(FeCrAl)_3C$ on materials with a high carbon content (steel 50, U8A), carbides are formed $(FeCr)_{23}C_6$. The layer is immediately adjacent to a carbon-rich transition zone, which is formed due to counter-diffusion of carbon, and behind it is a carbon-depleted ferrite zone.

The result obtained correlates with the hardness of the hardened zones. With increasing hardness, wear resistance increases. Hardness was measured on transverse sections on a PMT-3 device, according to the standard method. With an increase in the carbon content in steels, the microhardness of the surface layer increases. The microhardness of the surface layer during chromoaluminoboration is 15000 MPa, and on steel U8A 16000 MPa (phases $(Fe,Cr,Al)_2B$). With chromoaluminosiliconization $(Fe,Cr,Al)_3Si$ = 13500, and on U8A steel 14500 MPa.

When tested under conditions of sliding friction, chromoaluminoborated coatings have the best wear resistance among the coatings under consideration. Their wear resistance is 4.8—5 times higher than that of uncoated samples, chromoaluminosilicated and chromoaluminum-titanized 2.1—3.5 times. As can be seen from Fig. 3, the wear resistance for the considered friction pairs depends on the microhardness of the layer.

Conclusions

Modeling was carried out to search for optimal SHS powder mixtures to obtain intermetallic wear-resistant protective coatings on steel 50 and U8A using the technology of self-propagating high-temperature synthesis. The structures of protective layers and their wear resistance under sliding friction conditions have been studied. The best wear resistance, among the coatings under consideration, is chromoaluminoborated coatings. Their wear resistance is 4.8—5 times higher than that of uncoated samples, chromoaluminosiliconized and chromoaluminum-titanized 2.1—3.5 times

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МАТЕМАТИЧНЕ МОДЕЛЮВАННЯ ОТРИМАННЯ ЗНОСОСТІЙКИХ ПОКРИТТІВ З ВИКОРИСТАННЯМ ТЕХНОЛОГІЇ САМОРОЗПОВСЮДЖУВАЛЬНОГО ВИСОКОТЕМПЕРАТУРНОГО СИНТЕЗУ

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Реферат

У роботі розглянуто способи отримання хромоалітованих покриттів та представлено нову технологію формування захисних шарів на сталях в умовах саморозповсюджувального високотемпературного синтезу. З використанням методів математичного моделювання при отриманні зносостійких покриттів на деталях машин в умовах саморозповсюджувального високотемпературного синтезу розроблено оптимальні склади СВС сумішей. Алюмінування хромом може проводитися послідовно, хромувати, а потім алітувати. Дифузійне хромування є одним із прогресивних технологічних процесів хіміко-термічної обробки, що дає можливість отримувати матеріал з особливими фізико-механічними властивостями і водночас знизити вартість дорогих і важкооброблюваних сталей за рахунок використання більш економічні вуглецеві сталі.

Метою роботи є пошук оптимальних СВС порошкових сумішей, що дозволяють утворювати інтерметалічні захисні шари на сталі 50 та У8А в умовах саморозповсюджувального високотемпературного синтезу, дослідження структури захисних шарів та їх зносостійкості під тертя ковзання.

Отриманий результат корелює з твердістю загартованих зон. Зі збільшенням твердості підвищується зносостійкість. Твердість вимірювали на поперечних зрізах на приладі ПМТ-3 за стандартною методикою. Зі збільшенням вмісту вуглецю в сталях зростає мікротвердість поверхневого шару. Мікротвердість поверхневого шару при легуванні бором становить 15000 МПа, а на сталі У8А 16000 МПа (фази (Fe,Cr,Al)2B). При легуванні кремнієм (Fe,Cr,Al)3Si = 13500, а на сталі U8A 14500 МПа.

Вивчення зносостійкості хромоалітованих шарів на сталях 50 і У8А, легованих бором і кремнієм, дозволяє говорити про підвищення зносостійкості деталей машин і механізмів у 2—3 рази.

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