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## EFFECT OF MICROPARTICLES OF TITANIUM DIBORIDE AND NANOPARTICLES OF TITANIUM CARBONITRIDE ON THE STRUCTURE AND PROPERTIES OF DEPOSITED METAL

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Formation of composite structure in a wear-resistant metal obtained by introduction of refractory microparticles of titanium diboride and nanoparticles of titanium carbonitride charged with powder wire into the molten pool is considered. Dependences of the hardness and abrasive wear resistance of the deposited metal on the content of powder titanium diboride and carbon in the charged powder wire are determined.

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**Key words:** electroslag deposition, composite structure, titanium diboride, titanium carbonitride, powder wire, abrasive wear resistance.

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### INTRODUCTION

The operating properties of parts of oil- and gas-field, road-building, mining, and other equipment intensely wearing under the action of abrasive ambients can be raised by using processes of electroslag deposition (ESD) of wear-resistant alloys. At the same time, weld deposition of traditional alloys with a typical structure of natural composite does not provide enough wear resistance of parts under intense action of a set abrasive. Deposited materials with structure of artificial composite are more resistant to abrasive wear. Such materials can be obtained using covered electrodes (YuK-12, Bkh-2, KhR-19, etc.) [1, 2], filler powder mixtures (Bkh, KBKh, KhFV-10, etc.) [2, 5], and strip and tubular welding fillers. However, the manual method of deposition recommended for forming quality deposited metal are low efficient. Powder wires (PW) containing refractory hard components in the filler are more effective [3, 4]. Wires of the known compositions containing scarce and expensive constituents (WC, WC<sub>2</sub>, W<sub>2</sub>B<sub>5</sub>) and other less effective materials (CrB<sub>2</sub>) have not found wide application in the industry.

Sparingly alloyed PW specially developed for the electroslag process guarantee the transition of refractory hard microparticles into the deposited metal. It seems expedient to use titanium diboride (TiB<sub>2</sub>) in the composition of such PW filler for such particles. Titanium diboride possesses high physical and mechanical properties, is stable in steel and iron melts, and has a comparatively low cost.

In order to raise the wear resistance of deposited metal it is also expedient to use nanosize particles of titanium carbonitride (TiCN) in the composition of the PW filler. This is confirmed by the known data on elevation of the strength and ductility properties of nitrogen-alloyed alloys containing fine dispersed segregations of titanium carbonitride in the structure [6, 7] and of hypoeutectic cast irons inoculated with nanoparticles of TiCN [8].

The aim of the present work consisted in studying the effect of microparticles of TiB<sub>2</sub> and nanoparticles of TiCN contained in the PW filler on formation of the structure of an artificial composite and on the properties of electroslag-deposited wear-resistant metal.

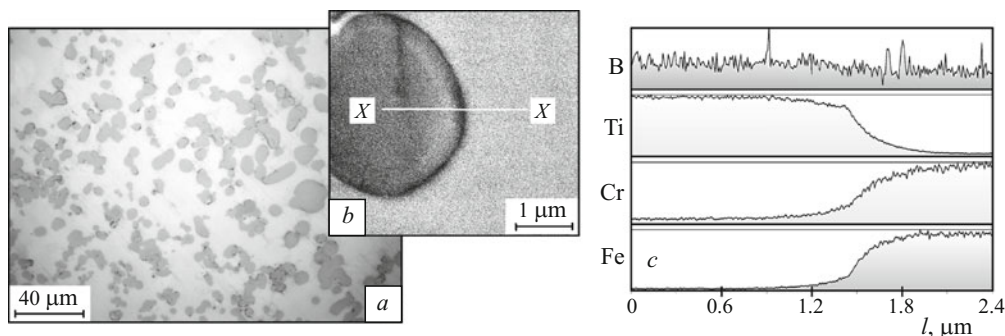
### METHODS OF STUDY

The specimens of deposited metal were obtained by electroslag deposition with the use of PW and a current-conducting mold, in which the hollow nonconsumable electrode and one of the sections were connected to the electrical network through a two-loop circuit [9]. Powder wire was fed into slag ANF-6 through the hollow electrode in an electrically neutral mode, which eliminated functional dependence of the rate of melting of the wire on the electrical parameters of the process of the deposition. This also made it possible to provide dozed heat input into the wire by varying the temperature of the near-electrode volume of the slag for uniform melting of the wire and lowering the degree of dissolution of the refractory particles contained in the molten drops.

The components for the powder filler of the experimental PW 3.8 mm and 3 mm in diameter with volume efficiency of

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**Fig. 1.** Microstructure of the metal with deposited PW 20Kh7G12N2 containing 28 wt.%  $\text{TiB}_2$  (a); inclusion of  $\text{TiB}_2$  in the metal with deposited PW 100Kh10N4 containing 25 wt.%  $\text{TiB}_2$  (b); distribution of chemical elements in the ‘boride (Fe, Cr)B – boride  $\text{TiB}_2$ ’ cross section over axis  $X-X$  ( $l$  is the length of the scanning line) (c).

0.65 and 0.5, respectively, were designed so as to obtain matrix alloys of two types (see Table 1).

The envelope of the wire was made of steel strip 08kp; the fillers were powders of metallic manganese Mn977, nickel ПНÉ-1, ferrochrome FKh010A, graphite GSM-2, and titanium diboride with a mean size of particles  $d_m = 10$  and  $35 \mu\text{m}$ . To inoculate the deposited metal, the mix of the tested PW was enriched with 2 wt.% composite powder consisting of nickel micropowder with particles less than  $60 \mu\text{m}$  in size (70 wt.%) and ultrafine particles of TiCN less than  $80 \text{nm}$  in size (30 wt.%).

The structure and the micromorphology of the deposited metal were studied using an Axiovert 40 MAT light microscope and a Quanta 200 3D scanning electron microscope. The content and the distribution of the alloying elements in the structural components were determined by means of energy dispersive analysis (an EDAX system). The phase composition of the metal was determined by x-ray diffraction analysis in copper radiation using a DRON-3M diffractometer. The topography of the surface of polished sections was studied with the help of a Solver Pro scanning probe microscope in the mode of half-contact atomic force microscopy. The probes were silicon cantilevers with tip sharpness of  $10 \text{nm}$ .

The hardness of the deposited metal was measured by the Rockwell method using a TK-2M device at a load of  $1.47 \text{kN}$ . The microhardness of the structural components was measured using a PMT-3 device by indenting a Vickers

diamond pyramid at a load of  $0.98$  and  $1.96 \text{N}$ . The tests of experimental specimens for abrasive wear were performed in the mode of friction against rigidly fastened abrasive in a Kh4-B-type machine. The static load on the specimen contacting the abrading surface (sandpaper P100) was  $936 \text{MPa}$ . The loss in the mass of the tested specimens and of the standard (annealed steel 45) was measured accurate to  $0.1 \text{mg}$  using a VSL-60/<F255D>0.1A analytical balance.

## RESULTS AND DISCUSSION

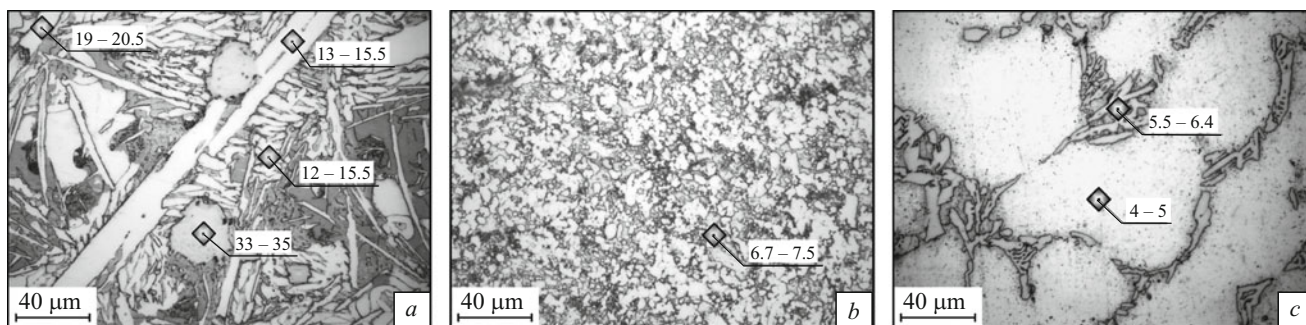
The structure of the deposited metal contained uniformly distributed inclusions (Fig. 1a) with microhardness of  $33.5 - 35 \text{GPa}$ , which were identified as particles of  $\text{Ti}_2\text{B}$  passed into the deposited metal from the PW filler.

The particles of  $\text{TiB}_2$  interacted actively with the metallic melt, and their finest fraction dissolved already in the stage of formation of a drop at the end of the wire at the moment when the temperature of the melt and the free energy of  $\text{TiB}_2$  were the highest. When the drops passed into the pool, the temperature and the intensity of the motion of the metallic melts decreased and so did the rate of dissolution of the  $\text{TiB}_2$  particles; a composite structure formed during crystallization in the deposited metal. Since the particles of  $\text{TiB}_2$  serve crystallization centers in the matrix melt, coarse primary crystallites of other borides and carboborides form around them. The distribution of alloying elements in the zone of the interaction between a particle of  $\text{TiB}_2$  and the (Fe, Cr)B boride formed around it (Fig. 1b and c) reflects the occurrence of diffusion processes in the transition zone about  $0.8 \mu\text{m}$  long and formation of strong chemical bonding between these borides.

If the composition of the wire filler includes chromium, which is a surface-active element, the contact angle of wetting of the  $\text{TiB}_2$  particles with the steel decreases considerably. Under such conditions their interaction with the metallic melt is activated and its intensity is determined by the thermodynamic parameters of the ‘ $\text{TiB}_2$  – metallic melt’ sys-

**TABLE 1.** Types of Tested PW

Type of PW	Matrix of deposited metal	Content of $\text{TiB}_2$ in the filler, wt.%
1	20Kh7G12N2	8
		18
		28
2	100Kh10N4	25
	200Kh10N4	
	300Kh10N4	



**Fig. 2.** Microstructure and microhardness (GPa) of deposited metal with matrix 20Kh7G12N2 at TiB<sub>2</sub> content of 28 (a), 18 (b), and 8 wt.% (c) in the wire filler.

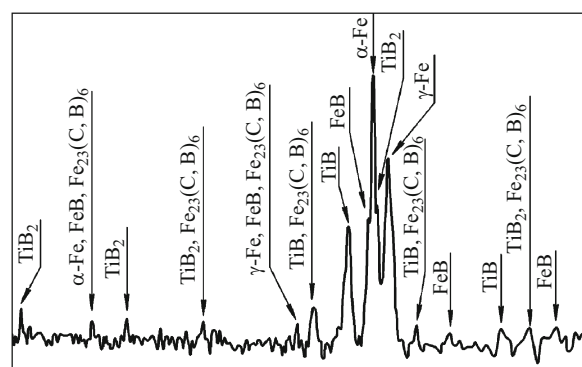
tem and by the area of the interphase interaction that depends on the specific surface  $S_{sp}$  of the boride powder.

It has been shown that the sizes of the TiB<sub>2</sub> inclusions (2 – 30 μm) in the deposited metal increases upon growth in the mean size of the TiB<sub>2</sub> particles in the PW filler and upon increase in the mass fraction of the TiB<sub>2</sub> powder in it. The latter circumstance seems to be a result of the fact that growth in the content of TiB<sub>2</sub> powder, which possesses a high specific heat capacity [168 J/(kg · K) at 1073 K] as compared to the alloyed chromium-nickel steel [586 J/(kg · K) at 1373 K], elevates the consumption of heat for heating the metallic drops containing refractory particles. They become microscopic refrigerators lowering the superheating of the molten metal of the drops and the degree of dissolution of the TiB<sub>2</sub> powder in the melt. Growth in the mean size of the boride particles in the filler of the wire from 10 to 35 μm is accompanied by substantial increase in the content of the TiB<sub>2</sub> inclusions in the deposited metal. This is explainable by lowering of the intensity of their dissolution in the slag and in the metallic melts due to the decrease in the specific surface  $S_{sp}$  of the powder.

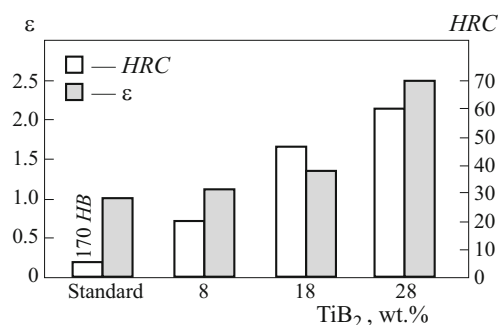
Metallographic analysis has shown that the structural and phase composition of the deposited metal with matrix of type 20Kh7G12N2 differ substantially at different contents of the boride introduced into the wire. At 28 wt.% TiB<sub>2</sub> the metal has a hypereutectic structure (Fig. 2a). The boride eutectic based on α-Fe and retained austenite has a microhardness of 12 – 15.5 GPa. In addition to TiB<sub>2</sub> (Fig. 3) the deposited metal contains excess segregations of TiB and inclusions of Fe<sub>23</sub>(C, B)<sub>6</sub> and FeB in the form of coarse and fine light-colored needles with microhardness 14.6 – 19.7 GPa. The elevated hardness (58 – 61 HRC) of the deposited metal (Fig. 4) is a result of the high hardness of the structural components.

Decrease in the mass fraction of the TiB<sub>2</sub> powder in the filler of the wire to 18 wt.% causes formation of a eutectic structure with reduced microhardness (6.7 – 7.5 GPa) and considerable fineness (see Fig. 2b). The hardness of the deposited metal is also reduced and amounts to 45 – 48 HRC.

When the content of TiB<sub>2</sub> in the wire is decreased to 8 wt.%, the structure of the deposited metal is represented by



**Fig. 3.** Diffractogram of the metal with deposited PW 20Kh7G12N2 containing 28 wt.% TiB<sub>2</sub>.

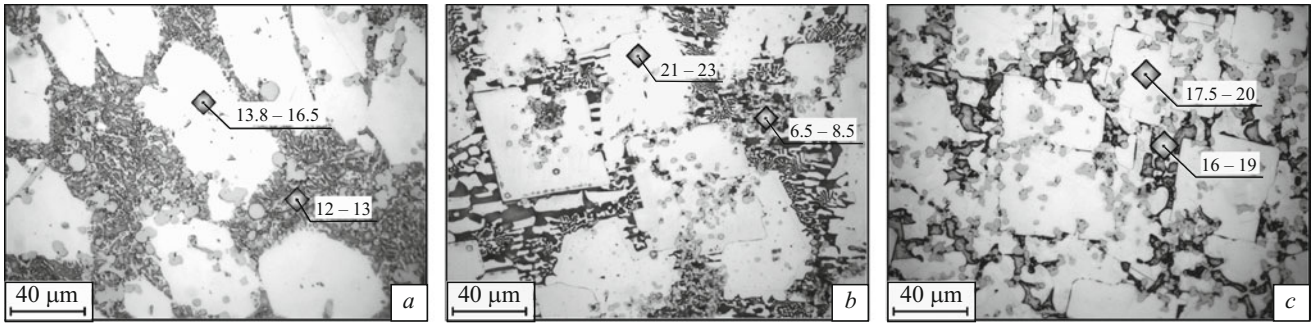


**Fig. 4.** HRC hardness and relative wear resistance  $\varepsilon$  (against a standard of annealed steel 45) of deposited metal as a function of the content of TiB<sub>2</sub> in the filler of PW 20Kh7G12N2.

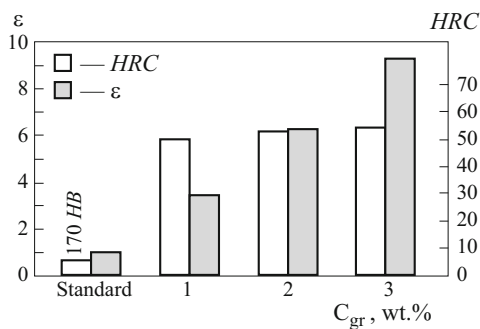
grains of alloyed austenite with microhardness 4 – 5 GPa surrounded with a crushed boride eutectic (see Fig. 2c). Its hardness is very low (17 – 20 HRC) due to the low content of eutectic in the soft and ductile austenite matrix.

The abrasive wear tests have shown (Fig. 4) that a 3.5-times increase in the content of TiB<sub>2</sub> in the PW filler causes only 2.5-times increase in the relative wear resistance of the deposited metal. This may be explained by the high brittleness of the matrix of the alloy, which is incapable of reliable fixing and keeping of the hardening phases of borides





**Fig. 5.** Microstructure and microhardness (GPa) of the metal with 100Kh10N4 matrix and content of graphite in the filler equal to 1 (a), 2 (b), and 3 wt.% (c).



**Fig. 6.** Dependences of the hardness  $HRC$  and relative wear resistance  $\varepsilon$  (against a standard of annealed steel 45) of deposited metal on the content of graphite  $C_{gr}$  in the charge of the wire (at 25 wt.%  $TiB_2$  in the filler of the wire).

and carboborides of lamellar and acicular shape, which play the role of stress concentrators [10].

In order to increase the volume fraction of the hardening solid phase and to provide bonding the titanium segregated in the metallic phase upon dissolution of  $TiB_2$  particles, we changed the content of graphite in the filler of the wire in a range of 1 – 3 wt.% at a constant content of  $TiB_2$  in the latter (25 wt.%). The elevated content of carbon promoted growth in the content of the segregated hard phases in the deposited metal, the volume fraction of which, including the  $TiB_2$  particles, amounted to 60, 74, and 92 vol.% at 1, 2, and 3 wt.% graphite in the wire, respectively.

In the whole of the carbon range the structure of the deposited metal was hypereutectic and contained different contents of primary borides  $(Fe, Cr)B$  and carboborides  $(Fe, Cr)(C, B)$  (Fig. 5). Inclusions of  $TiB_2$  were present both in the eutectic matrix of the alloy and in the coarse crystals of the hardening phase. The deposited metal contained globular inclusions of  $TiC$  carbide (2 – 5  $\mu m$  in size) segregated from the melt and a composite carboboride  $(Ti, Fe)(C, B)$ .

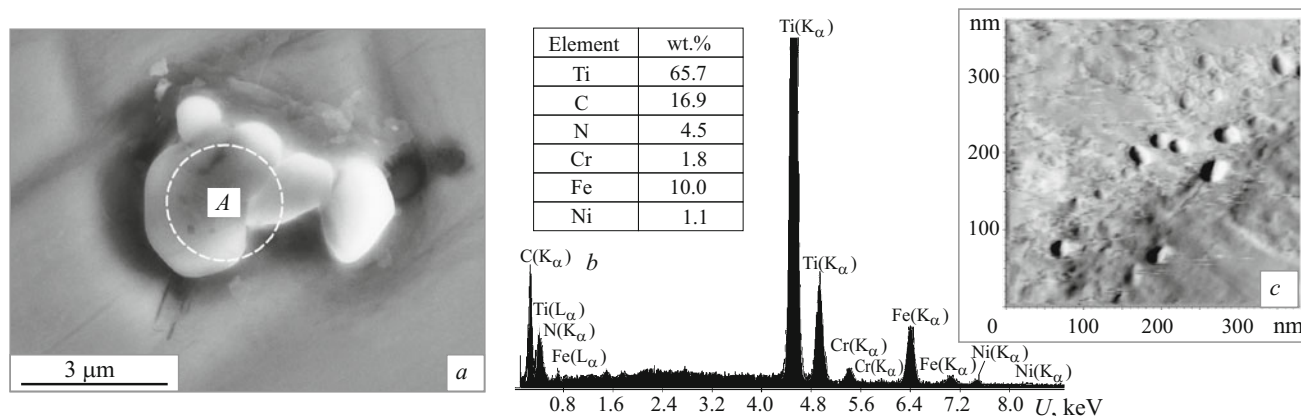
The hardness of the deposited metal increased upon growth in the graphite content in the PW filler from 1 to 3 wt.% from 50 to 54  $HRC$ . The microhardness of the iron-chromium borides and carboborides in the metal coated with PW 100Kh10N4 with 25 wt.%  $TiB_2$  in the filler va-

ried within 13.8 – 16.5 GPa; that of the eutectic varied within 12 – 13 GPa (Fig. 5a). Upon growth in the graphite content in the wire charge to 2 wt.%, the microhardness of the coarse crystals of the hardening phase increased to 21 – 23 GPa; that of the eutectic decreased to 6.5 – 8.5 GPa (Fig. 5b). When the graphite content was increased to 3 wt.%, the microhardness of the crystals of  $(Fe, Cr)(C, B)$  and  $(Fe, Cr)B$  decreased to 17.5 – 20 GPa (Fig. 5c). These crystals took virtually the entire volume of the deposited metal and were surrounded by a net of a carboboride eutectic with microhardness of 16 – 19 GPa.

We established that the increase in the carbon content provided growth in the wear resistance of the composite alloy due to formation of a large content of  $(Fe, Cr)(C, B)$  iron-chromium carboborides that possess enhanced resistance to the action of the abrasive as compared to  $FeB$  and  $Fe_{23}(C, B)_6$  and play, to some extent, the role of a matrix for the high-hardness particles of  $TiB_2$ ,  $TiC$ , and  $(Ti, Fe)(C, B)$  uniformly distributed in the volume of the deposited metal. The formation of a composite structure with high volume fraction of hardening phases increases the relative wear resistance of the deposited metal to 9.3 (Fig. 6).

To improve the weldability of the deposited metal we inoculated it with nanoparticles of titanium carbonitride  $TiCN$ . The ultrafine particles of  $TiCN$  affected the processes of crystallization of the metallic melt and changed the composition, morphology, distribution, and sizes of the excess phases. We detected considerable growth in the content of fine (up to 6  $\mu m$ ) inclusions represented by hard particles of titanium carbide, carbonitride, and nitride ( $TiC$ ,  $TiCN$ , and  $TiN$ ). The content and the sizes of the crystals of the  $(Fe, Cr)(C, B)$  carboboride and  $(Fe, Cr)B$  boride decreased, and the volume of the eutectic component in the metal increased.

The process of electroslog deposition is accompanied with dissolution and coagulation of a part of the nanosize particles of  $TiCN$  and subsequent formation of colonies of irregular particles 1 – 3  $\mu m$  in size (Fig. 7a and b). The nitrogen freed in an amount not exceeding 0.025 wt.% participated in formation of coarser inclusions of  $TiN$  titanium nitride 3 – 10  $\mu m$  in size segregated from the melt and visi-



**Fig. 7.** Electron image (a) ( $\times 26,000$ ) of a colony of TiCN particles, spectrogram of the content of elements in range “A” (b), and topography of the surface of the specimen (c).

ble in polished sections as trapeziums and squares. Using atomic force microscopy we established that the deposited metal contained inclusions 15 – 50 nm in size (Fig. 7c). It seems that a certain part of the particles of TiCN does not dissolve in the melt, and they become crystallization centers for other titanium compounds.

The relative wear resistance of the inoculated deposited metal has more than doubled as compared to the base alloy (PW 200Kh10N4 containing 25 wt.% TiB<sub>2</sub>) and attained 12.6, which is virtually 5 times higher than the respective parameter of one of the best commercial wear resistant alloys (150Kh15R3T2) with deposited standard PW (Np-170M).

## CONCLUSIONS

1. The content of TiB<sub>2</sub> particles no less than 30 μm in size in the filler of powder wires guarantees that a considerable part of them will pass into the deposited metal upon ESD and form in it a structure of artificial composite with elevated wear resistance under conditions of abrasive wear without impact loads.

2. The dissolution and diffusion processes between the particles of TiB<sub>2</sub>, the matrix of the deposited metal, and the iron-chromium borides and carboborides segregated in the process of its crystallization result in formation of strong chemical bonding between them and reliable fixation of the reinforcing particles in the composite formed.

3. The introduction of a low (up to 0.6 wt.%) content of nanosize particles of TiCN into the filler of the powder wire changes the morphology and composition of the hardening phases, increases the volume fraction of fine inclusions of refractory compounds in the eutectic matrix of the alloy, and thus raises considerably (by more than a factor of 2) the relative wear resistance of the deposited metal.

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## REFERENCES

1. N. A. Grinberg and A. B. Arabei, “Wear resistant fillers and composite materials for reinforcing rubbing surfaces under conditions of abrasive and hydroabrasive wear,” *Svar. Proizvod.*, No. 5, 7 – 9 (1992).
2. E. I. Leinachuk, *Arc Facing of Parts Subjected to Abrasive and Hydroabrasive Wear* [in Russian], Naukova Dumka, Kiev (1985), pp. 23 – 29.
3. V. D. Oreshkin and P. V. Popov, *Wear Resistant Deposited Material*, RF Patent No. 2290288, MPK<sup>7</sup> B 23K 35/36 [in Russian], VolgGASU (No. 2004126303), Appl. 30.08.2004.
4. E. N. Eremin, Yu. O. Filippov, A. E. Eremin, and A. S. Losev, *Powder wire*, RF Patent No. 2356714, MPK<sup>7</sup> B 23K 35/368 [in Russian], Omsk State Eng. University (No. 2007107746), Appl. 01.03.2007.
5. F. A. Kyazymov, V. D. Oreshkin, and E. T. Lobanova, “Interrelation between the wear resistance of carboboride coatings and their physicochemical properties,” in: *Physical Metallurgy and Strength of Materials, Coll. Works* [in Russian], Izd. VolgGTU, Volgograd (2001), pp. 47 – 53.
6. S. N. Popov and A. D. Antonyuk, “Effect of nitrogen on the structure and properties of high-boron carbon wear resistant deposited materials,” *Nov. Mater. Tekhnol. Metall. Mashinost.*, No. 2, 31 – 36 (2009).
7. N. S. Mochalina, *Reinforcing of Steel with Nanosize Segregations of Titanium and Niobium Carbonitrides, Author’s Abstract of Candidate’s Thesis* [in Russian], Novosibirsk (2010), 19 p.
8. G. N. Minnekhanov, O. A. Shuikin, and R. G. Minnekhanov, “Effect of inoculation with nanoparticles of titanium carbonitride and alloying with titanium on the structure and properties of hypoeutectic cast iron,” *Omskii Nauch. Vestn.*, No. 1, 22 – 25 (2009).
9. I. V. Zorin, G. N. Sokolov, A. A. Artem’ev, and V. I. Lysak, “Electroslag deposition on end surfaces of articles using two-circuit feeding of the slag pool,” *Avtom. Svarka*, No. 1, 12 – 16 (2008).
10. A. A. Artem’ev, Yu. N. Dubtsov, and G. N. Sokolov, “A study of the structure and wear resistance of deposited metal reinforced with granules of titanium diboride,” in: *News of the Volgograd State Engineering University, Ser. Problems of Materials Science, Welding and Strength in Machine Building* [in Russian], IUIL VolgGTU, Volgograd (2004), Issue 4, pp. 34 – 36.