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PRODUCING AND PROPERTIES OF DETONATION COATINGS BASED ON FeMoNiCrB AMORPHIZING ALLOY WITH ADDITION OF STRENGTHENING PHASES

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ABSTRACT

The structure and properties of amorphizing composite detonation coatings based on FeMoNiCrB alloy were studied. FeMoNiCrB + ZrB_2, FeMoNiCrB + (Ti, Cr)C, FeMoNiCrB + $FeTiO_3$ composite powders were used for coatings deposition, which were produced from a mixture of the composition powders by mechanical alloying. It is found that as a result of detonation spraying of all the powder compositions, the formed coatings have dense, lamellar, multiphase structure. The coating composition includes Fe(Ni, Cr) solid solutions, Mo_2FeB_2 and Fe_2B borides, dispersed inclusions of alloying additives (ZrB_2, (Ti, Cr)C, $FeTiO_3$) and oxides (ZrO_2 and $FeCr_2O_4$ or Fe_2O_3, or Fe_3O_4), as well as an amorphous phase, the amount of which in the coating structure has increased, as a result of the detonation spraying process. The values of microhardness, corrosion resistance, fatigue life and wear resistance of the composite detonation coatings are given.

KEY WORDS: detonation spraying, composite powders, amorphizing iron alloy, zirconium boride, titanium-chromium carbide, iron titanate, coating, corrosion resistance, wear resistance

INTRODUCTION

The complex of special physicochemical and mechanical characteristics found in materials with amorphous structure, opened broad prospects for their practical use for development of protective coatings operating in the conditions of higher wear and corrosion, as well as for coatings with special properties (magnetic, resistive, radiation resistant, etc.) [1–3].

One of the methods of producing coatings with amorphous structure is thermal spraying of coatings [3].

An important advantage of thermal spraying (TS) in the production of metallic materials with amorphous structure (MMA) over other methods (melt spinning, melt extrusion, producing of thin layers of MMA using laser, evaporation in vacuum, magnetron spraying, etc.), which allow producing foils, strips with a thickness of not more than 10–150 μm, is the possibility of forming layers of coating material with an amorphous structure of up to several mm thickness. The basis of the technology of TS coatings with amorphous structure consists in providing the cooling rate of the melt particles of the sprayed material at the moment of forming the coating on the surface of the base of not lower than the critical value that is characteristic of each amorphizing alloy. Most of such Ni-, Fe- and Co-based alloys have the following characteristics in the range of 10^5–10^6 K/s [1, 3], which is possible to provide in TS conditions by appropriate selection of sizes of the sprayed particles, parameters of the spraying process and cooling system of a product on which the coating is sprayed, when using almost all TS methods (flame, plasma and detonation). However, in flame and plasma spraying, the direct effect of a high-temperature gas jet on the sprayed surface requires the development of special cooling conditions of the spraying zone to avoid reduction in the rate of temperature drop of the sprayed particles below the required one. In this regard, the conditions of detonation spraying are more favorable to provide the cooling rates of the melt of the sprayed particles, necessary for the formation of the amorphous state of the sprayed coating structure. On the other hand, higher velocities of melt particles during detonation spraying at the moment of their hitting against the surface of the base, lead to the formation of deformed weave particles of smaller thickness, which provides higher cooling rates of the sprayed material and promotes amorphization of the coating material.

The accumulated experience of detonation spraying of amorphous coatings showed the prospects and effectiveness of their practical application for restoration of parts of internal combustion engines (ICE) ($Fe_{69}B_{15}C_{10}Si_6$, $Fe_{70}Cr_{10}B_{20}$, $Fe_{70}Cr_{10}P_{13}C_7$), strengthening of parts of metal-cutting machines and the stamp tool ($Fe_{61}B_{37}C_2$, $Fe_{67}Ti_7B_{24}C$, Ni_3B), for protection of parts of chemical mechanical engineering against wear and corrosion ($Fe_{70}Cr_{10}P_{13}C_7$, $Ni_{40}Ti_{40}Si_{20}$) [3]. One of the directions of further development of technologies of detonation spraying of coatings with amorphous structure, which can lead to increase of their service properties and expansion of areas of application, is the development of detonation composite coatings on the basis of alloys with amorphous structure.

The aim of the work was to study the process of structure formation and to determine the properties of detonation coatings from composite powders based

Table 1. Characteristics of source powders

Powder	Particles size, μm	Density ρ, g/cm³	Microhardness, MPa	Phase composition
FeMoNiCrB, (Fe – 36.2; Mo – 29.9; Ni – 23.6; Cr – 7.6; B – 2.7)	63–100	7.84	6170 ± 1170	Solid solution Fe(Ni, Cr), Mo_2FeB_2, Fe_2B, Cr_2B
FeMoNiCrB + ZrB_2	<80	7.42	6020 ± 1280	Solid solution Fe(Ni, Cr), Mo_2FeB_2, ZrB_2, APh
FeMoNiCrB + (Ti, Cr)C	<40	7.283	5650 ± 1100	Solid solution Fe(Ni, Cr), Mo_2FeB_2, (Ti, Cr)C, Cr_3C_2, APh
FeMoNiCrB + $FeTiO_3$	<80	7.52	5050 ± 660	Solid solution Fe(Ni, Cr), Mo_2FeB_2, $FeTiO_3$, APh

on FeMoNiCrB alloy with ZrB_2, (Ti, Cr)C and $FeTiO_3$ additives, produced by mechanical alloying.

OBJECTS OF STUDIES AND PROCEDURE OF EXPERIMENT

For detonation spraying of coatings, composite powders produced by mechanical alloying from a mixture of powder of amorphizing FeMoNiCrB alloy with 30 vol.% of refractory compounds ZrB_2, (Ti, Cr)C and $FeTiO_3$ were used. The method of producing composite powders is described in detail in [4], and their characteristics are presented in Table 1.

Detonation spraying of coatings was performed in the installation "Perun-S" using propane-butane as a detonating mixture (50 % C_3H_8 + 50 % C_4H_{10}) with oxygen in a ratio of 1:3 with the addition of air. As a transporting gas, air was used (Table 2). The spraying distance was constant — 110 mm, the frequency of cycles was 6.6 s^{-1}.

To study the structure and phase composition of the coatings, methods of metallography (microscope Neophot-32, equipped with the attachment for digital filming) were used; X-ray diffraction phase analysis (XDPA) was performed in a DRON-3 diffractometer in CuK_α radiation with a graphite monochromator at a step movement of 0.1° and exposure time at each point of 4 s with the subsequent computer processing of the obtained digital data. Phase identification was performed using the ASTM database.

Corrosion resistance of detonation coatings in the 10 % H_2SO_4, 3 % NaC1 and 5 % NaOH solutions was investigated by the potentiostatic method in the potentiostat P-5827 M at a scanning rate of 2 mV/s using a specially designed clamping cell that provides a one-sided access of the electrolyte to the coating and does not require protection of nonoperating surfaces. As a reference electrode, a silver chloride electrode filled with a saturated solution of potassium chloride was used, and as an auxiliary electrode, platinum served. Preparation of specimens before the corrosion tests was performed according to GOST R 9.905–2007 [5].

According to the experimental values, cathode and anode polarization curves were constructed in the coordinates:

$$E_c = f(\lg i_c),$$

where E_c is the corrosion potential, V; i_c is the current density, A/cm² [6, 7].

The rate and corrosion potential of coatings was determined graphically by polarization curves by extrapolation of Tafel regions of cathode and anode curves to $E = E_c$.

Using the values of corrosion currents determined according to the polarization curves, the weight and depth value of corrosion was calculated by the formulas [6]:

$$K_w = \frac{iA \cdot 1000}{nF},$$

where K_w is the weight index of corrosion, g/m²·h; i is the current density, A/cm²; A is the atomic weight of metal, g/mol; n is the valence of the metal ion that passed into the solution; F is the Faraday number (26.8 A·h/mol).

$$K_d = K_w = \frac{8.76}{\rho},$$

where K_d is the index of corrosion depth, mm/year; ρ is the metal density, g/cm³; 8.76 is the conversion fac-

Table 2. Conditions of spraying detonation coatings

Powder	Consumption of detonation mixture, m³/h			Consumption of transporting gas (air), m³/h
	Propane-butane C_3H_8+ C_4H_{10}	Oxygen	Air	
FeMoNiCrB	0.5	1.55	0.5	0.65
FeMoNiCrB + ZrB_2	0.5	1.55	0.9	0.35
FeMoNiCrB + (Ti, Cr)C	0.5	1.55	0.9	0.35
FeMoNiCrB + $FeTiO_3$	0.5	1.55	0.9	0.35

tor for transition from the weight index of corrosion to the calculation per 1 h to the depth index of up to 1 year, calculated from the number of hours per year (24 h·365 = 8760 h) and divided by 1000.

For the comparative characteristics of corrosion resistance, ten-point evaluation scale was used (GOST 13819–69), based on the use of depth index of corrosion (K_d) [6].

Wear resistance of coatings was studied in the conditions of abrasive wear by friction against a loosely fixed abrasive (GOST 23.208–79) [8]*. As an abrasive material for tests SiO_2 sand with a hardness of 11 GPa and B_4C carbide with a microhardness of 45 GPa were used; the particle size of the powders was 250–300 μm.

The index of wear resistance of the coating was evaluated by the loss of mass of the specimen after the experiment with an accuracy of 0.0001 g. For each type of coating, three specimens were tested.

The relative wear resistance (K_i) was evaluated by the formula [8]

$$K_i = \frac{G_e}{G_i}\frac{\rho_i}{\rho_e},$$

where ρ_e, ρ_i are the densities, and G_e, G_i is the loss of mass of reference and test materials, g.

As a reference specimen, steel 30KhGSA with the hardness *HV* 212–248 was used.

EXPERIMENTAL RESULTS AND DISCUSSION

The study of the microstructure of detonation coatings (Figure 1) showed that during spraying of both powders of the amorphizing FeMoNiCrB alloy as well as composite powders, the coatings are formed which are dense, uniform by thickness and with a lamellar structure, where alternation of light and dark lamellae is observed. The values of microhardness of both dark and light lamellae vary in wide ranges (Table 3), and in general, its higher values for dark lamellae can be noted, where, probably, oxide inclusions are concentrated. If we compare the averaged values of microhardness of coatings depending on the composition, their higher values for CP with (Ti, Cr)C carbide unlike ZrB_2 borides and $FeTiO_3$ oxide can be noted. The same pattern occurs in the case of source CP (Table 1). However, the microhardness of the sprayed coatings appeared to be lower than of the source powders. The reason for this difference probably consists in the different content of the amorphous phase [9].

X-ray structure phase analysis of detonation coatings shows that during spraying of CP of all compositions, an amorphous-crystalline structure is formed, which is evidenced by large areas of "halo" on the X-ray patterns (Figure 2).

The study of the kinetics of electrode potentials of detonation coatings (Figure 3) showed that their values stabilize within 15–40 min after immersion of the specimens in the electrolyte. Thus, in a 3 % NaCl solution with the introduction of additives ZrB_2, (Ti, Cr)C, $FeTiO_3$, the shift of the corrosion potential (E_c) occurs to the more positive direction from –0.35 to –0.28 V and the cathodic reaction of hydrogen evolution inhibits. If in the case of coatings from FeMoNiCrB powder, corrosion currents are in the range of $4\cdot10^{-6}$ A/cm^2, then with the introduction of additives, they are reduced for almost all coatings to $2–3\cdot10^{-6}$ A/cm^2. The absence of passivation of the coating in 3 % NaCl medium may be predetermined by the fact that this solution belongs to the aggressive media with a high content of Cl-, the presence of which gradually displaces oxygen from the protective film to the electrode surface. At the same time, the anode process of forming the pro-

Table 3. Characeristics of detonation coatings

XDPA	Composition	H_μ*, MPa	Characteristics of structure
APh, solid solution Fe(Ni, Cr), Mo_2FeB_2, Fe_2B, Fe_2O_3	FeMoNiCrB	4855 ± 1023	Dense homogeneous structure with hardly noticeable lamellarity and small amount of dark tiny (probably oxide) inclusions (Figure 1, *a*)
APh, solid solution Fe(Ni, Cr), Mo_2FeB_2, ZrB_2, Fe_2B, ZrO_2, $FeCr_2O_4$	FeMoNiCrB + ZrB_2	3830 ± 570	Dense fine-lamellar structure with alternating light and dark gray lamellae, whose microhardness differs slightly (respectively, 3270–4500 and 3040–5590 MPa) (Figure 1, *b*)
APh, solid solution Fe(Ni, Cr), Mo_2FeB_2, (Ti, Cr)C, Fe_2B, Fe_2O_3	FeMoNiCrB + (Ti, Cr)C	4450 ± 700	Dense lamellar structure with light inclusions of rounded shape, microhardness of which changes within the range from 3800 to 5700 MPa (Figure 1, *c*)
APh, solid solution Fe(Ni, Cr), Mo_2FeB_2, $FeTiO_3$, Fe_2B, Fe_3O_4	FeMoNiCrB + $FeTiO_3$	3750 ± 620	Dense fine-lamellar structure with light ($H\mu$ = 2220–4350 MPa) dark gray ($H\mu$ = 3000–3980 MPa) lamellae with a large number of both light and dark gray inclusions (Figure 1, *d*)

*Investigations were carried out at the participation of Cand. of Techn. Sci. V.F. Labunets.

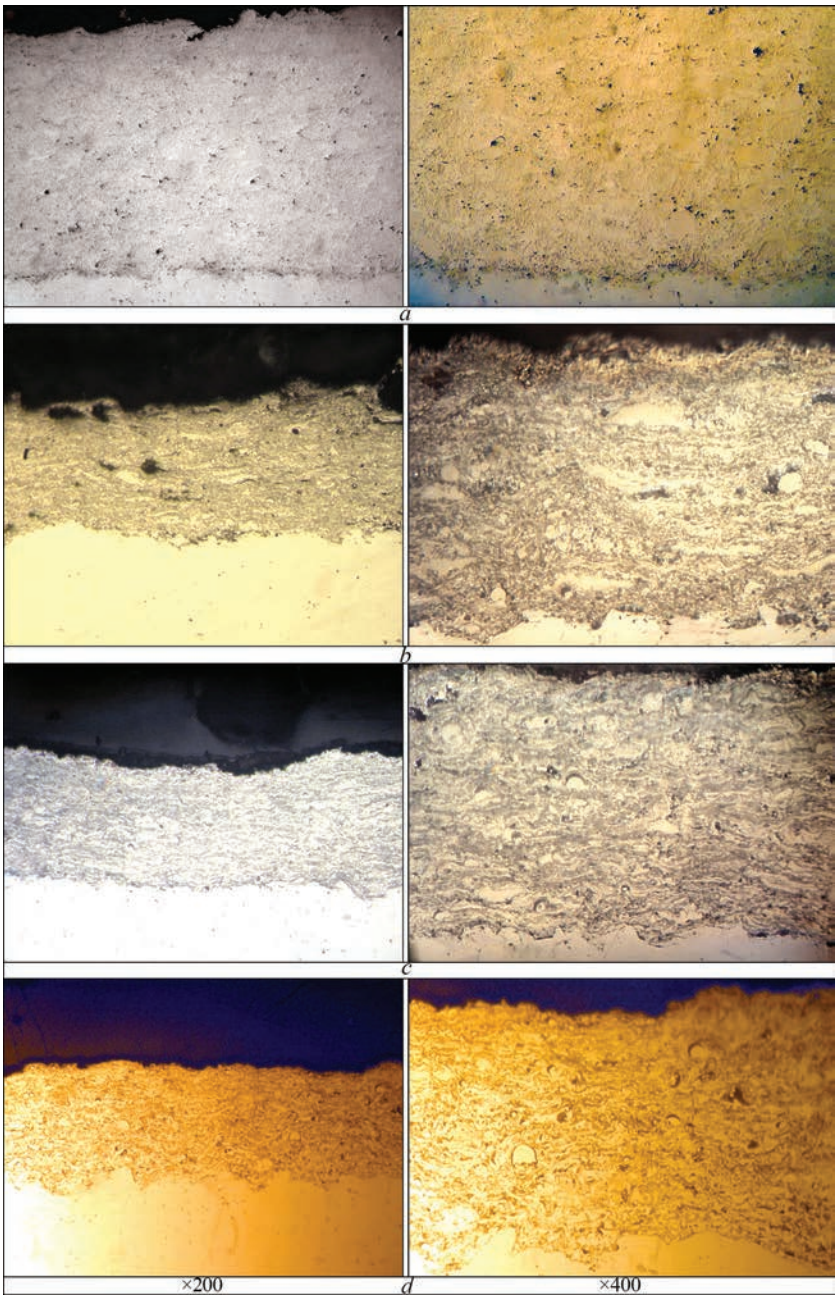

Figure 1. Microstructure of detonation coatings produced from powders FeMoNiCrB (*a*), FeMoNiCrB + ZrB_2 (*b*), FeMoNiCrB + (Ti, Cr)C (*c*), FeMoNiCrB + $FeTiO_3$ (*d*)

tective oxide is slowed down by the anodic process of formation of easily soluble compounds of metals with Cl- [10].

The study of the electrochemical behavior of detonation coatings in the 10 % solution of H_2SO_4 showed that the introduction of ZrB_2, (Ti, Cr)C, $FeTiO_3$ leads to the change of corrosion potential in a more positive direction from –0.12 to –0.044 V, corrosion processes occur with a hydrogen depolarization, corrosion currents are in the range of $1.6–1.8\cdot10^{-5}$ A/cm^2. The obtained anode polarization curves indicate the absence of passivation of coatings in a wide range of potentials. Pure chromium and nickel in sulfuric acid are well passivated [11, 12], while in the coatings, whose source powder includes these metals, they do not transfer into the passive state. This can be explained by the presence of the phases Mo_2FeB_2, ZrB_2, TiC in the layer structure, which are the cathodes relative to nickel and chromium. They prevent the formation of continuous oxide films on the surface of the coatings in the solution of sulfuric acid, as a result of which the system loses the ability to passivate.

Electrochemical studies of detonation coatings in the 5 % NaOH solution show that the introduction of additives ZrB_2, (Ti, Cr)C, $FeTiO_3$ shifts the corrosion potential in the positive direction from –0.48 to –0.34 V and reduces the corrosion currents from $5\cdot10^{-6}$ to $2\cdot10^{-6}$ A/cm^2.

Analysis of the results (Table 4) shows that for all the studied coatings, the maximum corrosion rate

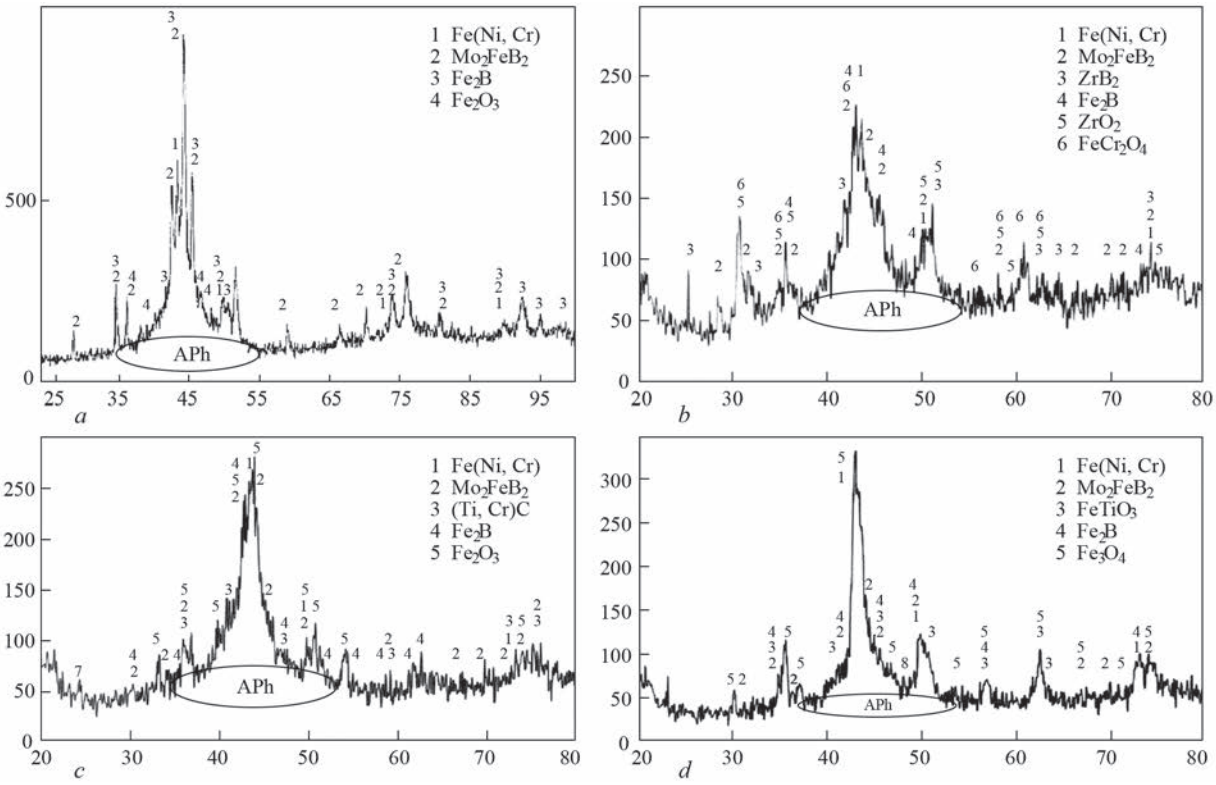

Figure 2. X-ray patterns of detonation coatings produced from powders: FeMoNiCrB (*a*), FeMoNiCrB + ZrB_2 (*b*) FeMoNiCrB + (Ti, Cr)C (*c*), and FeMoNiCrB + $FeTiO_3$ (*d*)

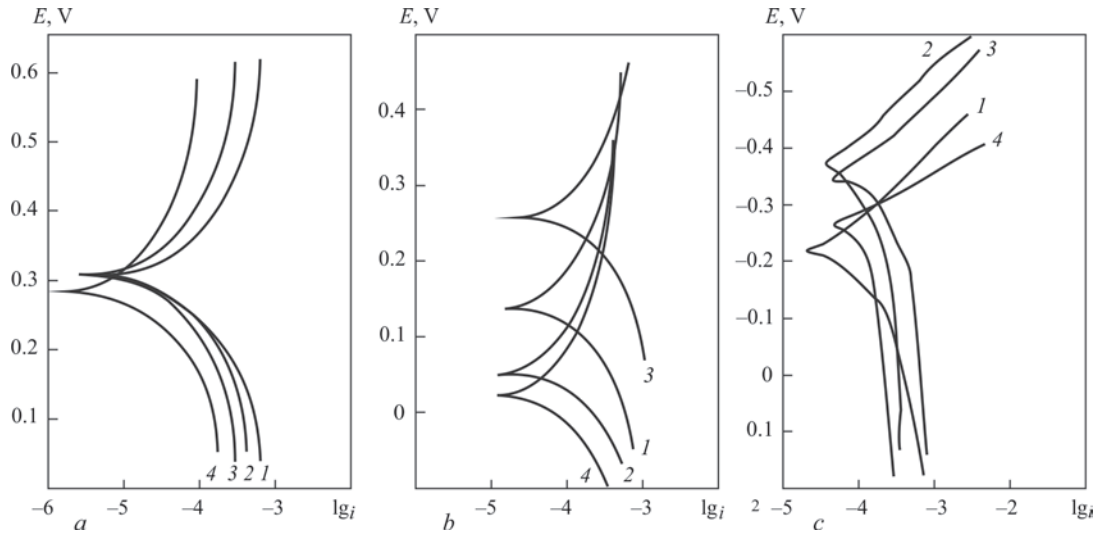

Figure 3. Polarization curves of detonation coatings: *a* — in 3 % NaCl; *b* — in 10 % H_2SO_4 solution; *c* — in NaOH (*1* — FeMoNiCrB; *2* — FeMoNiCrB + ZrB_2; *3* — FeMoNiCrB + (Ti, Cr)C; *4* — FeMoNiCrB + $FeTiO_3$)

Table 4. Results of electrochemical tests of detonation coatings (coating thickness is 500 μm)

Composition of coating	Electrolyte					
	3 % NaCl		5 % NaOH		10 % H_2SO_4	
	E_c, V	i_c, A/cm²	E_c, V	i_c, A/cm²	E_c, V	i_c, A/cm²
FeMoNiCrB	–0.35	$4\cdot10^{-6}$	–0.48	$5\cdot10^{-6}$	–0.12	$1.9\cdot10^{-5}$
FeMoNiCrB +ZrB_2	–0.31	$2.5\cdot10^{-6}$	–0.34	$2\cdot10^{-6}$	–0.24	$1.5\cdot10^{-5}$
FeMoNiCrB + (TiCr)C	–0.33	$3\cdot10^{-6}$	–0.33	$3\cdot10^{-6}$	–0.08	$1.6\cdot10^{-5}$
FeMoNiCrB + $FeTiO_3$	–0.28	$3\cdot10^{-6}$	–0.44	$3\cdot10^{-6}$	–0.04	$1.8\cdot10^{-5}$

Table 5. Indices of corrosion resistance of detonation CP based on FeMoNiCrB

Composition of coating	Corrosion rate index		Service life, year	Point of corrosion resistance	Group of corrosion resistance
	K_w, g/м²h	K_d, mm/ year			
3 % NaCl					
FeMoNiCrB	0.042	0.047	10.6	4	Resistent
FeMoNiCrBi + ZrB_2	0.026	0.029	17.2	4	Same
FeMoNiCrBi + (Ti, Cr)C	0.031	0.035	14.3	4	»
FeMoNiCrB + $FeTiO_3$	0.031	0.035	14.3	4	»
5 % NaOH					
FeMoNiCrB	0.047	0.052	9.6	4	Resistent
FeMoNiCrBi + ZrB_2	0.033	0.038	13.1	4	Same
FeMoNiCrBi + (Ti, Cr)C	0.038	0.04	12.5	4	»
FeMoNiCrB + $FeTiO_3$	0.04	0.043	11.1	4	»
10 % H_2SO_4					
FeMoNiCrB	0.2	0.22	2.3	6	Low-resistant
FeMoNiCrBi + ZrB_2	0.156	0.174	2.8	6	Same
FeMoNiCrBi + (Ti, Cr)C	0.166	0.186	2.5	6	»
FeMoNiCrB + $FeTiO_3$	0.182	0.21	2.4	6	»

Table 6. Test results of detonation coatings based on FeMoNiCrB on abrasion resistance by friction against a loosely fixed abrasive

Composition of coating	SiO_2 abrasive		B_4C abrasive	
	Given wear, g/km	Relative wear resistance	Given wear, g/km	Relative wear resistance
FeMoNiCrB	0.00875±0.00075	3.3	0.0509±0.002	1.9
FeMoNiCrB + ZrB_2	0.01065±0.00015	2.6	0.0419±0.0003	2.3
FeMoNiCrB + (Ti, Cr)C	0.01±0	2.7	0.031±0.001	3.0
FeMoNiCrB + $FeTiO_3$	0.00955±0.00595	2.9	0.0414±0.0003	2.3
Steel 30KhGSA	0.0291±0.00145	–	0.099±0.0002	–

occurs in a sulfuric acid solution, the minimum is in 3 % NaCl, i.e. the corrosion rate correlates with the pH value of the solution and decreases in the range from weakly acidic to neutral and alkaline solutions. Therefore, the corrosion rate in the 10 % H_2SO_4 solution (pH is 1) is higher than in the neutral 3 % NaCl (pH is 8.0) and in the alkaline 5 % NaOH solution (pH is 13).

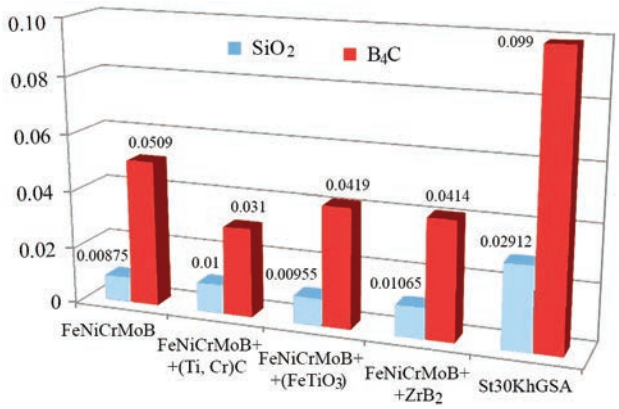

Figure 4. Test results of coatings on friction wear against SiO_2 and B_4C abrasives, g/km

Thus, electrochemical tests in the studied solutions showed that in detonation coatings with CP FeMoNiCrB + (ZrB_2, (Ti, Cr)C, $FeTiO_3$), corrosion current decreases from $2 \cdot 10^{-6}$ in the 3 % NaC1 and 5 % NaOH to $1.5 \cdot 10^{-5}$ A/cm$_2$ in the 10 % H_2SO_4. Introduction of ZrB2, (Ti, Cr)C, $FeTiO_3$ in all the coatings leads to a decrease in the corrosion current by 1.5–3.0 times as compared to the material of the base FeMoNiCrB depending on the type of additive in the direction $FeTiO_3 \rightarrow$ (Ti, Cr))C $\rightarrow ZrB_2$.

On the basis of the received experimental data, the comparative evaluation of fatigue life of the studied coatings of identical thickness in the considered corrosion media was carried out. The results of the calculation of the evaluated service life of the studied coatings at a thickness of 500 μm are given in Table 5.

The results of tests of wear resistance of detonation coatings are presented in Table 6 and in Figure 4.

When using the SiO_2 abrasive, the highest wear resistance is observed in the coatings produced from FeMoNiCrB powder, and in the case of B_4C abrasive, among the developed composite coatings, the coat-

ing produced from FeMoNiCrB composite powder +30 vol.% (Ti, Cr)C is the the most wear-resistant. This correlates with the average microhardness of the coatings (see Table 3), which in the case of FeMoNiCrB + (Ti, Cr)C amounts to 4450 MPa against ~3800 MPa in CP FeMoNiCrB + $FeTiO_3$ and FeMoNiCrB + ZrB_2.

CONCLUSIONS

1. The coatings deposited by detonation spraying of composite powders (CP) FeMoNiCrB – ZrB_2, (Ti, Cr) C, $FeTiO_3$, and FeMoNiCrB powder, have a dense lamellar multiphase structure. The microhardness of FeMoNiCrB coating is 4855 ± 1023 MPa, and in the composite coatings FeMoNiCrB + (ZrB_2, (Ti, Cr), FeTiO it is 3830 ± 570 MPa, 4450 ± 700 (20 MPa and 3750 ± 620 MPa, respectively).

2. All the produced coatings have an amorphous-crystalline structure. The composition of all the coatings includes solid solutions based on Fe and (Fe, Ni) and boride phases Mo_2FeB_2, Fe_2B, oxides, as well as the amorphous phase, the content of which in the spraying process grows as compared to the powder.

3. The carried out electrochemical studies showed that the corrosion resistance of detonation coatings depends on pH of the solution. In alkaline and neutral media, the corrosion resistance of coatings is by an order higher than in acidic medium, which is predetermined by the presence of SO_4^{-2} anions. The introduction of additives ZrB_2, (Ti, Cr)C and $FeTiO_3$ into the coating reduces the corrosion rate by 2–3 times in the 3 % NaCl solution and 5 % NaOH and has a weak effect on the corrosion rate in H_2SO_4. Detonation coatings, which were investigated in the 3 % NaCl and 5 % NaOH solutions are classified in accordance with GOST 308–85 at a thickness of 500 μm as resistant with a service life of 14–17 years and 11–13 years, respectively, and in the 10 % H_2SO_4 as low-resistant with a service life of 2.4–2.8 years.

4. The studies of wear resistance of the detonation coatings FeMoNiCrB and CP FeMoNiCrB under wear conditions in unfixed abrasives SiO_2 and B_4C showed that the relative wear resistance in relation to the reference “steel 30KhGSA” amount to 2.6–3.3 in SiO_2 medium and 1.9–2.9 in B_4C medium. The highest wear resistance 2.7–3.0 was achieved in the case of FeMoNiCrB + (Ti, Cr)C coating, having a microhardness of 4450 ± 700 MPa.

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CONFLICT OF INTEREST

The Authors declare no conflict of interest

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