ISSN 1070-4272, Russian Journal of Applied Chemistry, 2009, Vol. 82, No. 5, pp. 851−856. © Pleiades Publishing, Ltd., 2009.
Original Russian Text © V.I. Balakai, V.V. Ivanov, I.V. Balakai, A.V. Arzumanova, 2009, published in Zhurnal Prikladnoi Khimii, 2009, Vol. 82, No. 5, pp. 797−802.

APPLIED ELECTROCHEMISTRY AND CORROSION PROTECTION OF METALS

Analysis of the Phase Disorder in Electroplated Nickel–Boron Coatings

V. I. Balakai, V. V. Ivanov, I. V. Balakai, and A. V. Arzumanova

South-Russian State Technical University (Novocherkassk Polytechnic Institute), Novocherkassk, Rostov-on-Don oblast, Russia

Received December 11, 2008

Abstract—Probable state of the phase disorder in electroplated nickel–boron coatings was analyzed. The electrical resistivity of the coatings and the microhardness and wear resistance of their surface was modeled. The calculated parameters of the nickel–boron coatings were analyzed in comparison with the corresponding experimental data.

DOI: 10.1134/S107042720905019X

The high cost of noble metals (silver, gold, platinum, etc.) as materials for electric contacts restricts their use in electronic devices. At present, it is suggested to fabricate low-current sliding contacts that switch low-power currents under sliding friction conditions from nickel-based alloys having a comparatively low and stable-in-time contact electrical resistance, high electrical conductivity, and enhanced corrosion stability and mechanical wear resistance [1, 2].

A promising alloy for use in low-current sliding contacts is an electroplated nickel–boron alloy [1–3]. Despite that the resistivity and the contact resistance of a nickel–boron electroplated coating (EC) is 1.4–1.8 times lower than those of electroplated silver, their wear resistance and microhardness of nickel–boron coatings are 4.5–5 times those of silver [3]. The corrosion resistance of nickel–boron ECs exceeds that of nickel by a factor of 2.0–2.5. The experimentally recorded improvement of the electrical and mechanical properties of thermally treated nickel–boron ECs, compared with nickel, was attributed in [3] to formation of boron-containing phases Ni_3B and Ni_2B. However, the higher, compared with nickel, resistivity and the nature of the dependence of this quantity on the boron content of a coating indicate that the phase composition is not the only factor determining the electrical properties of ECs.

In this context, analysis of the qualitative and quantitative phase composition of thermally treated ECs, performed with allowance for the possible chemical modification processes and the distribution of phases throughout the coating volume, is necessary for a more precise interpretation of the known experimental data. It is noteworthy that the analytical method for solving this phase problem for ECs is nearly the only possible, as, e.g., in the case of ECs subjected to a tribological treatment [4, 5].

An analysis of the probable state of the phase disorder in thermally treated nickel–boron ECs, a modeling of the resistivity, microhardness, and wear resistance, and the subsequent analysis of the phase disorder on the basis of experimental evidence about the corresponding properties of the coatings is the aim of this study.

EXPERIMENTAL

We deposited electroplated coatings based on the nickel–boron alloy from a chloride electrolyte of composition (g l^{-1}): nickel chloride hexahydrate 200–300, nickel sulfate 2.5–5.0, boric acid 25–45, chloramine B 0.5–1.5, potassium dicarboundecarborane 0.5–4.0, at pH 1.0–5.0, temperature of 18–40°C, and cathode current density of 0.5–9 A dm^{-2} [6, 7, 8].

In accordance with [5], we name the state of a nickel–boron EC that is spontaneously formed under the action of external factors (thermal treatment, triboactivation) through chemical modification and physicochemical

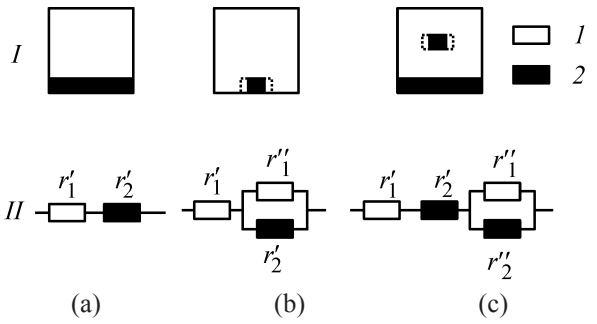

Fig. 1. Idealized images of (*I*) elementary volumes and (*II*) the corresponding simplest equivalent circuits for (a) heterogeneous, (b) homogeneous, and (c) combined distribution of (*2*) boron-containing phases Ni_3B, Ni_2B, or NiB in the matrix of (*1*) nickel phase in nickel–boron ECs.

transformations, the phase disorder state. The main characteristics of this state of EC are the qualitative and quantitative phase composition and the nature of distribution of each of the phases in the coating volume.

Analysis of the phase disorder on the basis of data on the coating resistivity. Let us consider the resistance of a nickel–boron EC in the direction *n* parallel to its surface. If the condition $l >> (db)^{1/2}$ (where *l* is the distance between two measuring probes; *b*, probe width; and *d*, coating thickness) is satisfied, we have a "rod-like" case [9]. In this case, the role of the resistivity in the direction *n* is played by the normal component of the resistivity tensor $n\rho n$, which determines the potential difference between the measuring probes, $U = (Il/db)n\rho n$. This means that the value of ρ of a multiphase EC is determined by the individual ρ_i of each *i*th phase, with allowance for the nature of their distribution in the coating "rod" being analyzed.

Let us select an elementary volume *V* of the coating as a parallelepiped whose average linear size satisfies the following condition

$$<a> << V^{1/3} << \rho/(\partial r/\partial x),$$

where <a> is the average parameter of the unit cells of all the crystalline phase of the composite EC (CEC), and $\rho/(\partial r/\partial x)$ is the formal wavelength characterizing the periodicity of the resistivity variation within the volume of the coating being analyzed.

Let us assume that we can neglect changes in resistivity when passing from one elementary volume to another, i.e., $\partial r/\partial x \approx 0$. In this case, the coating can be considered homogeneous. Then, two fundamentally different types of distribution of boron-containing phases in the EC volume can be formally assumed: quasi-homogeneous (with the maximum value of the disorder parameter, $\beta \approx 1$) and quasi-heterogeneous (with the minimum value of the disorder parameter, $\beta \approx 0$). A combined variant ($0 < \beta < 1$) is intermediate between the first two (Fig. 1).

Let us consider the effect of the bulk concentration of boron-containing phases on the resistivity of nickel–boron ECs for the variants listed above.

Heterogeneous coating (β = 0). Based on the corresponding equivalent scheme (Fig. 1a), we can write the resistance of an elementary volume of the coating as $r_h = r_1 + r_2$. Then we have for the resistivity of the heterogeneous coating:

$$\rho_h = (1 - \alpha)\,\rho_1 + \rho_2 \qquad (1)$$

where ρ_1 and ρ_2 are the resistivities of the nickel- and boron-containing phases, respectively, and α is the volume fraction of the boron-containing phase in the EC ($0 < \alpha < 1$).

Homogeneous coating (β = 1). According to the equivalent scheme Fig. 1b, the resistance of an elementary volume of the coating can be written as $r_g = r_1 + xr_1r_2(xr_1 + r_2) - 1$. Making simple rearrangements on the assumption that a part of the volume fraction *x* of nickel near a microparticle of the boron-containing phase can be considered to be connected in parallel to this particle, we have for the resistivity of the homogeneous coating: $\rho_g = (1 - x - \alpha)\rho_1 + \alpha x\rho_1\rho_2(x\rho_1 + \alpha\rho_2) - 1$. We assume that *x* is comparable with α, i.e., $x \approx \alpha$. In this case, we finally have

$$\rho_g = (1 - 2\alpha)\,\rho_1 + \alpha_1\rho_2\,(\rho_1 + \rho_2)^{-1} \qquad (2)$$

Combined coating (0 < β < 1). Based on the corresponding equivalent scheme in Fig. 1c, which is a combination of the first two schemes, we can write the resistance of an elementary volume of the coating as $r_c = (1 - \beta)r_h + \beta r_g$ and we have for the resistivity of a combined CEC:

$$\rho_C = (1 - \beta)\rho_h + \beta\rho_g = (1 - \beta)[(1 - \alpha)\rho_1 + \alpha\rho_2] + \beta[(1 - 2\alpha)\rho_1 + \alpha\rho_1\rho_2(\rho_1 + \rho_2)^{-1}]$$

or, finally,

$$\rho_C = [1 - \alpha(1+\beta)]\rho_1 + \alpha[1 - \beta\rho_2(\rho_1 + \rho_2)^{-1}]\rho_2. \qquad (3)$$

Table 1. Resistivity of thermally treated composite nickel–boron electrolytic coatings

Coating	Boron content, wt %	Volume fraction α, rel. units			Disorder parameter β	Resistivity $\rho \times 10^6$, ohm cm	
		Ni_3B	Ni_2B	NiB		calculation	experiment
Ni	0	0	0	0	0	8.60	8.6
		0.08	0	0	0.90	8.02	
Ni-B(1)	1.0	0	0.06	0	0.95	8.00	8.0
		0	0	0.03	1.00	8.52	
		0.26	0	0	0.88	7.21	
Ni-B(2)	1.8	0	0.18	0	0.90	7.16	7.2
		0	0	0.10	1.00	7.80	
		0.48	0	0	0.75	6.51	
Ni-B(3)	2.8	0	0.33	0	0.70	6.48	6.5
		0	0	0.18	1.00	6.82	

It is noteworthy that formula (3) can formally describe the properties of CECs also at parameter β equal to 0 or 1 [formulas (1) and (2), respectively].

We calculated the resistivity of the EC by formulas (1) and (2), with the parameter β accounted for by formula (3) and the following individual parameters of the solid phases used: for cubic nickel, $\rho_1 = \rho_{11} = 8.9 \times 10^{-6}$ ohm cm; for boron-containing phases with rhombic structures, $\rho_2 = (1/3)(\rho_{11} + \rho_{22} + \rho_{33}) = 21 \times 10^{-6}$ (Ni_3B) and 9×10^{-6} ohm cm (NiB), and for that with a tetragonal structure, $\rho_2 = (1/3)(2\rho_{11} + \rho_{33}) = 14 \times 10^{-6}$ ohm cm (Ni_2B) [10–13]. The dependences ρ(α), calculated on the assumption that only one of the three boron-containing phases is formed, and α(α, β), found with the inhomogeneity of the distribution of these phases throughout the coating volume taken into account, are presented in Fig. 2 and Table 1, respectively.

A comparison of the calculated and experimental data demonstrated that formation of the Ni_3B phase and, presumably, Ni_2B is the most probable in thermally treated nickel–boron ECs (Table 1). Formation of the NiB phase in thermally treated nickel–boron ECs is unlikely because data calculated on the assumption of the maximum degree of disordering of the nickel boride phase in the bulk of the coating (i.e., for β = 1) disagree with the experimental data obtained in [3] (Fig. 2c). Thus, taking into account the good agreement between the calculated and experimental data for Ni_3B and Ni_2B (Table 1), we can assume that boron-containing phases are represented in thermally treated nickel–boron ECs mostly by the Ni_3B phase with an admixture of Ni_2B.

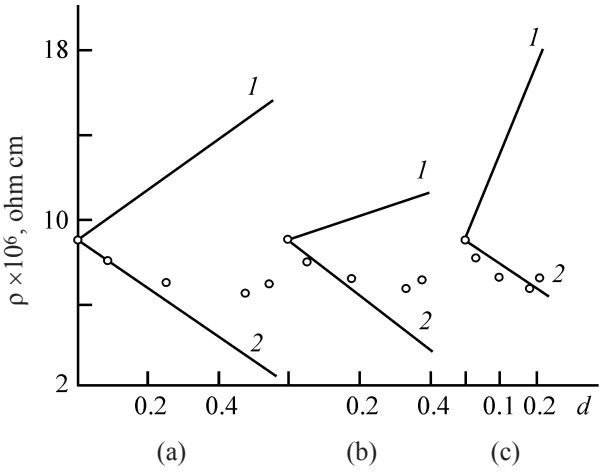

Fig. 2. Diagrams of the resistivity ρ against the volume concentration α of the low-boron phase for nickel–boron ECs, plotted on the assumption that (a) Ni_3B, (b) Ni_2B, or (c) NiB phase is present. The dependences were calculated by formulas (*1*), (*2*).

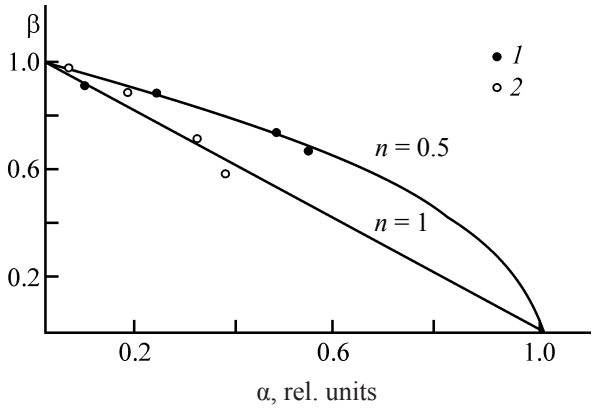

Fig. 3. Effect of the volume concentration α of (*1*) Ni_3B and (*2*) Ni_2B in nickel–boron ECs on the disorder parameter, *n*. exponent in the dependence of the type $\beta = (1 - \alpha)^n$.

Table 2. Microhardness of thermally treated electrolytic nickel–boron coatings

Coating	Boron content, wt %	Volume fraction α, rel. units			Disorder parameter β	Resistivity $\rho \times 10^6$, ohm cm	
		Ni_3B	Ni_2B	NiB		calculation	experiment
Ni	0	0	0	0	0	8.60	8.6
		0.08	0	0	0.90	8.02	
Ni-B(1)	1.0	0	0.06	0	0.95	8.00	8.0
		0	0	0.03	1.00	8.52	
		0.26	0	0	0.88	7.21	
Ni-B(2)	1.8	0	0.18	0	0.90	7.16	7.2
		0	0	0.10	1.00	7.80	
		0.48	0	0	0.75	6.51	
Ni-B(3)	2.8	0	0.33	0	0.70	6.48	6.5
		0	0	0.18	1.00	6.82	

It is noteworthy that the distribution of the boron-containing phases in nickel–boron ECs can be characterized as strongly disordered. However, the dependences $\beta = (1 - \alpha)n$ for both of the presumed phases in the coating are markedly different. A linear dependence of the type $\beta - (1 - \alpha)$ is more characteristic of the Ni_2B phase, whereas for the Ni_3B, $\beta = (1 - \alpha)1/2$, which is typical of the distribution of more highly dispersed phases (Fig. 3).

Analysis of the phase disorder on the basis of data on the microhardness of the coating surface. The microhardness as an important parameter of the surface can be estimated in the case of a homogeneous distribution of microparticles of two solid phases throughout the volume by the additive formula

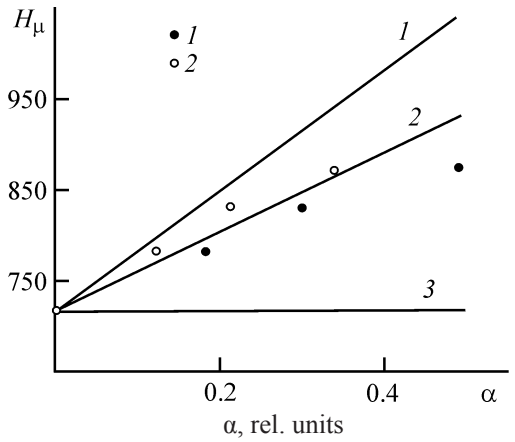

Fig. 4. H_μ–α diagram for nickel–boron ECs, plotted on the assumption that (*1*) Ni_3B or (*2*) Ni_2B phase is present. Dependences *1, 2* were calculated by formula (4), and dependence *3* by formula (5) at $\beta = 0$.

$$H_\mu = (1 - \alpha)H_{\mu,\,Ni} + \alpha H_{\mu,\,Ni-B}, \quad (4)$$

where $H_{\mu,Ni}$ and $H_{\mu,Ni-B}$ are individual characteristics of the surfaces of nickel and a boron-containing phase with a volume fraction α.

In the case of an inhomogeneous distribution of the boron-containing phase over the EC surface and in the absence of a concentration gradient across the coating thickness, we consider that the contribution of the microhardness $H_{\mu,Ni-B}$ in formula (4) is proportional to the phase order parameter $(1 - \beta)$. Then

$$H_\mu = (1 - \alpha)H_{\mu,\,Ni} + \alpha H_{\mu,\,Ni-B} + \alpha(1 - \beta)(H_{\mu,\,Ni-B} - H_{,\,Ni})$$

or

$$H_\mu = (1 - \alpha\beta)H_{\mu,\,Ni} + \alpha\beta H_{\mu,\,Ni-B} \quad (5)$$

To calculate the microhardness of the EC surface in terms of the refined additive model (5) with allowance for the parameter β, we used the microhardnesses (MPa) of individual solid phases: nickel 710, Ni_3B 1190, Ni_2B 1430, and NiB 1610 [10–12]. The results of our calculation of the microhardness of CEC on the assumption that one of the two boron-containing phases is formed in the coatings (with its inhomogeneous distribution over the surface taken into account) are listed in Table 2.

A comparison of the calculated and experimental data demonstrated that the formation probability of the Ni_3B phase and, possibly, Ni_2B is the highest (Table 2, Fig. 4).

The conclusion that the formation probability of the

NiB phase in thermal treatment of EC is low, which follows from the significant discrepancy between the calculated and experimental data, confirms the results obtained above by an analysis of the resistivity data.

Analysis of the phase disorder on the basis of the data on the wear resistance of the coatings. According to the synergic model of the "concentration wave" [4], the rate of the linear wear of an EC taken in a two-component approximation [solid (s) + lubricating (lu)] can be represented as

$$I_{lin} = \alpha I_{lin,s} + (1 - \alpha)I_{lin,lu} + 2\alpha^2(1 - \alpha)(1 + k_n)(I_{lin,s} - I_{lin,lu}), \quad (6)$$

where α is the volume fraction of the phases constituting the solid component of the coating; $I_{lin,s}$ and $I_{lin,lu}$, volume-averaged linear wear rates of the individual phases of the solid and lubricating components of the EC; and k_n, degree of nanostructuring, which characterizes the volume fraction of spherical or cylindrical nanoparticles of the phases constituting the solid components within the space between two mating surface of the tribosystem.

Previously, the most probable values of the parameter k_n in the synergic term of expression (6) have been determined for nickel–boron–fluoroplastic and nickel–fluoroplastic ECs to be 0.17 and 0.07, respectively [4, 14]. Taking this circumstance into account, we can assume that, under the same triboconjugation conditions, the fraction of boron-containing phases in nickel–boron ECs, $k_{n,Ni–B} \approx 0.10$, and that of nickel, $k_{n,Ni} \approx 0.07$. However, the lack of phases constituting the lubricating component in these ECs and, consequently, the absence of the synergism effect of the type (6) give no way of using this formula for calculation of tribotechnical characteristics. We employ for this purpose the additive model in which the volume fraction of boron-containing phases and the volume fraction of nickel are taken into consideration as follows: $\alpha(1 - k_{n,Ni–B})$ and $(1 - \alpha)(1 - k_{n,Ni})$, respectively. Then, we have for the linear wear rate of the EC surface:

$$I_{lin}^{o} = (1 - \alpha)(1 - k_{n,\,Ni})I_{lin,\,Ni} + \alpha(1 - k_{n,\,Ni–B})I_{lin.,\,Ni–B} \quad (7)$$

It is noteworthy that, even in the case of a quasi-homogeneous phase distribution in the coatings ($\beta \approx 1$), if the heterogeneity is manifested only on the surface of an EC that is not of gradient-type across its thickness, formula (7) can be used to estimate the linear wear rate in friction with the same CEC.

Table 3. Wear of electrolytic nickel–boron coatings under conditions of boundary friction against St.45 steel

Coating	Boron content, wt %	Volume fraction α, rel. units		Linear wear rate I_{lin}, μm h^{-1}	
		Ni_3B	Ni_2B	calculation	found
Ni	0	0	0	1.288	1.30
Ni-B(1)	1.0	0.18	0	1.220	1.21
		0	0.12	1.226	
Ni-B(2)	1.8	0.30	0	1.114	1.11
		0	0.21	1.118	
Ni-B(3)	2.8	0.48	0	0.982	0.98
		0	0.34	0.984	

The effect of the substrate (St.45 steel in the given case) on the wear resistance of the surface of a nickel–boron CEC was taken into consideration as follows [15]:

$$I_{lin} = I_{lin}^{o} + \alpha\{(8\alpha - 6\alpha^2 - 1)I_{lin,Ni}I_{lin,St.45}(I_{lin,Ni} + I_{lin,St.45})^{-1} + (I_{lin,St.45} - I_{lin,Ni})\}, \quad (8)$$

where I^0_{lin} is found using formula (7).

The calculation was performed using the following wear resistances (μm h^{-1}) of individual phases constituting the solid component of the EC: Ni 1.1, Ni_3B 0.9, Ni_2B 0.75, NiB 0.6, and St.45 1.2, which corresponded to the steady stage of the boundary friction mode of the corresponding pairs of identical materials at a specific load of 3 MPa and friction speed $V = 0.048$ m s^{-1} [4]. Experimental data on the wear resistance of ECs in friction pairs with St.45 steel are in satisfactory agreement with the corresponding calculated values not only on the assumption that the Ni_3B or Ni_2B phase is present in the coatings, but, presumably, also at their arbitrary concentration ratio. (Fig. 5, Table 3).

This conclusion does not contradict the principal results of the analysis of the phase disorder, obtained from data on the resistivity of the coatings and on the microhardness of their surface.

CONCLUSIONS

(1) The phase disorder state in thermally treated nickel–boron electrolytic coatings is characterized by the presence of the nickel phase and boron-containing phases Ni_3B and Ni_2B, with the inhomogeneity of their distribution over the coating surface increasing as the

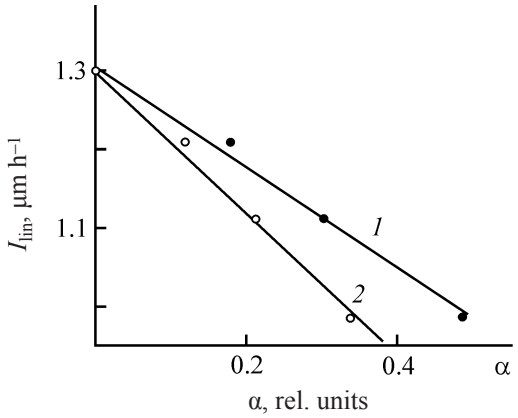

Fig. 5. I_{lin}–α diagram for nickel–boron ECs, plotted on the assumption that (*1*) Ni_3B or (*2*) Ni_2B phase is present. Dependences *1, 2* were calculated by formula (8).

boron content of the alloy becomes higher. The NiB phase can also be formed in the course of friction.

(2) Formation of spherical or cylindrical nanoparticles of the solid phases Ni, Ni_3B, Ni_2B, and NiB on the surface of the electrolytic coatings is possible under boundary friction conditions. These nanoparticles improve the antifrictionalty and wear resistance of the coatings.

(3) An increase in the volume fraction of the boron-containing phases in a coating makes higher its surface microhardness and improves the corrosion resistance of the composite electrolytic coating. A change in the nature of the distribution of these phases over the surface from homogeneous to heterogeneous leads to a decrease in the electrical resistivity of the coating and enables its use in low-current sliding contacts.

REFERENCES

1. Kudryavtseva, I.D., Sysoev, G.N., Balakai, V.I., et al., in *Prikladnaya elektrokhimiya. Gal'vanotekhnika: Mezhvuzovskii sbornik* (Applied Electrochemistry, Electroplating: Intercollegiate Coll.), Kazan: Kazan. Khim. Tekhnol. Inst., 1988, pp. 105–110.
2. Kudrjavtzeva, I.D., Degtjar, I.A., Dubov, B.V., and Kukoz, F.I., *Trans. IMF*, 1999, no. 77(3), pp. 123–126.
3. Balakai, V.I., Kudryavtseva, I.D., and Shevchenko, V.V., Abstracts of Papers, *Mezhdunarodnaya nauchno-prakticheskaya konferentsiya* (Proc. Int. Sci.-Pract. Conf. on Problems of Synergism in Tribology, Triboelectrochemistry), Novocherkassk, November 8, 2002, pp. 40–44.
4. Ivanov, V.V., Balakai, V.I., Ivanov, A.V., and Arzumanova, A.V., *Zh. Prik. Khim.*, 2006, vol. 79, no. 4, pp. 619–621.
5. Ivanov, V.V., *Kombinatornoe modelirovanie veroyatnykh struktur neorganicheskikh veshchestv* (Combinatorial Modeling of Probable Structures of Inorganic Substances), Rostov-on-Don: SKNTs VSh, 2003.
6. USSR Inventor's Certificate, no. 1387528.
7. Balakai, V.I., Kudryavtseva, I.D., and Balakai, I.V., Abstracts of Papers, *II Vserossiiskaya konferentsiya molodykh uchenykh* (2nd All-Russia Conf. of Young Scientists), Saratov, April 26–29, 2005 pp. 82–85.
8. Karakuleva, L.V., Abstracts of Papers, *XII Vserossiiskoye soveshchaniye* (XII All-Russia Symp. On Improvement of the Technology of Electroplated Coatings), Kirov, Kirov: Vyat. Gos. Univ., 2003, p. 35.
9. Sirotin, Yu.I. and Shaskol'skaya, M.P., *Osnovy kristallofiziki* (Fundamentals of Crystal Physics), Moscow: Nauka, 1979.
10. Samsonov, G.V., Serebryakova, T.I., and Neronov, V.A., *Boridy* (Borides), Moscow: Atomizdat, 1975.
11. Samsonov, G.V. and Vinitskii, I.M., *Tugoplavkie soedineniya: Spravochnik* (High-Melting Compounds: Reference Book),Moscow: Metallurgiya, 1976.
12. *Gal'vanicheskie pokrytiya v mashinostroenii: Spravochnik* (Electroplated Coatings in Machine Building: Reference Book) Shluger, M.A., Ed., Moscow: Mashinostroenie, 1985, vol. 1.
13. Samsonov, G.V., Markovskii, L.Ya., Zhigach, A.V., and Valyashko, M.G., *Bor, ego soedineniya i splavy* (Boron, Its Compounds and Alloys), Kiev: Akad. Nauk UkrSSR, 1960.
14. Ivanov, V.V., Kukoz, F.I., Balakai, V.I., et al., *Izv. Vyssh. Uchebn. Zaved., Sev.-Kavk. Region, Tekhn. Nauki,. Special issue*, 2007, pp. 94–99.
15. Ivanov, V.V. and Shcherbakov, I.N., Abstracts of Papers, *Mezhdunarodnaya nauchno-prakticheskaya konferentsiya* (Proc. Int. Sci.-Pract. Conf. on Problems of Synergetics in Tribology, Triboelectrochemistry, Materials Science, and Mechanotronics), Novocherkassk, November 4, 2005, pp. 25–26.