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Synthesis and properties of nanoscale titanium boride

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Abstract. This work reports the scientific and technological grounds for plasma synthesis of titanium diboride, including thermodynamic and kinetic conditions of boride formation when titanium and titanium dioxide are interacting with products resulting from boron gasification in the nitrogen - hydrogen plasma flow, and two variations of its behavior using the powder mixtures: titanium - boron and titanium dioxide - boron. To study these technology variations, the mathematical models were derived, describing the relation between element contents in the synthesized products of titanium and free boron and basic parameters. The probable mechanism proposed for forming titanium diboride according to a "vapour - melt – crystal" pattern was examined, covering condensation of titanium vapour in the form of aerosol, boriding of nanoscale melt droplets by boron hydrides and crystallization of titanium - boron melt. The comprehensive physical - chemical certification of titanium diboride was carried out, including the study of its crystal structure, phase and chemical composition, dispersion, morphology and particle oxidation. Technological application prospects for use of titanium diboride nanoscale powder as constituent element in the wettable coating for carbon cathodes having excellent physical and mechanical performance and protective properties.

Introduction

Titanium diboride TiB_2 is a synthetic super hard, heat resistant, high melting and wear resistant material, which is popular on the market for the production of cermets, refractory and other coatings for various purposes [1, 2]. The relatively new and important field as to application prospects is its use in aluminum electrolytic melting as a component for the wettable coating for electrolysis' cathodes, protecting them against destructive effects of cryolite-alumina melting [3,4]. For obtaining such a coating, an aqueous slurry containing 68 - 70% of solids (90% - TiB_2, 10% -Al_2O_3) is prepared. Physical and chemical bindings between the Al_2O_3 colloidal particles and TiB_2 particles in the slurry lead to the formation of jelly-like viscoelastic state. This material does not bleed and behaves as a solid after drying. The slurry is applied by spraying or staining with intermediate drying in air after applying every layer. The total drying time is 24 hours. The coating 1.0-2.0 mm in thickness provides the wetting of a cathode with aluminum; has a high resistance to sodium dissolution; at the same time combines a sufficient hardness, bending strength, wear resistance, and adhesion to the base material; reduces the voltage dropping in cathodes and increases the cathode efficiency relative to aluminum yielding.

For producing aluminum in foreign countries, basic materials for cathode coatings to protect aluminum electrolytic cells are supplied by JSC "Moltek" under trademarks TINOR A, TINOR M and thick TINOR. When the coating is 1 mm thick, the TiB_2 consumption is 2.3 kg/m^2 of a cathode surface [5, 6] that indicates the need for further development of technological capacities to produce it. Currently, the basic process to obtain TiB_2 intended for wettable cathode coatings is a self-propagating high-temperature synthesis [7]. Despite the relative simplicity as to technological solutions, this technology is low efficient, and allows obtaining TiB_2 in the form of a coarse powder with a particle size in the 3-10 microns range. There are good grounds to suggest that adding TiB_2 to the slurry as a fine powder having particles with a size equitable or smaller than the size of Al_2O_3 particles (0.1-1 microns) will improve mechanical and physical properties and protective capabilities of the coating.

The aim of the research

In this connection, the aim of this study is to develop scientific and technological foundations for titanium diboride plasma synthesis with its physical and chemical certification and identify basic technological parameters for the technology.

The reactor for the synthesis of titanium diboride and its characteristics.

For the synthesis process of titanium diboride, an industrial plasma metallurgical complex was used based on a triple torch direct current plasma reactor having a power of 150 kW [8]. This complex together with the reactor includes plasma torches (plasmatrons), with the structural design improved by the authors, a mixing chamber, a dosing device for fine-dispersed non-free-flow basic material, a continuous sleeve filter; and systems for electrical, gas, water supply and ventilation. Three electric arc plasma torches EDP - 104A of 50 kW each used to generate a plasma flux are fitted in the mixing chamber at an angle of 30º to the reactor's axis. The powder and gaseous basic material is introduced through a water cooled lance into the zone of plasma jets' collision. In this case, the reaction mixture of a specified composition is formed; the nano dispersed products are synthesized and formed. The main parameters of the reactor are given in Table 1. In terms of its parameters, the reactor can be classified as modern electrothermal equipment.

Table 1. Plasma reactor basic parameters

Parameters	**Value**
Power, [kW]	150
Reactor type	Triple-jet, direct-current, vertical,
Type of plasma torch (plasmatron), Power, [kW]	EPD-104A, 50
Plasma forming gas	Nitrogen
Mass of heated gas, [kg/h]	32.5
Internal diameter, [m]	0.054
Reactor capacity, [m^3]	0.001
Refractory lining of reactor channel	Zirconium dioxide
Temperature of plasma flow, [K]	5400 (L* = 0) – 2200 (L = 12)
Temperature of refractory lining, [K]	1549 (L = 0) – 770 (L = 12)
Specified electrical output power, [MBW/m^3]	2142
Service life, [h]: -anode -cathode	3125 112
Impurity of titanium diboride with eroded material, % -anode -cathode	Cu – 0.0000954 W – 0.0000002

*L – relation between the reactor length and its internal diameter

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Powered basic materials for the synthesis of titanium diboride.
We simulated the interaction of plasma flow and feedstock flow in order to choose appropriate titanium-containing basic materials. The relevance of this approach is confirmed in [9-11].

Due to the availability of titanium, titanium dioxide and boron powders, hydrocarbons - methane and plasma forming gas – nitrogen, the following mixtures: B - H- N, Ti - O - C - B - H - N, Ti - B - H – N were taken as objects in the thermodynamic simulation. The compositions of gaseous and condensed products required for the analysis were calculated using the "const" programming, which is based on the simultaneous solution to the following equations: the law of mass action, mass balance, the total number of moles of gas mixture, existence of the condensed phase, Dalton's law. The calculations were performed using a computer simulation program for high temperature complex chemical equilibria «PLASMA», having an integral database of interacting products for oxide -, boride -, carbide- and nitride forming systems. When calculating, the 1000 - 6000 K temperature range at a total pressure of 0.1 MPa in the system was taken into consideration.

Results of calculating the equilibrium compositions in the B - H - N system are shown in Figure 1 a, b. It can be seen that in the investigated system gasification of boron occurs that increases with the dilution of the system with hydrogen. Gasification of boron is caused by the high thermodynamic stability of boron hydride in BH_2 composition in the temperature range 2650 - 3250 K. When the ratio of B: H = 1: 6, the conversion degree of boron into BH_2 reaches 1. Condensation of boron from the gaseous state is thermodynamically possible at temperatures below 2650 K. Thus, it is necessary to accept the dilution of the system with hydrogen efficient and predict the effect of hydrogen concentration within the gaseous state on completeness of boride formation in the plasma flow. Quasi-equilibrium compositions of the B - H - N system (Figure 1 c, d) are described by significant extension of temperature limits required for the stability of boron hydride BH_2, corresponding to 2150 - 3250 K.

In the boride forming systems, titanium diboride can be obtained in the range of temperatures 3500-2300 K and when all relations between components are considered. The following gaseous chemical reactions in the boride formation process are thermodynamically possible:

$Ti_г + BH_{2г} = TiB_{2к} + 2H_{2г}$ (1), $Ti_г + 2B_г = TiB_{2к}$ (2), $Ti_г + 2BH_г = TiB_{2к} + H_{2г}$ (3),

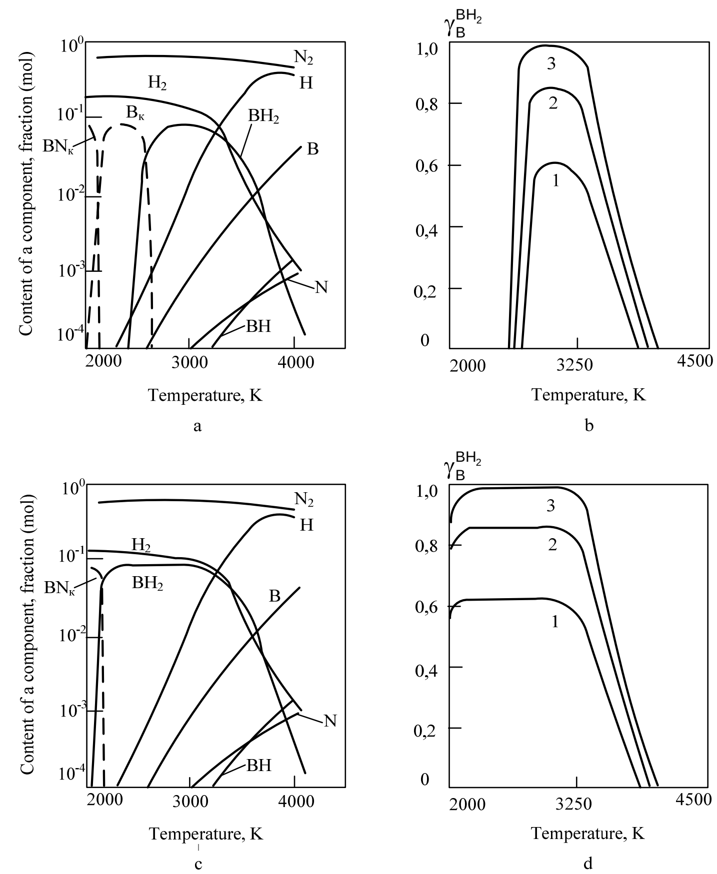
$$Ti_г + 2BO_г + 2HCN_г = TiB_{2к} + 2CO_г + H_{2г} + N_{2г} \quad (4),$$
$$2TiO_г + 2HCN_г + 2BH_{2г} = 2TiB_{2к} + 2CO_г + 5H_{2г} + N_{2г} \quad (5).$$

The fractional conversion of titanium into diboride may be 0.85 according to reaction (1). The 100% conversion of titanium into diboride is achieved at the stoichiometric ratio of components in the temperature range 3200 - 2450 K (Figure 2). With the excessive boron and carbon in the systems in equilibrium when in the condensed phase, boron nitride and free carbon with a concentration for both dependent on the ratio between B/Ti and C/O can be present together with diboride at a temperature below 2800 K. The nitride formation process is thermodynamically possible at a temperature of 2300 K and below

$$2TiB_{2к} + 3N_{2г} = 2TiN_к + 4BN_к \quad (6)$$

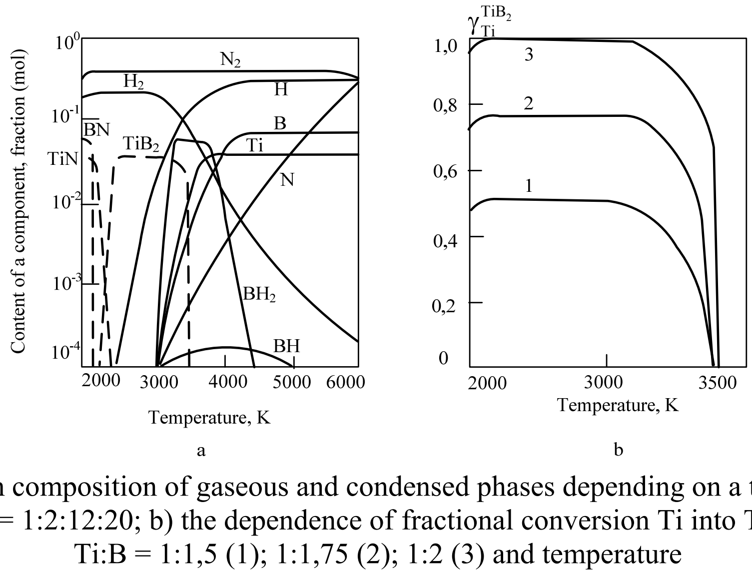
The formation of titanium nitride together with diboride is possible, but at higher temperatures and deficient boron in the system.

Conditions for the effective processing of boron- and titanium-containing basic materials were defined using an improved mathematical model relative to the plasma and material flow interaction, with this model allowing for the influence of heat transfer gas on the heat exchange with walls, basic materials and artificial channel insulator [11]. The model is based on a simultaneous solution to equations of motion for basic material particles, the inter-component heat exchange and heat exchange between the plasma flow and reactor walls.



a) the equilibrium composition of gaseous and condensed phases depending on a temperature at the ratio of B:H:N = 1: 6: 20; b) the equilibrium dependence of fractional conversion B into BH_2 on the ratio of B:H = 1: 2 (1); 1: 4 (2); 1: 6 (3) and temperature; c) the quasi-equilibrium composition of gaseous and condensed phases depending on a temperature at the ratio of B:H:N = 1: 6: 20; d) the quasi-equilibrium dependence of fractional conversion B into BH_2 on the ratio of B: H = 1: 2 (1); 1: 4 (2); 1: 6 (3) and temperature

Figure 1. Results of thermodynamic calculations in the B - H – N system



a) the equilibrium composition of gaseous and condensed phases depending on a temperature at the ratio of Ti:B:H:N = 1:2:12:20; b) the dependence of fractional conversion Ti into TiB_2 on the ratio of Ti:B = 1:1,5 (1); 1:1,75 (2); 1:2 (3) and temperature

Figure 2. Results of thermodynamic calculations in the Ti – B – H – N system

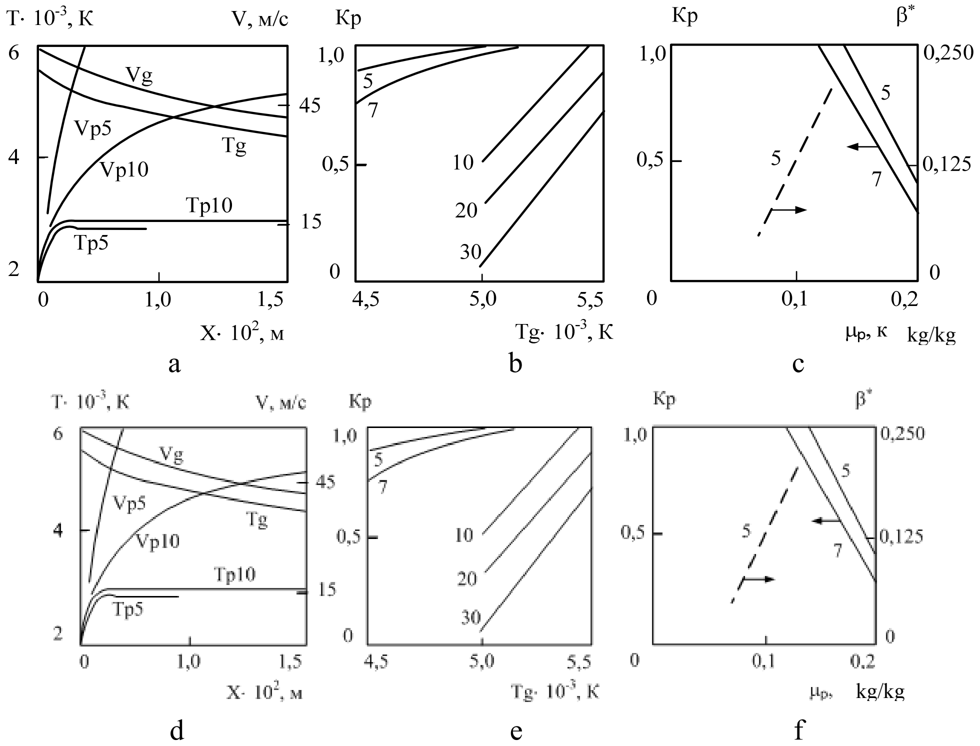
A distinctive feature of the implemented model variant is the use of calculation dependency for heat exchange between the plasma flow and the reactor's channel walls, with this calculation dependency obtained by the authors for real life conditions used in the formation of titanium boride in a plasma reactor and not included into the known equations (7): an industrial reactor power of 150 kW; a triple - jet mixing chamber with an angle of plasma jets at 30º, providing forced turbulence of the plasma flow; a 0.005 m thick lining of the reactor channel in zirconium dioxide, reducing the heat transfer by 20% from the plasma flow; introduction of fine dispersed basic powders (titanium, titanium oxide, boron) different in terms of phase composition, thermal and physical properties and dispersion of the plasma flow; the consumed mass concentration of fine dispersed basic powders 0.12 kg / kg, near to the maximum value and reducing the heat transfer by 15% from the plasma flow. The equation has the following form:

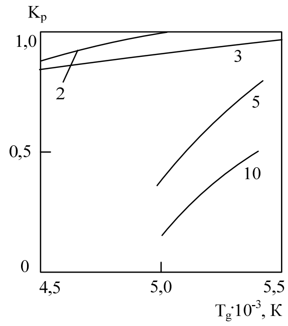
$$St = (0.672 \pm 0.155) R_{f,x}^{-0.425 \pm 0.081} . \tag{7}$$

Where St, Re, Pr are the Stanton, Reynolds, Prandtl numbers;

x and f are the indices corresponding to a bulk temperature of flow and an axial coordinate.

A rate of plasma evaporation of boron- and titanium-containing dispersed materials is determined by such factors as energy and hydrodynamic parameters of the plasma flow, particle sizes and their heat properties, mass flow concentration. The studies were carried out on the three-torch reactor under the following operation conditions: the mass flow rate of plasma forming gas (nitrogen) is 9 · 10-3 kg /s, the gas is fed to the mixing chamber of 75 kW. The results of the study are given in Figure 3.





g

a) variations in bulk temperature, plasma flow rate (T_g,V_g) and titanium particles (T_p,V_p) lengthwise of the reactor; b) the influence of initial temperature of the plasma flow (T_g) on the evaporation rate of titanium particles (K_p); c) the influence of mass flow concentration (μ_p) on the evaporation rate of titanium particles (K_p) and the energy fraction transferred to particles (β^*); d) variations in bulk temperature, plasma flow rate (T_g,V_g) and titanium dioxide particles (T_p,V_p) lengthwise of the reactor; e) the influence of initial temperature of the plasma flow (T_g) on the evaporation rate of titanium dioxide particles (K_p); f) the influence of mass flow concentration (μ_p) on the evaporation rate of titanium dioxide particles (K_p) and the energy fraction transferred to particles; g) the influence of initial temperature of the plasma flow (T_g) on the evaporation rate of boron particles (K_p). 2, 3, 5, 7, 10, 15, 20, 30 are particle sizes in microns.

Figure 3. Hydrodynamic and energy conditions for processing titanium (a-c), titanium dioxide (d-f), and boron (g)

When titanium metal powder is used as a basic material, an optimal combination of thermal and physical characteristics, primarily coefficients of conductivity, heat of melting and evaporation, makes possible the process with the acceptable for processing flow concentration (0.10-0.14 kg/kg) of particles sized 5-10 microns. And, a coefficient of thermal efficiency for the flow with particles of up to 5 micron reaches 0.20. The established behaviors do not depend on the initial velocity of particles when it varies in the range 1-3 m/s. The operating reactor parameters ensure complete evaporation of titanium dioxide particles with a size of from 3 to 5 microns, with the particles interacting with the flow at similar velocities, making 32-60 m/s for 3 micron particles and 28-55 m/s for 5 micron particles, in a time respectively $15 \cdot 10^{-5}$ - $18 \cdot 10^{-5}$ and $54 \cdot 10^{-5}$-$85 \cdot 10^{-5}$s. It should be noted that an increase to a certain value of mass flow concentration for dioxide has no influence on its evaporation rate. The maximum mass flow concentration when the complete processing of TiO_2 is possible is 0.12 kg/kg for 5 micron particles and 0.14 kg/kg for 3 micron particles. The optimal loading of the reactor enables increasing a fraction of energy transferred to particles, i.e., the coefficient of thermal efficiency for the flow, for example, with 5 micron particles, increases from 0.075 to 0.20. Varying in feed rate of powder TiO_2 from 1 to 3 m/s practically does not cause any changes in the hydrodynamic behavior of the flow, and, therefore, does not affect its inter-component heat exchange. When the mass flow concentration is 0.077 kg/kg, boron particles of a 2 - 3 micron size are completely evaporated with the extreme energy characteristics for the plasma flow, corresponding to an initial temperature of 5400.

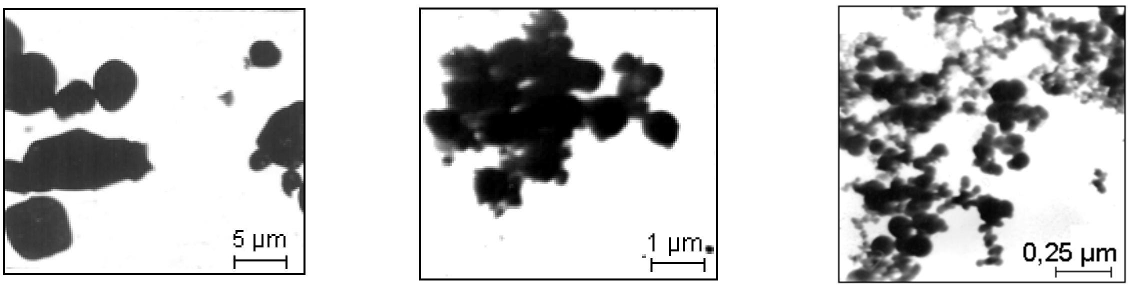
Plasma synthesis and titanium diboride characteristics.

The basic powders and gases – a reducing agent and an exchange gas – were identified according to the results of simulating the interaction of the plasma and feedstock flows. Their characteristics are given in Table. 2.

Table 2. Main characteristics of powdered basic materials and processing gases.

Powdered basic material and processing gases	**Content of base material , [%] min**	**Dispersivity, [µm]**
Finely dispersed powder of titanium PTMk	99.9	0,5-5
Titanium dioxide pigment R-1 GOST 9808-84, rev.	99.0	-1
Amorphous Boron B99	99.0	-1
Methane (natural gas)	93.6 (ethane -3.0; propane -2.18; butane -1.18)	-
Hydrogen for industrial use GOST 3022 – 80, rev.	99.8	-
Nitrogen for industrial use GOST 9293-74, rev.	99.5 (a content of oxygen is 0.5 max)	-

With photomicrographs of powdered basic material samples taken for the study, an ensemble of particles having a spherical shape is clearly observed, and the linear dimensions can be measured (Figure 4). Titanium powder (Figure 4 a) is largely represented by spherical or elliptical shape particles with the linear dimensions from 0.4 to 4.5 microns. The powder of titanium dioxide is characterized by spherical particles having a size ranging from 0.1 to 1 micron (Figure 4 b). Boron powder significantly differs from other basic material components in terms of high dispersivity and some tendency to aggregate (Figure 4 c). Hence, the boron powder particles of a predominantly spherical shape with a size widely ranging 50 to 250 nm may form aggregates ranging in size from 250 to 400 nm, containing up to 10 particles.



a b c

Figure 4. Photomicrographs of powdered basic materials used for the titanium diboride synthesis: (a) titanium powder, (b) titanium dioxide powder, (c) boron powder

The dispersed composition of powdered basic material is shown in Figure 5. Examining an array with 985 particles shows that the titanium powder is characterized by a particle size of 0.5 - 4 microns, the average particle size is 2.0 microns (Figure 5 a) and the particles are distributed as to fractions as follows: +0.5 - 2 microns - 48.2%, + -4 microns - 51.8%. The titanium dioxide powder has an average particle size of 0.5 micron (Figure 5 b), and the studied particles in quantity of 770 are within the size range 0.2 - 1.0 micron, with particles of a + - 0.5 micron fraction making 48.7% and + 0.5 - 1.0 micron - 51.3 %. The boron powder is the most highly dispersed basic material used (Figure. 5): 760 particles in the size range 50 - 250 nm, an average size of 112 nm and they are distributed in terms of fractions: + 50 - 125 nm - 53.2%, + 125 - 250 nm - 46.8 %.

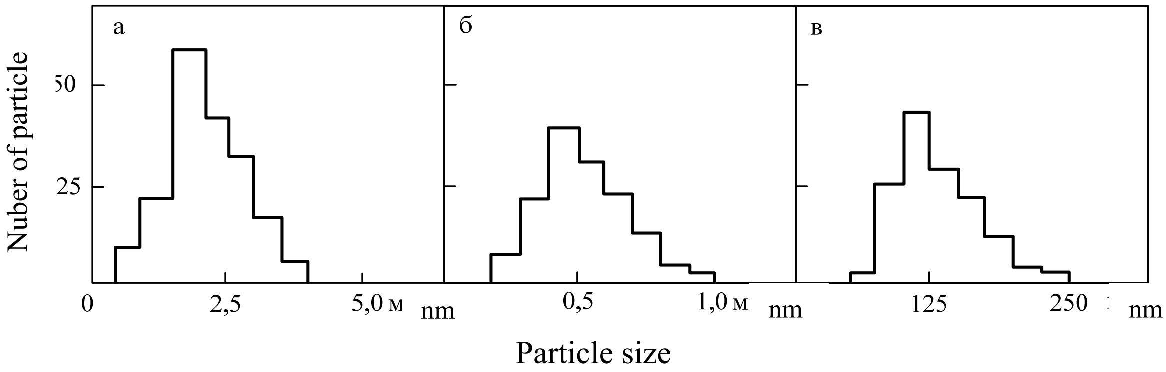


Figure 5. The dispersed composition of powdered materials:
(a) titanium powder, (b) titanium dioxide powder, (c) boron powder

The synthesis process of titanium diboride was examined using an arc power of 80 - 150 kW at a flow rate of the plasma forming gas (4.6 - 9.0) • 10^{-3} kg/s, that corresponds to the initial temperature of the plasma flow 5400 - 5500 K. The mass flow concentration was 0.10 kg of powder per 1 kg of plasma forming gas. The synthesized products were hardened by nitrogen injected through a hardening ring mounted on the reactor outlet. The hardening temperature was controlled by varying the reactor's length. The hardening gas flow was (1.0 - 2.0) · 10^{-3} kg / s.

Solid synthesis products were investigated by the following methods: X-ray, chemical, mass spectrometry, electron microscopy, thermal gravitational analysis and BET method. For the various problems of the research to solve, we examined the samples taken from the plasma flow using a water-cooled metal probe to avoid any contact with air as well as the nano powders' samples taken from the recovery system after filter depressurizing. The gaseous and thermal desorption products were analyzed using the chromatographic method.

Two process variants were investigated using the following mixtures: 1 - ($Ti + B + H_2$), 2 - ($TiO_2 + CH_4 + B$). With this, their contents are optimized in the products of titanium diboride synthesis. The following equations describing the dependence of the titanium diboride content on main technological factors:

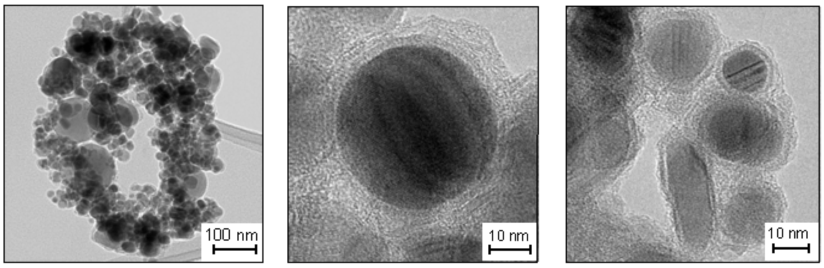
$$[TiB_2\,(1)] = -\,412.41 + 0.09489T_0 + 2.196[B] + 0.1597\{H_2\} - 0.00061T_0[B]; \quad (8)$$

$$[TiB_2\,(2)] = 4.59 + 0.0156\,T_0 + 0.00213T_з - 0.0688\{CH_4\} - 0.214[B]\cdot\{H_2\} \quad (9)$$

Where T_0 is the initial temperature of the plasma flow (5000 – 5400 K);
$T_з$ is the hardening temperature (2600 – 2800 K);
[B] is the content of boron in the charging mixture (100 – 120% of stoichiometrically required);
$\{CH_4\}$ is the amount of the reducing agent (methane) (100 – 120% of stoichiometrically required);
$\{H_2\}$ is the concentration of hydrogen in the plasma forming gas (0-0.25 %).

The basic parameters of the synthesis process and characteristics of titanium diboride are described in Table. 3. Two variations of synthesis are compared with the purpose of identifying the most suitable titanium powder for boriding. The titanium diboride nano scale powder is evidenced by spherical aggregates in 120 - 200 nm size range formed by combining round particulates in the appreciably wide size range 10 to 60 nm (Figure 6). The round shape of titanium diboride nanoparticles proves the possibility of forming according to the "vapour - melt - crystal" pattern, supposedly in interacting titanium aerosol with boron hydrides.

It is assumed that the proposed method for producing titanium diboride is competitive as to the phase and chemical composition, dispersion, main technological parameters, and this method can be accepted as a principle technology used for diboride intended for protective aluminum-wettable cathode and galvanic composite coatings [3-6].



a b c

Figure 6. Photomicrographs of titanium diboride nanopowder (a – ensemble of particles and aggregates; b – morphological pattern of aggregates; c – single particles)

Table 3. Basic parameters of the synthesis and characteristics of titanium diboride

Synthesis parameters and characteristics of titanium diboride	**Synthesis technology variants**	
	1(Ti + B +H_2)	**2(TiO_2 + B + CH_4)**
Exchange gas composition, [% об.]		
- Nitrogen	74.0	
- Hydrogen	25.0	
- Natural gas (methane)	1.0	
Fineness of titanium-containing basic material, [μm]	0.5…4.0	0.2…1.0
Fineness of boron-containing basic material, [μm]	0.25…0.40	
Boron content in charging powder mixture, [% of stoichiometric]	100 – 120	
Amount of reducing agent (methane), [% of stoichiometric]	-	100-120
Initial temperature of plasma flow, [K]	5400	
Hardening temperature, [K]	2600 - 2800	
Chemical analysis, [%]		
TiB_2	92.0 – 93.0	90.05 – 91.30
Free boron	1.30 – 1.15	1.91 – 1.04
Free titanium	1.91 – 1.45	-
Free carbon	-	1.42 – 0.92
Oxygen	2.29 – 1.83	3.72 – 3.52
Nitrogen	2.05 – 1.92	2.26 – 2.11
Volatiles	0.45 – 0.65	0.64 – 1.11
Specific surface area, [m^2/kg]	46000 –48000	35000 - 37000
Particle shape	round	
Oxidation degree of powders x10^7, [kg O_2/m^2 of specific surface area]	3.82 – 4.98	9.51 – 10.63
Basic material flow capacity, [kg/h]	3.6	
Capacity TiB_2 , [kg/h]	3.42	2.35
Rate, [kg/h·m^3]	1556	1070

Conclusions

It has been established that titanium diboride can be obtained in the form of nano particles using titanium - boron and titanium dioxide - boron powder mixtures under the nitrogen - hydrogen and nitrogen - hydrocarbon plasma flows. The behavior of the boride formation process has been identified and discussed. The two variants of the synthesis process are compared with the purpose of identifying the most suitable titanium powder for boriding. The method proposed for titanium diboride production is competitive in terms of its phase and chemical composition, dispersion, main technological parameters, and this method can be accepted as a principle technology to produce this material used in protective aluminum-wettable cathode and galvanic composite coatings.

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