Plasma metallurgical production of nanocrystalline borides and carbides

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Abstract. The experience in production and study of properties of nanocrystalline borides and chromium carbides, titanium, silicon was summarized. The design and features of the vertical three-jet once-through reactor with power 150 kW, used in the plasma metallurgical production, was described. The technological, thermotechnical and resource characteristics of the reactor were identified. The parameters of borides and carbides synthesis, their main characteristics in the nanodispersed state and equipment-technological scheme of production were provided. Evaluation of engineering-and-economical performance of the laboratory and industrial levels of borides and carbides production and the state corresponding to the segment of the world market was carried out.

1. Introduction

In 2011 for the first time in the world more than 1.5 billion tonnes of steel – the most demanded construction material were produced. In the structure of constructional materials the percentage of iron-based alloys accounts for 95%, non-ferrous metals and alloys – 4%, the rest – less than 1%. However, the latter group is represented by a wide range of special-purpose materials vital for modern civilization. It includes materials corresponding to such criteria as “infusibility”, “superhardness”, “heat-resistance” and “refractoriness”, which helps to solve many scientific and technological innovation and design problems. Therefore, in this group the materials based on carbides, borides, nitrides, silicides, and their composites occupy an important place. In the development of their national technological base the following steps can be distinguished. In the 50-60’s mainly the Institute for Problems in Materials Science and the Institute of Superhard Materials of NAS of Ukraine investigated the properties and developed technologies for their production and use. In the 70-80’s a number of territorial research centres on the basis of academic institutions in Moscow, Kiev, Riga, Novosibirsk made efforts to develop the production and implement these materials in the high-dispersed state. The 2000’s were marked by the rise of technology, which is still ongoing and covers the development of nanotechnologies and nanomaterials at a new level.
At present, Russia is among the leading countries in terms of the volume of conducted nanotechnology research, but is significantly inferior in its production of nano-products and their export [1-8]. In accordance with the President’s initiative of April 24, 2007 a system of state support for scientific and applied research into these issues was created, providing unification of state resources and private businesses and their concentration, development of the national nanotechnology infrastructure, improving the efficiency of commercialization and transfer of nano-developments, focus of efforts on the most attractive in commercial terms directions. Such directions include functional, structural and compositional nanomaterials.

In the Siberian region of the Russian Federation the foundation of plasma metallurgical nanotechnologies of high superhard materials was laid by the scientific school of Academician M.F. Zhukov. In the early 70’s he brought together efforts of several research teams of academic, industrial and educational institutions in Western and Eastern Siberia in the direction of the laboratory production and application of nanopowders for different purposes. The results are reflected in the published afterwards in Russia and abroad multi-volume series “Low-temperature plasma” (Chief-editor Academician of RAS M.F. Zhukov), “Thermal plasma in the technology of new materials” (Science-editor Academician of RAS M.F. Zhukov), “Nanomaterials and nanotechnologies in the production of silicon carbide” (Scientific-editor Prof. G.V. Galevsky), etc. The studies confirmed the operability of plasma technological equipment, the possibility for synthesis of carbides, borides, nitrides in nanostate and their application in new areas. However, socio-economic changes, which took place in Russia at the turn of the 90’s, led to the cessation of investments into this area, made it impossible to transit to an industrial level and commercialize the research.

In the XXI century in conditions of nano-technological recovery it seems that the continuation of previous studies for organization of industrial plasma metallurgical production of high-temperature chemical compounds, and identification of priority areas of their application in ceramic, electroplating, metallurgical and other technologies is an important scientific and economic problem relevant to the State program “Development of science and technology for the period till 2020”.

The purpose of this paper is to summarize rich experience and the results achieved by Siberian State Industrial University (SibSIU) in creating a profile equipment and development of technologies for production of nano-dispersed borides and chromium carbides, titanium and silicon. The choice of production technology of borides and carbides as a study object is conditioned by a favorable combination of their consumer properties (hardness, refractoriness, wear resistance and heat resistance); availability of raw materials; relative simple furnace synthesis as a base technology; strong demand from consumers, especially as materials coating, coating of functional materials and modifying complexes, increasing the life cycle of products and tools in 3-4 times; a real opportunity to achieve new effects when used in the nanostate.

2. Plasma technological equipment: design, operation, characteristics

For the experimental study of synthesis of borides and carbides and their production SibSIU together with NPF “Polimet” created plasma technological industrial complex (Figure 1), surpassing the experimental variants developed before. The construction of plasmatrons, mixing chamber, the charge dosing device, bag filter are protected by patents of the Russian Federation No. 66877, 107440, 108319, 184916. The main characteristics of the reactor are given in Table I. More detailed thermal engineering, resource and technological characteristics of the reactor are described in [9]. The plasma technological complex includes a three-jet reactor and systems of electricity, gas, water supply and ventilation, instrumentation and automation equipment, charge dosing, nano-dispersed products capture and neutralization of the exhaust gases.

To generate the plasma flow three arc electric gas heaters (plasmatrons) EDP-104AM with power up to 50 kW each are installed in the mixing chamber at an angle of 30° to the reactor axis. Plasmatrons EDP-104AM operate on the direct current with the following parameters of the electric arc: the arc voltage is up to 250 V, current – up to 200 A. The stabilization of the electric arc – gas-swirling due to the tangential injection of the plasma-forming gas through a special ring. The
Plasmatron anodes are made of copper, water-cooled with internal diameter 0.008 m with a practically unlimited service life in the presence of cooling and operation in the mixing chamber with an angle of inclination of the plasma jets 30°. Cathodes of plasmatrons consist of water-cooled copper shells and cathode inserts from thoriated tungsten (to reduce the electron work function) with a diameter of 0.003 m with service life of 100-120 hours. Plasmatrons activation is carried out by means of an oscillator.

In contrast to the base model in the plasmatrons EDP-104AM commercially pure nitrogen with oxygen content up to 1.5-2.0% can be used as the plasma-forming gas, that at the moment corresponds to the actual composition of the supplied commercial nitrogen. Plasmatrons power supply is carried by a thyristor converter unit of series AT4-750/600 having a steep volt-ampere characteristic and the following operating parameters: power, kW – 450; rectified voltage, V – 600; rectified current, A – 750; efficiency at a nominal speed, % – 96; supply voltage, kV – 6.

![Figure 1. Industrial plasma technological facility.](image)

| Table 1. Basic characteristics of the reactor. |  |
| --- | --- |
| Characteristics | Values |
| Power, kW | 150 |
| Reactor type | Three-jet once-through vertical |
| Type of plasmatron, power, kW | EDP-104А, 50 |
| Plasma-forming gas | nitrogen |
| Weight of the heated gas, kg/h | 32,5 |
| Internal diameter, m | 0,054 |
| Reactor volume, m³ | 0,001 |
| Lining of the reactor channel | dioxide zirconium |
| Temperature of the plasma flow, K | 5400 (L*=0) – 2200 (L=12) |
| Lining temperature, K | 1549 (L=0) – 770 (L=12) |
| Specific electrical power, MW/m³ | 2142 |
| Service life: | 3125 |
| - anode |  |
The mixing chamber design provides the effective injection of high-disperse raw materials into the reactor, its mixing with the plasma flow and a practically unlimited service life of the plasmatron anodes. The mixing chamber is connected to a sectional water cooled channel having an internal diameter of 0.064 m. The mixing chamber and the reactor sections are made of stainless steel. Feeding of high-disperse raw materials into the mixing chamber is carried out by water-cooled tuyere. The tuyere is also used for supplying the gaseous hydrocarbon to the reactor. To reduce the radial temperature gradient in the near-wall zone the channel of the reactor is lined inside with high-temperature insulation material.

For dosing of powdered raw material the intermittent dosing device of combined electromechanical and gas-swirl type with removable cylinder – receiver of the powdered raw material intended for low-loose high-disperse materials is used.

The capture system includes a settling chamber where the temperature of the process gases is reduced to 2800-2000 K and up to 10% of nanopowder is captured, and two alternately operating bag filters (trapping up to 85% of nanopowder). Into the settling chamber with the help of a water-cooled probe the reagent, passivating and coagulating nanopowders, are introduced. Filters are made with a water-cooled housing, regeneration of filter sleeve by reverse blowing with a compressed gas (nitrogen). Filter cloth is a gauze from chrome-nickel steel with a twill weave.

Plasma technological complex exceeds the known laboratory and pilot-scale variations in power in 4-5 times, service life in 3-4 times, performance in 2.5-3.5 times.

3. Production and properties of nano-powders of borides and carbides

The study results of plasma technological options of borides and carbides productions and their implementation are described in detail in a number of publications issued at different times including [10-11].

Development and launching of plasma technological production of borides and chromium carbides, titanium and silicon comprises two stages: 1) study of the processes of boride and carbide formation and chemical and physical properties of borides and carbides in the nanostate; 2) commercial development of the investigated technological options.

At the first stage the plasma flows and raw material interaction is simulated, experimental study, discussion of the mechanism of boride and carbide formation, physico-chemical certification of nano-dispersed products take place. Below the equations describing the dependences of borides and carbides content on the basic technology factors (1)-(5) are provided, as well limits for parameters change of borides and carbides formation in the industrial reactor with capacity of 150 kW, the main characteristics of borides and carbides (Table 2) and micrographs (Figure 2).

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\begin{align*}
[\text{CrB}_2] &= -413.53 + 0.09695 T_0 + 2.283 \{B\} + 0.1736 \{H_2\} - 0.00058 T_0 \{B\}; \\
[\text{Cr}_3(\text{C}_{0.8} \text{N}_{0.2})_2] &= -66.12 + 0.03 T_0 - 0.42 \{H_2\} - 0.14 \{N\} - 0.00002 T_0 \{N\}; \\
[\text{TiB}_2] &= -412.41 + 0.09489 T_0 + 2.196 \{B\} + 0.1597 \{H_2\} - 0.00061 T_0 \{B\}; \\
[\text{TiC}] &= 17.3211 + 0.0105 T_0 - 0.0156 T_h + 0.1859 \{\text{CH}_4\} - 3.432 \{H_2\} - 0.4078 \{N\}; \\
[\text{SiC}] &= 86.50 + 0.00273 T_0 - 0.0064 T_h - 0.144 \{\text{CH}_4\} + 0.00007 T_h \{\text{CH}_4\},
\end{align*}
\]

where \(T_0\) – initial temperature of the plasma stream, K;
\(T_h\) – hardening temperature of borides and carbides formation products;
\{B\} – content of boron in the mixture (in % from stoichiometrically required);
\{CH\} – quantity of hydrocarbon (in % from stoichiometrically required);
{H$_2$} – hydrogen concentration in the plasma-forming gas, % vol;
{N} – amount of atomic nitrogen in the plasma-forming gas (in % from stoichiometrically required for the formation of hydrogen cyanide).

At the second stage specifications and technical documentation (specifications and manufacturing processes) and equipment-technological schemes of the proposed for implementation in the conditions of NPF “Polimet” technological options for production of borides and carbides are developed; the main technical and economic indicators are identified. Figure 3 shows an example of equipment-technological scheme of production of carbonitride (I) and chromium carbide (II).

![Figure 2](image1.png)

**Figure 2.** Micrographs of boride and chromium carbonitride nanopowders (a, b), boride and titanium carbide (c, d), silicon carbide (e, f).

**Table 2.** Permissible limits of change in parameters of borides and carbides synthesis in the industrial reactor with power 150 kW and their main characteristics.

| Parameters of synthesis and its characteristics | CrB$_2$ | Cr$_3$(C$_{0.8}$N$_{0.2}$)$_2$ | TiB$_2$ | TiC | SiC |
|-----------------------------------------------|---------|----------------|---------|-----|-----|
| Composition of the coolant gas,% vol.:        |         |                 |         |     |     |
| - nitrogen / hydrogen / methane               | 74/25/1 | 99/-/-         | 74/25/1 | 99/-/1 | 99/-/1 |
| Technological variant of synthesis            | Cr+B+H$_2$ | Cr+CH$_4$ | Ti+B+H$_2$ | Ti+CH$_4$ | Si+CH$_4$ |
| Performance, kg/h                             | 3.6     | 3.1            | 3.6     | 3.2  | 3.0  |
| The amount of boron in the mixture, % from stoichiometric | 100-120 | –              | 100-120 | –   | –    |
| Amount of carbonizer, % from stoichiometric   | –       | 120-140        | –       | 120-140 | 120-140 |
| Initial temperature of the plasma flow, K     | n.l. 5400 | n.l. 5400 | n.l. 5400 | n.l. 5400 | n.l. 5400 |
| Hardening temperature, K                      | 2600-2800 | 2000-2200     | 2600-2800 | 2600-2800 | 2800-3000 |
| Phase composition                             | CrB$_2$ | Cr$_3$(C$_{0.8}$N$_{0.2}$)$_2$ | TiB$_2$ | TiC | β-SiC |
| Content of the main phase, %                  | 92-93   | 92-93.5        | 92-93   | 93-93.5 | 91-92 |
| Yield of the main phase, %                    | 91-92   | 90.5-91.5      | 91.5-92.5 | 92-92.5 | 87-90 |
| Performance, kg/h                             | 3.0     | 3.4            | 3.4     | 3.7  | 4.05 |
| Intensity, kg/h·m$^3$                         | 1364    | 2010           | 1980    | 2105 | 2200 |
Specific surface area, m²/kg

|        | 33000-35000 | 46000-48000 | 33000-35000 | 40000-44000 |
|--------|-------------|-------------|-------------|-------------|

Size* of the particles, nm

|        | 42.0        | 34.0        | 36.0        | 35.0        | 55.0        |
|--------|-------------|-------------|-------------|-------------|-------------|

Particles shape

|        | Spheroidal | Spheroidal | Spheroidal | Facet, cubic | Facet       |
|--------|------------|------------|------------|--------------|-------------|

Nano-powder oxidation** x10⁷, kg O₂/m²

|        | 9.0-9.7    | 8.0-10.0   | 5.8-7.6    | 8.5-9.5      | 6.5-8.0     |
|--------|------------|------------|------------|--------------|-------------|

* Calculated with value of specific surface;
** Determined after exposure in the air for 24 h.

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**Figure 3.** Equipment and technological scheme of carbonitride (I) and chromium carbide (II) production: 1 – charge dosing; 2 – synthesis; 3, 4 – separation of the desired product; 5 – absorptive version of exhaust gases neutralization; 6, 7 – refinement of chromium carbonitride and control of its characteristics; 8, 9 – refinement of chromium carbonitride and its additional carbonization; 10 – control of chromium carbide characteristics.

4. Economic evaluation

The transition to industrial production of borides and carbides nanopowders creates real preconditions for their widespread introduction into the market, at least in the domestic market of nanomaterials. Table 3 presents the comparison of main technical and economic indicators of production of carbide, chromium boride and silicon carbide in the laboratory and industrial conditions.

**Table 3.** Comparison of technical and economic indicators of nanopowders production in the laboratory and industrial conditions.

| Feasibility indicators                  | Cr₂B₂   | Cr₃C₂  | SiC   |
|----------------------------------------|---------|--------|-------|
| Maximum capacity of the reactor, kW    | 150/50  | 150/50 | 150/50|
| Content of the main phase,%             | 95.0*/81.0** | 96.0/81.0 | 99.0/94.0 |
| Oxidation x10⁷, oxygen kg/m²            | 8-10/18-20 | 12-14/9-11 | 0.8/6.7    |
| Productivity, tonne/year per reactor   | 3.2/0.5  | 3.6/0.6 | 3.1/1.8   |
| Intensity, kg/h²                       | 1365/265 | 1360/245 | 1210/605  |
| Specific energy consumption, thousand kW-h/tonne | 75/145  | 69/140  | 74/115    |
| Prime cost, thousand rubles/kg         | 6.2/15.8 | 6.6/14.5 | 6.0/11.0  |

*/*** commercial and laboratory levels.
The main developers and manufacturers of nanomaterials based on borides and carbides abroad are scientific-production companies “Nanostructured & Amorphous Materials, Inc.” (USA), “Tokyo Tekko Co” (Japan), “Hefei Kaier Nanotechnology & Development Ltd. Co” (China), “NEOMAT Co” (Latvia), “Plasma Chem GmbH” (Germany) offering them at a price about 1200 USD/kg at a comparable level of quality and dispersion [5-9].

5. Conclusions
The performed analysis confirms the achievement by the plasma technological production of high temperature titanium borides and carbides, chromium, silicon of the industrial level in the usage of a three-jet once-through reactor with power 150 kW as a base model of a technological complex. This transition ensures qualitative and technical and economic parameters comparable with foreign counterparts, and competitiveness of the scientific and technical developments.

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