A study on the production of titanium carbide nano-powder in the nanostate and its properties

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Abstract. The plasma synthesis of titanium carbide nano-powder in the conditions close to industrial was studied. Titanium carbide TiC is a wear- and corrosion-resistant, hard, chemically inert material, demanded in various fields for the production of hard alloys, metal-ceramic tools, heat-resistant products, protective metal coatings. New perspectives for application titanium carbide in the nanostate can be found in the field of alloys modification with different composition and destination.

1. Introduction
The developed in the 80s of the 20th century the technology of plasma synthesis of titanium carbide is based on a carbothermic reduction of titanium oxide in the gas phase and is implemented using a three-jet once-through reactor. For plasma flow generation three electric arc plasmatrons EDP-104A are used with the total capacity up to 50 kW. Implementation of the proposed plasma-metallurgical technology provides titanium carbide production in the form nano-powders with nano-particles size 50-70 nm. Along with the advantages there are following disadvantages in this technology: technological and economic inefficiency of using technical propane-butane mixture, requiring for the processing a complex in composition and generation the nitrogen-ammonia-hydrogen plasma, and plasma-metallurgical reactor of the laboratory level.

In this regard, the aim of this work is to study the plasma synthesis of titanium carbide nano-powder in the conditions close to the industrial. In order to achieve this goal the following tasks need to be solved: analysis of the current state of the production and use of titanium carbide; characterization of the three-jet once-through reactor; model-mathematical study on interaction of plasma and raw materials flows; prediction of the basic technological parameters of plasma-metallurgical production of titanium carbide, its physical and chemical attestation and definition of economic indicators.

2. Experimental research and results
To achieve these objectives the three-jet once-through plasma reactor of industrial level was used with power (150 kW), for which the heating engineering, resource and technological characteristics were investigated. The average weight temperature of the plasma flow at the length of the reactor 12 calibres ranges within (5400÷1750) K for a non-lined channel and (5500÷1900) K with its insulation by the cylinder from zirconium dioxide 0.005 m thick; the temperature of the inner surface varies within (942÷490) K and (855÷1549) K, respectively. The specific electrical power reaches 2142
MW/m³, which is much higher than this indicator for a traditional electro-thermal equipment (usually about 0.2 MW/m³). The estimated life of the electrodes is 3125 hours for a copper anode and 112 hours for a tungsten cathode. The predicted titanium carbide contamination with products of electrode erosion is 0.00012% of copper and 0.000019% of tungsten. On the aggregate characteristics the three-jet plasma reactor of 150 kW can be attributed to a highly efficient, reliable modern electro-thermal equipment.

The plasma synthesis is a metallurgical process difficult to study. This is due to its transience, high temperatures and low volume of carbide formation zone. In such conditions the model-mathematical approach is rather promising involving thermodynamic modeling of synthesis processes, modeling of the interaction of titanium-containing raw materials and gas-coolant, an experimental investigation with use of the planned experiment method. The methodology of this approach is described in detail in [1, 2]. During simulation all kinds of titanium-containing raw materials available were examined: chrome and its oxide TiO₂. The natural gas, plasma gas – nitrogen were used as a hydrocarbon raw material.

The thermodynamic modeling of synthesis processes is carried out in order to predict the optimal parameters for producing titanium carbide (ratio of components and temperature), the definition of equilibrium parameters of the synthesis process (conversion degree of raw materials into carbide, composition of gaseous and condensed products), evaluation of the influence of gas-phase reactions on carbide formation, providing an efficient processing of the dispersed raw material in the conditions of plasma metallurgical technologies.

In connection with the use in the synthesis of titanium, oxide TiO₂, hydrocarbon raw material – methane and plasma-forming gas – nitrogen as a titanium-containing raw material the examination objects were the systems C-H-N, Ti-O-C-H-N, Ti-C-H-N. The necessary for the analysis compositions of gaseous and condensed products were calculated by the “constant” method, based on a joint solution of the equation of the mass action, material balance, total number of gas mixture moles, existence of a condensed phase, Dalton’s law with the use of software modeling high-complex chemical equilibria “PLASMA” (ISSC SB RAS), which has a built-in data base for the reaction products for oxide-, boride-, carbide- and nitride-forming systems [3]. In the calculations the temperature range 1000-6000 K at a total pressure of 0.1 MPa in the system was considered. Thermodynamic analysis of the selected process variants showed that in the system C-H-N, simulating a high-temperature pyrolysis of methane, in the equilibrium conditions within the temperature range 2800-3800 K the main carbonaceous components of the gas phase are HCN, C₃H and C₂H. In the system Ti-O-C-H-N the titanium carbide formation is possible at a temperature below 3500 K at a stoichiometric and abundant amount of carbon. In the system Ti-C-H-N the formation of titanium carbide is possible in the equilibrium and quasi-equilibrium conditions. In equilibrium conditions when changing the ratio of Ti:C=0.25:(0.0625-0.25) the degree of titanium conversion into carbide varies from 0.25 to 1, and at 1.5-fold abundance of carbonizer carbide comprises 9.1% of free carbon. In the conditions of quasi-equilibrium carbon condensation does not occur. In both cases, titanium carbide formation is thermodynamically possible according to the gas phase reactions involving vapour of titanium and hydrogen cyanide, i.e. according to the scheme “vapour-crystal” that allows us to predict the possibility for reaching its high yield in real conditions of synthesis.

On the basis of model-mathematical research and the experimental data the prediction of technological parameters of titanium carbide production was performed (Table 1). The results of the model-mathematical and experimental studies have allowed us to predict the technological characteristics of the plasma metallurgical production of titanium carbide for various types of titanium-containing raw material and choose the best technology option (Table 2).

| Table 1. Technological parameters of titanium carbide production. |
| --- |
| Raw material | TiO₂ | Ti |
| Power, kW | 150 | 150 |
| Consumption of plasma-forming gas, kg/s | 9·10⁻³ | 9·10⁻³ |
Cooling water consumption, m³/h  
3.7  
3.7  
The initial temperature of the plasma flow, K  
5400  
5400  
Quenching temperature, K  
2800  
2800  
Mass consumption concentration, kg/kg  
0.12  
0.10  

During calculations the losses of raw materials in the reactor in the amount of 4% and the losses of synthesis chemicals in the capture system 5% were considered.

**Table 2.** Technological parameters of plasma metallurgical production of titanium carbide.

| Technological variant | Variant I (TiO₂ + natural gas) | Variant II (Ti + natural gas) |
|-----------------------|-------------------------------|-------------------------------|
| Conversion degree     | 0.94                          | 0.94                          |
| Product yield, %      | 92.0                          | 92.0                          |
| Productivity, kg/h    | 2.66                          | 3.7                           |
| Intensity of production, kg/m³/h | 2956      | 4111                          |
| Consumption of titanium-containing raw material, kg/kg | 1.46 | 0.87 |
| Gas consumption – coolant gas, kg/kg | 9.10 | 9.10 |
| Natural gas consumption, kg/kg | 0.26 | 0.26 |
| Energy consumption, kW·h/kg | 56.4 | 40.5 |

On the basis of model-mathematical research and the obtained experimental data the prediction of technological parameters of plasma metallurgical production of titanium carbide was carried out. The optimal technological variant is the process of titanium carbonization by natural gas. The titanium carbide production was carried out in the conditions of NPF “Polimet” on the basis of industrial complex with power 150 kW.

For generation of the plasma flow three electric arc heaters (plasmatrons) EDP-104A were used with power up to 50 kW each, installed in the mixing chamber at the angle of 30° to the reactor axis, were used. The mixing chamber includes a steel water-cooled body with three welded fittings to it with threaded connections for three water-cooled evenly spaced on the plasmatrons circumference and the flange for the camera to be docked with the reactor section and a device for the input of highly dispersed raw material [1]. For injection of finely dispersed raw material a water-cooled tuyere was installed. Its inner diameter was 0.004-0.008 m, so that its lower end was removed from the impact point of the plasma jets at a distance of 0.5-1.0 calibers. The mixing chamber and reactor sections were made of stainless steel. The change in the reactor length and injection of a cold gas (nitrogen) into the plasma flow through the quenching ring, installed at the reactor outlet, makes it possible to quench the synthesis products in different temperature zones. The quenching ring is a hollow metal disk with thickness 0.008 m. The equipment keeping the reactor functioning includes systems of electro-gas and water supply, test instrument, automation, controlling the composition of the plasma-forming and the exhaust gas from the reactor, dosing of the charge and capture of products. Features of a three-jet reactor are given in Table 3.

**Table 3.** Characteristics of the three-jet reactor.

| Reactor characteristics | Values |
|-------------------------|--------|
| Arc power, kW           | 30 42 55 66 80 110 150 |
| Consumption of plasma-forming gas (nitrogen), 10⁷ kg/s | 22.20 28.50 32.00 38.10 44.00 57.15 78.30 |
| Service life of plasmatrons*, h | 120 110 110 110 110 100 100 |

*
*cathodic insertions from thoriated tungsten

Plasmatrons EDP-104A, the design of which is presented in [4, 5], operate on direct current with the following parameters of the electric arc: the arc voltage is up to 250V, current – up to 200 A. The stabilization of the electric arc – gas-swirl due to the tangential entry of the plasma-forming gas and methane through the swirl-insulator. Plasmatrons anodes are copper water-cooled with internal diameter 0.008 m with a practically unlimited service life in the presence of cooling. Plasmatron cathodes consists of copper water-cooled housings and cathode insertions of tungsten, pressed into the body up to its surface (to reduce the electron yield work) with a diameter of 0.003 m and with service life 100-120 hours. Ignition of the electric arc is carried out by breakdown of the gap between the cathode and the anode with high voltage pulse. The arc is drawn into the anode stabilized on the plasmatron axis by the swirled flow of nitrogen. The thermal efficiency of the plasmatrons with power of 50 kW at the minimum consumption of plasma forming gas is 50-52%. This design makes it possible to achieve the following: to reduce the specific erosion of the electrodes and improve their operational life to commercially acceptable levels; apply a more efficient performance of the cathode and the swirl-insulator for the working and the protective gases; install plasmatrons in the mixing chamber of the three-jet once-through reactor without changing its geometric and thermal characteristics.

Power supply of the industrial plasma reactor is carried out by a thyristor of the converter unit series AT4-750/600 having a steeper volt-ampere characteristic and the following operating parameters: power 450 kW; rectified voltage, V-600; rectified current, A-750; efficiency at nominal speed, 96%; supply voltage, kV-6.

Technical nitrogen with an oxygen content of 0.5% is used as a plasma-forming gas. Natural gas with a methane content up to 94% of volume is used as carbonizer. For dosing of the powdered raw material the dosing device of a mixed electromechanical and gas-swirling type with intermittent action and removable cylinder – receiver of the powdered raw material constructed by the Institute of Solid State Chemistry and Mechanochemistry of the Siberian Branch of the Russian Academy of Sciences [6].

Titanium carbide capture system includes a settling chamber where up to 10% of nanopowder is captured and the process gas temperature decreases to 60°C, and two alternately working bag filters (trapping up to 85% of nanopowders) [7, 8]. The bag filter for trapping nanoscale powders, including a housing with a cooling jacket and with pipes for supplying gas powder mixture and the discharge of treated gases, trapping sleeve, regeneration system with the installed coaxially outside the sleeve chamber with radial gas-tight partitions and pipes for supplying the regenerating gas, collector for the nanodispersed powder with a slide gate device. With the nanopowder accumulation the gate device is periodically opens and nanopowder falls out into the collector. The filter cloth is a metal gauze from chromium-nickel steel of twill weave. The use of the bag filter of this design allows to separate titanium carbide from gases, enhance the degree of its trapping, prevent particle coarsening and their surface oxidation, reduce the volume of regenerating and cleaning gas, reduce the necessary filter surface. Plasma synthesis products were investigated by X-ray, chemical, electron microscopy, derivatographic analyses, as well as by BET to determine their specific surface. Also methods of transmission (TEM) and scanning electron microscopy (SEM) were used.

The plasma synthesis product is the titanium carbide TiC. Titanium carbide content in the products of synthesis is 92.88-93.42%. The micrographs of titanium carbide are given in Figure 1. The nanopowder titanium carbide is represented by spherical aggregates ranging in size from 150 to 600 nm, formed by the particles of the cubic form within a wide size range – from 10 to 60 nm. The faceted form of titanium carbide particles indicates their formation according to the mechanism of “vapour – crystal”, presumably during the interaction of titanium vapour and hydrogen cyanide.

The presence of aggregates of various volumes in the synthesis products indicates a high possibility for the further nanoparticles coarsening by their coagulation when the temperatures are lowered.
Carbide is accompanied by free carbon represented by spherical particles of sizes preferably 10-30 nm.

![Image](image1.jpg)

**Figure 1.** Micrographs of titanium carbide nanopowder – SEM: a – in the condition after synthesis; b – morphological pattern of the aggregate; c – ensemble of nanoparticles; d – a cube-shaped nanoparticle.

The optimal values of technological factors, and the main characteristics of titanium carbide correspond to the following: titanium powder fineness – 5 µm; quantity of number carbonizer, % from the stoichiometric – 120-140; the initial temperature of the plasma flow, K – not less than 5400; quenching temperature, K – 2600-2800; titanium carbide yield, % mass – 92; productivity, kg/hr – 3.7; rate, kg/h·m³ – 4111 (which is 30-50 times higher than the rate of traditional metallurgical productions); specific surface, m²/kg – 33000-35000; particle size, nm 34-36; shape of the particles – spherical

The synthesis products contain titanium monocarbide with a face-centered cubic lattice with the parameter a=0.4323 nm, which is 0.0004 nm less than of the bulk crystals. This may be due to a non-equilibrium state in the particles smaller than 100 nm of near-surface layers, resulting in deformation (compression) of crystal lattices, atoms shift from ideal positions, the appearance of micro stresses [9, 10]. Microstress of the lattice, evaluated by the ration value Δa / a is (0.92 ± 0.10)-10-3. Free pyrolytic carbon is formed, presumably, during methane decomposition in the amorphous state and does not appear in the diffraction patterns.

Estimation of economic efficiency of the plasma metallurgical production of titanium carbide shows that at the sale price of 305 USD/kg it can be competitive on the world market of nanomaterials, where today the leading foreign manufacturers of carbide nano-powders established the price ranging within 500-2000 USD/kg.

**3. Conclusions**

On the basis of the model-mathematical and technological research the optimal values of parameters for nano-titanium carbide synthesis and its physical and chemical characteristics are found. It is found that during carbidization of titanium powder by methane in the conditions of plasma nitrogen flow within the temperature range 5400-2600 K the product of plasma synthesis is titanium carbide TiC.
The phase and chemical compositions, dispersion, morphology and oxidation of synthesis products were investigated. The following main technical and economic parameters of the proposed technology as productivity, intensity, cost, and a sale price were defined.

4. References

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