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Titanium Carbide: Nanotechnology, Properties, Application

G V Galevsky [1,a], V V Rudneva [1,b], A K Garbuzova [1,c], D V Valuev [2,d]

[1]Siberian State Industrial University, Novokuznetsk, Russia
[2]National Research Tomsk Polytechnic University, Yurga Technological Institute branch of Tomsk Polytechnic University 652050, Kemerovo region

[a]e-mail: kafcmet@sibsiu.ru, [d]e-mail: valuevden@rambler.ru

Abstract. The paper develops scientific and technological bases for fabrication of titanium carbide which is a nanocomponent of composite materials. The authors determine optimum technology specifications and the main titanium carbide properties: fineness of titaniferous raw materials, carbide-forming agent quantity, set temperature of plasma flow, tempering temperature, titanium carbide yield, productivity, specific surface, size and shape of particles. The paper includes equations to describe how the major specifications of the fabrication technique influence the content of titanium carbide and free carbon in the end product.

Introduction

Titanium carbide is a synthetic, super-hard, high-melting, heat-resistant material which is widely used for manufacturing metal-working tools, protective coatings and carbide steel. Producing nanocondition titanium carbide allows new applications including different types of composite materials [1 – 3].

The tests were carried out by means of an industrial plasma assembly based on a three-spool direct-flow vertical plasma reactor with the capacity of 150kW [4 – 6]. The plasma assembly consists of a mixing chamber with 3 plasmatrons EDP-104A which are fixed at an angle of 300, a reactor and a sedimentation chamber. Alongside with the reactor the plasma assembly includes a charge-conveying system, electricity-, gas- and water-supply systems, a synthesis product trapping system and a ventilation system. Powder and gas raw materials are fed into the plasma jet impact area with the help of a water-cooled lance. As this takes place a reaction mixture with predetermined composition is produced and nanodispersed particles are synthesized. Table 1 shows the main engineering specifications of the reactor.

Table 1. Reactor specifications

Feature	Values
Capacity, kW	150
Reactor type	three-spool direct-flow vertical
Plasmatron type, capacity, kW	EDP-104A, 50
plasma-supporting gas	nitrogen
Heated gas weight, kg/h	32.5

Feature	Values
Inside diameter, m	0.054
Reactor volume, m^3	0.001
Reactor channel lining	zirconium dioxide ZrO_2
Plasma flow temperature, K	5400 (L=0) – 2200 (L=12)
Lining temperature, K	1549 (L=0) – 770 (L=12)
Specific electric power, MW/m^3	2142
Operational life of anode cathode	3125 112
Titanium carbide erosion contamination, % anode weight cathode weight	Cu-0.0000954% W-0.0000002%

The specifications of the reactor prove that it is an up-to-date electro-thermal device.

The experiments were carried out in the reactor heat-insulated by zirconium dioxide lining with wall thickness of 0.005m and outside diameter of 0.066m which reduces its diameter to 0.056m. Titanium powder (alternative 1) and titanium dioxide (alternative 2) powder were chosen as raw materials, natural gas with methane content of 96% was used as carbide-forming agent. Table 2 shows properties of raw materials and plasma-supporting gas for titanium carbide synthesis.

Table 2. Raw materials and plasma-supporting gas

Raw materials	Base material content, not less than %	Dispersity, µm
Fine titanium powder PTMk	99.9	0.5-5
Titanium dioxide pigment R-1 (National State Standard 9808-84)	99.0	-1
Methane (natural gas)	93.6 (ethane-3.0; propane -2.18; butane -1,18)	-
Nitrogen (National State Standard 9293-74)	99.5 (oxygen content not more than 0.5)	-

Having taken into consideration properties of raw materials and plasma-supporting gas as well as reactor operating conditions we have developed the necessary specifications for thermodynamic and kinetic process simulation which are described in papers [7, 8]. The results of the simulation and mathematical calculations let us project specifications for production of titanium carbide by plasma method.

The experimental research demonstrated that the content of titanium carbide and free carbon in the end products has increased. The following equations for titanium carbide production are obtained. They allow estimating the influence of different factors on synthesis parameters, optimizing and controling the processes.

$$[TiC(1)]=17.3211+0.0105\cdot T_0-0.0156\cdot T_3+0.1859\cdot[CH_4]-3.432\cdot\{H_2\}-0.4078\cdot[N]+0.000004562\cdot T_0\cdot T_3+0.000782\cdot T_0\cdot\{H_2\}-0.0000567\cdot T_3\cdot[CH_4]-0.000435\cdot T_3\cdot\{H_2\}+0.0001353\cdot T_3\cdot[N]; \qquad (1)$$

$$[TiC(1)-C_{free}(1)]=-53.95+0.01152\cdot T_0+0.0476\cdot[CH_4]+0.1325\{H_2\}+0.09257\cdot[N]-0.00000576\cdot T_0\cdot$$

$$\begin{gathered}\cdot T_3 - 0.002938\cdot T_3 - 0.00000876\cdot T_0\cdot[CH_4]-\\ -0.00000588\cdot T_0\cdot\{H_2\}+0.00000728\cdot T_3\cdot[CH_4]-0.000053\cdot T_3\cdot[N]+\\ +0.000417\cdot\{H_2\}\,[N];\end{gathered}\tag{2}$$

$$\begin{gathered}[TiC(2)]=-182.277+0.05187\cdot T_0+0.000927\cdot T_3+0.9428\cdot[CH_4]-\\ -0.4464\cdot\{H_2\}-0.1208\cdot[N]-0.0001878\cdot T_0\cdot[CH_4];\end{gathered}\tag{3}$$

$$\begin{gathered}[TiC(2)-C_{free}(2)]=-13.162+0.01157\cdot T_3+0.01588\cdot[CH_4]-\\ -0.1244\cdot\{H_2\}+0.00013\cdot[N]-0.000001162\cdot T_0\cdot T_3+0.00279\cdot T_0+\\ +\,0.000057\cdot T_3\cdot\{H_2\}+0.005707\cdot\{H_2\}\cdot[N]\end{gathered}\tag{4}$$

where T_0 is set temperature of plasma flow, K; T_3 is tempering temperature, K; $[CH_4]$ is hydrocarbon percentage of the amount stoichiometricaly needed for producing titanium carbide, %; $\{H_2\}$ is concentration of hydrogen in plasma-supporting gas, % of volume; [N] –percentage of atomic nitrogen in plasma-supporting gas of the amount stoichiometricaly needed for producing hydrogen cyanide, %. Titanium carbide content in both cases depends on carbide-forming agent concentration, set temperature of plasma flow and tempering temperature.

Table 3 shows the main synthesis specifications and properties of titanium carbide. Having compared the two alternatives, we determined that carbidising titanium powder with methane is preferable. General properties of the synthesized titanium carbide meet requirements to nanodisperse components of composite materials.

Table 3. Synthesis indices and properties of titanium carbide

Synthesis indices and properties of titanium carbide	Alternative I (TiO_2 + natural gas)	Alternative II (Ti + natural gas)
Exchange gas composition, % of volume – nitrogen	99.5	99.5
Carbide-forming agent composition, % of volume	93.6	93.6
-methane	3.0	3.0
-ethane	2.2	2.2
-propane	1.2	1.2
-butan	-	-
Titaniferous raw material fineness, µm	1-3	5
Percentege of carbide-forming agent, % of stoichiometric one	120-140	120-140
Set temperature of plasma flow, K	5400	5400
Tempering temperature, K	2600-2800	2600-2800
Chemical composition, % of weight		
-TiC	91.62-92.13	92.88-93.42
- titanium dioxide	6.56-6.82	-
-free titanium (Ti+O)	-	5.37-5.68
-free hydrogene	1.31-1.56	1.21-1.44
- volatile matter	0.82-0.97	0.97-1.11
Titanium carbide yield, % of weight	92	92
Specific surface, m^2/kg	29000-32000	33000–35000
Particle size*, nm	38-42	34-36
Particle shape	facetted, cubic	facetted, cubic
Titanium carbide nonopowder oxidation $^{**}\times10^7$, kg O_2/m^2	12.5	8.6
Productivity, kg/h	2.8	3.7
Note: *this index is calculated according to the size of specific surface **this index was measured after exposure of the air during 24h.		

The end-product contains titanium monocarbide with cubic face-centered space lattice in which a = 0.4323 nm, which is by 0.0004nm less than that with massive crystals. It is stipulated by nonequilibrium conditions of near-surface layers particles less than 100 nm in size, which leads to deformation (compression) of space lattices, displacement of atoms from ideal positions, generating microstresses. With the first alternative titanium carbide is accompanied by dioxide with rutile and anatase space lattice. Free pyrolytic carbon which accompanies carbide is generated due to amorphous methane decomposition and it cannot be seen on the diffractograms. With alternatives I and II, the end products contain the following percentage of the weight (%): TiC – 91.88 and 93.15; $C_{free.}$ – 1.44 and 1,33; N – 0.90 and 1.00, and have specific surface 30000 and 34000 m^2/kg.

Titanium carbide nanopowder consists of round-shape aggregates from 150 to 600 nm in size formed by cubic particles with quite wide range of dimensions: from 10 to 60 nm. Facet shape of titanium carbide particles proves that they are formed according to “vapor – crystal” pattern when titanium and hydrogen cyanide vapors undergo a reaction. Aggregates of different sizes which can be found in the end product indicate that further aggregation of nanoparticles by coagulation at lowered temperatures is highly prabable.

A characteristic feature of pyrolytic carbon nanopowder is its ability to form micro-aggregates up to 100 – 150 nm in size with 6 – 10 particles 30 – 40 nm in size. Evidently the obtained titanium carbide greatly differs by its nanolevel and morphology from its micropowder obtained by mechanical dispersion of carbide of carbomechanical furnace synthesis.

Conclusion

Scientific bases of titanium carbide fabrication in plasma reactor including thermodynamic conditions of carbide forming and kinetic laws of evaporating titanium raw material are worked out.

It is proved that carbidization of titanium is a preferable method of titanium carbide plasma fabrication. This technology applies PTMk metallic titanium, nitrogen (National State Standard 9293-74) as plasma-supporting gas, methane as carbide-forming agent. Optimal technological indices and titanium carbide properties are determined.

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