Nanopowders Synthesis of Oxygen-Free Titanium Compounds—Nitride, Carbonitride, and Carbide in a Plasma Reactor

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Abstract The synthesis of titanium nitride, carbonitride, and carbide nanopowders from titanium tetrachloride vapor in the stream of hydrogen or hydrogen–nitrogen plasma, generated by an electroarc torch, in a confined-jet flow reactor has been experimentally studied. Single-phase nanopowders with a NaCl-type cubic crystal lattice as assemblies of preferably cube-shaped nanoparticles of a 20–150 nm size and aggregates based on them have been obtained in the experiments. By varying the synthesis parameters, it has been possible to prepare titanium nitride nanopowders with a specific surface area in the range of 11–39 m²/g containing 18.8–22.5 wt% nitrogen, which corresponds to the empirical formula TiN_{0.79}–TiN_{0.99}. The titanium carbonitride nanopowders had a specific surface area of 13–23 m²/g, carbon and nitrogen contents of 7.5–13.6 and 13.5–5.1 wt%, respectively. The titanium carbide nanopowders had a specific surface area of 14–45 m²/g and carbon contents of 17–21 wt%. Most reached yield of main products was 94%.

Keywords Titanium • Nitride • Carbide • Carbonitride • Tetrachloride Nanopowder • Synthesis • Thermal plasma • Reactor

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Introduction

Oxygen-free titanium compounds (OFTC)—Nitride, carbonitride, and carbide—have a unique combination of physicochemical and mechanical properties: high melting point, thermal conductivity, chemical stability, and hardness, including those at high temperatures [9, 12]. Owing to these properties, OFTC are of great interest for the creation of materials used in the manufacture of cutting tools, wear-resistant articles and coatings, biocompatible materials and coatings, structural elements operating at high temperatures, etc. For the creation of new nanostructured materials with improved properties compared to the conventional ones, their designers pay a good deal of attention to nanosized powders of inorganic compounds of elements, including OFTC [3, 4]. To date, various methods for the synthesis of titanium nitride, carbonitride, and carbide nanopowders have been proposed, of which processes carried out in a flow of thermal electric-discharge plasma using various titanium-containing feedstocks—titanium metal and its compounds, such a hydride, tetrachloride, and dioxide—are the most widespread place [2, 5–7, 13–17]. Nonetheless, there is no information about commercialization of plasma processes for producing OFTC nanopowders.

For practical implementation of nanopowders synthesis of titanium nitride, carbonitride, and carbide, the most appropriate feedstock is titanium tetrachloride manufactured on an industrial scale to produce titanium metal and titanium dioxide (global production of the titanium sponge alone was about 190,000 tons in 2014 [8]). Titanium tetrachloride has a low boiling point (410 K) and can be easily transferred to the vapor state, making it possible to conduct the plasma-assisted synthesis involving gaseous reactants to produce the desired nanopowders with a uniform particle-size composition. The practical implementation of the production of nanopowders in thermal plasma requires the creation of equipment that ensures the necessary performance of the process and has a long service life. The most effective solution in this line is the use of plasma reactors based on arc plasma torches. To date, electric arc gas heaters (plasma torches) are among the most common devices for generating a low-temperature plasma [18]. This is due to a number of advantages provided by the use of plasma torches: the possibility of heating any gas or mixture to a relatively high-weighted average temperature (1000–5000 K), a high efficiency of heating (90%), a long continuous operating life (to 1000 h), relative simplicity of design of experimental facilities, and sufficient ease in managing operating modes with simultaneous high reliability and robustness.

Plasma-enhanced nanopowder production processes can be conducted in the steady-state continuous mode using a confined-jet flow reactor, in which the nanopowder is deposited on the reactor wall having a temperature that does not permit sintering of the deposited particles and the resulting layer is periodically removed from the wall [1].

The aim of this study was to implement on a laboratory-scale process for the manufacturing of titanium nitride, carbonitride, and carbide nanopowders in an embodiment that is the most suitable for its subsequent commercialization. In view

of the foregoing, a process of this kind can be the synthesis of the desired products by reacting titanium tetrachloride vapor (or its mixture with methane) with arc torch-generated hydrogen–nitrogen thermal plasma in a confined-jet flow reactor. The possibility of commercialization of the process implies the availability of source of raw materials, existing technical solutions to create efficient thermal plasma generators operating over a wide power range, and technical solutions for the plasma reactor design with long service life.

Technique of Experimental Researches

Experimental study of the synthesis of titanium nitride, carbonitride, and carbide nanopowders was performed using a plasma unit, based on an arc torch-generating thermal plasma at a rated power of 25 kW, by reacting a mixture of titanium tetrachloride vapor and nitrogen with a hydrogen–nitrogen–argon thermal plasma. In the synthesis of titanium carbonitride and carbide, methane was added to the titanium tetrachloride–nitrogen mixture. To generate plasma, a dc arc plasma torch at a nominal power of 25 kW was used. The experimental setup is shown in Fig. 1. The reactor of 600 mm in length and 200 mm in diameter had water-cooled walls; the reactor design provided for the possibility of placing inside the reactor a quartz tube of a 150 mm diameter with attached thermocouples for measuring the temperature of the powder deposition surface.

Fig. 1 Experimental plasmachemical unit. 1 TiCl_4 supply and evaporation system, 2 Plasma generator, 3 Powder removal system from reactor walls, 4 Reactor, 5 Product collectors, 6 Cleaning system of plasma generator nozzle, 7 Filtration device, 8 Off-gases purification system

In the reactor volume, the mixing of the reactants and their chemical transformation occurred to form OFTC nanoparticles, which were deposited on the reactor walls and carried over on the bag filter. After the filter, the gaseous products entered into a bubbling absorber, where the chlorine-containing products were absorbed. The range of variation of the parameters of the titanium nitride and carbonitride nanopowder production processes is shown in Table 1.

Complex instrumental analysis of the obtained nanopowders included the following:

X-ray diffraction (XRD) performed using a RIGAKU Ultima-4 diffractometer in filtered Cu K α radiation with a high-speed detector D/teX, the software package PDXL, and the PDF-2 database;

measurement of the BET specific surface area of the powders with a Micromeritics TriStar 3000 surface area and porosity analyzer;

measurement of the particle-size composition of the powders with a Mastersizer 2000 M laser-diffraction particle-size analyzer;

electron microscopic examination with an FEI Versa 3D, Helios 650 and Scios scanning microscope (SEM) and an FEI Tecnai G2 F20 transmission microscope (TEM);

determination of total carbon and nitrogen using LECO (model CS-400 and TS-600 analyzers, respectively);

determination of total chlorine.

Results and Discussion

The results of earlier calculations for OFTC receiving processes in the approximation of equilibrium thermodynamic model testify to a possibility of synthesis of titanium nitride, carbide, and carbonitride at the interaction of titanium tetrachloride

Table 1 Variation range of process parameters

Parameter		Range	Unit
Flow rate of TiCl ₄		0.1–1.0	kg/h
Flow rates of plasma gases	H ₂	0.2–1.4	n. m ³ /h (STP)
	N ₂	0.2–0.8	n. m ³ /h (STP)
	Ar	0.0–2.5	n. m ³ /h (STP)
Flow rate of gases fed to TiCl ₄ supply line	N ₂	0.0–1.1	n. m ³ /h (STP)
	Ar	0.1–0.2	n. m ³ /h (STP)
	CH ₄	0.00–0.17	n. m ³ /h (STP)
Atomic ratio of elements	H/Cl	2–47	
	N/Ti	10–129	
	C/Ti	0–2.1	
Plasma jet enthalpy, <i>I</i> _{pl}		3.0–6.3	kW*h/m ³
Temperature of nanopowder deposition surface, <i>T</i> _{quar}		400–815	°C

with nitrogen, methane, and their mixes, respectively, in the presence of hydrogen [10]. For the supply of main products yield come nearer to 95%, tenfold hydrogen excess in comparison with required stoichiometrical is necessary; thus, synthesis coproducts are the lowest titanium chlorides. Dependence of all main products yield on temperature has extreme character and the maximum of titanium nitride, carbide, and carbonitride yield are in the temperature range of 1100–1500, 2000–2200, and 1200–1800 K, respectively. During titanium carbide and carbonitride synthesis, there can be a condensed carbon as a part of equilibrium products; however, the condensed carbon is absent on the overhead temperature boundary line of the maximum yield of titanium carbide and carbonitride and at higher temperatures.

Strong inhomogeneity of the temperature and flow-rate fields in the confined-jet flow plasma reactor [11] can be responsible for the presence of titanium chloride impurities in the product because of differences in time–temperature conditions of chemical transformations. Since the titanium chlorides TiCl_3 and TiCl_4 have boiling points of 1230 and 410 K, respectively, the separation of titanium nitride nanopowder from the gas dispersion stream of the products at a temperature above 1000 K (given the significant dilution of TiCl_3 vapor with nitrogen and hydrogen) should exclude the presence of chloride impurities in the final product; however, the following reaction is thermodynamically allowed in this case:

The results of preliminary experiments were carried out in the reactor with the water-cooled wall, onto which the produced titanium nitride was directly deposited, showed that the yield of TiN under these conditions was no more than 50% and the product powder contained a significant amount of total chlorine as an impurity. The product yield was determined as the ratio of the mass of the resulting nanopowder to the theoretical mass of titanium nitride $\text{TiN}_{1.0}$, that could be obtained from the titanium tetrachloride consumed. When a quartz tube of a 180-mm-diameter was inserted in the reactor and maintained at a temperature of 670–1090 K, the titanium nitride yield increased to 70–94% and the total chlorine content was reduced to percent shares. These results suggest that reaction (1) hardly proceeds under the experimental conditions and all further experiments were carried out in the reactor with the quartz insert. Using the quartz insert not only elevated the temperature of the product deposition surface, but also provided an extension of the high-temperature zone in the reactor, leading to an increased yield of titanium nitride.

It was established experimentally that the interaction of TiCl_4 vapor with hydrogen–nitrogen plasma in the presence of nitrogen, methane, and their mixes in the confined-jet flow reactor results in the formation of titanium nitride, carbide, and carbonitride nanopowders, respectively. According to X-ray diffraction data, the product nanopowders are single phase and have a cubic crystal lattice of the NaCl type (Fig. 2a); their total chlorine content is at the level of tenths parts of percent, which was reached at a titanium tetrachloride flow rate of 0.2 kg/h. Increasing the feedstock flow rate to 0.4 kg/h resulted in decrease of main product

yield and increase in the total chlorine content of a few percent; X-ray diffraction pattern manifests the presence of hydrolyzed titanium trichloride $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ phase (Fig. 2b). The appearance of this phase is due to the sorption of TiCl_3 on the surface of nanoparticles and their interaction with water vapor present in the air during the removal of the nanopowder from the reactor wall, an operation that is carried out in contact with air.

The results of electron microscope examinations have shown that all powders are assemblies of nanoparticles of preferably cubic shape with a size of 20–150 nm and aggregates on their basis (Fig. 3). In the nanopowders found to contain $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$,

Fig. 2 X-ray diffractograms of titanium nitride, carbonitride, and carbide nanopowders

Fig. 3 Typical microphotographs of titanium nitride (a), carbonitride (b), and titanium carbide (c) nanopowders

a change in their morphology was noted, mostly faceted shape of the particles was replaced by a rounded shape, which was caused by the formation of a $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ shell on the originally cubic nanoparticles of titanium nitride (Fig. 4).

The nitrogen content of the titanium nitride nanopowders varied in the range of 18.8–22.5 wt%, which corresponds to the empirical formulas $\text{TiN}_{0.79}$ – $\text{TiN}_{0.99}$ and it is within the region of homogeneity of titanium nitride. The specific surface area of titanium nitride, carbonitride, and carbide nanopowders ranged within 11–39, 13–23, and 14–45 m^2/g , which corresponds to the average particle-size range of 100–27 nm.

The energy level of the processes in thermal plasma, which is defined by the plasma flow enthalpy, determines the temperature distribution in the reactor volume and is one of the most important factors on which both the physicochemical properties of the resulting nanopowders and the characteristics of the implemented process (reactants conversion, yield of the end product, and power consumption for its production) depend. As a result of the experiments, it was found that the change in enthalpy of the plasma jet has the strongest influence on the particulate composition of the titanium nitride. As the plasma jet enthalpy increases, the specific surface area of the resulting OFTC nanopowders decreases and, hence, the average nanoparticle size calculated from the measured values of the specific surface area increases (Fig. 5).

Fig. 4 Microphotographs of titanium nitride nanopowder with a $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ impurity

Fig. 5 Dependence of the specific surface area of titanium nitride (a) and carbide (b) nanopowder on the plasma flow enthalpy. The TiCl_4 flow rate is 0.2 kg/h, the element ratios are $\text{H}/\text{Cl} = 11$ –24, $\text{N}/\text{Ti} = 22$ –71 (a), $\text{H}/\text{Cl} = 38$ –41, $\text{C}/\text{Ti} = 1.4$ –1.5 (b)

For the titanium tetrachloride flow rate of 0.2 kg/h, increase in the plasma jet enthalpy from 3.0 to 5.6 kW*h/m³ leads to decrease in the specific surface area from 24.0 to 4.7 m²/g; this corresponds to change in the average particle size from 46 to 230 nm. Since the formation of titanium nitride nanoparticles in the plasma process occurs via the crystal–vapor macroscopic mechanism (indicated by the presence of faceted particles), the increase in the average particle size with an increase in the plasma jet enthalpy suggests a prevalence of the particle growth rate over to the rate of their formation. Unlike the case of titanium nitride synthesis, an increase of the plasma flow enthalpy in the receiving of titanium carbonitride results in increasing the specific surface area of the nanopowder, although the chemical composition remains definitely unchanged (Table 2). The changes in the specific surface area and, consequently, the average size of nanoparticles could be due to the formation of carbon nuclei during the pyrolysis of methane, which are additional centers of condensation in the formation of titanium carbonitride nanoparticles.

Increase in the specific surface area of the titanium carbonitride nanopowder from 13 to 20 m²/g was observed with increase in the C/Ti atomic ratio from 0.6 to 2, which could be caused by change in the condensed-phase nucleation rate with increase in the concentration of methane in the high-temperature zone and also the emergence of free carbon as an impurity.

The phase composition of the products remained unchanged with increase in the plasma jet enthalpy and, hence, the average particle size (Fig. 6a), but this led to some reduction in the nitrogen content of the resulting nanopowder: at maximum enthalpy of 5.6 kW*h/m³, the nitrogen content was 18.8 wt%. The introduction of methane admixed to titanium tetrachloride vapor into the plasma during the synthesis resulted in the substitution of carbon for nitrogen atoms in the nitride lattice; thus with increase in the C/Ti atomic ratio increased the carbon content and decreased the nitrogen content, maintaining their overall concentration at almost constant level (Fig. 6). The carbonitride nanopowders contain 7.5–13.6 wt% of carbon and 13.5–5.1 wt% nitrogen and the carbide nanopowders contain 17–21 wt % of carbon; their chemical composition was determined predominantly by the C/Ti atomic ratio in the reaction mixture (Fig. 6).

Table 2 Properties of titanium carbonitride nanopowders obtained by different plasma flow enthalpies

Enthalpy kW*h/m ³	TiCl ₄ flow rate (kg/h)	H/Cl ratio	C/Ti ratio	Specific surface area (m ² /g)	[N] (wt%)	[C], (wt%)
3.5	0.2	17.9	0.68	15.9	12.1	8.0
5.2	0.2	18.1	0.64	21.1	13.1	7.5

Fig. 6 Dependence of carbon (2), nitrogen (3), and the total content (*I*) in the titanium carbonitride (a) and carbon content in the carbide (b) nanopowders depending on the C/Ti ratio. **a** The plasma flow enthalpy is 4.6 kW·h/m³ (a), 3.0–3.2 kW·h/m³ (b), the TiCl₄ flow rate is 0.2 kg/h; the atomic ratios are H/Cl = 18 (a), 38–43 (b), N/Ti = 95

Conclusions

In this experimental study, we have shown the feasibility for synthesizing of titanium nitride, carbonitride, and carbide nanopowders from titanium tetrachloride vapor in the hydrogen, hydrogen–nitrogen plasma stream, generated by an arc plasma torch, in the confined-jet reactor. The yield of the main nanopowders has been achieved up to 94% by upgrading the reactor design with providing of wall temperature elevation in the reactor in the range of 670–1090 K, with the amount of total chlorine impurities being reduced to less than 0.1 wt%.

Single-phase nanopowders with a NaCl-type cubic crystal lattice as assemblies of preferably cube-shaped nanoparticles of a 20–150 nm size and aggregates on their basis have been obtained in the experiments. Varying the synthesis parameters has made it possible to prepare titanium nitride nanopowders with a specific surface area in the range of 11–39 m²/g containing 18.8–22.5 wt% nitrogen, which corresponds to the empirical formula TiN_{0.79}–TiN_{0.99}. The titanium carbonitride nanopowders had a specific surface area of 13–23 m²/g, carbon and nitrogen contents of 7.5–13.6 and 13.5–5.1 wt%, respectively. The titanium carbide nanopowders had a specific surface area of 14–45 m²/g and carbon contents of 17–21 wt%. Most reached yield of main products was 94%.

The study has demonstrated the feasibility of the synthesis OFTC nanopowders from titanium tetrachloride vapor in a reactor having a long service life. Further investigation should focus on optimizing the process to ensure the maximum yield of the desired products and minimum power consumption for the manufacturing of the products with a given set of physicochemical properties.

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