

Titanium nitride plasma-chemical synthesis with titanium tetrachloride raw material in the DC plasma-arc reactor

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Abstract. The possibility of plasmochemical synthesis of titanium nitride is demonstrated in the paper. Results of the thermodynamic analysis of $\text{TiCl}_4 - \text{H}_2 - \text{N}_2$ system are presented; key parameters of TiN synthesis process are calculated. The influence of parameters of plasma-chemical titanium nitride synthesis process in the reactor with an arc plasmatron on characteristics on the produced powders is experimentally investigated. Structure, chemical composition and morphology dependencies on plasma jet enthalpy, stoichiometric excess of hydrogen and nitrogen in a plasma jet are determined.

1. Introduction

Titanium nitride possesses unique physicochemical and physicomechanical properties [1, 2]. This results in a wide range of applications on TiN basis, such as production of the cutting tools with wear proof coatings. The newly developed nanomaterials processing techniques can improve the resulting wear properties in comparison with traditional techniques. Thus there is a great interest in nano-powders based on inorganic compounds, including titanium nitride. Processes using low-temperature plasma for production of titanium oxygen-free compound powders are currently used [3-5]. Plasma synthesis is the most universal method for nano-powder production for various size and chemical compositions. Nevertheless, information on commercial realization of plasma processes of titanium nitride nano-powders production is absent.

For practical realization of titanium nitride nano-powder synthesis the most common raw material is the titanium tetrachloride, which is commercially used for titanium and titanium dioxide production. Titanium tetrachloride has a low boiling temperature (410 K) and can be easily transferred to the gaseous state, providing possibility of plasma synthesis with participation of other gaseous reagents and production of uniformly graded nano-powders.

Practical realization of nanopowder production in thermal plasma requires an equipment design, which provides the necessary processes efficiency and has along service life. Plasma reactors on the basis of arc plasmatrons are known to be the most efficient in this field. Today an plasma-arc gas heater (plasmatron) is one of the most widespread devices for low-temperature plasma generation [8, 9]. Its advantages are the possibility of heating of any gases and mixes to rather high average mass temperatures (1000-5000 K), effective efficiency of heating (up to 90%), a high resource of long-term operation life (up to 1000 h), relatively simple of experimental installations design, sufficient ease in management of operating modes at simultaneous high reliability and stability.

The main goal of this work was the realization of titanium nitride nano-powders synthesis in the laboratory scale with an option for future commercialization. For this purpose the synthesis of target products based the interaction of titanium tetrachloride vapor (or its mixes with methane) with the hydrogen-nitrogen thermal plasma generated in the arc plasmatron in the reactor with a limited jet current was chosen.

Possibility of process commercialization depends on the existence of a raw material source, the existing technical solutions for effective generators of thermal plasma working in the wide power range and also design of the plasmachemical reactor with a long service life.

2. Thermodynamic analysis

It is necessary to define the reaction products and titanium nitride output quantity in the reaction of titanium tetrachloride with nitrogen in the hydrogen at high temperatures and the process power consumption. In the presented work calculations of equilibrium structures and thermodynamic properties of $\text{TiCl}_4 - \text{H}_2 - \text{N}_2$ system are performed. For these calculations TERRA program complex for modeling of phase and chemical equilibrium in multicomponent systems is used [6, 7]. For the calculations it is assumed that the reactions take place in isobaric and isothermal conditions at temperatures in the range from 400 to 4000 K and a pressure of 0.1 MPa. Further calculation parameters are given in Table 1.

Table 1. Main parameters and relations of calculations of equilibrium structures and thermodynamic properties of $\text{TiCl}_4 + x \text{H}_2 + y \text{N}_2$ system

x	y	H/Cl	N/Ti
8	0.5	4	1
8	5	4	10
8	20	4	40
20	0.5	10	1
20	5	10	10
20	20	10	40

Based on the calculations results of equilibrium compositions and thermodynamic properties of $\text{TiCl}_4 + x\text{H}_2 + y\text{N}_2$ reactions products the following equilibrium characteristics of processes were defined:

- titanium nitride output TiN,

$$\{\text{TiN}_{\text{output}}\} = \frac{[\text{TiN}]}{Ti_{\text{sum}}}, \quad (1)$$

with [TiN] as titanium nitride content, mole/kg,

Ti_{sum} – total titanium content in the system, mole/kg,

- titanium chlorides TiCl_m output,

$$\{\text{TiCl}_{m\text{output}}\} = \frac{[\text{TiCl}_m]}{Ti_{\text{sum}}}, \quad (2)$$

with $[\text{TiCl}_m]$ as titanium chloride content, mole/kg,

- energy consumption necessary for 1 kg of titanium nitride produce at the set temperature of mixture, MJ/kg,

$$\{\text{Energy consumption}\} = \frac{(I_{T\text{sum}} - I_{0\text{sum}})}{[\text{TiN}] * Mr(\text{TiN})}, \quad (3)$$

where $I_{T\text{sum}}$ - total full enthalpy of equilibrium mixture at temperature T, kJ/kg,

I_{0sum} – total full enthalpy of initial reagents ($TiCl_4$ temperature is 500 K, other reagents – 298 K), kJ/kg, and $Mr(TiN)$ – TiN molecular weight;

- enthalpy of nitrogen-hydrogen plasma, which provides equilibrium mixture at the set temperature,

$$\{\text{Plasma enthalpy}\} = \frac{(I_{Tsum} - I_{0sum})}{(x + y) \cdot 22.4} \cdot 1000, \quad (4)$$

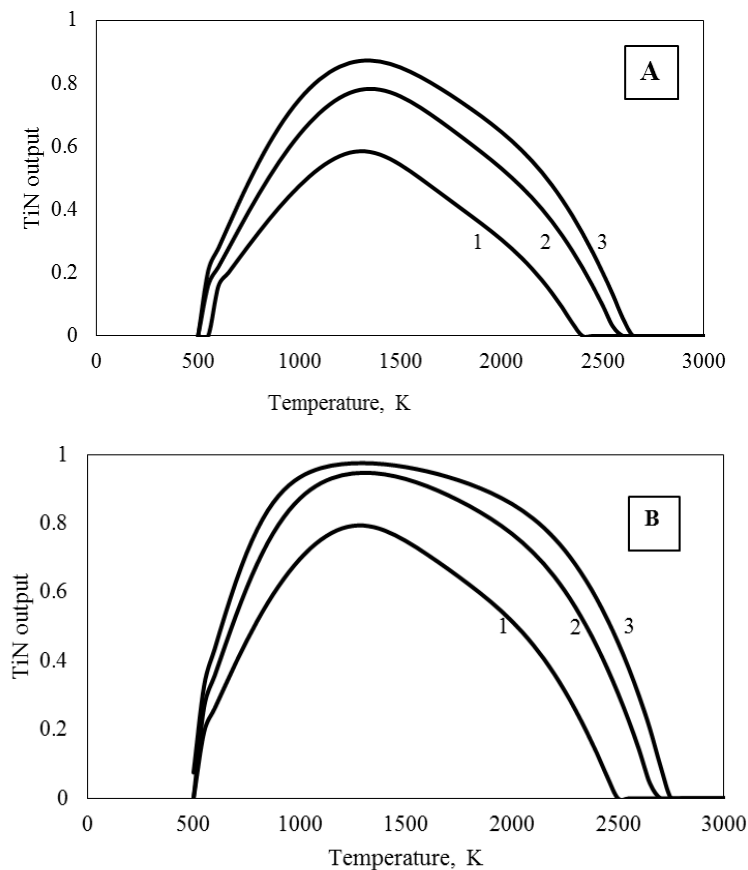


Figure 1. Dependency of TiN output on temperature at various compositions of initial reagents for (A) H_2 ratio $x=8$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$ and (B) H_2 ratio $x=20$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$.

As a result of the calculations dependencies of TiN output on temperature and a ratio of initial reagents are established (figure 1). It is calculated that values above 95% of TiN output are provided at $x = 20$ and at $y \geq 5$ and temperature 1300 – 1400 K.

At a temperature exceeding 1400 K there is a decrease in titanium nitride output. Thus in the whole system there is a formation of mainly $TiCl_3$ and $TiCl_2$ up to the temperature of 3000 K (figure 2). At a temperature below 1300 K titanium nitride transforms to tetrachloride $TiCl_4$.

It follows from calculations that in the equilibrium conditions during the synthesis of titanium nitride the main impurity will be $TiCl_3$ and $TiCl_4$. These components have a boiling temperature of 1230 and 410 K [10]. In order to decrease the concentration of these impurities in the product thermal vacuum processing can be used, considering that titanium nitride is a refractory compound.

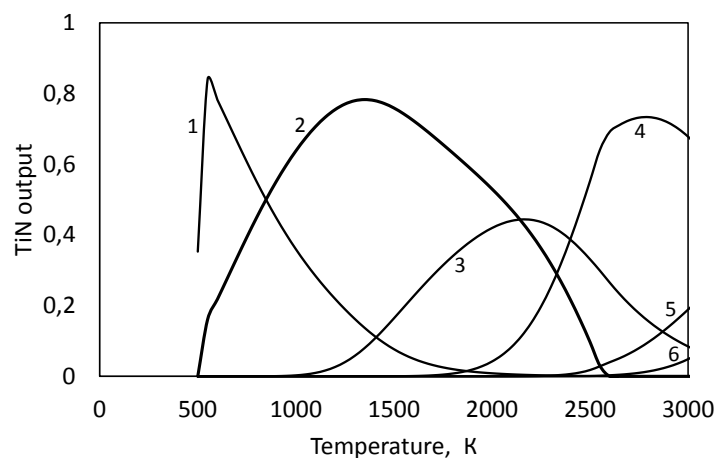


Figure 2. Dependence of titan ferrous components output on temperature at $x=8$, $y=5$.

1 – TiCl_4 , 2 – TiN , 3 – TiCl_3 , 4 – TiCl_2 , 5 – TiCl , 6 – Ti

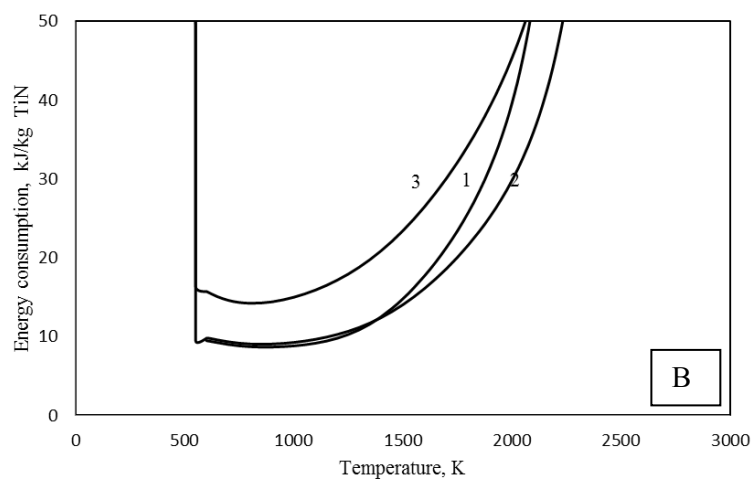
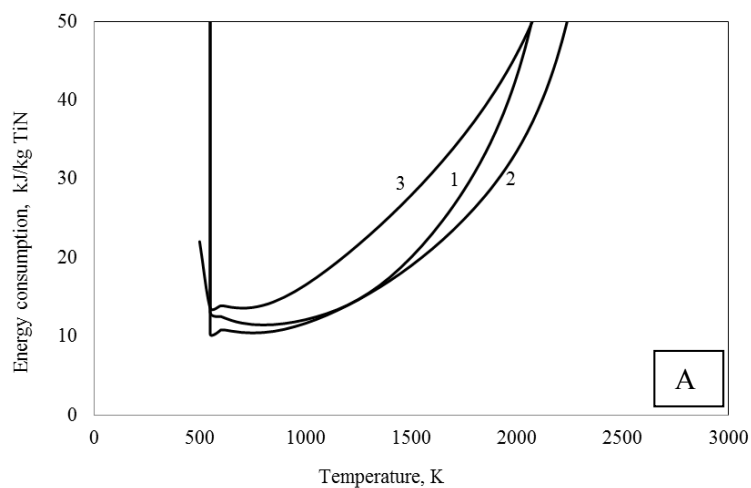


Figure 3. Dependence of energy consumption of titanium nitride produce on temperature at various compositions of initial reagents (A) H_2 ratio $x=8$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$ and (B) H_2 ratio $x=20$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$.

In the temperature field of the maximum titanium nitride output the energy consumption of its synthesis is 16 – 20 MJ/kg depending on excess of nitrogen (figure 3). The absolute minimum of energy consumption is in the temperature range of 550 – 750 K (at $x=20$) and 800 – 900 K (at $x=8$). However in these conditions titanium nitride output does not exceed 55 – 70%.

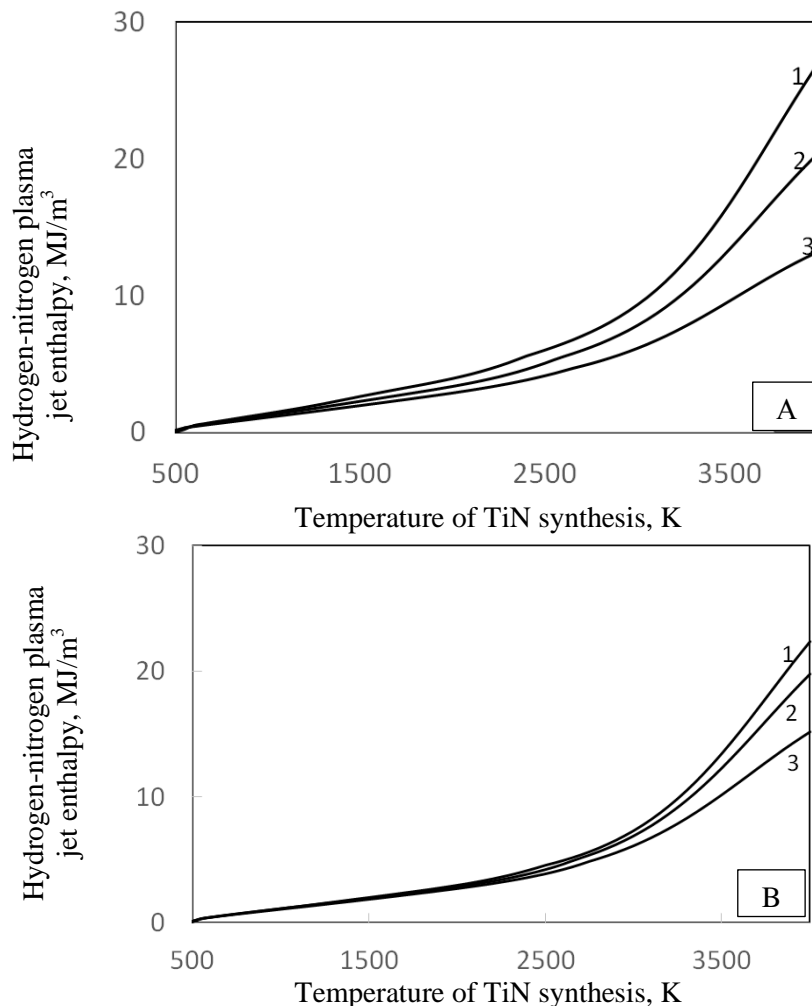


Figure 4. Dependence of hydrogen-nitrogen plasma jet enthalpy on TiN process synthesis temperature at various compositions of initial reagents (A) H_2 ratio $x=8$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$ and (B) H_2 ratio $x=20$ and N_2 ratio (1) $y=0.5$, (2) $y=5$; (3) $y=20$.

For providing the maximum titanium nitride output at $x=20$ and at $y \geq 0.5$ (process temperature - 1300 K) the necessary value of nitrogen-hydrogen plasma enthalpy is about 1.5 MJ/m³ (figure 4). This enthalpy can be easily provided and exceeded when using the existing designs of arc plasmatrons.

3. Experimental setup

Experimental investigations of titanium nitride nano-powder synthesis were conducted using a plasma setup based on the thermal plasma arc generator (figure 5). In this setup a power of 25 kW is necessary to provide interaction in the titanium tetrachloride - nitrogen mixture with hydrogen-nitrogen-argon thermal plasma.

In the reactor chamber a mixture of initial reagents and their chemical transformations used for formation of TiN nanoparticles are present. The nanoparticles were accumulated on reactor walls, and

also were taken out on the bag filter. After the filter gaseous products of reaction come to a bubbling absorber where there absorption of chlorine-containing products takes place.

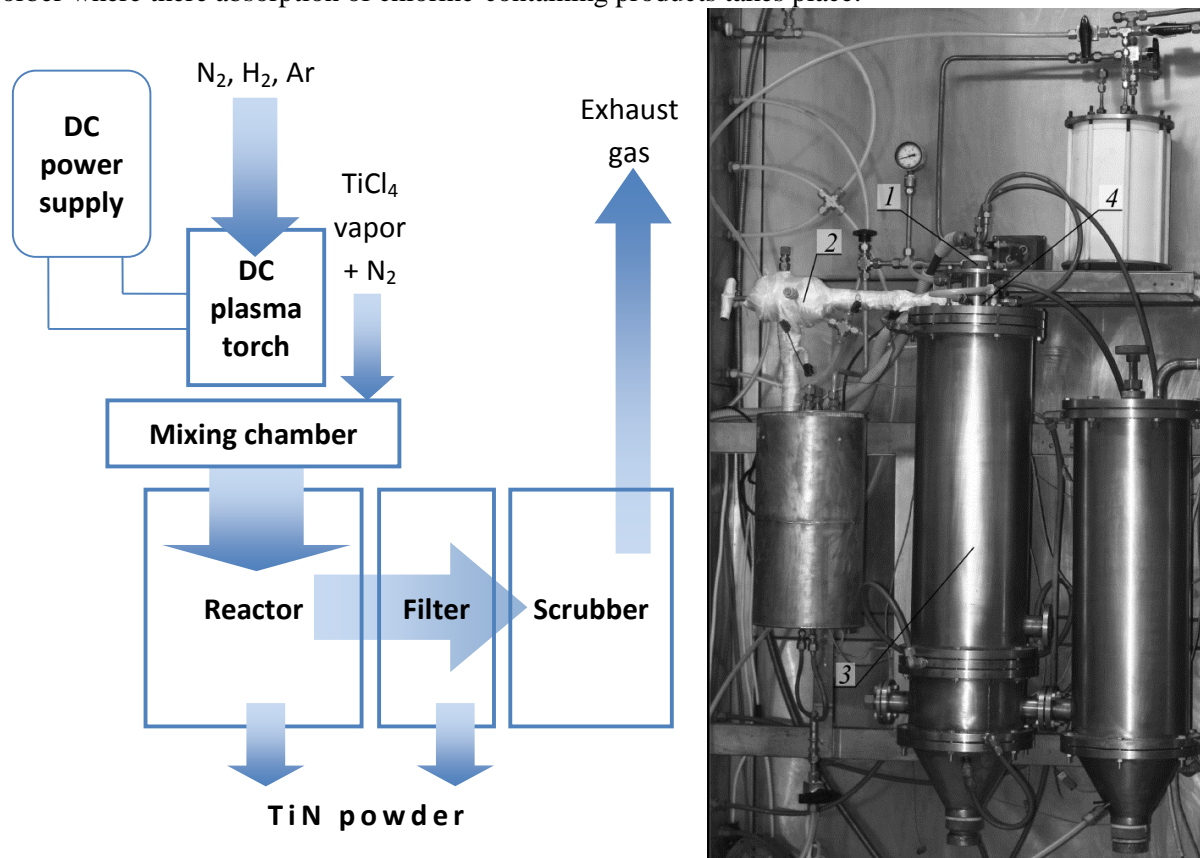


Figure 5. Experimental setup.

1 – DC plasma torch, 2 – $\text{TiCl}_4 + \text{N}_2$ steam line, 3 – reactor, 4 – mixing chamber

All heat loaded setup units are cooled with water. The cooling water thermal losses in each unit were defined by calorimetry. The heat of Q_i determined by a calorimetry which is taken away with water from a unit i (thermal losses) was calculated as:

$$Q_i = \frac{(T_i - T_0) \cdot G_i}{860}, [\text{kW}] \quad (5)$$

where T_i – water temperature at the exit from unit, °C; T_0 – water temperature on an entrance, °C; G_i – consumption cooling a water unit, kg/h.

The enthalpy of a plasma jet I_{pl} was calculated as the difference between the power N brought from a DC power source to a plasmatron and thermal losses Q_{pl} in plasmatron related to a total consumption of plasma-forming gases $\sum V_j$:

$$I_{pl} = \frac{N - Q_{pl}}{\sum_j V_j}, [\text{kWh/n.m}^3]. \quad (6)$$

Ratio of hydrogen of plasma and chlorine in TiCl_4 and ratio of nitrogen of plasma and titanium in TiCl_4 were set by change of a ratio of titanium tetrachloride and plasma-forming gases consumptions.

Liquid titanium tetrachloride fed the dosing pump in a high-temperature zone of the evaporator. Titanium tetrachloride vapor was injected by the transporting gas at a temperature of 200 °C in a plasma jet. As the transport gas nitrogen was used.

The complex physical and chemical analysis of the produced nanopowders included:

- the X-ray phase analysis (RFA) which is carried out on the RIGAKU Ultima-4 diffractometer in the filtered Cu K α radiation with the high-speed detector "D/teX", a software package of "PDXL" and the databank "PDF-2";
- measurement of powders specific surface by BET method on the analyzer of a specific surface and porosity "Micromeritics TriStar 3000";
- measurement of particle size distribution of the produced powders by laser diffraction method "Mastersizer 2000 M";
- electron microscopy on the scanning microscope (SEM) "JSM-6700F" ("Jeol Company") and on the translucent microscope (TEM) "Tecnai G2 F20" ("FEI Company");
- measurement of the total nitrogen content on the LECO TS-600 analyzer;
- measurement of the total chlorine content by Sheniger's method.

Produced TiN powder mean particles size depends on process parameters. Distribution by the size is normal for each operation. TiN powders dispersion changed in the range 230 – 30 nm, it includes the range of nanopowders with the size below 100 nm.

Main parameters of plasma process and the analyzed physical and chemical properties of the produced nano-powders TiN_x are specified in table 2.

Table 2. Main parameters of plasma process and the analyzed physical and chemical properties of the produced nanodimensional powders TiN_x

parameter	range	dimension
Mass rate of flow TiCl ₄ , G_{TiCl_4}	0,1 – 0,5	kg/h
Concentration Ti, C_{Ti}	$3,4 - 27,1 \cdot 10^{-3}$	mol Ti/mol gas
H ₂ consumption in plasma, $G_{\text{H}_2}^{\text{pl}}$	0,2 – 1,4	n.m ³ /h
N ₂ consumption in plasma, $G_{\text{N}_2}^{\text{pl}}$	0,2 – 0,8	n.m ³ /h
Ar consumption in plasma, $G_{\text{Ar}}^{\text{pl}}$	0,0 – 1,6	n.m ³ /h
N ₂ consumption in transport gas, $G_{\text{N}_2}^{\text{tr}}$	0,0 – 1,1	n.m ³ /h
Temperature of powder accumulation surface, T_{qz}	401 – 815	°C
Average integrated temperature of powder accumulation surface, $T_{\text{qz}}^{\text{av}}$	557 – 687	°C
Plasma jet enthalpy, I_{pl}	3,0 – 6,3	kWh/m ³
Ratio of hydrogen of plasma and chlorine in TiCl ₄ , $H_{\text{pl}}/\text{Cl} = (2 G_{\text{H}_2}^{\text{pl}}/22,4)/(4 G_{\text{TiCl}_4}/\text{Mr}(\text{TiCl}_4))$	2 – 47	mole/mole
Ratio of nitrogen of plasma and titanium in TiCl ₄ , $N_{\text{pl}}/\text{Ti} = (2 G_{\text{N}_2}^{\text{pl}}/22,4)/(4 G_{\text{TiCl}_4}/\text{Mr}(\text{TiCl}_4))$	10 – 129	mole/mole
Specific surface, S_{sp}	5 – 39	m ² /g
Medium particle size, $d = 1103,24/S_{\text{sp}}$	28 - 234	nm
Nitrogen mass concentration, [N]	5,1 – 22,5	mass. %
Chlorine mass concentration, [Cl]	<0,10 – 4,45	mass. %

4. Results and discussion

It is experimentally established that at interaction of TiCl₄ vapors with hydrogen-nitrogen plasma leads to formation of titanium nitride powder. According to the X-ray phase analysis (figure 6) the produced single-phase nano-powders also have a cubic crystal lattice like NaCl with the total ratio of chlorine of ~0.1%. This was provided due to the consumption of titanium tetrachloride of 0.2 kg/h. The resulting particle size lies in a wide range and depends on process parameters.

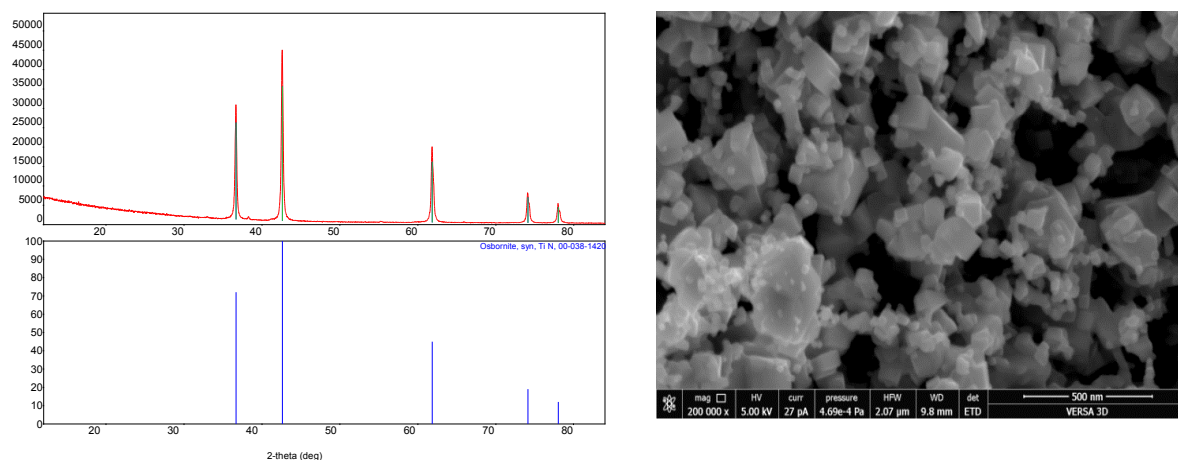


Figure 6. X-ray and SEM results for TiN nano-powders

The increase in consumption of raw materials to 0.4 kg/h led to decrease in a target product output and increase in the total content of chlorine to ~1%. Thus on a x-ray diffraction pattern the phase of the hydrolyzed titanium trichloride $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ was identified. Presence of this phase is caused by sorption of TiCl_3 on surface of titanium nitride nanoparticles and their interaction with the water vapors, which are present in the surrounding atmosphere during operation of removal of nano-powder from the wall of the reactor performed in air.

In the produced titanium nitride nanopowders the content of nitrogen changed in the range of 18.8–22.5 mass.%. That corresponds to formulas $\text{TiN}_{0.79}$ – $\text{TiN}_{0.99}$ and is within the range of homogeneity of titanium nitride. Results of SEM investigations has shown that all produced powders represent ensembles of nanoparticles mainly of cubic form with sizes of 20–150 nanometers and aggregates on their basis (figure 7, A). In nano-powders in which presence of $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ was detected, change of their morphology is noted – mainly faceted form of particles was replaced with roundish that is caused by formation of a cover of $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ on originally cubic nanoparticles of titanium nitride (figure 7, B).

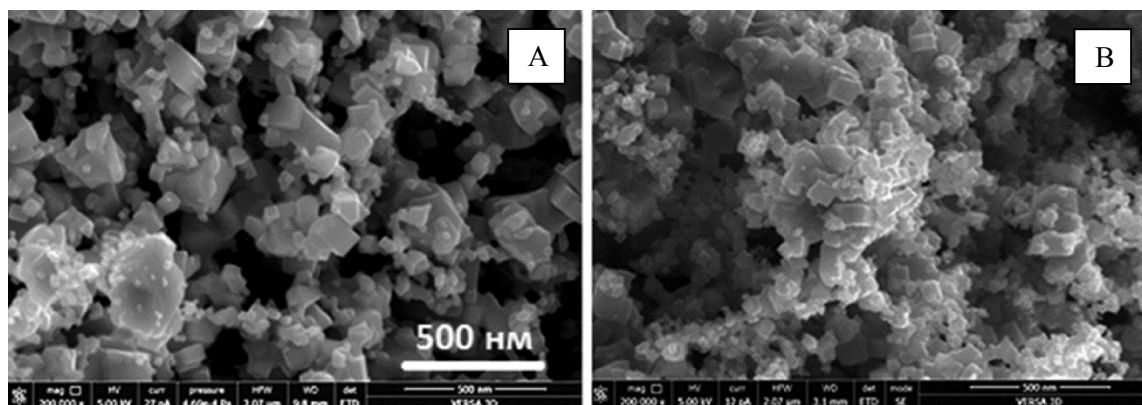


Figure 7. TiN (A) and with $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ (B) presence nanopowders produced SEM results

Formation of $\text{TiCl}_3 \cdot 6\text{H}_2\text{O}$ cover of titanium nitride nano-powder is undesirable. Therefore removal of the produced titanium nitride from the reactor has to be carried out without contact with air.

The specific surface of titanium nitride nano-powders varied within 11–39 m^2/g . That corresponds to the range of the average size of particles of 100–28 nm. This value is calculated from ratio $d=6/(\rho_{\text{TiN}} \cdot S)$, where d is the average size of particles, ρ_{TiN} density of nitride of the titan and S the size of a specific surface.

The energy level at which the process was performed is defined by a plasma jet enthalpy, which defines distribution of temperatures in the volume of the reactor. It is one of the major factors influencing both physical and chemical properties of the produced nano-powders and characteristics of the process, such as conversion degree of initial reagents, a target product output and the electric power consumption.

As a result of the executed experiments it is established that change of an enthalpy of a plasma jet has the strongest impact on particle size of the produced titanium nitride. With growing plasma jet enthalpy the specific surface of the produced titanium nitride nano-powder decrease is observed. Thus, the average size of nanoparticles calculated from the measured value of a specific surface increases (fig. 8).

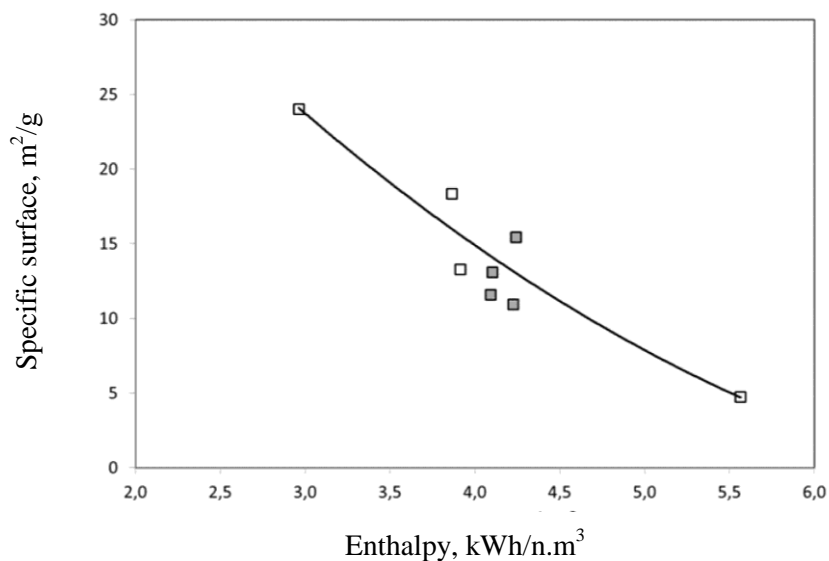


Figure 8. Produced TiN specific surface dependence on plasma jet enthalpy

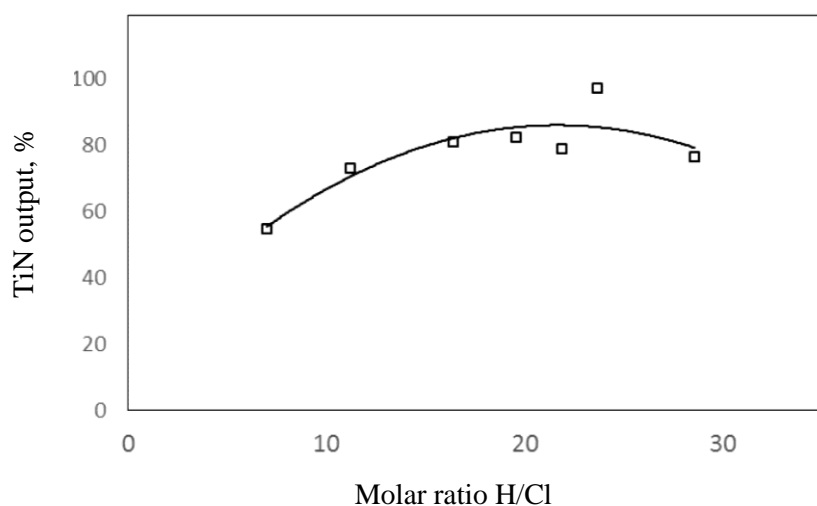


Figure 9. Produced TiN output dependence on molar ratio H/Cl

For a consumption of titanium tetrachloride of 0.2 kg/h the increase in enthalpy of a plasma jet of 3.0-5.6 kWh/m³ leads to decrease of a specific surface 24.0–4.7 m²/g. This corresponds to change of the average size of particles of 46-230 nm. Existence of a facet of particles indicates that titanium nitride nanoparticles in plasma process is formed on the “vapor - crystal” macromechanism, The

increase in the average size of particles with growth of the enthalpy of the plasma jet suggests that the prevailing growth rate of particles is related to the speed of their formation.

The phase structure of the received products remained invariable when increasing the plasma jet enthalpy and the average size of particles, respectively. However it led to some decrease in the content of nitrogen in the produced nano-powder. At maximum enthalpy of 5.6 kWh/m³ the content of nitrogen is 18.8 mass.%. Change of a molar ratio of the H/Cl elements within a range of 10-30 had no essential impact on the size of a specific surface of nano-powder of titanium nitride, however, influenced its output (figure 9).

The increase in the H/Cl ratio in the range of 7-20 led to growth of titanium nitride output. When further increasing the ratio, the output decreased a little. Existence of an extremum in the considered dependence is caused by influence of opposite operating factors – growth of a ratio of H/Cl (surplus of a reducer) leads to increase of the output. But at the same it time reduces process temperature at the expense of increase in amount of the hydrogen entering the reactor. Therefore the considered dependence has a maximum.

5. Conclusions

The presented investigations have shown the possibility of synthesis of titanium nitride nano-powders from vapors of titanium tetrachloride in a stream of the hydrogen-nitrogen plasma generated in an arc plasmatron.

From results of the carried-out thermodynamic calculation of equilibrium mixture can be concluded, that providing the target products output close to 95% requires tenfold excess of hydrogen in comparison to the stoichiometrically necessary amount, thus by-products of synthesis are the lowest titanium chlorides. Dependence of all target products output on temperature has extreme character and a maximum of titanium nitride output are obtained for the process temperature in range of 1100-1500K. The minimum energy consumption for production of 1 kg of target products in the vicinity of their maximum output is 20 MJ/kg.

The target nano-powders output reached in experiment is up to 94%, thus the total content of impurity of chlorine could be minimized to less than 0.1 mass.%.

In experiments single-phase nanopowders with a cubic crystal lattice like NaCl and the representing ensembles of nanoparticles of mainly cubic form with sizes of 20-150 nm and aggregates on its basis are produced. Change of parameters of synthesis allowed producing the titanium nitride nano-powders with a specific surface in the range of 11-39 m²/g containing 18.8–22.5 mass.%. This corresponds to gross - formula TiN_{0.79}-TiN_{0.99}.

Further investigations have to be performed in order to optimize the process, which can provide the maximum output of target products and the minimum consumption of the electric power when receiving target products with the set of physical and chemical properties.

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