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Thermodynamic Model of High-Temperature Synthesis of Oxygen-Free Titanium Compounds from Titanium Tetrachloride

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Abstract

Technological characteristics and equilibrium energy of plasma synthesis for titanium nitride, carbide and carbonitride - final product output and composition, energy consumption, plasma enthalpy required are calculated for the reactions:

- $TiCl_4 + x\ H_2 + y\ N_2$ (TiN synthesis);
- $TiCl_4 + x\ H_2 + z\ C_mH_n$ (TiC synthesis);
- $TiCl_4 + x\ H_2 + y1\ N_2 + z1\ C_mH_n$ (TiCN synthesis).

Calculations are carried out in the temperature range of 500 – 4000 K at the total pressure in system of 0.1 MPa and in the range of reagents ratio of: x = 8, 20; y = 0.5, 5, 20; z = 0.9, 1.0, 1.1; y1 = 5; z1 = 0.4, 0.5, 0.6.

Keywords: Thermal plasma, chemical equilibrium, characteristics, reactions, energy consumption, output, nitride, carbide, carboninride, tetrachloride, titanium

Introduction

Oxygen-free compounds of the titanium – carbide, nitride and carbonitride – possess unique specified of physicochemical and physico-mechanical characteristics: high values of melting temperature, heat conductivity, chemical stability, hardness, durability, including at high temperatures [1-3]. These properties of the specified compounds define wide application of materials on their basis in various technical applications, in particular in production of the cutting tool, wearproof details and coatings, biocompatible materials and coatings, structural element, working in high temperatures conditions. Considerable interest is represented by nanostructural materials, possessing increased properties in comparison with traditional materials, and receivable from nanodimensional powders of the considered oxygen-free titanium compounds [4].

Plasma synthesis is the most universal method of nanopowder production of elements and their various inorganic compounds and compositions in a controllable gas aerosphere – inert, reduction and oxidative.

To the present time, there are experimental works, in which possibility of production of observed oxygen-free titanium compounds from tetrachloride in plasma processes is shown [5-7].

The main advantages of plasma synthesis of nanopowders are defined:

- possibility of production of various types of nanopowders – individual elements, compounds and compositions;
- possibility to control of physicochemical properties of obtained powders in the course of plasma synthesis and production of base products with specified characteristics;
- high velocities of plasma processes and small sizes of reacting equipment;
- use of traditional raw materials;
- possibility of scaling with creation of production setup with high unit productivity.

Plasma synthesis of titanium nitride, carbide and carbonitride nanopowders can effectively be based on interacting of following reagents in the unified plasma reactor:

- $TiCl_4 + H_2 + N_2$ (TiN production);
- $TiCl_4 + H_2 + C_mH_n$ (TiC production);
- $TiCl_4 + H_2 + N_2 + C_mH_n$ (TiCN production),

where processes are carried out in streams of thermal plasma of hydrogen and a hydrogen -nitrogenous mix.

The work objective is calculations of energotechnological parameters of plasma processes group for production of observed oxygen-free titanium compounds - composition and output of final products, energy consumption for their production, necessary enthalpy of plasma stream - at interacting of specified above reagents based on equilibrium thermodynamic model.

Calculations method

To determine reaction products composition and output of titanium nitride, carbide and carbonitride at interacting of titanium tetrachloride with nitrogen, methane and hydrogen at heats, and also energy characteristics of process - calculations of equilibrium compositions and thermodynamic properties of systems

Ti – Cl – H – N, Ti – Cl – H – C and Ti – Cl – H – N – C with use of the program complex TERRA for modelling phase and chemical equilibria in multicomponent systems with respective database of thermodynamic properties of components are executed [8].

The used database consist of following titaniferous components: gaseous – Ti, TiCl, $TiCl_2$, $TiCl_3$, $TiCl_4$, TiN and condensed – Ti, $TiCl_2$, TiCl3, $TiCl_4$, TiC, TiN.

Titanium nitride, carbide and carbonitride are the compounds of variable composition having wide area of homogeneity [9,10] and element composition of these compounds, as well as their content in equilibrium system, generally should be defined as a result of calculations. The used program complex TERRA does not directly provide such possibility, therefore some titanium carbides, nitride and carbonitride are observed as the compound of constant composition, which matches to upper bound of homogeneity region.

Titanium nitride and carbide (TiN and TiC) have an equal crystal structure with a lattice of type NaCl and can form an infinite series of solid solutions TiC – TiN (titanium carbonitride), in which atoms of non-metals substitute each other. Thermodynamic properties of such solid solutions depending on their composition are absent in the literature and in database of the program complex TERRA, therefore titanium carbonitride is observed in approach of ideal solid solution TiC – TiN (TiC_xN_{1-x}).

Equilibrium compositions and thermodynamic characteristics of reactions products are counted at the compositions of initial reagents specified more below and relationships of corresponding elements:

$$TiCl_4 + (x\,H_2 + y\,N_2)_{plasma} \quad (1)$$

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

$TiCl_4 + z\ CH_4 + (x\ H_2)_{plasma}$ (2)

x	z	H/Cl	C/Ti
8	0,9	4,9	0,9
8	1	5	1
8	1,1	5,1	1,1
20	0,9	10,9	0,9
20	1	11	1
20	1,1	11,1	1,1

$TiCl_4 + z\ CH_4 + (x\ H_2 + y\ N_2)_{plasma}$ (3)

x	y	z	H/Cl	N/Ti	C/Ti
8	5	0,4	4,4	10	0,4
8	5	0,5	4,5	10	0,5
8	5	0,6	4,6	10	0,6
20	5	0,4	10,4	10	0,4
20	5	0,5	10,5	10	0,5
20	5	0,6	10,6	10	0,6

Calculations are executed under condition of reactions proceeding in isobar-isothermal conditions in the interval of temperatures 500 – 4000 K with step of 50 K at the general pressure in system 0.1 MPa.

Based on calculations results of equilibrium compositions and thermodynamic properties of reactions products (1-3) following equilibrium characteristics of processes are defined:

- output of titanium nitride TiN (reaction (1)),

{TiN output } = [TiN] / Ti_{sum},

where [TiN] – the content of titanium nitride, mole/kg,

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

- output of titanium carbide TiC (reaction (2)),

{TiC output} = [TiC] / Ti_{sum},

where [TiC] – the content of titanium carbide, mole/kg,

- output of titanium carbonitride TiC_xN_{1-x} (reaction (3)),

{TiC_xN_{1-x} output } = ([TiC] + [TiN]) / Ti_{sum},

- output of titanium chloride $TiCl_m$,

{$TiCl_m$ output } = [$TiCl_m$] / Ti_{sum},

where [$TiCl_m$] – the content of titanium chloride, mole/kg,

- composition of titanium carbonitride TiC_nN_{1-n},

{n} = [TiC] / ([TiC] + [TiN]),

- the energy consumptions, necessary for 1 kg production of titanium nitride, carbide or carbonitride at the specified temperature of composition, MJ/kg,

{Energy consumptions } = $(I^T_{sum} – I^0_{sum}) / (g_i*M_i)$,

where I^T_{sum} - a total full enthalpy of equilibrium composition at

To temperature T, kJ/kg,
I^0_{sum} – A total full enthalpy of initial reagents
($TiCl_4$ temperature is 500 K, for other reagents – 298 K, kJ/kg,
g_i – [TiN], [TiC], ([TiN] + [TiC]),
M_i – molecular weight of TiN and TiC;

- plasma enthalpy of nitrogen-hydrogen mix (reaction (1) and (3)) and hydrogen (reaction (2)), providing production of equilibrium composition at the specified temperature,

$$\{\text{Plasma enthalpy}\} = (I^T_{sum} - I^0_{sum}) / ((x + y) *22.4)/1000.$$

Results and discussion

Composition and output of reactions products

As a result of calculations for interacting of titanium tetrachloride with reagents in reactions (1-3) dependences of composition of reactions products and the output of titanium nitride, carbide and carbonitride from temperature and a relationship of initial reagents (fig. 1) are installed. In the observed range of parameters change, the output of matching oxygen-free titanium compounds can attain to 95 – 97 % and its magnitude increases with increase in a relationship of elements H/Cl in observed systems. In the field of maximum output of base products, the basic impurity is gaseous titanium chloride, and for titanium carbide and carbonitride – the condensed free carbon. Impurity of titanium chloride can be brought in to the final product in actual plasma processes if quenching (fast cooling) high-temperature composition of systems is carried out. Titanium chlorides $TiCl_3$ and $TiCl_4$ have boiling temperatures accordingly 1230 and 410 K [11] and for their removal thermo-vacuum treatment of resulting products can be effectively used, considering, that observed oxygen-free titanium compounds are refractory components.

Free carbon impurity in titanium carbide and carbonitride are absent in equilibrium compositions at the temperatures, which is a little exceeding temperatures of their maximum output. In figures 1 – 3 the thicker lines sections of the output of oxygen-free compounds match to the output of titanium carbide, nitride and carbonitride, that exceeds 90 %, and thus in titanium carbide and carbonitride there are no free carbon impurity.

TiN output (not less than 90 %) are provided for x=20 at temperature in the interval 1050 – 1650 K and y=5, and also in the interval temperatures 950 – 1850 K at x=20 and y=20 (fig 1a). The increase in relationship H/Cl expands a temperature range of 90 percent output of titanium nitride. At the temperatures exceeding specified overhead values, the output of titanium nitride decreases, and thus in system the lowest titanium chloride – mainly $TiCl_3$ and $TiCl_2$ are formed at the temperatures to 3000 K, and at the temperature low then 1050 and 950 K titanium nitride turns in tetrachloride $TiCl_4$.

The values of TiC output, exceeding 90 %, are provided at x=20 and z =1 over the range temperatures 1700 – 2400 K at z = 1 and over the range 1700 – 2500 K at x=20 and z=1.1, however temperature ranges in which there is no free carbon are 2100 – 2400 K and 2350 – 2500 K accordingly (fig. 1b). The increase in value of factor z (relationships of elements C/Ti) above unit narrows a range of 90 percent output TiC in which free carbon does not exist. As well as in the case of titanium nitride synthesis, the main titaniferous impurity of a base product is a titanium chloride.

Temperature dependences of the titanium carbonitride output at various relationships of initial reagents represent per se superposition of separate dependences of titanium nitride and carbide outputs from temperature, since, titanium carbonitride was observed in approach of the ideal condensed solution of titanium carbide and nitride.

It was gained, that the titanium carbonitride output more than 90 %, in which there is no free condensed carbon, is provided at x=20 in ranges of temperature 1650 - 1800 K (z=0.4), 1700 – 1900 K (z=0.5) and 1750 – 1950 K (z=0.6) – fig. 1c. The composition of titanium carbonitride (parameter *n* in formula TiC_nN_{1-n}) in the specified ranges of temperature practically remains constant and numerically equal to value of parameter z. However, in all temperature range of titanium carbonitride existence value of parameter n changes from 0 to 1 with temperature growth, that matches to transferring from titanium nitride to carbide.

Results of calculations shows that temperature areas of titanium nitride and carbide existence are located below melting temperatures of specified compounds. It follows from this, that in streams of thermal plasma as the result of chemical condensation from a gas phase, the formed particles cannot be in liquid condition in the processes of synthesis of these compounds, having the respective spherical form and growth of particles cannot occur on the coagulative mechanism. Earlier it was noted for titanium nitride synthesis in the plasma processes [12], that the presented calculations of titanium carbide and carbonitride synthesis allows to propagate this leading-out to synthesis of these compounds.

Energy characteristics of processes

Temperature dependences of the energy consumption necessary for production of 1 kg titanium nitride, carbide and carbonitride, are presented in figure 2, and dependence on process temperature of plasma enthalpy providing production equilibrium composition at the specified temperature of process, presented in figure 3. All dependences of energy consumption on process temperature have extreme character and have a minimum; however, for all observed compounds in the field of absolute minimum the output of base products much lower than achievable maximum, and in the case of titanium carbide and carbonitride in reaction products there is a free carbon considerable quantity. Therefore it is expedient to observe energy characteristics of processes in the ranges of parameters changing, in which the output of base products not less than 90 % is provided, and for titanium carbide and carbonitride there is no free carbon Temperature intervals of process proceeding, in which performance of these conditions is provided at different values of parameters, are shown in figures by broader lines.

In the temperatures field of the maximum titanium nitride output the energy consumptions for its fabrication is 16 – 20 MJ/kg, depending on excess of nitrogen (fig. 2a). For providing of the maximum titanium nitride output ($x=20$, $y\geq5$, temperature of process 1300 K) necessary magnitude of the enthalpy of nitro-hydrogen plasma should be ~1,5 MJ/m^3 (fig. 3a).

Near to the temperature 2100 K, matching to the maximum output of titanium carbide (94 %, $x = 20$) and to absence of free carbon, energy consumptions for its production is 31 MJ/kg, the enthalpy of the hydrogen plasma providing specified equilibrium temperature of process 2100 K, should be equal 3.9 MJ/m^3.

The minimum power inputs at which titanium carbonitride does not contain some free carbon and its output exceeds 90 %, is 25 MJ/kg and match to reaction temperature at 1700 K, the enthalpy of the nitro-hydrogen plasma providing conducting of process at the specified temperature, should be 2.6 MJ/m^3.

From comparison of power characteristics for production processes of oxygen-free titanium compounds follows, that the least energy consumptions are required for production of titanium nitride, and the greatest – for titanium carbide production. It is caused by temperatures at which the maximum output of titanium carbide above respective temperatures for titanium nitride production and achievement of higher temperatures demands the raised consumptions of energy.

The counted values of the enthalpy of high-temperature streams for hydrogen-nitrogenous mixes and hydrogen, being over the range 1.5 – 3.9 MJ/m^3, could be confidently provided by existing electric discharge generators of thermal plasma [13].

Conclusions

The executed calculations of processes in approach of equilibrium thermodynamic model testify to possibility of synthesis of titanium nitride, carbide and carbonitride at interacting of titanium tetrachloride accordingly with nitrogen, methane and their mixes in the presence of hydrogen. For the providing of the output of base products which are coming nearer to 95 % tenfold excess of hydrogen in comparison with stoichiometrically necessary is required, thus synthesis coproducts is the lowest titanium chlorides. Temperature dependence of the output of all base products has extreme character and the maxima of titanium nitride, carbide and carbonitride output are in temperature range of 1100-1500, 2000-2200, 1200-1800 K accordingly. Under the synthesis of titanium carbide and carbonitride, equilibrium products can contain condensed carbon, however on the overhead temperature boundary line of the maximum output of titanium carbide and carbonitride and at higher temperatures, the condensed carbon is absent.

The minimum energy consumptions for production of 1 kg base products in the field of their absolute maximum output and under condition of the condensed carbon absence for titanium carbide and carbonitride are 22, 31, 25 MJ/kg for titanium nitride, carbide and carbonitride accordingly.

Presented energotechnological characteristics of processes group for synthesis of oxygen-free titanium compounds are gained in equilibrium approach and should be observed as some limit values, characterizing chemically reacting system in conditions when the residence time of system at the specified parameters is not less, than times of the chemical relaxation, and relaxation times of transport processes.

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Figures

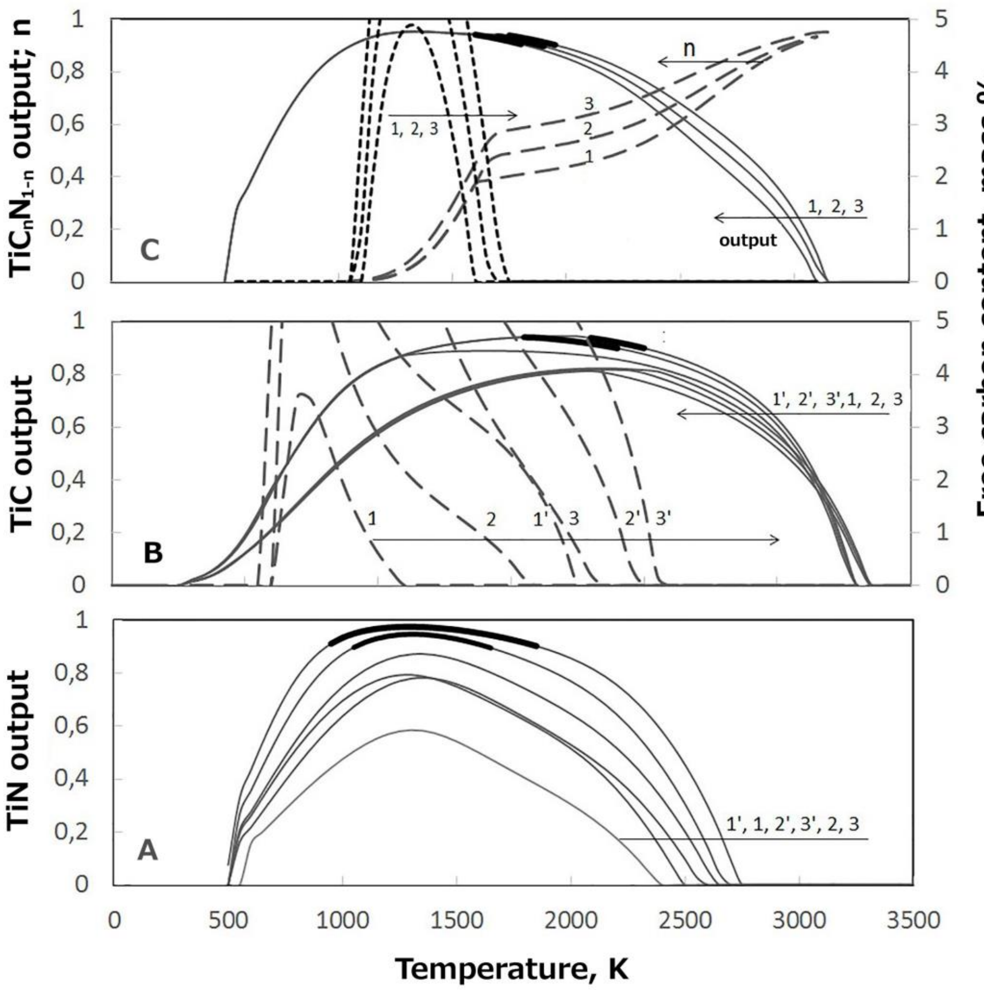

Fig. 1

Temperature dependences of output of titanium nitride, carbide and carbonitride, the free carbon content in titanium carbide and carbonitride, and atomic carbon content in titanium carbonitride composition.

A — TiN synthesis: 1' – x = 8, y = 0.5; 2' – x = 8, y=5; 3' – x = 8, y = 20; 1 – x = 20, y = 0.5; 2 – x = 20, y = 5; 3 – x = 20, y = 20.
B — TiC synthesis: 1' – x = 8, z = 0.9; 2' – x = 8, z = 1.0; 3' – x = 8, z = 1.1; 1 – x = 20, z = 0.9; 2 – x = 20, z = 1.0; 3 – x = 20, z = 1.1.
C — TiC_nN_{1-n} synthesis: 1 – x = 20, y = 5, z = 0.4; 2 – x = 20, y = 5, z = 0.5; 3 – x = 20, y = 5, z = 0.6.

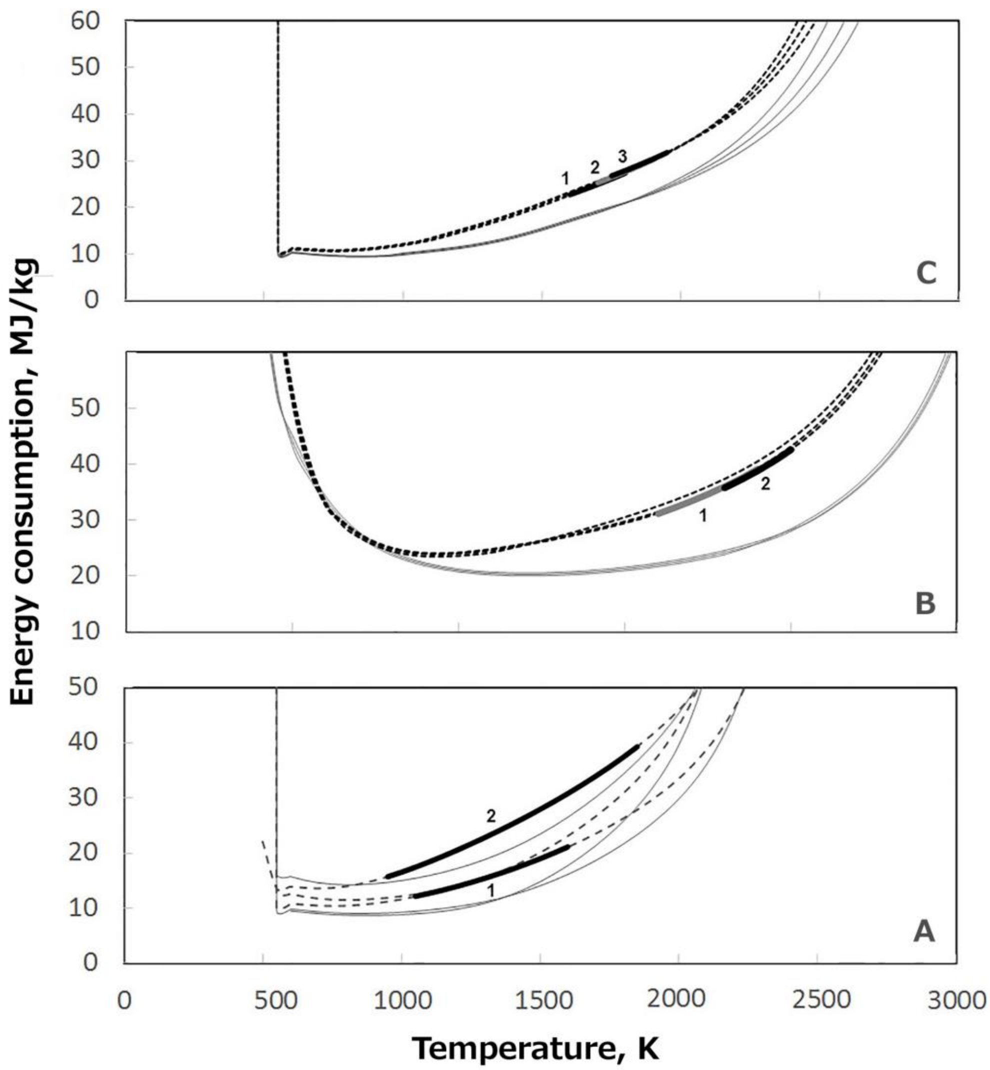

Fig. 2

Temperature dependences of energy consumption on production of titanium nitride, carbide and carbonitride.
A — TiN synthesis: 1 – x = 20, y = 5; 2 – x = 20, y = 20.
B — TiC synthesis: 1 – x = 20, z = 1.0; 2 – x = 20, z = 1.1.
C — TiC_nN_{1-n} synthesis: 1 – x = 20, y = 5, z = 0.4; 2 – x = 20, y = 5, z = 0.5; 3 – x = 20, y = 5, z = 0.6.

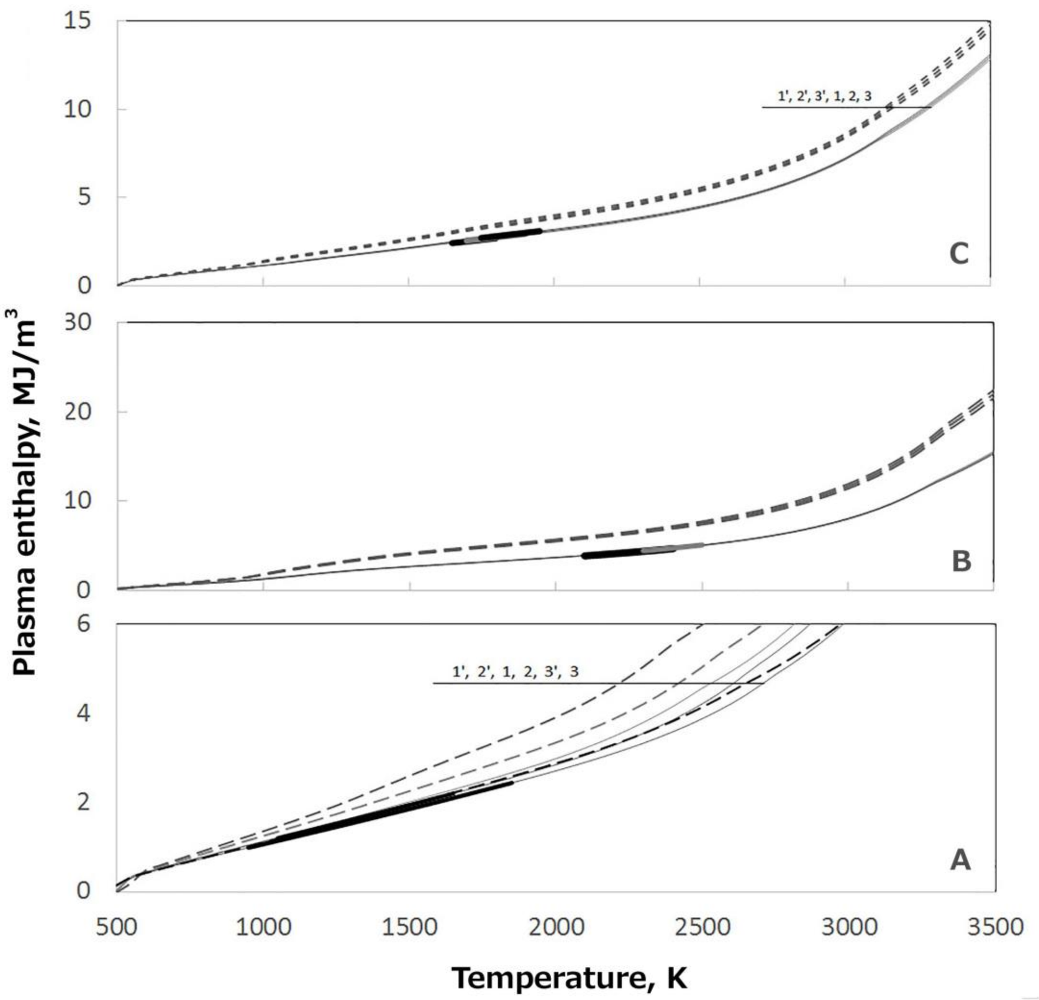

Fig. 3

Dependences of plasma stream enthalpy on production process temperature of titanium nitride, carbide and carbonitride (accordingly – hydrogen-nitrogenous plasma, hydrogen plasma and hydrogen-nitrogenous plasma).
A —TiN synthesis: 1' – x = 8, y=0.5; 2' – x = 8, y=5; 3' – x = 8, y = 20.
1 – x = 20, y = 0.5; 2 x = 20, y = 5; 3 – x = 20, y = 20.
B —TiC synthesis: **- - - - x** = 8, ——— **x** = 20.
C —TiC_nN_{1-n} synthesis: 1' – x = 8, y = 5, z = 0.4; 2' – x = 8, y = 5, z = 0.5; 3' – x = 8, y = 5, z = 0.6; 1 – x = 20, y = 5, z = 0.4; 2 – x = 20, y = 5, z = 0.5; 3 – x = 20, y = 5, z = 0.6.

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