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MATHEMATICAL MODELING OF PLASMA TECHNOLOGY FOR TiO_2 FINE POWDER PRODUCTION

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This paper presents the physical characteristics of plasma in presence of vapor of metal (Ti). The scheme of an evaporator of TiO_2 powder based on a plasma torch of combined type is presented. That scheme is characterized by reducing of the equipment cost by decreasing of RF power in comparison to application of usual ICP torches. An analysis of thermo-physical processes of plasma generation as well as heating of fine TiO_2 particles is presented. The results were a basis for creating of equipment for the production of fine TiO_2 materials and nanostructured TiO_2 materials with lower radio frequency (RF) power consumption.

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1. Introduction

In recent years an annual production of fine powders and nanopowders is 1-1.5 billion USD in the world. An industry of nanopowders is the most developed commercial segment of the nanomaterials market. Average annual growth rates of that industry are 15%. Thus needs for fine powders and nanopowders in the world are increasing every year.

By now a large number of technologies of fine powder and nanopowder production were developed. All existing methods of fine powder and nanopowder production can be divided into two groups: mechanical methods and physical and chemical methods.

To produce fine powders and nanopowders by a mechanical way various types of mills are used in which grinding of material is achieved due to abrasion and impacts [1]. The disadvantages of that technique include a possibility of pollution of powder by abrade materials as well as a difficulty of obtaining of powders with a narrow particle size distribution.

Physical and chemical methods of fine powders and nanopowders production are the followings: a vacuum deposition, a sol-method, plasma methods, a laser ablation, etc [2]. In the majority of these methods the initial material is evaporated, moved to the place of deposition and then it is condensed in the form of fine particles and nanoparticles due to intense forced cooling by quenching gas (the exception is the sol-method in which the powder is formed by a chemical reaction of the two solutions). In some cases, the desired product is formed by chemical reactions in the gas phase while the starting reagents are common and readily available materials.

A plasma synthesis of nanoparticles is a very promising method allowing to achieve a high efficiency of the process and a precise control of parameters of the final product [3, 4].

In plasma process the evaporation of initial material and chemical reactions (if required) occur in the thermal plasma. High temperature allows all the initial materials to transit into gaseous state and their subsequent reactions and products condensation. The desired dispersion of produced particles is achieved by controlling of the cooling rate of plasma flow in which a process of condensation from the gas phase occurs.

To produce thermal plasma the industry mainly uses two types of electrical discharges: an arc and a radio frequency (RF) inductively coupled plasma (ICP). Applied to the production of nanopowders the ICP torches have higher technological features compared to the arc plasma

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torches such as: a generation of plasma in a large volume; a purity of plasma due to the lack of electrodes, simple design; an ability to wide change of a velocity of plasma flow; a simplicity of materials feeding into a plasma stream; a long residence time of material in the plasma jet; a long service life; reliability; an ability of operation with any gas environment, including corrosive one; scalable up to a power of about 10 MW.

A disadvantage of application of RF plasma is a necessity of using of quite expensive RF power supplies. Moreover, the cost of those power supplies is significantly increased with increasing of RF power. A combined plasma torch was proposed in order to reduce the cost of equipment by decreasing of RF power. In that kind of plasma torch an existence of inductively coupled plasma and its ignition is provided by a DC arc plasma torch [5].

The article describes the plasma process of TiO_2 fine powder and nanopowder production on the basis of the combined plasma torch as well as analysis of thermo-physical processes of the plasma generation, motion and heating of fine TiO_2 particles in plasma.

2. Experimental set-up

Fig. 1 represents a scheme of a technological process of TiO_2 fine powder and nanopowder production. Plasma created by a plasma torch is used to heat the initial powder. Powder is fed to the outlet of the plasma torch (this method of powder feeding does not affect the generation of plasma inside the torch). Being inside the plasma jet the powder is heated and is completely vaporized (goes into the gaseous phase) in the zone of the evaporator. It is well known that nanopowders can be obtained by a condensation of vapor phase during the quenching [6]. Therefore a mixture of plasma gas and evaporated material passes through a nozzle of small diameter wherein it is cooled by cold gas flow.

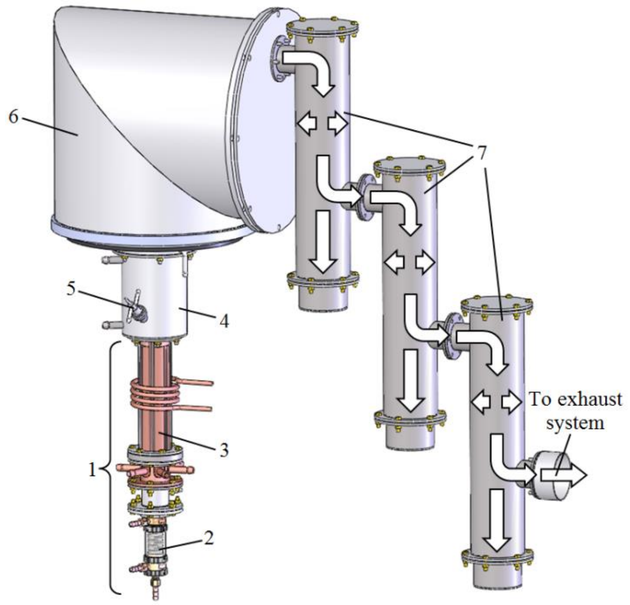

Fig. 1 - Scheme of the technological process of fine powder and nanopowder materials production: 1 – combined plasma torch; 2 – DC part of the combined plasma torch; 3 – RF part of the combined plasma torch; 4 – evaporating chamber (reactor); 5 – powder feeding tube;6 – condensing chamber; 7 – trap modules

The resulting fine powder containing nano-sized fraction is collected in a special device namely a trap having a modular structure. The principle of operation of the trap is based on the mechanism of the powder condensation and its deposition on the water-cooled walls. A design of the trap module provides the existence of the zone of stagnant gas that lead to increase the deposition rate of powder. The largest fractions of powder are deposited in the first trap module, the smaller ones are deposited in the following ones. A quantity of trap modules can be changed depending on the powder feed rate.

The above-described features of ICP torch are valid for the combined plasma torch, they are undoubted advantages when the combined plasma torch is used for the synthesis of fine powders and nanopowders.

Large plasma volume allows to realize its uniform loading by the initial material. Slow plasma flow leads to big residence time in plasma (compared to the plasma flow generated by arc plasma torches), so that the initial material are better treated and the final product is more uniform in quality. In addition, high temperature and large plasma volume allow to produce fine powders and nanopowders with high efficiency, and produced powders have a narrow size distribution.

The plasma torch PN-V1 produced by a company "Association Polyplasma" [7] with a channel diameter of 12 mm was chosen as the basic design of the arc plasma torch [8–10]. It was decided to increase the diameter of the channel and the nozzle of the plasma torch up to 20 mm. The selected diameter will provide a low velocity of plasma so that a steady laminar operation of plasma jet exists at sufficiently high flow rates of plasma gas.

Geometry of developed ICP torch (with a diameter of 56 mm) was chosen based on preliminary experiments.

The design features of the combined plasma torch namely a distance between an output end of the arc plasma torch and the inductor coils was initial data for the design of the arc plasma torch. Their consideration shows that the length of generated jet of the arc plasma torch should be in the range of 250–350 mm to provide a reliable ionization of a zone of generation of inductively coupled plasma (i.e. inductor zone).

Thus, the foregoing suggests that the plasma process of fine powder and nanopowder production using a combined plasma torch includes the following steps:

- Generating of plasma in the combined plasma torch (in arc part and ICP part);
- Feeding of a fine powder into the plasma jet and its evaporation;
- Cooling of the vapor phase and condensing of material in the form of nanoparticles.

3. Calculation of plasma composition in presence of Ti vapor

The working gas is a mixture of argon and oxygen in the combined plasma torch. The initial TiO_2 powder with a mean diameter of 15 μm is fed into plasma jet inside the evaporation chamber and that powder evaporates completely. Plasma jet containing TiO_2 vapor is cooled by cold oxygen gas flow in the condensation chamber.

To analyze processes that take place in the gas mixture of Ar + O_2 containing TiO_2 vapor, a composition of such multicomponent plasma was calculated.

Calculation of multicomponent plasma composition was carried out by constant method i.e. by solving a system of nonlinear equations written on the basis of the mass action laws, mass balance equations, the quasi-neutrality equation and Dalton's law. A Newton's method for increment of the logarithms of unknown values was applied to solve such system. The method of solution is described in detail in [11, 12]. A special program created by authors was used for these calculations.

In the calculation there were taken into account the following species: O_2, O_2^-, O_2^+, O, O^+, Ar, Ar^+, TiO_2, TiO, TiO^+, Ti, Ti^+, Ti^{2+}, e.

Results of calculations for the mixture of 49.5% O_2 + 49.5% Ar + 1% TiO_2 (% means mole percent) at pressure of 1 atm are shown in Fig. 2 for the temperature range 300–10 000 K.

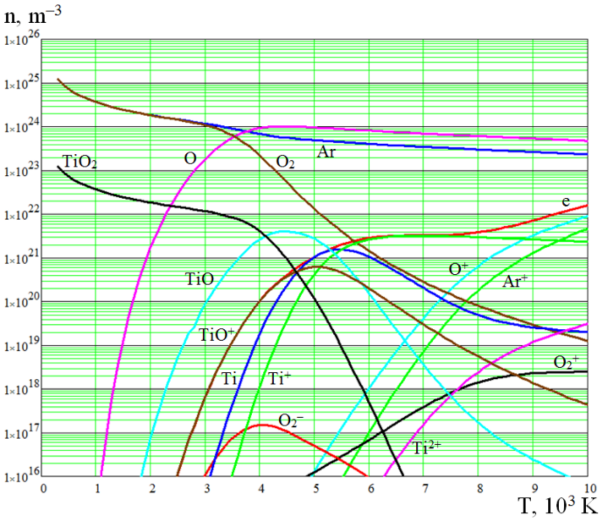

Fig. 2 – Temperature dependence of the composition (species number densities) of mixture of 49.5% O_2 + 49.5% Ar + 1%TiO_2 at 1 atm

From Fig. 2 which presents the temperature dependence of plasma composition (i.e. number densities of different species in plasma as functions of the plasma temperature) one can draw the following conclusions:

- Titanium oxide TiO_2 is chemically stable compound at low temperatures in the presence of large amounts of oxygen;
- The decomposition of TiO_2 takes place at a temperature of 4000-5000 K;
- At temperatures below 8000 K the electrical conductivity of investigated gas mixture is completely determined by the presence of vapor of titanium (Ti) and a molecular component TiO due to lower ionization potentials of these species compared with oxygen and argon.

4. Mathematical model

For a better understanding of the processes taking place in the combined plasma torch and in the zone of plasma jet mathematical modeling of these processes was carried out.
The simulation was performed using the software ANSYS Fluent 13.0. A 2D axisymmetric case was considered. By the software it was possible to solve simultaneously the following equations: energy equation, continuity equation, motion equation.

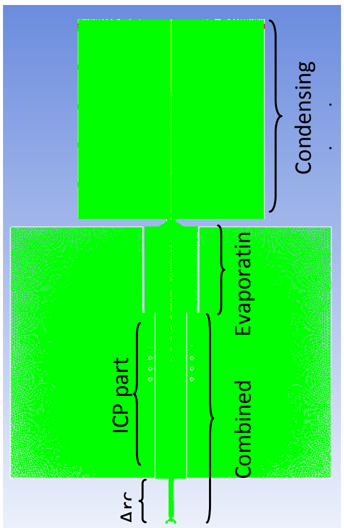

Fig. 3. Schematic drawing representing the computational domain of plasma process

The ability to apply user-defined functions (UDF) allowed to introduce into the simulation an electromagnetic problem and nonlinear thermophysical properties of plasma (for the sake of simplicity we used pure Ar at 1 atm).

Two separate simulations were obtained, for the arc plasma torch and for the ICP plasma torch. The computational domain was divided by mesh onto about 300 000 cells (see Fig. 3). Boundary conditions for each of the required values are defined at each boundary of the computational domain using simple physical considerations.

The conditions of laminar flow of the arc plasma torch were created to obtain the required length of the arc plasma jet [13]. Arc plasma power was changed in the range of 10–15 kW, argon flow rate – in the range of 15–37 slpm.

5. Results and discussion

The results of the calculation are shown in Fig. 4 that presents the distributions of plasma temperature and axial velocity of the plasma jet of the arc plasma torch at a power of 14.5 kW and an argon flow rate of 25.9 slpm. In this case the plasma velocity not exceeds 10 m/s and plasma temperature not exceeds 3000 K in the inductor zone of the ICP torch.

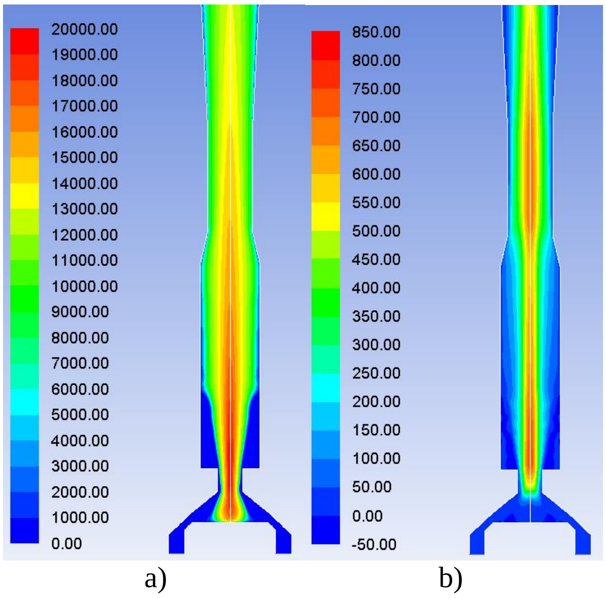

Fig. 4 – Results of calculation for arc plasma torch (arc voltage is U=70 V, power in plasma is P=14.5 kW, argon flow rate is G=25.9 slpm): a – temperature, K; b – axial velocity, m/s

In order to select an operation mode of the ICP torch providing the power of plasma jet that is sufficient to vaporize the initial TiO_2 powder a series of calculations was carried out in which the power was varied between 20 and 40 kW, the gas flow rate was between 18.5 and 148 slpm, the coil current frequency was 1.76 and 5.28 MHz (values from standard range of frequencies in Russian Federation).

Results of a calculation of the ICP part of the combined plasma torch are shown in Fig. 5 for operation at a power of 30 kW and a gas flow rate of 100 slpm.

Calculation showed that a power of the plasma jet (a power at the outlet of the plasma torch) is about 20 kW in that operation mode. It is most effectively provided at a frequency of 5.28 MHz.

The results of calculations show that the maximum temperature (~ 10,000 K) is observed in the area of energy dissipation about the same distance from the axis and the wall (see Fig. 5, a). This is explained in the following way. The electromagnetic field induces a ring of current into the plasma. Although the maximum electric field is located on the wall of the plasma torch, the maximum current density of plasma is formed at a certain distance from the wall. The plasma current density decreases near the axis of the plasma torch due to the skin effect [14].

The maximum temperature is situated in the zone of energy dissipation. The plasma temperature decreases to 7–8 thousand K at the exit of the plasma torch.

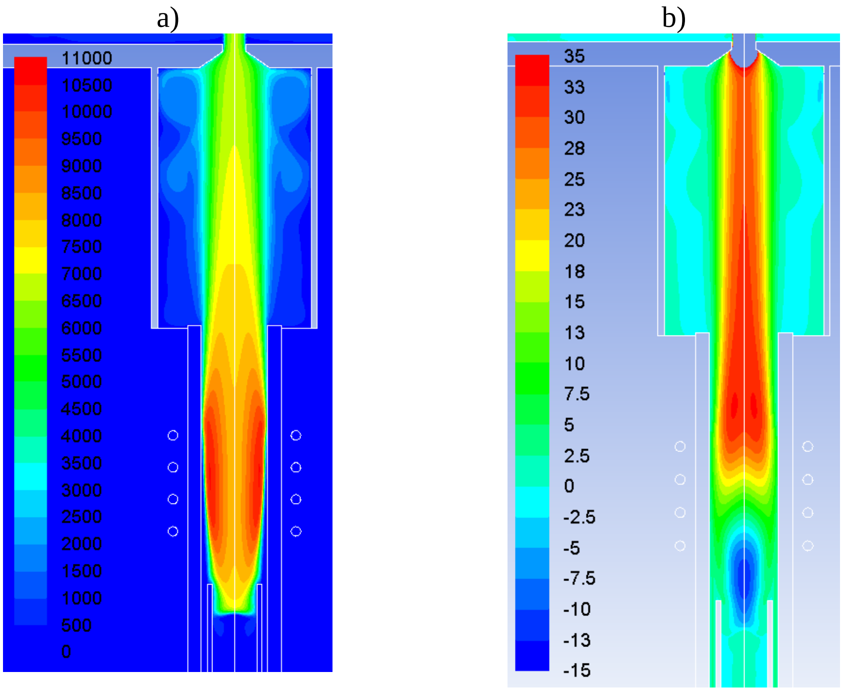

Fig. 5 – Results of calculation for ICP torch (RF power is P=30 kW, coil current frequency is f=5.28 MHz, argon flow rate is G=100 slpm): a – plasma temperature, K; b – axial plasma velocity, m/s

A recirculation zone of the plasma flow is observed near the inlet of the plasma torch (the so-called frontal vortex – see Fig. 5, b). The front boundary of that zone coincides with the boundary of the plasma, and this recirculation zone exists up to almost the middle of the inductor coils. Lines of the stream function are closed in the recirculation zone, i.e. some quantity of plasma rotates continuously in the zone, not leaving it. The cold gas at the torch inlet is discarded to the wall of the plasma torch and does not penetrate into the recirculation zone. Major role in the plasma recirculation zone formation is played by the electromagnetic force.

The cold gas going from the torch inlet meets the frontal vortex of plasma at the zone of the internal tube end. Interaction of the cold gas and the plasma vortex directs the cold gas to the torch wall. After that the cold gas flowing between plasma and the torch wall is heated gradually by plasma. It becomes conductive, and the electromagnetic force starts to act onto it. As a result the gas begins to penetrate into the plasma core in the middle zone of the inductor coils. However the most part of gas does not penetrate the plasma core, it flows along the torch wall.

The results obtained in the previous step (namely the distributions of plasma temperature and velocity at the plasma torch outlet) were used as input data for calculation of plasma jet loaded by initial fine powder.

Calculations were carried out using the software ASYS Fluent 13.0 in 3D setting. This is due to the fact that the powder feeding carried out radially using special water-cooled tube that disturbs an axial symmetry of the geometry.

Results of calculation of plasma jet without the powder feeding are shown in Fig. 6. It is seen that the axial symmetry of the plasma jet is generally preserved.

A series of calculations of plasma jet at different powder feed rate (2–5 kg/h) and various start velocities (5–15 m/s) was carried out [15].

Initial powder was TiO_2 with a mean diameter of 15 μm.

Best results (optimal trajectory of particles and its heating) were obtained at a powder feed rate of 4 kg/h and a start velocity of 10 m/s (see Fig. 7).

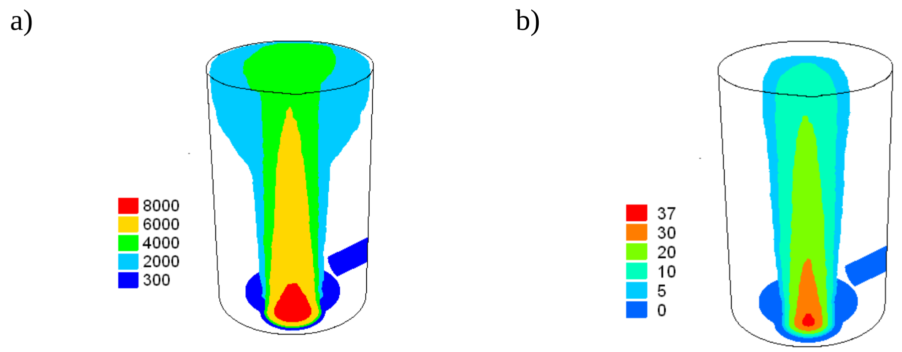

Fig. 6 – Results of calculation of plasma jet without powder feeding: a – plasma temperature, K; b – axial plasma velocity, m/s [15]

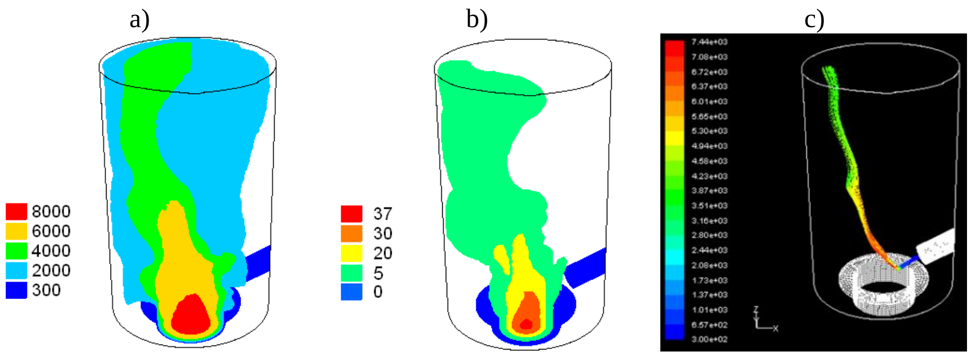

Fig. 7 – Results of calculation of plasma jet with powder feeding (powder feeding rate is 4 kg/h, start velocity is 10 m/s): a – plasma temperature, K; b – axial plasma velocity, m/s; c – trajectory and temperature of TiO_2 particles with a mean diameter of 15 μm [15]

Evaporation of particles of the initial powder was not taken into account for the presented calculations. However, this aspect will be taken into consideration in our future work. Evaporation will result in a change of the plasma composition and thereby to change its properties. The calculation of such plasma composition (see Fig. 2) shows that plasma in the presence of vapors of titanium is more uniform, with a higher thermal conductivity (due to greater influence of electrons) which will increase the efficiency of the evaporation of the powder.

The process of cooling of gas flow containing vapor and condensation of fine powder also expected to consider in next steps using the model described in [16].

5. Conclusions

The new scheme of plasma process of fine TiO_2 powder production based on a combined plasma torch is proposed. That scheme is characterized by reducing of the equipment cost by decreasing of RF power in comparison to to application of usual ICP torches.

An analysis of thermo-physical processes of plasma generation as well as heating of fine TiO_2 particles is presented. The results were a basis for creating of equipment for the production of fine and nanostructured TiO_2 materials with increased efficiency and lower power consumption.

Based on these investigations a combined plasma torch for fine powder and nanomaterials production was developed. That torch consists of series-connected two parts: the arc plasma torch and the ICP torch.

The arc plasma torch is the plasma torch PN-V1 with increased diameter of the channel (20 mm), it operates with a power of 10–15 kW and an argon flow rate of 14.8–37.0 slpm.

ICP torch has the following parameters: the frequency is 5.28 MHz, the inner diameter of the torch is 56 mm, the plasma power is 30 kW and the gas flow rate is 74.0–110.0 slpm.

A patent [17] was obtained on the base of this investigation.

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