# Thermodynamic modelling of plasma-chemical nanopowders production

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Nanosized powders of elements and their inorganic compounds are the basis for the creation of various nanostructured materials, such as nanostructured functional ceramics, hard alloys with increased wear resistance and impact strength, dispersion-hardened and modified structural alloys with improved performance characteristics, nanostructured protective thermal and corrosion-resistant - and wear-resistant coatings, polymer composites with fillers and modifiers from inorganic nanoparticles, etc. [1-9].

Nanopowders can be synthesised by various methods in gas-phase, liquid-phase, solid-phase and combined processes, including physical and chemical deposition from the gas phase, precipitation from solutions, mechanical grinding, etc.

Gas-phase processes are based on homogeneous nucleation from supersaturated vapours and subsequent condensation and coagulation growth of the resulting nanoparticles. Supersaturated vapours can be obtained by cooling saturated vapours, as well as by chemical reactions. Depending on the method used for obtaining supersaturated vapours, gas-phase processes for obtaining nanopowders include synthesis in flames, evaporation under the action of highly concentrated energy flows (laser radiation, accelerated electron flow, focused microwave radiation flow), and synthesis in low-temperature plasmas of electric discharges.

Plasma-chemical synthesis is the most universal method for obtaining nanopowders of elements, inorganic compounds, and compositions in a controlled gas atmosphere, which can be inert, reducing or oxidising.

Thermodynamic modelling is widely used in the development of pyrometallurgical processes, making it possible to estimate the range of parameters for optimal process operation [10–12]. The use of thermodynamic modelling for high-temperature flow apparatuses implies that the characteristic times of equilibrium establishment processes (chemical reactions and transfer phenomena) are much shorter than the residence time of the reacting system in the apparatus.

Thermodynamic modelling is also used in research and development of processes carried out in thermal plasma flows, including the synthesis of nanosized powders of elements and their inorganic compounds [13-18]. Traditionally, the thermodynamic analysis of plasma-chemical processes is based on calculations of the equilibrium compositions of multicomponent multiphase systems under isobaric-isothermal conditions with obtaining the dependences like 'system phase and chemical composition vs temperature' for a set of various elemental compositions in the system under consideration.

Using temperature as process parameter makes it extremely difficult to apply thermodynamic calculations results for interpretation of experimental results, because determination of even average values of temperature and component composition in a real gas-dispersed high-temperature, chemically reacting flow is a very difficult task.

In this regard, the use of temperature as a parameter that controls the process and the comparison of the thermodynamic model calculations, and the experimental data of real plasma-chemical process becomes practically impossible.

As an alternative to the plasma-chemical process temperature, it is advisable to use the enthalpy of the thermal plasma flow, which is uniquely related to temperature.

Let's consider this option using a specific example of a plasma-chemical process implemented in a flow reactor. The processes of obtaining nanopowders of elements and their inorganic compounds using thermal plasma are predominantly implemented according to the following scheme (Figure. 1).

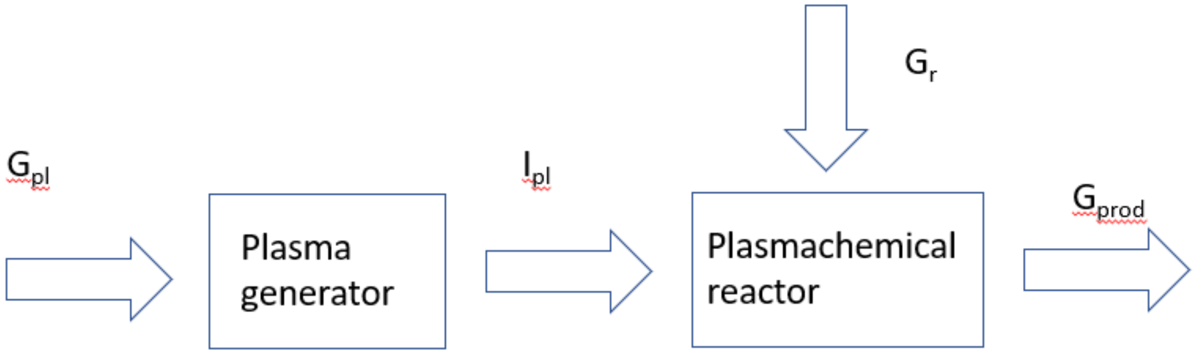

*Figure 1. Typical plasmachemical process of nanoparticles production.*

In the thermal plasma generator, the gas (heat carrier gas or reagent gas) is supplied at a flow rate $G_{pl}$ (kg/s) and heated when passing through an electric discharge, acquiring a mean mass enthalpy $I_{pl}$ ( MJ/kg). Reagents are introduced into the thermal plasma flow in a gaseous or condensed (dispersed) state with a flow rate of $G_r$ (kg/s). As a result of their interaction, vapours of the target product are formed. When the high-temperature flow is cooled below the condensation temperature, nanoparticles of the target product are formed.

Plasma-chemical processes are predominantly implemented in reactors with confined jet flow, where the plasma jet is cooled because of heat transfer to the reactor wall. As a result of condensation, the target nanoparticles are formed. Some of the nanoparticles are deposited on the reactor wall; the rest are carried out together with the gas flow and subsequently separated at the filter.

In the plasma-chemical process implemented in the above reactor, the control parameters are the consumption of the reagents involved in the process, and the net power supplied ($N_p$). The net power input is defined as the difference between the electrical power input ($N_e$) and the power removed with the water cooling of the thermal plasma generator ($N_{hl}$). The mass-average enthalpy of the thermal plasma flow is calculated as $I_{pl} = (N_e - N_{hl})/G_{pl}$ , where $G_{pl}$ is the mass flow rate of the plasma gas.

In the thermodynamic model, the equilibrium mean mass enthalpy of the plasma flow ($I_{epl}$, kJ/kg) can be calculated from the relation: $I_{epl} =( H^T_{sum} - H^{T0}_{sum0})/m^0_{pl}$, where $H^T_{sum}$ is the total total enthalpy of the equilibrium mixture of components at temperature T, kJ/kg; $H^{T0}_{sum0}$ is the total enthalpy of the initial components at the initial temperature, kJ/kg; $m^0_{pl}$ is mass fraction of plasma-forming gases in the initial components, kg/kg.

As an example, the process of obtaining titanium carbide powder by the interaction of titanium chloride $TiCl_4$ vapour with methane $CH_4$ in a flow of thermal hydrogen plasma according to the overall reaction

$$x\ H_2\ \text{plasma} + TiCl_4 + CH_4 = TiC + 4\ HCl + (x - 2)\ H_2 \qquad (1)$$

The typical dependence of the equilibrium yield of Ti-containing components on temperature for a total pressure in the system of 0.1 Mpa and $x = 20$ is shown in Figure. 2 and in Figure. 3.
The equilibrium characteristics of the process (yield of the target product and energy consumption for its production) are shown depending on the enthalpy of the plasma flow. The temperature is used as a parameter of the thermodynamic model initially at the stage of calculating the equilibrium composition and total enthalpy of the system, and then on their bases the values of the specific enthalpy of the plasma flow are calculated, which is then used as a process parameter.

The use of the specific enthalpy of the plasma flow as a process parameter implemented in a flow-through plasma-chemical reactor makes it possible to conveniently compare the results of experiments and calculations using a thermodynamic model, and evaluate the compliance or possible deviation of the process from the equilibrium trajectory.

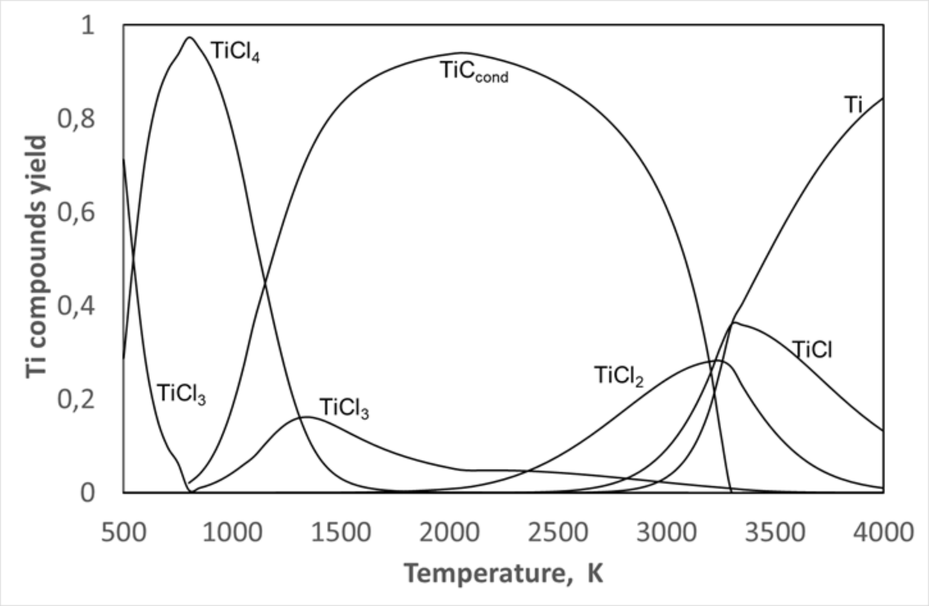

*Figure 2. Temperature dependence of the equilibrium yield of Ti-containing components.*

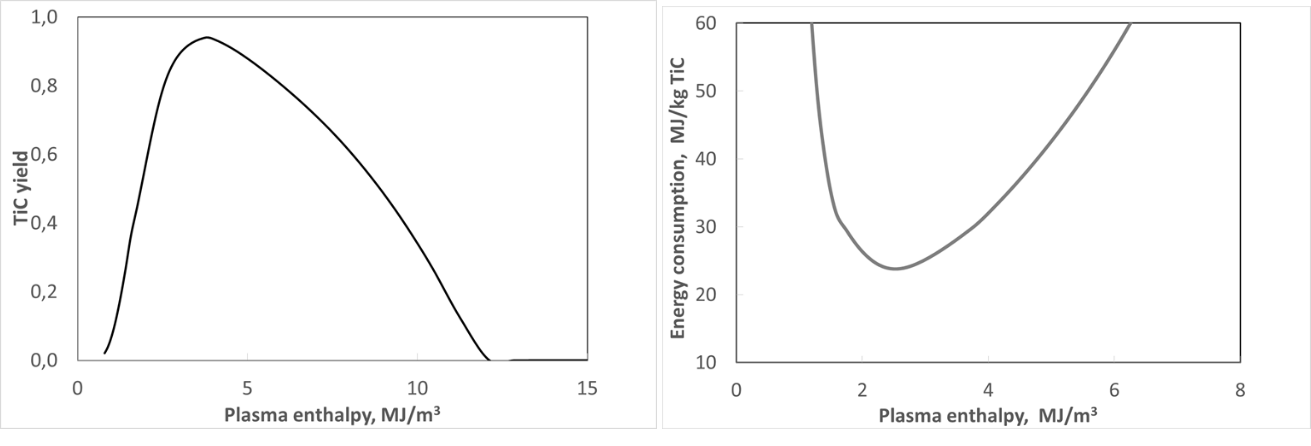

*Figure 3. Dependence of the equilibrium yield of TiC and energy costs for its production on the plasma enthalpy.*

The granulometric composition is one of the most important characteristics of nanopowders, which determines the possibility and direction of their use in practical applications.

According to the results of numerous studies, all nanopowders obtained in plasma-chemical processes are polydisperse and consist of primary particles having an equiaxed shape.

The formation of nanoparticles from the gas phase under the conditions of plasma-chemical synthesis occurs according to the macro mechanisms' 'vapour - liquid – crystal' (VLC), 'vapour - crystal' (VC) and hybrid, including a combination of these mechanisms (VLC-VC). The VLC mechanism implies that when a high-temperature stream containing vapours of a condensing component is cooled, liquid nanoparticles are initially formed, and further crystallised under conditions of decreasing temperature. This mechanism is realised if the temperature at the onset of condensation exceeds the melting point of the component. When liquid nanoparticles collide in a gaseous medium, they coalesce. The conditions of coalescence determine the formation of a dispersed composition in accordance with the coagulation mechanism. Due to surface tension forces, liquid nanoparticles have a spherical shape, which is retained during their crystallisation. If the temperature at the onset of condensation is below the melting point of the component or the component does not have a liquid state, then the nanoparticles are formed by the VC mechanism and have faceting. When such particles collide, they do not coalesce completely, but aggregates of nanoparticles are formed. The macromechanism of nanoparticles formation in a specific plasma-chemical process can be explained using thermodynamic calculations of the temperature dependence of the equilibrium yield of a nanopowder substance. Let us assume that the substance under consideration exists in a liquid and solid state, and its yield depends on temperature. Let us denote $T^*$ as the minimum temperature, which corresponds to the maximum yield of the nanoparticle substance, $T_c$ is the maximum temperature at which the nanoparticle substance exists in a condensed state, and $T_m$ is the melting point of the substance. The process of equilibrium condensation is carried out in the temperature range $T^* \ldots T_c$ and occurs at a decreasing temperature. Condensation starts at $T_c$ and ends at $T^*$, when the vapour completely passes into condensate. The conditions for the formation of a condensed phase according to the above macro-mechanisms can be written as:

VLC mechanism will be realised when $T_m<T^*<T_c$, all particles have a spherical habit (Figures 5a; 4-1);
VC mechanism will be realised when $T^*<T_c<T_m$, all particles have faceted crystal habit (Figures 5b; 4-2);
VLC-VC mechanism will be realised when $T^*<T_m<T_c$; particles have both spherical and faceted crystal habit (Figures 5c; 4-3).

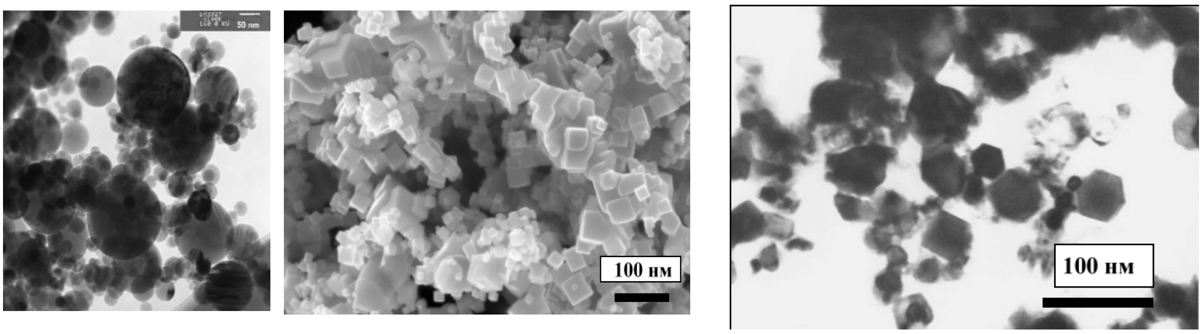

*Figure 4. Micrographs of $Al_2O_3$ (1), TiCN (2), and W (3) nanopowders obtained in plasma-chemical processes.*

The VLC mechanism is implemented if, under conditions of decreasing process temperature, the maximum yield of the condensed phase substance is ensured at temperatures above the melting point (Figure 5a). In turn, the VC mechanism determines the formation of nanoparticles if the formation of the nanoparticle substance occurs at temperatures below the melting point of the nanoparticle substance (Figure 5b) or the substance does not exist in the liquid state at all. If nanoparticles undergo crystallisation (solidification) during process temperature decline before the maximum nanoparticles yield is reached, then the particle formation mechanism changes from VLC to VC, and both spherical and faceted particles will be present in the resulting product (Figures 5c, 6).

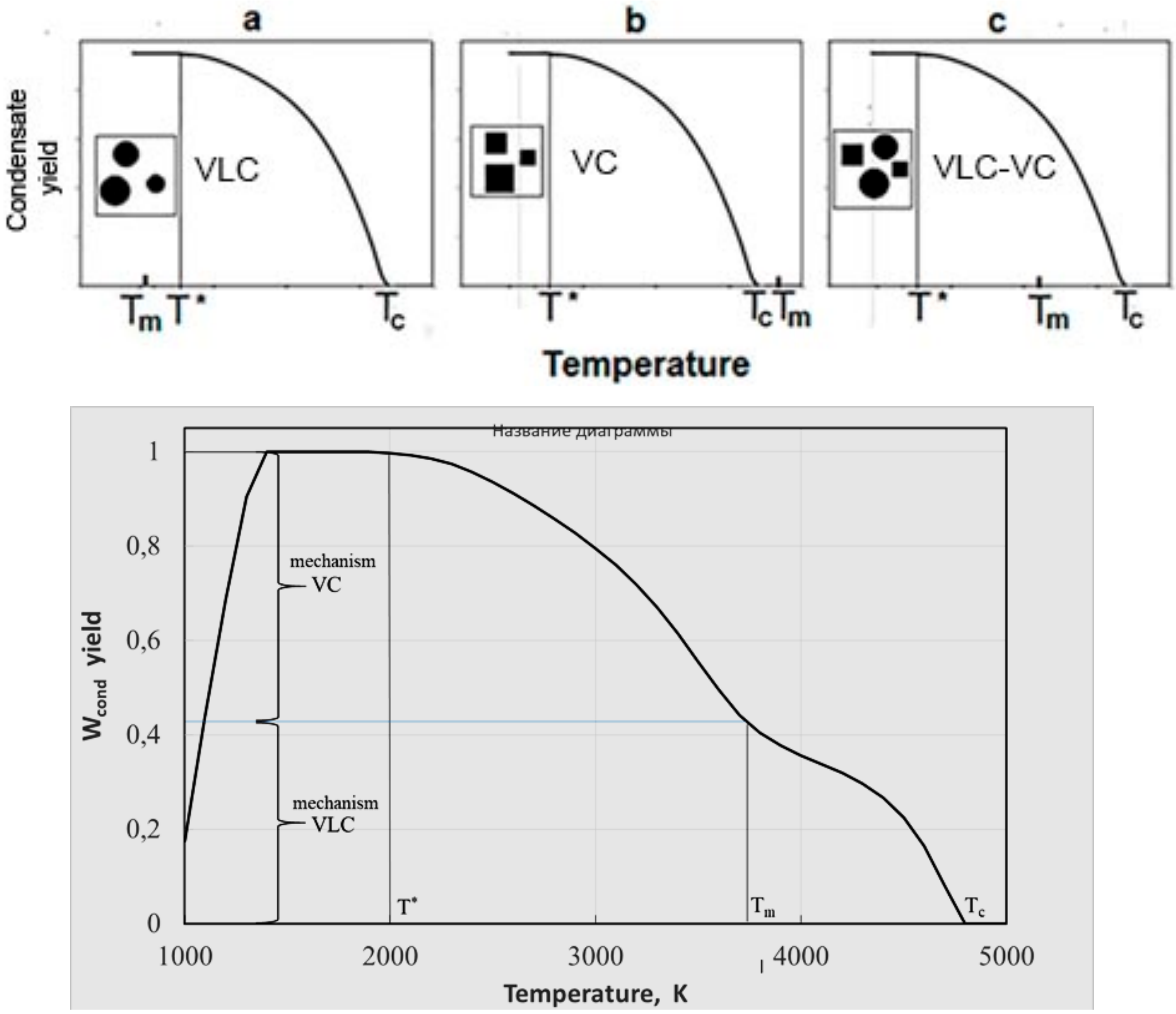

*Figure 6. Temperature dependence of the equilibrium yield of condensed tungsten in the* $WO_3 - 6H_2$ *system.*

Micrographs of nanopowders obtained in plasma-chemical processes (Figure 4) indicate that under these conditions, the formation of nanoparticles can occur according to all three of the indicated mechanisms VLC, VC and VLC-VC.

## CONCLUSION

Plasma flow-specific enthalpy could be used as a process parameter to conveniently compare the results of experiments in a flow-through plasma-chemical reactor and thermodynamic calculations, and evaluate the compliance or possible deviation of the process from the equilibrium trajectory.

Thermodynamic modelling serves as a helpful tool to evaluate the macromechanism (vapour–liquid–crystal or vapour–crystal) of metal and complex inorganic nanoparticles formation during chemical condensation from the gas phase under conditions of equilibrium cooling of high-temperature flows containing vapours of the condensing component.

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