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Plasma-Cryogenic Synthesis of the High Purity Nanomaterials

Arkadiy Bessarabov*, Mark Ivanov, Aleksey Kvasyuk, Tatiana Stepanova, Andrei Vendilo

Science centre "Low-tonnage chemistry" (SCLC), Krasnobogatyrskaya st. 42, 107564 Moscow, Russian Federation
a.bessarabov@mtu-net.ru

High purity nanomaterials (silicon, tungsten carbide, oxides of silicon, tin, iron, titan) are widely used in the innovative and science-intensive fields of economy. In manufacture of these substances it is exceedingly important that a by-product of synthesis should not contaminate the target products or interact with process equipment. Otherwise it will take up an additional amount of impurities. A promising way to tackle with this problem is application of low-temperature plasma. It allows to create a set of modern apparatus with the minimum microimpurity background. The advantage of this technique is that it can yield nanodispersed powders which is virtually impossible with other high purity technologies.
It is known that plasma allows receiving a various level of structural conditions. But difficulties of realization of the given conditions always rested against necessity of their instant fixing. However, it is possible only in cryogenic jets of hydrogen, nitrogen, oxygen, argon, helium, etc. Reactors used earlier had a lack of this possibility. Creation of a new class for cryogenic plasmachemical technologies for obtaining of the high purity nanomaterials was the purpose of the given work.
During the researches there was examined the influence of the following 3 factors for the dispersion of the final product: the aggregate state of the original substance, the components ratio (heads of high-speed plasma jet and jet injected gas) and the speed of cryogenic tempering. Development of cryogenic plasmachemical nanotechnologies was spent on the basis of the CALS-technologies (Continuous Acquisition and Life cycle Support).

1. Development of the universal plasmachemical apparatus for obtaining of high purity nanomaterials

To obtain nanodisperse materials the universal plasmachemical apparatus was developed. It allows applying not only initial hardphase product by means of powder feeder, but liquid-phase reagents with the help of special sprayer (Bessarabov et al., 2011a). Universality of the plant allows obtaining nanodisperse oxide of metals of 2nd, 3rd and 4th group of the periodic system. Depending on amount of the parent material, plasma-formation gas flow and power insertion it is possible to obtain nanopowders of different dimension series.
The plasmachemical process was developed in the framework of the most modern and promising computer-support system, CALS technology (Saaksvuori and Immonen, 2010). The CALS concept is based on a set of unified information models and on standardization of access ways to information and its adequate interpretation in conformity with international standards (ISO-10303 STEP). This provides unified methods for control over processes and enables interaction between all those involved in the development process. Nowadays it is almost impossible to sell at the foreign market any high-tech products without electronic documentation conforming to international CALS standards (ISO-10303 STEP). Another significant advantage of application of CALS-technologies is the ability to control all the products generated in the process of production. It allows you to adjust the volumes of wastes and to achieve the least negative impact on the environment (Lam et al., 2011). Thus, use of CALS technologies is a must for the most promising projects.

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In the development of a plasmachemical process for synthesis of nanodispersed tin oxide a type scheme (application protocol) “Initial data for designing” was created in the framework of the CALS project (Figure 1). In conformity with the chemical industry’s standard, the structure of the input data includes 17 necessary sections. All these sections are incorporated in the CALS project. In the screen form (Figure 1), additional subitems are only displayed in section no. 12 (data for calculation and choice of the process equipment). However, additional specific to chemical industry information is actually input into the CALS project for all the sections.

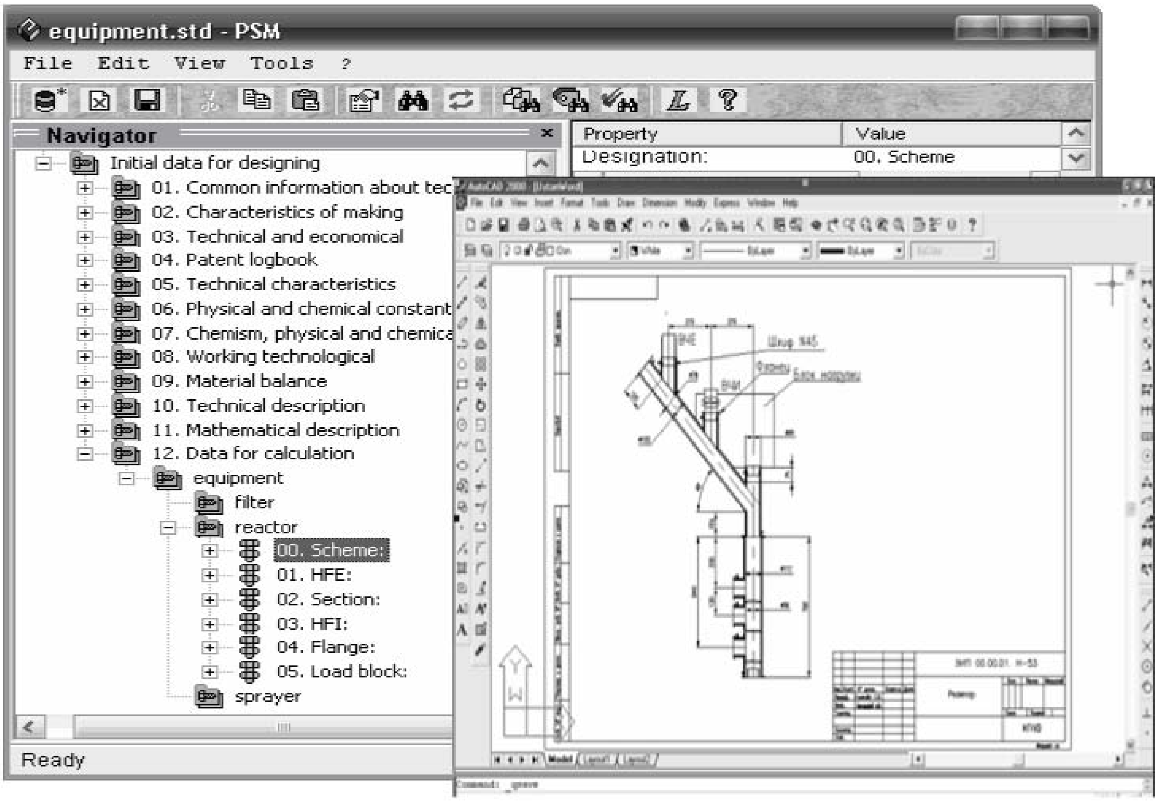

Figure 1: Element of design CALS-project of universal plasmachemical apparatus for synthesis of nanomaterials: reactor.

Design electronic description according to STEP standard (Figure 1) contains the structure and variants of item configuration, geometrical models and drawings, properties and features of components. At the element of this scheme universal plasmachemical apparatus is shown allows transferring to reactor not only the initial solid product by means of powder feeder, but the liquid reagents (chlorides and alchoxides) with a special sprayer.

For this CALS-project of apparatus (Figure 1) includes metering device for the transfer of initial materials powders, pulverizer for transfer of plasma-creating gas, filter for the product recovery and plasma torch. Apparatus universality allows obtaining nanodisperse compounds of tin, iron, silicon, titan (Ampelli et al., 2011), tungsten on it.

2. Thermodynamic researches

Section no. 11 (mathematical description of the process) of the CALS project (Figure 1) presents the results obtained in simulating the plasmachemical synthesis. Analysis of chemical and heat-and-mass exchange processes at elevated temperatures leads to severe difficulties already in the stage of formulation of the simulation problem. It is appropriate to use thermodynamic simulation methods as a first approximation. These methods presume that in the processes under consideration the working body forms a conditionally closed, isolated system in which a local thermodynamic equilibrium (LTE) is attained. In this approximation the state of the system is only determined by the content of chemical elements in the system and by values of two parameters of state (Bessarabov et al., 2007). The use of the thermodynamic equilibrium approximation is justified by the high concentration of energy in the volumes under

consideration and by the resulting high rates of conversion processes, which instantaneously bring the system in the LTE state.
A calculation of equilibrium for isolated multicomponent thermodynamic systems can be reduced to a problem of determination of a state with the minimum entropy. Therefore, to compose the sought-for system of equations it is necessary to find an analytical relationship between the entropy of a unit mass of the working body and the thermodynamic parameters determining its composition, properties, and existence conditions.
A thermodynamic calculation of the equilibrium states of the system is performed in a wide range of basic parameters of the plasmachemical process: starting component ratios, temperatures, and pressures (Figure 2). A thermodynamic simulation makes it possible to choose the synthesis conditions, analyze the environmental safety of the production process, and assess the mechanism of thermal dissociation of the starting compounds.

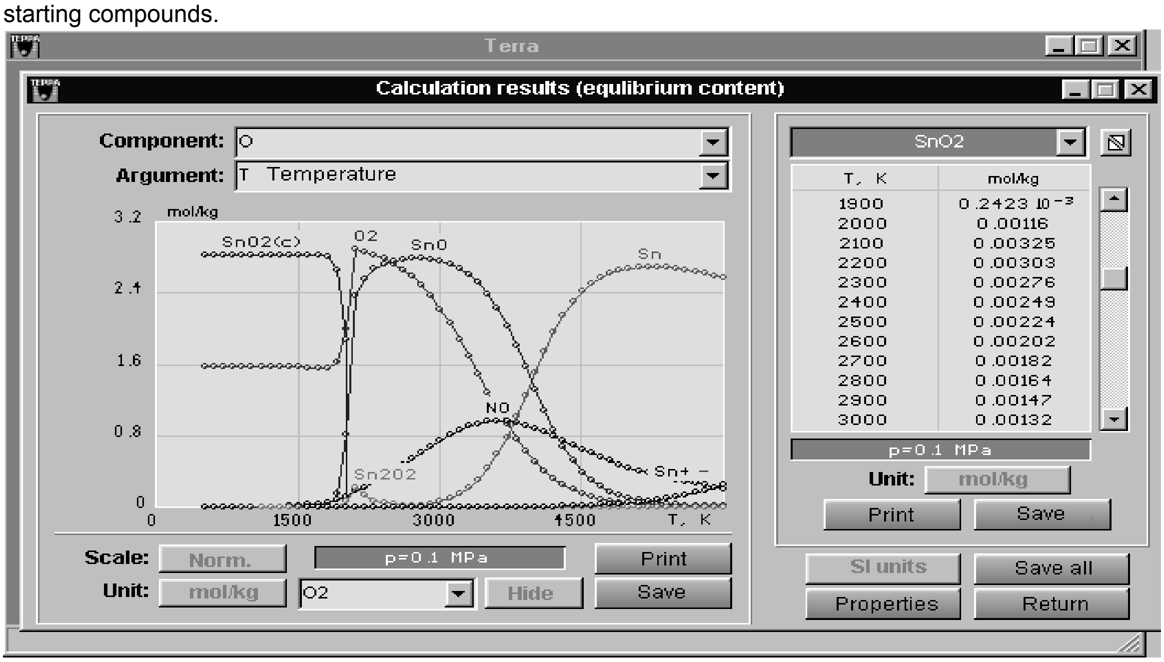

Figure 2: Screen form of the results of thermodynamic simulation of the plasmachemical synthesis (on example of the tin oxide).

In the general case, a gaseous system is constituted by neutral and electrically charged (ionized) components of the gas phase and separate condensed phases. The equation of state for an ideal gas is valid for the gas phase as a whole and for each of its components. The condensed phase will be considered single-component and immiscible. The content of the components of the gas phase and of separate condensed phases in the system will be expressed in moles per unit mass.
Determination of the parameters of the equilibrium state consists in finding all the dependent variables, including the number of moles of the components and the number of phases at which entropy reaches a maximum. This problem of a search for the extremum of the entropy of the system with account of constriction equations was solved using Astra-4 software developed at Bauman Higher Technical School in Moscow (Vatolin et al., 1994).

3. The main characteristics of the plasma-cryogenic synthesis

In this chapter we consider the process of plasma-cryogenic synthesis on the example of nanodispersed silicon. It was carried out on the plasma induction apparatus with a capacity of 20 kW and frequency of 4.75 MHz. The apparatus had two inductors, and at first there was supplied power of 5 kW, for the second – 15 kW. As the plasma gas there was used an argon-hydrogen mixture, with 15 % vol. of hydrogen. Plasma gas flow was 1.5 nm^3/h. With the introduction of the separation of power, the efficiency ratio was 75 %. The plasma gas was injected into the upper part of the reactor through special slotted holes.
This allowed the plasma-making gas to flow along a wall in laminar mode and then formed to the plasmoid. Reacting mixture of silane-argon was supplied under a cut of the upper inductor through water-cooled probe with a high-speed pressure of 0.1 m/s. The diameter of the discharge chamber was 40 mm. The

diameter of the reactor was 400 mm. There was made the classic ratio of 1/10. This outlet allowed to provide virtually laminar flow regime with the number of Re not more than 20 at the exit of the discharge chamber. Consumption of hardening gas (argon) in liquid component was: is 0.1, 0.5 and 1 g/s. Temperature measurement was carried out with the assistance of calorimetric sensor.
Deviation amounted to 500 K. At maximum power of the charge, the temperature on a exit cut under the bottom of the inductor amounted to 8,000 K. Measuring the temperature and flow parameters were carried out at the reactor intended for diagnostic measurements. This reactor had the geometry of similar size factors of technological reactor.
Obtaining of the nanoparticles of inorganic substances in the plasma jet is a complex, multifactorial task (Fridman, 2012). From the point of view of plasma technology the most favorable nanosystems, are the systems in which the original substance is injected into the plasma jet in the form of gas, vapor-gas or aerosol mixture. The greatest difficulties appear when you enter the solid particles. This is due to the effect of the isotropic plasma reacting jets.
In our work (Bessarabov et al., 2007) there was given screen form of the CALS-project with the subcategory «Modeling of the granulated contents of nanodispersed powders» on the example of the synthesis of nanodispersed SiO_2. To the information model there were included studies, associated with the influence of the dispersion of a two-parametric complexes (Figure 3): the aggregate state of the original substance; the ratio of high-speed heads (B) of the plasma jet and jet of the injected gas (g/sec).
The research of the influence of the dispersion of an aggregation state of the original substance was carried out in plasma-chemical synthesis of SiO_2 nanopowders (required granulated content: d = 10 nm). In the work (Bessarabov et al., 2007) it was shown (Figure 3-a) that to obtain the required granulated content when using gas of the original substance (tetraethoxysilane – TEOS), the B should be equal to 1. When you enter the liquid TEOS through the nozzle, the B should be equal to 12. When the quartz powder (d_0 = 10 mcm) is entering through the feeder for the obtaining of nanodispersed SiO_2 (10 nm) there is required the high value of the B (50).

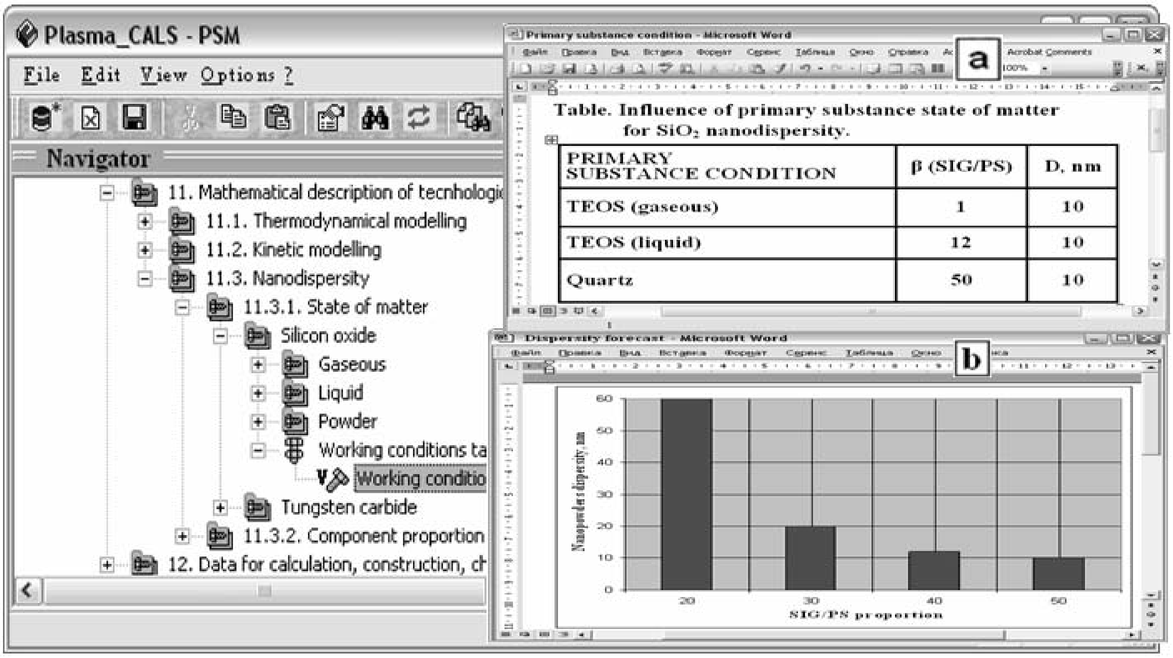

Figure 3: Element of CALS-project «Modeling of nanopowders dispersity: silicon oxide» (influence on dispersity: a – aggregate condition; b - ratio of SIG/PS).

When studying the influence of the B to the dispersity, the quartz powder (d_0 = 10 mcm) was used as the initial product. The ratio was ranged from 20 to 50. The result was the nanopowders with the diameter from 60 to 10 nm (Figure 3-b).
In whatever form the original substance was introduced to the plasma jet (whether in the form of gas, liquid or in solid form), always in the zone of input will be the difference in temperature, density, and high-speed fluctuations. Therefore, the time and energy relations will be very different for reacting heterogeneous systems which in turn affect the choice of the design features of the plasma reactor and the type of low-temperature plasma.

Analysis of the structure of nanodispersed silicon particles that we have received was carried out using x-ray powder method. Analysis of the particle size distribution was carried out on disc centrifuge DCS 5000. The measurement error of this unit is a plus/minus 1 nm. All of the samples had a x-ray amorphic structure.

Because the obtained silicon was planned for use in the manufacture of solar batteries, there was held chemical and spectral analysis of samples for the content of admixtures. The obtained samples belong to the class of high pure substances, due to the fact that the content of admixtures of heavy and alkali metals is at the level of $1*10^{-5}$ % of the amount of metals: Fe, Ni, Co, Mn, Cr, V, Na, K, Ca, Mg, as well as oxygen. All of these elements are subsequently affect the emission current in the solar battery.

We have studied the three modes of tempering with the flow of the product (mixture of silane with argon), respectively, of 0.1, 0.5 and 1 g/s. It was shown that the very narrow fraction was obtained by means of the largest active flooding of the combined-cycle plasma jet by the flow of liquid argon (1 g/s). The most interesting thing is that all 3 modes, which differ by a factor of ten, give the variation in the maximum length parameter of not more than 3 nm (from 2 to 5 nm). This once again points to the high efficiency of cryogenic tempering. Calculations based on high-speed flow using the Navier-Stokes equations and phases of the active mixture (number of Re up to 500) made it possible to assess the speed of tempering, which amounted to 10-11 seconds. I.e. after mixing, steam and gas flow turns into an isotropic nanodispersed dust mixture, solid component (nanopowder) of which separated by the bag filters. In the next hour passivation of powder in an argon atmosphere was carried out.

Advantages of the cryogenic tempering consist in the fact that it allows you to record any thermodynamic states of matter, related to the level of temperatures of up to 10,000 K. Cryogenic tempering gives possibility to transfer the clusters of level of 4,000-10,000 K to the condensed state (Hayes, 2010). And this means that at normal temperatures, we have the substance with properties inherent to the level of plasma-state conditions, i.e. it is about the solid ionic states.

4. Analytical quality monitoring

Low-temperature plasm allows obtaining of high purity nanomaterials. It is connected with the fact that by-product of synthesis does not pollute target products and does not interact with the technology apparatus, taking additional contamination. For a choice and the analysis of initial reagents and target high purity nanodispersed products of plasmachemical synthesis there was developed a system of computer quality management (CQM, Figure 4).

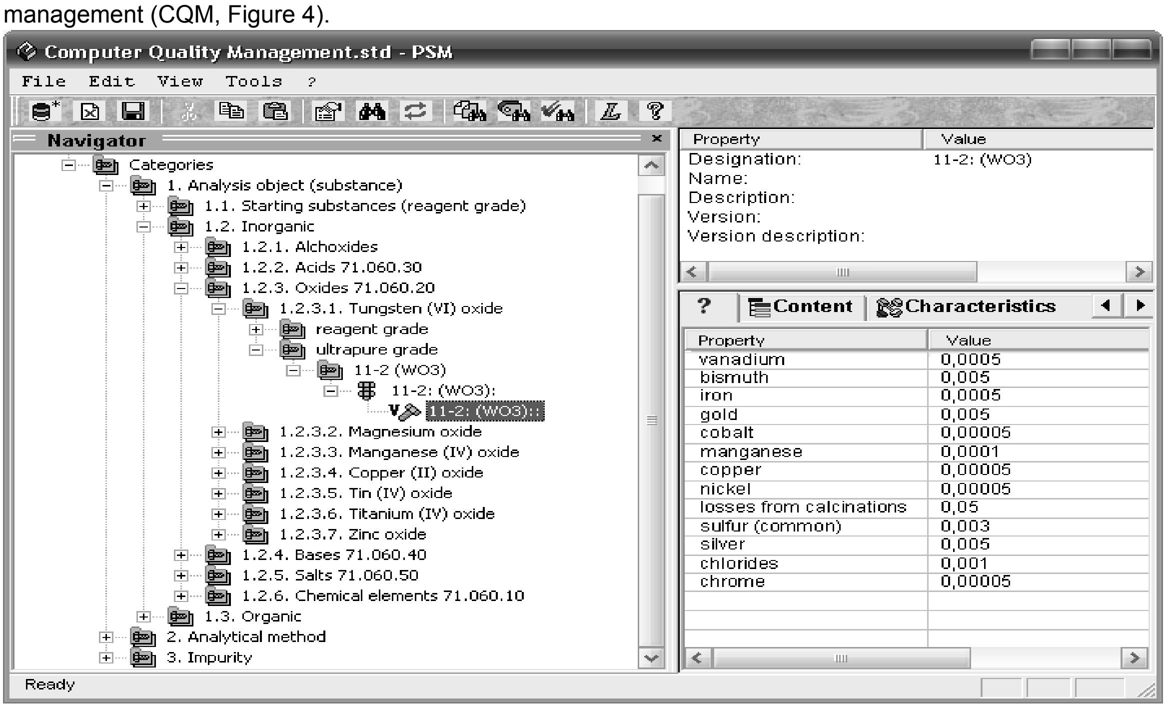

Figure 4: Element of CALS-project CQM-system in category «Analysis object» (tungsten oxide).

The system (Figure 4) has hierarchical structure of databases. Three basic information categories are allocated: «Analysis object»; «Analytical Method» and «Impurity».

The developed information structure allows choosing optimum methods of the analytical control for as much as possible exact definition of qualitative characteristics of analyzed products. On the basis of information model the program complex of the CALS-project of analytical monitoring is developed (Bessarabov and Zhdanovich, 2005). The program interface is performed taking into account an optimality of work of the user. The special procedures and the screen forms including a complex of modern elements of representation of the information and interaction with the user are developed for each stage of functioning of the system.

For assortment of initial reagents considered by us and target products of plasmachemical synthesis the following inorganic clusters are entered into the first category (Figure 4): «alchoxides» (tetraethoxysilane, tetrabuthoxytitan); «oxides» (oxides of silicon, titan, tin, iron, and tungsten); «salts» (tungsten carbide).

The chosen structure of classification of nanomaterials corresponds to the applied All-Russian qualifier of standards, a part of Uniform system of classification and coding of the technical and economic and social information of the Russian Federation. The qualifier is harmonized with the International qualifier of standards and the Interstate qualifier of standards.

5. Conclusions

Design features of the induction reactor with a cryogenic hardening used in our work allows you: to work on laminar flow; have at least two high-temperature plasma zones with controlled temperature of not less than 15,000 K; to implement the gradient less tempering at the times close to 10^{-8} seconds; to make the transition from virtually any of the available high-temperature plasma state to the normal thermodynamic conditions. It opens the way for a new class of nanopowders with developed chemically active surface.

Application of the concept of CALS in this paper allows considerably reducing the time of research and improving the quality of the work performed. The selected information technology allows to create not only an effective system design and control of quality of products, consistent with international standards, but also to integrate successfully to the production control system.

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