Pulse Plasmachemical Synthesis of Nanodispersed Oxides SiO_2 and TiO_2.

D. V. Ponomarev, G. E. Remnev

High Voltage Research Institute
2a Lenin av., Tomsk, 634050, Russia, e-mail: den@hvd.tpu.ru

Abstract – In the paper the research results of synthesis process and principal characteristics of nanodispersed oxides of silicon and titanium. The method of plasmachemical synthesis from gas-phase mixture of oxygen, hydrogen and tetrachlorsilane (titanium tetrachloride) was applied. The synthesis process was initiated by pulsed electron beam and had a chain-reaction character. The research results of synthesized powders by electron microscope are shown as well as the results of X-ray phase analysis and X-ray luminescent analysis. It is shown that the nanosized silicon dioxide is X-ray amorphous, and nanosized TiO_2 powders have crystal structure. The energy input for synthesis process was calculated.

1. Introduction

1990-s brought the discovery of new crucial perspectives on application of particular and even unique physical, chemical, mechanical and biological properties of nanosized particles and nanosized particle-based materials. The application of these technologies is considered a key technology of twenty first century compared to the already-developed computer information and bio technologies. The main parts of the applied nanoparticles are oxides (61.3 % in 1996, 73.4 % in 2000). At that the following oxides are more widely used: SiO_2 (28.5 %), $A1_2O_3$ (22.1 %) и TiO_2 (8.8 %) [1]. The wide application of nanodispersed powders and compacted nanomaterials with unique properties is often suppressed by a high cost of their generation. That is why at present time several laboratories in the world make researches on the development of technologies of their generation [2].

Modern industrial high-dimension methods of nanodispersed oxides synthesis use mainly the thermodynamic processes. For example, nanosize silicon dioxide (silica) is produced by the flame hydrolysis of tetrachlorsilan. The process of flame hydrolysis is carried out in the gas phase of air-hydrogen flame plasma at the temperature of 1100-1400 ^{0}C [2]. The thermodynamic equilibrium processes are characterized by the significant energy losses both for reaction chamber and initial products heating. The significant progress in the investigation and application of non-equilibrium plasmochemical processes achieved for last years allows to use the advantages of non-equilibrium processes in the chemical industry [3].

The electric explosion of wires production of powders presents interest since a considerable overheat of the metal and the non-equilibrium process allow preparing powders with new properties and those, which are expensive or difficult to produce by other methods [4]. In this case the powder represents a mixture of residual micrometer-sized particles and nanoparticles. However, special separating systems allow extracting up to 30 wt % nanoparticles. The production rate is 100-200 g/h of the nanofraction. Explosion of reactive metals in air leads to the formation of oxide nanoparticles. It was found that at the electric explosion of wires in air and the concentration of O_2 > 20 vol. % in its mixture with an inert gas the degree of oxidation reaches 100 % and the specific surface of the powder is 2-2.5 times larger than the specific surface of metal powders synthesized under similar conditions. The oxide particles have a nearly spherical shape and a relatively smooth surface. It was found out that crystal structure of titanium dioxide is formed, with the type of crystal lattice (rutile or anatase) being determined by the conditions of the synthesis [5].

The unique plasma qualities formed at the influence of pulsed electron beam (high degree of non-equilibrium, uniform excitation of large gas volumes at high pressures, high excitation velocity) allow to realize new physical principles of chemical reaction initiation. To these reactions belong: dissociation of oscillatory-excited molecules [3], chain plasmochemical processes [6], plasma-catalytic reactions [7] and others.

2. Experimental Set-up

In order to make research of non-equilibrium plasmochemical synthesis of nanodispersed ixodes of silicon and titanium at the influence of pulse electron beam the pulsed electron accelerator “”TEU-500” was used [8, 9, 10, 11, 12]. The accelerator parameters are the following: electron energy is 400-500 keV, pulse duration at the half-height is 60 ns, energy in pulse is up to 200 J, repetitive rate is 5 Hz. The electron beam was injected from the face plate in the closed reactor which represents a glass cylinder with inner diameter of 14 cm and volume of 3 liters. The pressure in the reactor was controlled by the low-inertial differential sensor of pressure [13]. Before introducing the gas mixtures the reactor volume was pumped-out by the roughing-down pump. The geometric size of synthesized powder was evaluated according to the pictures obtained by the transmission electron microscope. The selection volume at the histogram making was 1000-1200 measurements.

3. Synthesis of Nanodispersed Silicon Dioxide

The nanosize silicon dioxide was synthesized at the pulsed electron beam injection into the gas-phase mixture of tetrachlorsilane, oxygen and hydrogen. The pulsed electron beam initiated the chain reaction of hydrogen oxidation which was accompanied by both the OH radicals and O and H atoms formation. The action of active radicals and atoms on the initial tetrachlorsilane led to its decomposition with the formation of nanodispersed silicon dioxide. The investigations showed that the process had the oscillatory character similar to the cold flame mode under the hydrocarbon oxidation [14]. For 70 Torr O_2 + 130 Torr H_2 + 2 ml $SiCl_4$ mixture the complete tetrachlorsilane decomposition took place for one electron beam pulse. At the electron beam energy of 100 J for one pulse the energy consumptions of electron beam for tetrachlorsilane decomposition were 2.2 kJ/mole and taking into consideration the electron accelerator efficiency (35-40 %) [10] did not exceed 6.2 kJ/mole. These energy imputs are significantly lower than the energy of tetrachlorsilane decomposition which equals 425 kJ/mole [15].

The process of tetrachlorsilane destruction in the mixture with hydrogen and oxygen at the pulsed electron beam injection was of explosive nature what together with low limit of reagent mixture ignition and low energy imputs indicates the chain ramified character of silicon dioxide synthesis process at the $SiCl_4$ decomposition.

The carried out investigations showed that under the tetrachlorsilane decomposition in the chain plasmochemical process initiated by the pulsed electron beam the nanosize silicon dioxide is formed. Fig. 1 shows the powder picture obtained by the transmission electron microscope and the histogram of particle distribution according to the geometrical size after single beam action. The particles have the size of 40-120 nm (the average size is 66 nm).

The carried out composition analysis of the formed powder by the method of Rutherford backscattering showed that the powder consists of SiO_x by 99.76 % (in atomic per cents) at x=1.76. It is important to note the complete absence of chlorine (within the limits of device sensitivity) in the formed solid state. The analysis of microdiffraction of electron beam showed that in our conditions the amorphous silicon dioxide forms (Fig. 2). The presence of amorphous structure of synthesized silicon dioxide is confirmed by the X-ray phase analysis (Fig. 3).

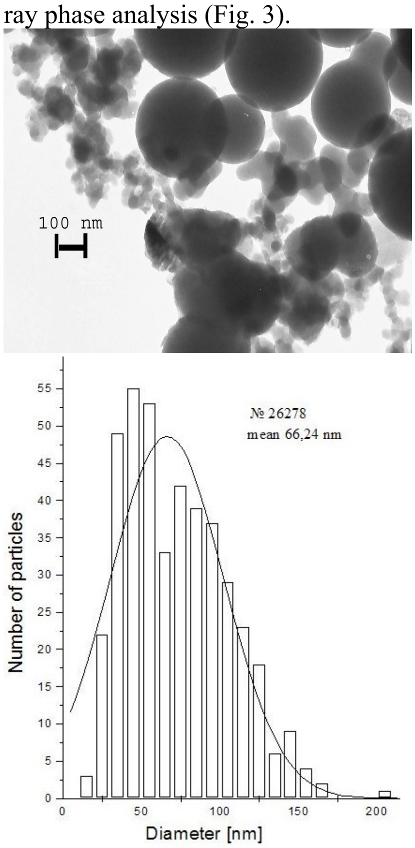

Fig. 1 The picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size Initial mixture is 70 Torr of O_2 + 130 Torr of H_2 + 2 ml of $SiCl_4$

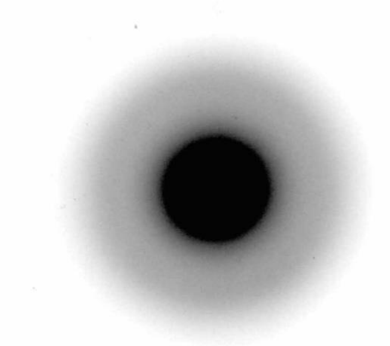

Fig. 2 Microdifractogram of nanodispersed silicon dioxide

The chemical composition of the synthesized powder was determined also by the energy dispersed roentgen fluorescent spectrometer "Oxford ED2000". The composition of nanosize powder (in relative units) was the following: Si = 99.50 ± 0.08, Fe = 0.22 ± 0.01, Cu = 0.058 ± 0.004, Zn = 0.04. The given installation allows to record the elements with the sequence number of more than 10 (Na and higher) and that is why there are no data concerning the content of oxygen.

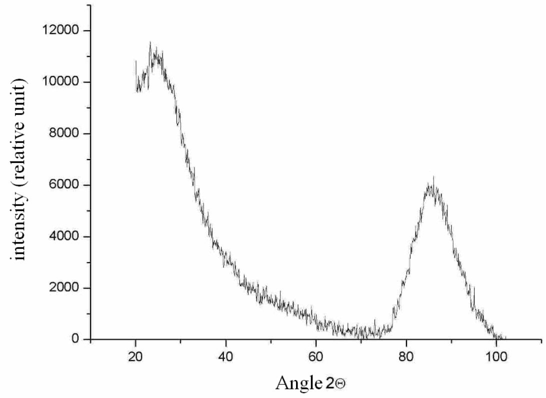

Fig. 3 The X-ray phase analysis of nanodispersed silicon dioxide

4. Synthesis of Nanodispersed Titanium Dioxide

At the synthesis of nanodispersed silicon dioxide the amorphous particles were obtained. It is known that silicon dioxide is a material with several crystalline structures. The type of the crystalline lattice is determined by the synthesis temperature. The titanium dioxide was chosen to determine the possibility of this method application for the synthesis of nanopowders with crystalline structure.

The use of closed plasmochemical reactor and pulsed character of the synthesis process allow making calculations of temperature variation in the synthesis process by the pressure change in the reactor. Fig. 4 shows the dependence of temperature in the reactor on the time. The presented data show that the temperature of gas-phase mixture in the synthesis process does not exceed 900 K, and the process duration is less than 0.1 s. The $TiCl_4$ deduction in the mixture with hydrogen and oxygen at the pulsed electron beam injection has an explosive character.

The energy of pulsed electron beam was 100 J. The destruction 13 mmole of $TiCl_4$ went for one pulse. As the result 0.2 to 0.3 g of TiO_2 powder was synthesized. Taking this into consideration it is possible to calculate the energy input (by beam) for the final product which was 0,1-0,15 kW·hr/kg. Together with the threshold limit of mixture ignition (by pressure) and low energy input this indicates the chain ramified character of TiO_2 synthesis process at the $TiCl_4$ conversion in the mixture of oxygen and hydrogen.

The performed research showed that at the destruction of titanium tetrachloride the nanodispersed titanium dioxide was formed. It had a crystalline structure . The type of the crystalline lattice (anatase or rutile) was determined by the synthesis conditions (composition of mixture, reagents, total pressure and so on). Fig.5 shows the X-ray patterns of nanodispersed TiO_2 powder. In the table 1 the data on the correlation of rutile and anatase phases for different samples of TiO_2 generated at different concentration of $TiCl_4$ in the initial mixture are presented.

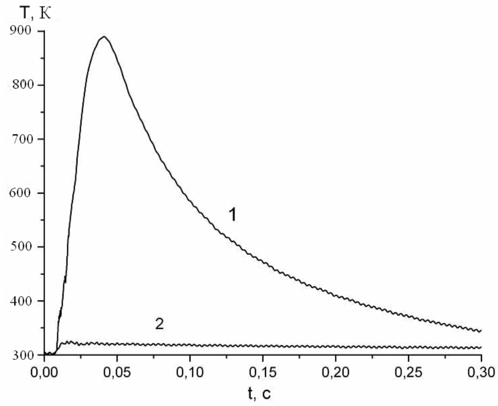

Fig. 4. Temperature change in plasmochemical reactor during the process of nanodispersed oxides (curve 1). Curve 2 shows the change of temperature only due to the heating of gas mixture by electron beam (without ignition).

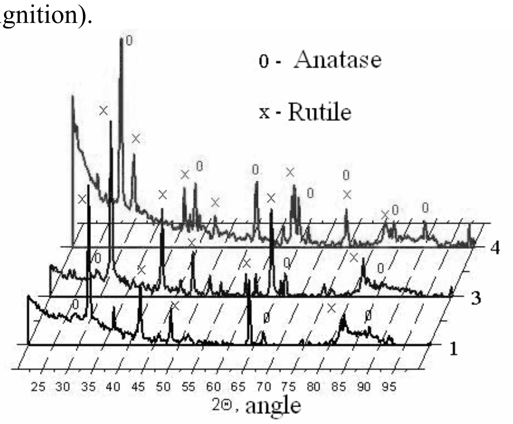

Fig. 5 – X-ray patterns of nanodispersed powder of titanium dioxide (1, 3 and 4 correspond to Table 1)

The initial gas-phase mixture had the following composition: $H_2 + O_2 + TiCl_4$ (50:25:n) (mmole). The high degree of coincidence of X-ray pattern peaks with the data of model specters of crystalline titanium dioxide indicates low content of amorphous phase and faults of crystalline structure in the synthesized TiO_2 samples.

Table 1. Results of X-ray phase analysis of nanodispersed titanium dioxide.

Sample	Concentration n $TiCl_4$, mmole	Rutile, %	Anatase, %
1	5	93	7
2	5	90	10
3	10	86	14
4	15	33	67
5	10 (+Ar)	39	61

On spite of the fact that the temperature of the gas-phase mixture in the synthesis process did not reach 1000 K, comparing to the other TiO_2 generation methods, in our conditions the crystalline nanoparticles with crystalline lattice structure in the form of rutile were formed. This is caused by the non-equilibrium character of synthesis process. The increase of $TiCl_4$ concentration in the initial mixture or the addition of inert gas (argon) led mainly to the formation of lattice of anatase type. This associates with the specific energy used by $TiCl_4$ molecules decreases.

The chemical composition of the synthesized powder was determined also by the energy dispersed roentgen fluorescent spectrometer "Oxford ED2000". The composition of nanosized powder (in relative units) was the following: Ti - 99,09±0,08, Si - 0,24±0,04, Cr - 0,10±0,01, Fe - 0,48±0,04, Cu - 0,03±0,01, Zn - 0,03±0,01. The given installation allows to record the elements with the sequence number of more than 10 (Na and higher) and that is why there are no data concerning the content of oxygen. Taking into consideration the oxygen content in the synthesized powder of titanium dioxide the calculated concentration of admixtures does not exceed 0,6 %.

5. Conclusion

The performed experiments research showed that in the non-equilibrium plasmochemical process initiated by pulsed electron beam from the gas-phase mixture of oxygen, hydrogen and silane tetrachloride (or titanium tetrachloride) the nanodispersed particles of silicon (titanium) dioxides forms.

The organization of chain plasmochemical process at the synthesis of nanodispersed silicon dioxide allows providing high productivity at high uniformity of powder on size and composition.

In the non-equilibrium plasmochemical process initiated by the pulsed electron beam from gas-phase mixture of oxygen, hydrogen and $TiCl_4$ the crystalline nanodispersed TiO_2 powder was obtained. The produced oxides have a typical form with cutting without inner cavities.

The change of initial mixture composition allows changing the crystalline structure, form and size of particles of synthesized TiO_2.

A peculiarity of the developed method is a significant decrease of synthesis temperature of particles with crystalline structure (rutile and anatase) what is caused probably by the non-equilibrium character of the going processes.

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