Investigation of Mode Influence of Plasmochemical Synthesis on the Size and Dispersibility of Silicon Dioxide Powder

G.E. Remnev, A.I. Pushkarev, D.V. Ponomarev

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

Abstract – In the paper the investigation results of dependence of geometrical size and dispersibility of nanosize silicon dioxide on the mode of plasmochemical synthesis execution are presented. The powder synthesis process out of gas-phase mixture of silicon tetrachloride, hydrogen and oxygen was initiated by the high-current pulsed electron beam.

Introduction

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 °C [1]. 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 [2]. 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 [2], chain plasmochemical processes [3], plasma-catalytic reactions [4] and others. The carried out investigations showed that under the influence of pulsed electron beam on the gas-phase mixture of silicon tetrachloride, oxygen and hydrogen the nanosize silicon dioxide is synthesized [5]. With the aim of determination of possibility of this nanodispersed powder synthesis method to control the size of synthesized particles the investigations of plasmochemical synthesis modes influence on the particle size were carried out.

1. Experimental Set-up

The works were carried out at the specialized high-current pulsed electron accelerator developed for investigation execution on non-equilibrium plasmochemical processes initiation [6]. 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 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.

2. Influence of Silicon Tetrachloride Concentration in the Initial Reagent Mixture

The carried out investigations showed that the process of nanodispersed silicon dioxide synthesis at the initiation by pulsed electron beam had a volumetric character [5]. With the aim of influence determination of initial concentration of $SiCl_4$ in the initial reagent mixture on the geometrical size of synthesized powder the investigations at the silicon tetrachloride content change and constant partial oxygen and hydrogen pressure were carried out.

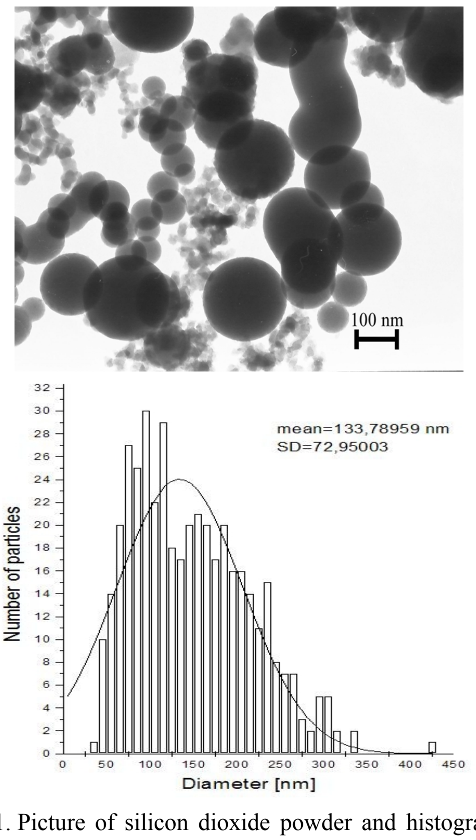

Fig. 1. Picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size. Initial mixture is 66 Torr of O_2 + 100 Torr of H_2 + 2 ml of $SiCl_4$

Figure 1 presents the picture and histogram of particle distribution of silicon dioxide. The initial mixture content is the following 66 Torr of O_2 + 133 Torr of H_2 + 2 ml of $SiCl_4$. From the histogram it is seen that the average size of the synthesized particles is 134 nm.

The decrease of silicon tetrachloride content in the initial mixture leads to the decrease of the geometrical size of the synthesized particles. In Fig. 2 the picture and histogram of particle distribution according to their geometrical size is presented with the following initial mixture content 66 Torr of O_2 + 100 Torr of H_2 + 1 ml of $SiCl_4$.

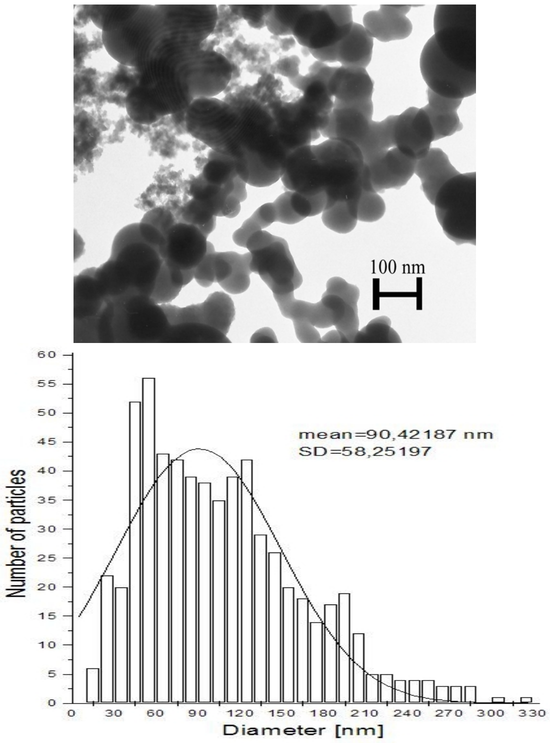

Fig. 2. Picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size. Initial mixture is 66 Torr of O_2 + 133 Torr of H_2 + 1 ml of $SiCl_4$

From the histogram it is seen that the average size of the synthesized powder decreases and is 90 nm.

3. Buffer Gas Influence

The nanodispersed particle synthesis at pulsed electron beam influence goes through the condensation of silicon dioxide molecules. That is why the presence of inertial buffer gas which prevents the condensation process must reduce the synthesized particle size. As a buffer gas the nitrogen was used. The nitrogen application in the nanoparticle synthesis process was carried out also with the aim of determination of air usage possibility instead of pure oxygen. Figure 3 presents the picture and histogram of particle distribution according to their geometrical size at the following initial mixture content: 66 Torr of O_2 + 133 Torr of H_2 + 264 Torr of N_2 + 1 ml of $SiCl_4$. The decrease of geometrical size of nanopowder should be noted when the nitrogen was added to the initial mixture.

The average particle size decrease down to 43 nm from 134 nm (see Fig. 1).

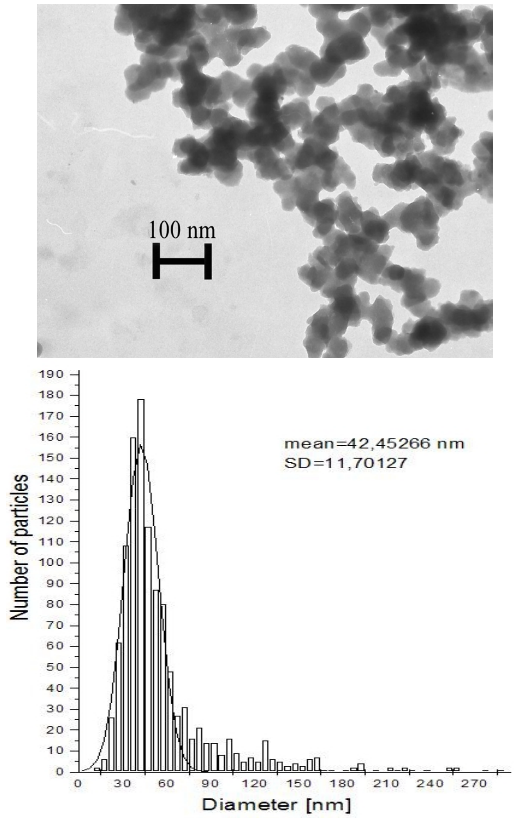

Fig. 3. Picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size. Initial mixture is 66 Torr of O_2 + 133 Torr of H_2 + 264 Torr of N_2 + 1 ml of $SiCl_4$

The decrease of silicon tetrachloride content from 2 ml to 1 ml in the initial mixture contained 66 Torr of O_2 + 133 Torr of H_2 + 264 Torr of N_2 leads to the further decrease of geometrical particle size. The average geometrical particle size at that was 27 nm.

4. The Influence of Initial Reagent Mixture Content

With the aim of possibility determination of simultaneous nanodispersed oxide synthesis of different materials the experiments on gas-phase mixture excitation of oxygen, hydrogen and tetrachlorsilan and titanium tetrachloride by the pulsed electron beam and also of O_2 + H_2 + $SiCl_4$ + CCl_4 were carried out.

4.1. Synthesis of Composite Nanodispersed oxides Si-Ti-O_x

Figure 4 shows the picture of Si-Ti-O_x powder obtained at the transmission electron microscope and histogram of particle distribution according to the geometrical size. The initial mixture was the following 66 Torr of O_2 + 133 Torr of H_2 + 2 ml of $SiCl_4$. The decrease of geometrical size of composite (SiO_2 + TiO_2) powder in comparison to the pure nanosize silicon dioxide from 134 nm to 29 nm should be noted. This can be connected with the condition change of formed particles at the new material introduction.

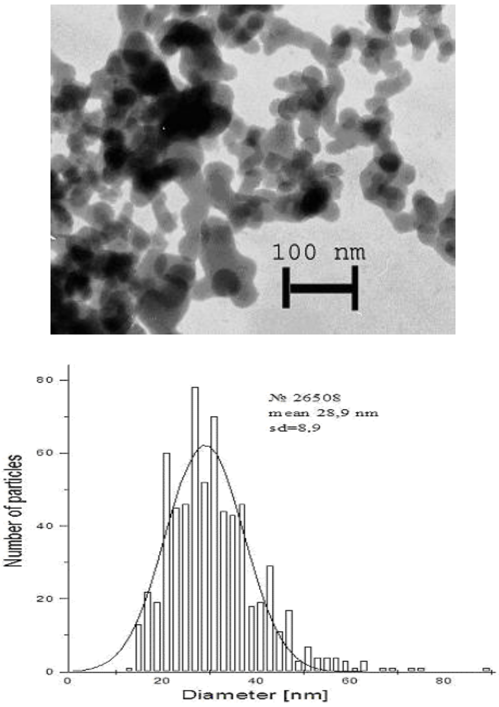

Fig. 4. Picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size of the powder Si-Ti-O_x. Initial mixture is 66 Torr of O_2 + 133 Torr of H_2 + 2 ml of $SiCl_4$ + 2 ml of $TiCl_4$

4.2. Synthesis of composite Nanodispersed oxides Si-Ti-Ox

Figure 5 shows the picture of Si-Ti-O_x powder and histogram of particle distribution according to the geometrical size. Initial mixture is 66 Torr of O_2 + 133 Torr of H_2 + 2 ml of $SiCl_4$ + 2 ml of CCl_4. The particle size of obtained composite powder Si-C-O_x is also smaller than pure nanodispersed silicon dioxide. The average particle size decreases from 134 to 47 nm.

5. Influence of Subsequent Effect of Pulsed Electron Beam

Process of nanodispersed oxide synthesis after single influence of pulsed electron beam finishes. With the aim of influence determination of subsequent electron beam effect on the synthesized powder the analysis of powder sizes at different number of subsequent pulsed electron beam influences was carried out. The particle enlargement was found out at the subsequent pulsed electron beam influence [7]. In all the experiments the similar mixture was used: 140 Torr of O_2 + 210 Torr of H_2 + 1.5 ml of $SiCl_4$. The mechanism of nanosize particle distribution according to the sizes depending on the number of subsequent electron beam pulses influence on the nanodispersed SiO_2 was investigated. After ten subsequent beam pulses the average particle size increased from 30 nm up to 140 nm. But also the significant number of particles with the size smaller than 30 nm was observed. Probably theses particles did not fall under the influence of pulsed electron beam.

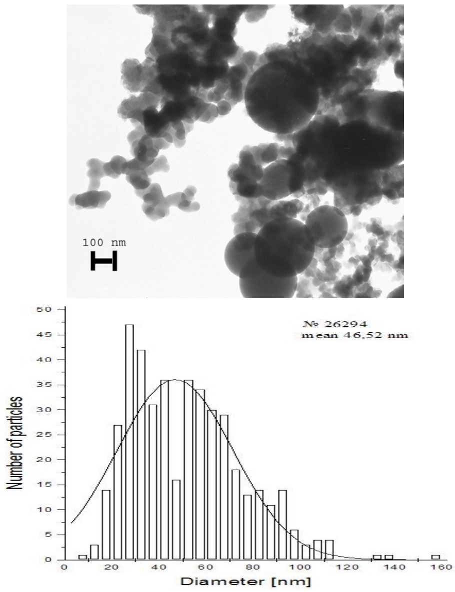

Fig. 5. Picture of silicon dioxide powder and histogram of particle distribution according to the geometrical size of the powder Si-C-O_x. Initial mixture is 66 Torr of O_2 + 133 Torr of H_2 + 2 ml of $SiCl_4$ + 2 ml of CCl_4

The quantity of electron beam influences on the gas mixture with formed particles of silicon dioxide leads to their enlargement according to a definite mechanism. The particle formation with regular spherical shape with large size is typical. Obviously the process of amalgamation goes due to the surface energy of primary nanosize particles.

Conclusion

The carried out investigations showed that the developed plasmochemical process of nanosize silicon dioxide can be easily controlled. The decrease of silicon tetrachloride in the initial mixture, addition of buffer gas lead to significant decrease of particle geometrical size. This confirms the volumetric character of synthesis process. At the synthesis of two-component oxides the particle size also decreases comparing to one-component particles. This effect indicates the important role of the initial stage of nucleation on the condensation velocity. The size of formed powder depends on the quantity of subsequent influences of pulsed electron beam. It is important to note that the synthesized nanodispersed particles do not have inner cavities.

References

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