IN SEARCH OF EFFECTIVE WAYS FOR GENERATION OF TiO_2 NANOPARTICLES BY MEANS OF FIRING Ti-CONTAINING PYROTECHNIC COMPOSITION

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ABSTRACT

The characteristics are studied of TiO_2 aerosol formed in combustion of Ti particles of few hundreds micron size moving in air with the velocities up to 15 m/s. The oxide particles were sampled by thermophoretic precipitator and examined with use of electronic microscope. The features of aerosol particles structure are described and compared with those obtained in combustion of Ti particles moving with the velocity not exceeding 5 m/s. Aerosol particles are fractal-shaped aggregates consisting of primary nano sized particles-spherules. When burning Ti particle velocity increases, the spherule size decreases from 23±2 nm up to 17±2 nm while fractal dimension of aggregates increases from 1.55 to 1.79. At the same time relatively large (mean size ca. 200 nm) particles appear in the aggregate structure that leads to decrease in a specific surface of aggregates. The mass fraction of large particles in aggregate may reach about 80% that makes it necessary to take account of their contribution into specific surface determined from the data of electronic microscopy.

INTRODUCTION

It is known that the nano sized TiO_2 particles possess photocatalytic properties, which provide effective destruction of various harmful substances. Such photocatalytic nanoparticles may be produced via different ways [1]. The data were reported that in some cases the nanoparticles in rutile crystal form demonstrated higher reactivity than nanoparticles in anatase crystal form [2]. The photocatalytic efficiency of the combustion-synthesized TiO_2 may exceed one for the commercial product. In particular, under identical conditions of UV exposure, the initial degradation rate of phenol with the combustion-synthesized TiO_2 appeared to be 2 times higher than that with commercial TiO_2 "Degussa P-25" [3]. It is supposed that the combustion-synthesized TiO_2 can be used for deactivation of a cloud of the poisonous gas appeared as a result of accident or an act of terrorism [4]. For real-time production of nano sized TiO_2 particles in situ the firing of the pyrotechnic compositions containing powdered Ti seems to be promising.

Compositions for obtaining smoke-like TiO_2 have to meet specific requirements. The formulation of such compositions should not contain ammonium perchlorate (AP), because the presence of chlorine worsens photocatalytic properties of particles, and should not contain other components forming condensed combustion products of metal oxide type (except TiO_2). The known from literature pyrotechnic compositions with titanium, including those with KNO_3 [5] and dinitramide salts KN_3O_4 and CsN_3O_4 [6] do not meet these requirements.

Recently, we conducted experiments on the combustion synthesis of nano sized TiO_2 with AP based pyrotechnic compositions [7] and determined the main parameters of TiO_2-smoke. However, as it is pointed above, the use of AP is undesirable. Therefore, a search was continued with use of ammonium nitrate as oxidizer with the Ti mass content in the range of 15-29% [8]. Unfortunately, these compositions exhibited rather low burning rate (about 0.4 mm/s at P = 1 atm) and intense sintering of the titanium. Even at relatively low (15%) content of titanium the slag formed in the shape of a skeleton consisting of sintered and partially oxidized particles of the titanium. With increase in the titanium content the burning rate increased, but the mass of slag also increased and completeness of the titanium combustion decreased. As a result of Ti particles sintering and incompleteness of metal combustion the yield of smoke particles with size less than 5 microns comprised ca. 5% of available Ti mass. The analysis of experimental data has allowed concluding that for the skeleton destruction it is necessary to raise the burning rate up to 0.6 mm/s.

In addition, it was revealed in [9] that when burning Ti particles move in air, the consecutive explosions occur, which promote particles' faster and more complete combustion.

The results of preliminary studies [7-9] allowed formulating the following recommendations. To increase the smoke oxide yield, it is necessary:

- to fire the pyrotechnic composition with enhanced burning rate;
- to ensure relatively fast motion of burning Ti particles in air.

The aim of the present work was the search of firing schemes and chlorine-free composition, providing enhanced yield of TiO_2 smoke and to decrease in the TiO_2-nanoparticle size (or increase in the particle's specific surface).

EXPERIMENTAL TECHNIQUES

The combustion of pyrotechnic composition consisted of 14% Ti, 24% of energetic binder and 62% of N_2H_4*HNO_3 – hydrazinium mono nitrate (HMN) [10, 11] has been investigated. Combustion of samples of 10 mm in diameter and height was carried out in small size chamber with nozzle that has allowed us to raise the burning rate (due to increased pressure in the chamber) as well as to provide enhanced speed of burning Ti particles motion. To increase further the burning rate, the Ti + __N mixture has been treated mechanically in a mill of CEM type [12] during 3 to 5 hours. Firing experiments were recoded with video camera. The burning rate was estimated by the burning time.

For sampling smoke particles the experimental set up with use of vertical ∅84_1870 mm quartz tube was assembled (volume ≈10 liters). The chamber with nozzle is mounted on a bottom of a tube; the connecting armature is mounted on the tube top cover. Figure 1 shows the experimental set up in details. Figures 2 and 3 illustrate the peculiarities of the firing experiments. It is worth noting that the combustion of Ti particles proceeds mostly in air environment, not in the flame of pyrotechnic composition pyrolysis products.

The following sampling techniques have been used:

1. Petryanov's aerosol filter of AFA type [13] (weighing the total residue);
2. Five-cascade impactor BP-35/25-4 of Andersen type (sampling with the aerosol fractions separation) [14];
3. Thermophoretic precipitator [15] (samples for transmission electron microscope TEM). The details of TEM-images treatment are presented in [16-18].

EXPERIMENTAL RESULTS

Burning rate and velocity of burning particles

Table 1 summarizes the results obtained with different nozzle throat diameters. It is seen from Table 1 that when using 2-mm nozzle, the burning rate reaches 0.7 mm/s. It is important to note that a skeleton at burning of composition used was not formed.

The experiments on smoke particles sampling were conducted with 2-mm nozzle. At these conditions the characteristic velocity of burning particles moving in air is about 5-15 m/s. The size of burning Ti-particles ejected from the nozzle reached 1 mm.

Table 1.
Burning rate of pyrotechnic composition fired in chamber with nozzle and the particles' motion parameters *) for milled mixtures Ti + __N

Nozzle diameter, mm	Burning rate, mm/s	Particles' lifting height, cm	Particles' velocity, m/s
5	0.5	100-150	3-5
4	0.6	130-160	3-5
3	0.6	160-190	5-6
2	0.7	180-220	8-9
2	0.8-1.0*	150-230*	5-15*

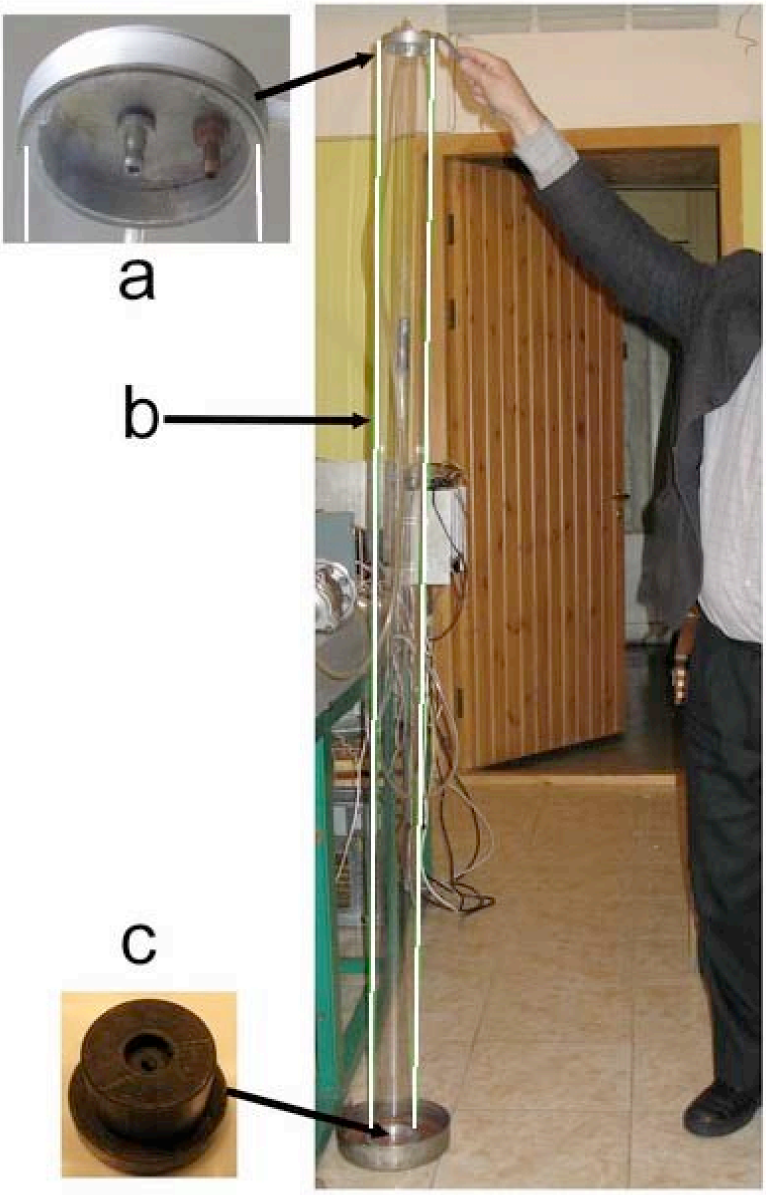


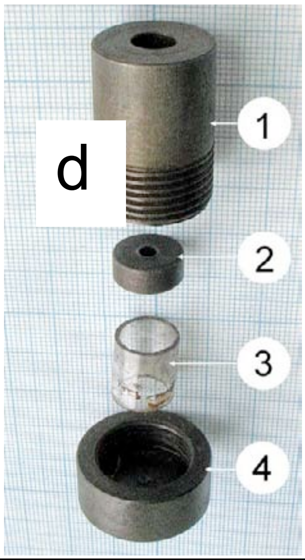
Fig. 1. Installation for sampling the smoke formed in combustion of Ti particles ejected from the nozzle:

a) The top cover of the main quartz tube with branch hoses for sampling the aerosol.

b) Main tube. Two white parallel lines are drown to mark out main tube.

c) The combustion chamber which has to be established on a bottom of the main tube with nozzle directed upward.

d) Details of the chamber (c): 1- casing, 2- nozzle insert, 3- pyrex tube for holding pyrotechnic composition, 4- bottom cover.



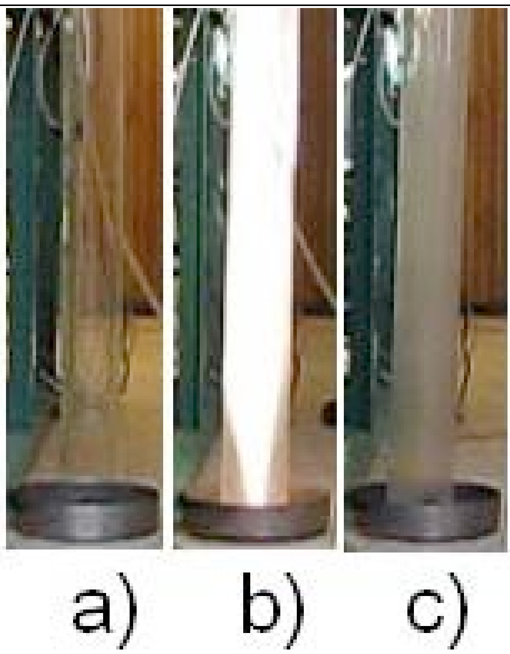


Fig. 2.
Fragments of the video recording the firing experiment.

a) Main tube before experiment is transparent. (One can see the things behind a tube).

b) The tube during firing. The jet of the combustion products discharged from the nozzle is visible. The tube is filled with the burning particles.

c) After combustion of the sample the tube is filled with the smoke particles and is not transparent.

Fig. 3.
Two examples illustrating the Ti-particles exploding combustion. The burning particles are ejected from the nozzle. The experiment without main quartz tube. High resolution photographic registration with use of digital camera “Canon EOS 350D” (the vertical size of the image equals 2264 pixels). Parameters of shooting: objective Sigma DC18-200 mm, focal length 125 cm; diaphragm f/5.6; exposure time 10 ms, sensitivity ISO800.

Smoke particle characteristics

Sampling of a smoke on the filter of AFA type is carried out with the purpose of obtaining the total smoke mass. Aerosol sampling started just after ignition of the sample and finished 2 minutes after complete combustion of the sample. Sampling rate comprised 20 liters per minute. Notice that the main tube volume is about 10 liters, and the burning time of the sample is about 10 seconds. The increment mass of the filter due to smoke particles precipitation comprised 7% of the titanium content in the sample.

The X-ray phase analysis of products performed on the Bruker D8 Advance diffractometer has shown that the TiO_2 particles sampled were basically in the rutile crystal form, with the crystallite size being equal to 60-80 nanometers. Also there were observed non-identified peaks.

Sampling of a smoke by the five-cascade impactor was performed with the aim to estimate the smoke size distribution. Sampling rate of aerosol was equal to 60 l/min. Table 2 shows the mass distribution for the particles precipitated on the impactor cascades in percentage of a lump mass of the collected particles. The total mass of particles sampled by the cascade impactor was 12.2 % of the titanium mass content in the sample.

Table 2. Mass distribution of particles entrapped on impactor's cascades

Cascade →	1	2	3	4	5
Characteristic size d_{50} for cascade, μm	17.8	13.5	3.65	1.27	N/A*
Mass, %	48.4	5.5	5.2	9.2	31.7

*) the AFA-type filter was used as the fifth cascade

The total fraction of the residue mass precipitated on the cascades No. 3, 4 and 5 comprised 46.1 %. Therefore the yield of smoke particles with less than 3.65 microns size from a mass unit of the titanium can be estimated as $12.2\%\times0.461\approx5.6$ %. For comparison: in [8], when firing the composition based on ammonium nitrate with full aerosol sampling, the mass fraction of smoke particles with size less than 5 microns comprised about 5.2 % of the Ti mass in pyrotechnic composition. It is obvious that in the present experiments some part of smoke particles has precipitated on the quartz tube walls and has been lost. Nevertheless, some greater mass yield of the smoke particles has been recorded. To confirm this conclusion the full particles sampling is required.

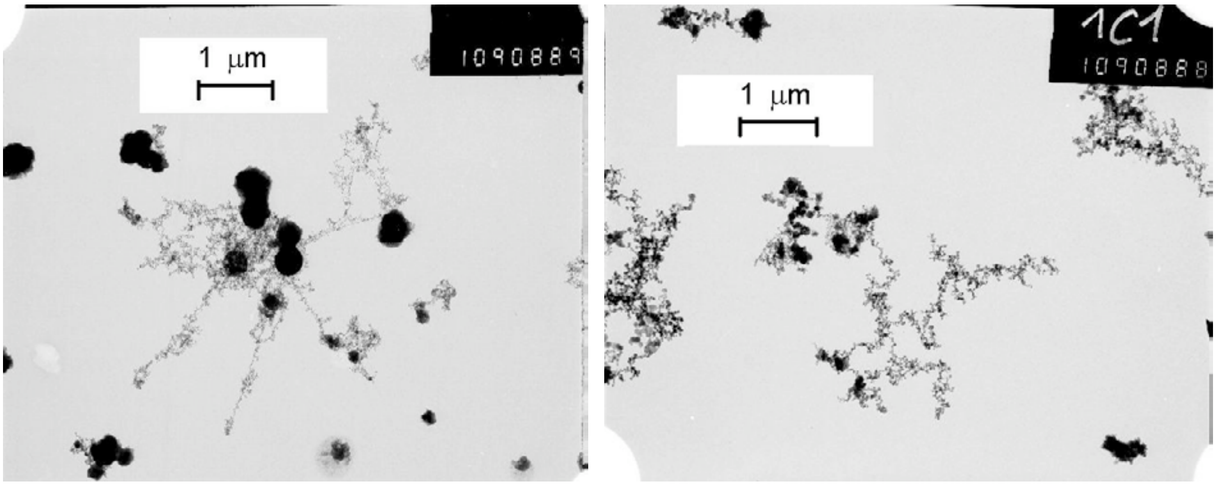
Necessity of the account for smoke particles sedimentation on a tube walls is specified by the following issue. When sampling with the 20 l/min rate an aerosol from a tube on the filter, the mass of the collected particles comprised 7 % of the mass of titanium in sample, while with the 60 l/min rate it comprised 12.2%. This distinction is caused presumably by the fact that in the first case some more particles precipitated on the tube walls due to longer period of sampling.

Thermophoretic precipitator have been used for sampling the aerosol particles for subsequent electron-microscopic analyses with the purpose of examining the sizes of primary particles (spherules) and fractal structure of TiO_2 aggregates.

Let us analyze the TEM-data. Figure 4a presents the typical images of TiO_2 aerosol aggregates sampled with thermophoretic precipitator. For comparison the image of the comparable size aggregates from [8] is presented in Figure 4b. Apparently, there are some differences in morphology of aggregates:

- in the case of present work rather large particles are observed in the aggregate structure;
- the spherule chains (present work) show the tendency to the rectilinear form while spherule chains in aggregates [8] contain "turns".

We explain the appearance of large particles by the fact that in the present work burning particles moved more quickly and intensively fragmented. Presumably, the fragmentation of burning particles is responsible for the formation of rather large particles in the combustion products. Such large particles can be resulting from the combustion of fragments in a heterogeneous mode. Rectilinearity of spherule chains is probably owed to charging effects and Coulomb interaction. The fact that in [8] the sets of rather small aggregates have been observed composed of up to several tens of spherules can testify in favor of this assumption. In experiments of the present work such aggregates practically were not observed. Notice that an aerosol "age", i.e. the time interval from firing the sample till the moment of sampling, in case of the present work was rather short (≈2 min in this work and 10 min in [8]).



a) b)

Fig. 4. TEM-images of the smoke oxide obtained at 10000_ magnification. Typical forms are of chain-branched aggregates.

a) Present work: pyrotechnic specimen fired in chamber with nozzle, fast moving burning Ti particles, hydrazinium mononitrate based composition. Sampling in course of combustion was performed continuously from the upper part of 10-liter tube, see Figs. 1 and 2.

b) Ref. [8]: pyrotechnic specimen burned in 20-liter vessel, slowly moving burning Ti particles, ammonium nitrate based composition. Sampling was performed in 10 min after complete specimen combustion.

Fractal dimension. By definition, the aggregate fractal dimension D_f equals the exponent in power correlation between the aggregate mass M and characteristic size D, _ $\sim D^{D_f}$. Following [16-18], fractal dimension of aggregates has been determined in the present work by the express method based on estimation of the aggregate mass via measuring the projection area of its image. It is known [19] that the fractal dimension of a 2D-projection is equivalent to fractal dimension of 3D-object, if $D_f<2$. We used as characteristic size so called "gabarite" size D_{gaba} defined as $D_{gaba} = \sqrt{LW}$. It is a geometrical average of length L and width W of an aggregate, which are the sides of circumscribing rectangle with minimal area LW.

The D_f value has been determined as angular factor of the straight line approximating dependency of M on $D_{gaba}{}^{D_f}$ in logarithmic coordinates, Fig. 5. Notice that such procedure gives the fractal dimension averaged over a set of aggregates. Over the set of 82 aggregates the value D_f = 1.79±0.04 has been obtained. For comparison, the dependency _$(D_{gaba}{}^{D_f})$ from [8, 9] with D_f = 1.55±0.02 is also presented in Fig. 5. It has to be mentioned that experiments [9] have been conducted with compositions based on the ammonium nitrate. The same fractal dimension value D_f = 1.55 has been determined earlier for compositions based on AP [9].

As is noted above, many aggregates examined in the present work contain large size particles (Fig. 4). Presence of these particles leads to underestimating the mass of aggregates when using an express method of mass determination based on the area of aggregate image projection, and, accordingly, to underestimating the D_f value. Thus, it can be stated with confidence that the aggregates generated in conditions of present work have greater fractal dimension than aggregates examined in [8, 9], and accordingly, they are more compact in average.

It is worth noting that in all cases the titanium particles combustion actually proceeded in air, therefore it is difficult to expect essential influence of a pyrotechnic composition formulation on the Ti particles combustion and formation of oxide aerosol. Apparently, observable distinctions in the combustion products characteristics are caused by fast motion of burning particles.

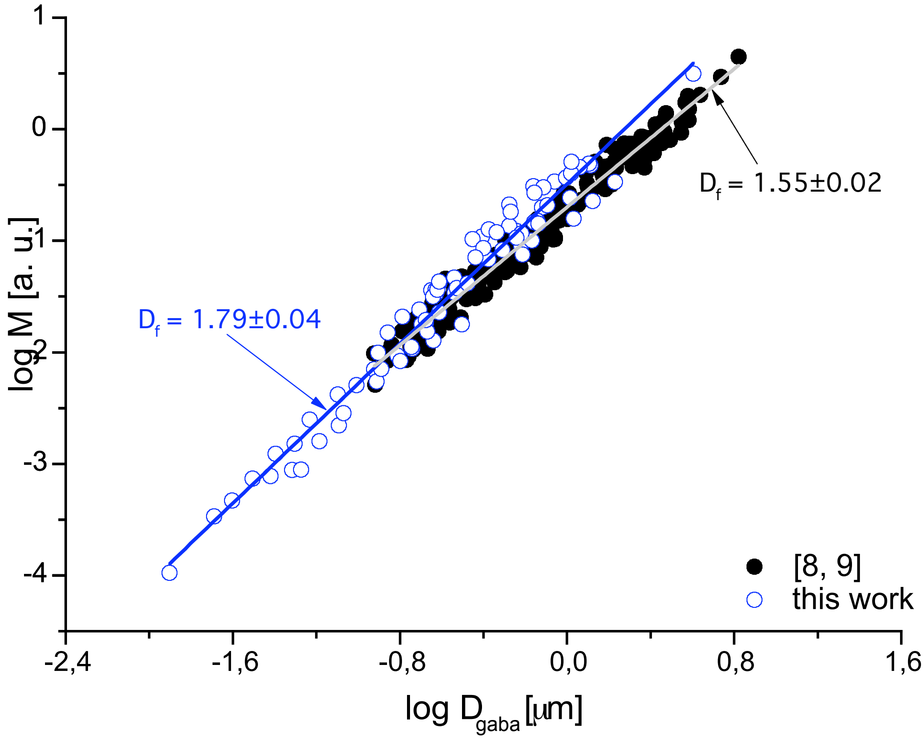


Fig. 5. Determination of fractal dimension of aggregates via measuring the slope of dependency _($D^{D_f}{}_{gaba}$). Comparison between the data obtained in present work and in [8, 9].

<u>Size of spherules</u>. The images with magnification 28000_ were used for measurement of the spherule sizes, Fig. 6. Totally 5435 spherules belonging to 30 randomly chosen aggregates have been measured. Figure 7 shows particle size distributions for these spherules (curve 1) and for 7393 spherules analyzed in [8, 9] (curve 2) processed in the same manner. The curves are presented as normalized number of spherules with given diameter and fitted by use of log-normal distribution. As a result of statistical treatment of histograms with size interval of 2 nm, the following characteristic parameters have been determined: D_{10} = 17 nm, D_{20} = 19 nm, D_{30} = 21 nm, D_{32} = 26 nm, D_{43} = 33 nm, $\sigma = \sqrt{D_{20}^2 - D_{10}^2}$ = 5 nm, K_{var} = σ/D_{10} = 0.44. Here D_{mn} are commonly used mean diameters determined as $D_{mn} = \sqrt[m-n]{\left(\sum_{i=1}^{k} D_i^m \cdot N_i\right) \Big/ \left(\sum_{i=1}^{k} D_i^n \cdot N_i\right)}$, where D_i is the midpoint and N_i is the number of particles in *i*-th histogram size interval; σ is the standard deviation, K_{var} is the coefficient of variation. We can notify that in [8] it has been found D_{10} = 23 nm, σ = 12 nm, K_{var} = 0.47 as a result of similar processing the detailed TEM-images. Value D_{10} = 23 nm has been also obtained [8] with use of diffusion aerosol spectrometer DSA. Same value D_{10} = 23 nm has been reported in [9] for compositions based on AP.

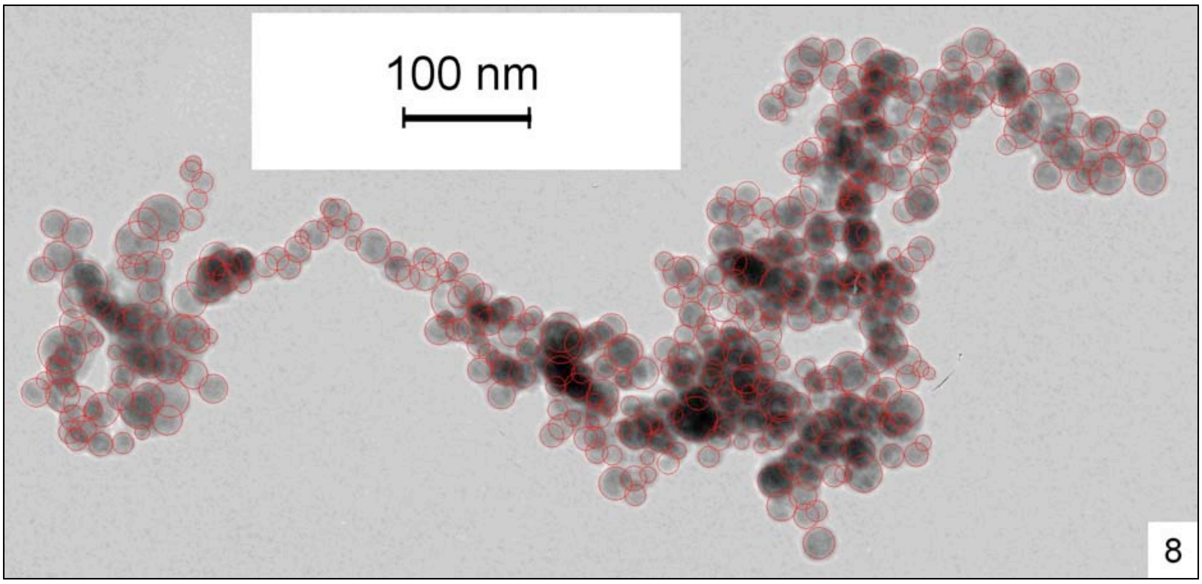


Fig. 6. Example of the spherule sizes determination by use TEM-image at 28000_ magnification. The aggregate No. 8 consists of 394 spherules and has overall sizes L = 0.9 μm, W = 0.4 μm, D_{gaba} = 0.6 μm. The characteristic sizes of spherules are: D_{10} = 19 nm, D_{30} = 21 nm, D_{43} = 25 nm, σ= 6 nm. Calculated value of S_{sp} comprises 66 m^2/g.

Each spherule is encircled. These circles are the results of the computer processing of image.

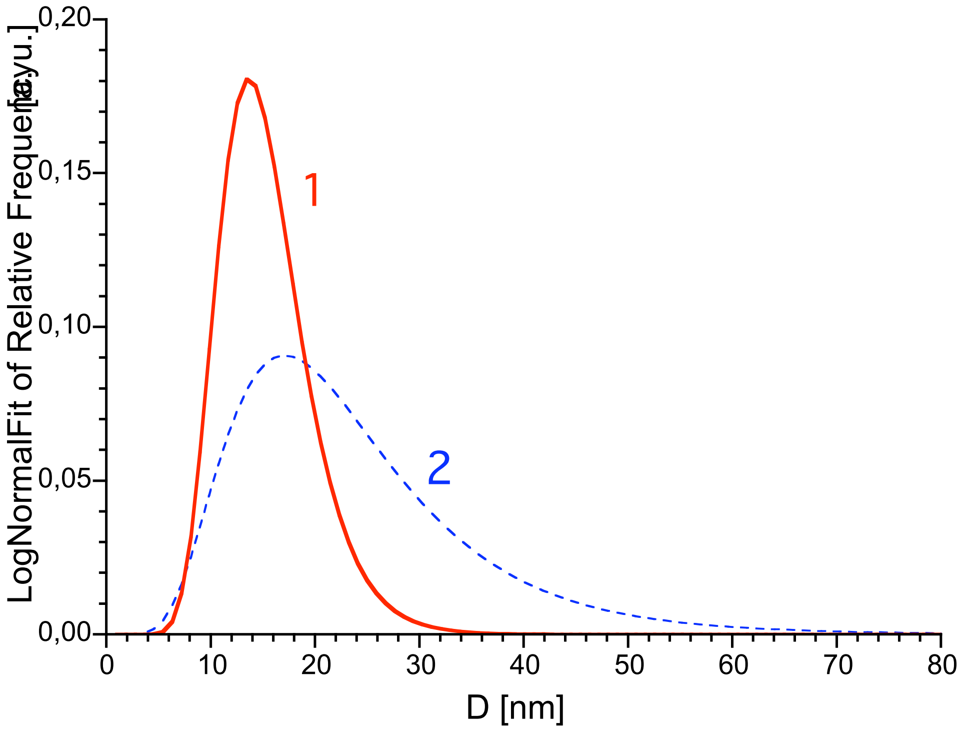


Fig. 7.

Comparison between size distributions for spherules obtained in present work (curve 1) and in [8, 9] (curve 2).

Specific surface. The particles specific surface value is of special interest from the point of view of catalytic activity. A formal estimation of specific surface S_{sp} has been made with D_{32} = 26 nm and ρ=3.95 g/cm^3 (TiO_2 density) by using the relationship $S_{sp}=6/(D_{32}\cdot\rho)$. It was obtained rather high value S_{sp} = 58 m^2/g. However, as shown above, one of the basic features of oxide aerosol, formed in conditions of the present work, is the presence of large particles in structure of aggregates. It is obvious that presence of these particles leads to essential decrease in an effective specific surface. Some efforts have been undertaken for an estimation of the scale of this effect. The large particles have been measured in all recorded aggregates on available photographic plates. The size of large particles exceeds 50 nanometers that allows one to easily distinguish them from the "ordinary" spherules. This set of totally 94 large particles is characterized by the following statistical parameters: D_{10} = 180 nm, D_{20} = 200 nm, D_{32} = 260 nm, D_{43} = 300 nm, σ = 90 nm. Using this D_{32} value the magnitude of specific surface has been found, S_{sp} = 5.8 m^2/g. Whereas there is a linear dependence between S_{sp} and D_{32}, the real specific surface can be estimated as $S_{sp} = 58(1-\xi)+ 5.8\xi$ [m^2/g], where ξ is mass fraction of the large particles. The value of ξ, estimated on the basis of available aggregates images, is equal to 0.8 that leads to decrease in a specific surface of aerosol to S_{sp} = 16 m^2/g instead of S_{sp} = 58 m^2/g evaluated from the mean size of spherules.

CONCLUSIONS

Fast motion of burning Ti particles, accelerated via use of chamber with nozzle up to the velocity of about 15 m/s results in changing the TiO_2 smoke particles parameters as compared with the case of motion with velocity of about 2-5 m/s which is typical for normal combustion of pyrotechnic composition specimen in open air (without chamber with nozzle).

The following specific features characterize the morphology of aerosol aggregates formed in the case of relatively fast moving burning Ti particles. (1) The spherule chains exhibit the tendency to get the rectilinear form while the spherule chains in aggregates of slow moving burning Ti particles contain "turns". (2) The aggregates contain relatively large particles (on the average of 180 nm in size). Such particles may contribute up to 80 % into total aggregate mass and this fact must be taken into account when calculating of a specific surface of aerosol. (3) Fractal dimension of aggregates increased up to D_f = 1.79±0.04 (in case of slow motion D_f = 1.55±0.02).

The main finding is the dependency of the size of TiO_2 spherules on the velocity of burning Ti particles. When burning particle velocity increases from 5 to 15 m/s the mean arithmetic spherule diameter D_{10} decreases from 23±2 nm to 17±2 nm.

The data obtained demonstrate the principal possibility to control the characteristics of the combustion-generated TiO_2 nanoparticle aerosol.

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