Nanosized metallic oxide produced by Ultrasonic Spray Pyrolysis

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Abstract

Nanosized titanium dioxide was synthesised from organometallic solution by ultrasonic spray pyrolysis. The influences of different process parameters (gas flow rate, decomposition temperature, retention time, etc.) on particle size, distribution and morphology were determined. Droplet size distribution was measured with a laser diffraction system (Malvern Spraytec) without dilution of the aerosol and at same atomization and carrier gas parameters like in the synthesizing process parameters. Obtained nanopowder was characterized by various methods (SEM, EDS, and SMPS) with respect to structure and constitution. The most sensitive process steps were determined, and solutions for improvement of those critical points will be shown. A reaction mechanism of synthesis is proposed, as well as optimal experimental conditions for obtaining nanopowder with specific particle size, distribution and morphology. The goal was to produce nanopowder with spherical particles; in size range 100-300nm. Obtained oxidic nanopowder is going to be applied in gold layers of electrical contacts with a goal to increase the mechanical properties and life time of these coatings, without decreasing electrical conductivity.

1 Introduction

Titanium dioxide (TiO_2) is today a highly-valued material with various applications and one of the most used particulate material in the world. Because its high refractive index and inertness colour titanium dioxide is widely used as pigment. This is one of the most common application of it, and for this application is used TiO_2 in particle form. Some newer TiO_2 applications are result of its photocatalytic and semiconducting properties, for example photodegradation of organic pollutants, water purification, waste water treatment, air purification or utilisation in solar cells and self-cleaning paints. Titanium dioxide may be produced by various synthetic methods like sol-gel method, vapour decomposition and different hydrothermal technique, etc. [1-3]. In case of hydrothermal methods, process is based on preparation of precursor (titanium salt solution), thermal decomposition, where heat source can be different (flame, wall heated reactor, plasma), particle generation and final nanopowder collection. On obtaining certain particle size and morphology, heating grade, evaporation rate, retention time and other process specific parameter have influence.

Ultrasonic spray pyrolysis as a nanopowder process belongs into group of solution aerosol thermolysis, which is general group of processes for particle production which are based on precursor atomisation (droplet size 1-100µm), aerosol transport through a temperature and atmosphere regulated reactor. Particle morphology in these processes is result of droplet size, precursor concentration and physical characteristics, operating temperature and evaporation rate [4]. Inside furnace it is assumed that the following steps are taking part: evaporation of solvent, diffusion of solutes, precipitation, decomposition and densification. [5] These process steps are simplified and their understanding is base for controlling the particle formation process. Most previous investigation took process temperature, droplet size and evaporation rate as the main parameters that influence particle morphology. [6-8] Jayanthi et al. defined in their model relative time constants for different process steps and have shown that droplet shrinkage and solute diffusion are the slowest steps. [7]

In the present work the influence of those parameters on titanium dioxide nanopowder through modelling first process step-evaporation stage was tested. Main aim was to produce spherical nanoparticles in size range 100-300nm, with high homogeneity of particle size distribution, and to achieve maximal productivity of a process. Particle size was regulated by droplet size and precursor concentration. Morphology was determined with temperature and carrier gas flow rate. Beside on morphology, carrier gas flow rate has influence on productivity of process. By increscent of carrier gas flow rate more precursor solution can be tranported in form of aerosol and this way more naopowder can be obtained. But carrier gas flow rate is limited by its influence on evaporation rate. This relationship was also investigated and optimal conditions were proposed.

2 Experimental

Tetra-n-butyl orthotitanate $C_{16}H_{36}O_4Ti$ (Merck, Darmstadt, Germany) was used as precursor for the synthesis of titanium dioxide nano powder by ultrasonic spray pyrolysis. The solutions were prepared by mixing of equivalent amount of corresponding salt in deionised water and addition of hydrochloric acid. Tetra-n-butyl orthotitanate reacts very fast with water to form butanol and reactive titanium oxide hydrate or titanium dioxide that directly precipitates as a white powder. To prevent this and prepare stabile solution, hydrochloric acid is added. Equipment used for experiments is described in previous work of Bogovic et al. and presented in Fig.1. [9]

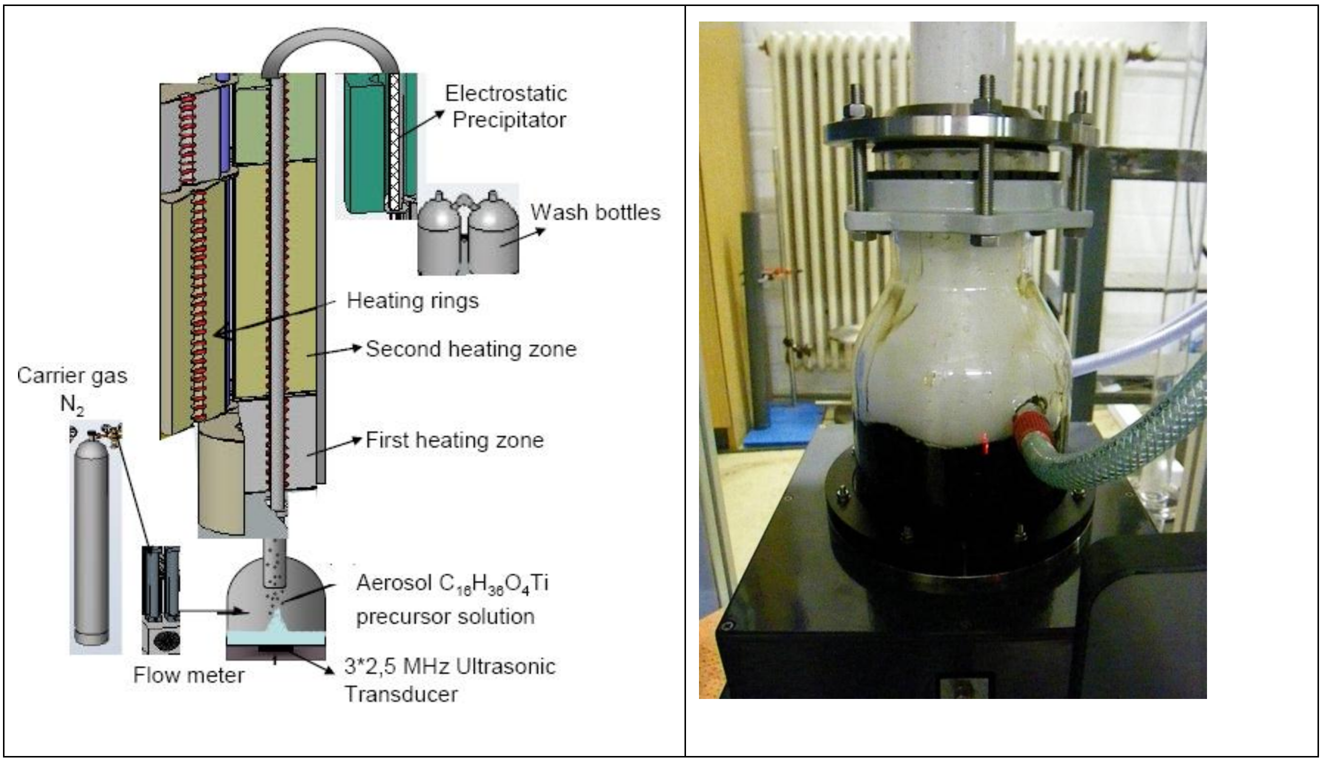

Figure 1: Experimental set-up and close up to 3*2,5MHz ultrasonic transducer

The equipment can be separated in three groups that are corresponding to three main process steps (aerosol generation, thermal decomposition, nanopowder collection). Process begins with aerosol generation through atomisation of tetra-n-butyl orthotitanate solution in an ultrasonic atomizer (Gapusol 9001, RBI/France) with three transducers operating at resonant frequency of 2,5 MHz. This generator is specially developed with a goal to increase aerosol production and this way also nanopowder production rate. Influence of more transducers in one generator on droplet size was also determined. Liquid lever in generator and solution temperature were maintained constant through whole process by continual re-filling and thermostat. Droplet size distributions were measured without dilution of the aerosol and at same atomization and carrier gas parameters like in the synthesizing process parametrs (Institute of Process Engineering in Life Sciences, Section I: Food Process Engineering, Karlsruhe Institute for of Technology (KIT)). A laser diffraction system (Malvern Spraytec) equipped with a 300 mm focusing lens was utilized for these investigations. Size measurement by laser diffraction is based on the size dependent scattering angle of light at a droplet or particle and therefore the scattering signal from the aerosol is detected in order to determine the droplet size distribution. Generated aerosol is carried in the reaction zone with nitrogen flow rate 3,5-10 l/min. The reaction zone (quartz tube l=1,8m, d=42mm) is situated in furnace with three separate regulated heating zone with temperature range 0-1100°C. So called “pre-heating” zone and “cooling” zone are situated at entrance and exit of the furnace with length of 0,4m, and in the middle is “reaction” zone with length 1m. Whole system was under inert atmosphere and small vacuum (980mbar). Produced nanopowder was collected in electrostatic precipitator. For the characterisation of the obtained titanium dioxide nanopowder was used scanning electron microscope. SEM images were used for observation of particle morphology, structure, size and size distribution. Qualitative analyses of obtained powders was done by energy disperse spectroscopy (EDS) analysis with a Si(Bi) X ray detector, connected with SEM and multi-channel analyzer. Particle size and particle size distribution was determined with on-line measurements with SMPS Scanning Mobility Particle Sizer system with DMA Differential Mobility Analyser (Grimm, Germany) after second heating zone and one more time after powder collection by SEM image analyses with ImageJ softer, while experimental data were processed by the computer program Origine8.

3 Results and discussion

Experimental conditions for the preparation of titanium dioxide nanopowder are given in Table 1. The goal of experiments was to determine influence of evaporation rate, temperature and carrier gas flow rate on morphology and particle size of produced nanopowder. All experiments were conducted with 6 g/l $C_{16}H_{36}O_4Ti$ precursor solution.

Table 1: Experimental Conditions for the three heating zones of the pyrolysis reactor

No. Experiment	Temp. [°C]	Flow rate N_2 [l/min]
1	800-800-300	4
2	800-800-300	7
3	800-800-300	10
4	250-800-300	4
5	250-800-300	7
6	250-800-300	10

Influence of concentration of precursor solution on oxidic nanoparticle was studied in previous work. [9] Based on these results, possible low concentration was selected in order to obtain nanopowder in certain particle size range.

Experimental data were chosen in way to test influence of different evaporation condition on particle formation. Carrier gas flow rate and temperature were regulated that way to simulate evaporation of droplet in low and high temperature zone, and by different velocity of droplet in those zones. Since the goal of titanium dioxide nanoparticle production was to produce spherical nanoparticle with maximal homogeneity, in size range 100-300nm, particle size distribution was also determined. Ultrasonic spray pyrolysis is based on assumption that from each droplet one particle is produced and that all droplets are going through same process steps by same conditions [10-11]. From this reason first step in partice size distribution determination is to determine droplet size distribution. Droplet size distribution is presented in Fig.2, for 6g/l $C_{16}H_{36}O_4Ti$ precursor solution and 3*2,5MHz transducer.

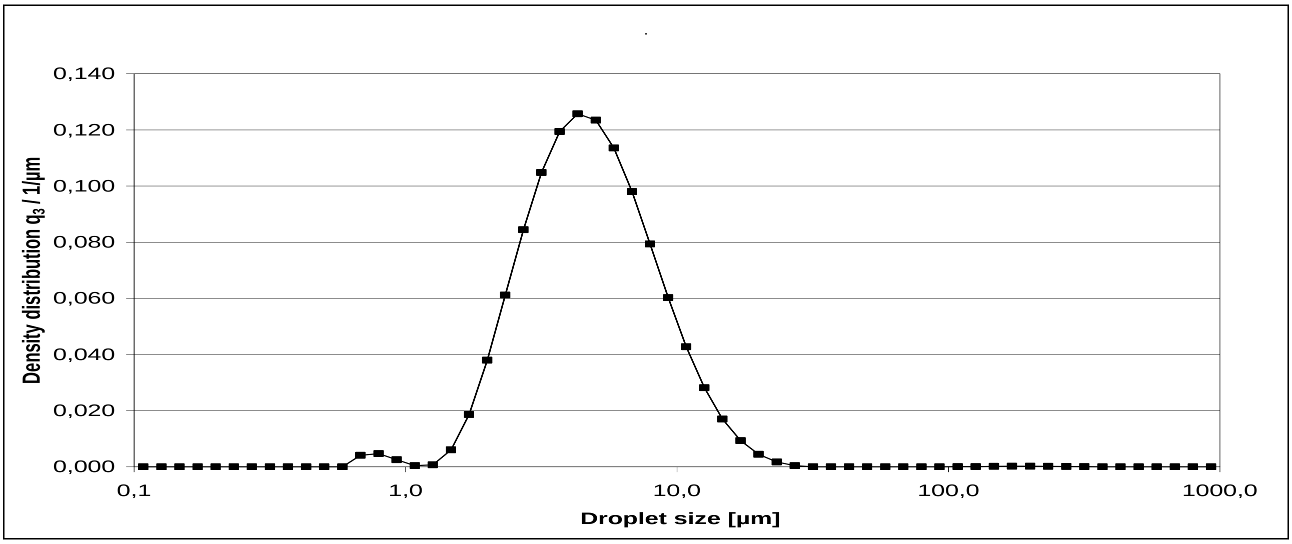

Figure 2: Droplet size distribution

From droplet size distribution it is obvious that it can’t be talked about single value of droplet size but droplet size distribution must be used, where droplets are in range 1-15µm with highest probability of droplet diameter in range of 4-6µm. By knowing droplet size distribution it is expected to get similar distribution of particle size, just in range of 100-400 nm. In theory there is model to predict average droplet size, by knowing influence of physical properties of the atomized solution and frequency of the ultrasound and it was studied by Lang et al. [12]. This model is defined with next formula:

$$D = 0{,}34 \cdot \left(\frac{8 \cdot \pi \cdot \gamma}{\rho \cdot f^2} \right)^{1/3} \tag{1}$$

(D: mean droplet diameter; γ: surface tension of the solution; ρ: density of the solution; f: ultrasound frequency)

After measuring surface tension and density of precursor solution, average droplet size for used frequency was calculated and it is 2,8 µm. When this value is compared with experimental result (4-6µm), it can be determined that theoretical average droplet size is not adequate and from this reason theoretical model is not going to be followed in further investigation. A reason for this might be coagulation that occurs between droplets in tube that connects generator with furnace. In theoretical formula influence of coagulation wasn’t taken into account. It is possible that coagulation rate is also influenced with generator construction, application of multiple transducers and experimental parameters. From this reason in this paper droplet size distribution was measured for generator used in experiment and by experimental parameters. All conclusions in this paper are going to be based only on experimental results and based on them model is going to be proposed. After conducted experiments, first information about produced nanopowder can be obtained from SEM (Scanning Electron Microscopy) images. SEM images were used to observe the surface morphology of particles formed at different experimental parameters sets and to get first information about particle size distribution range. SEM images of produced powders in experiments are given in Fig. 3 and Fig. 4.

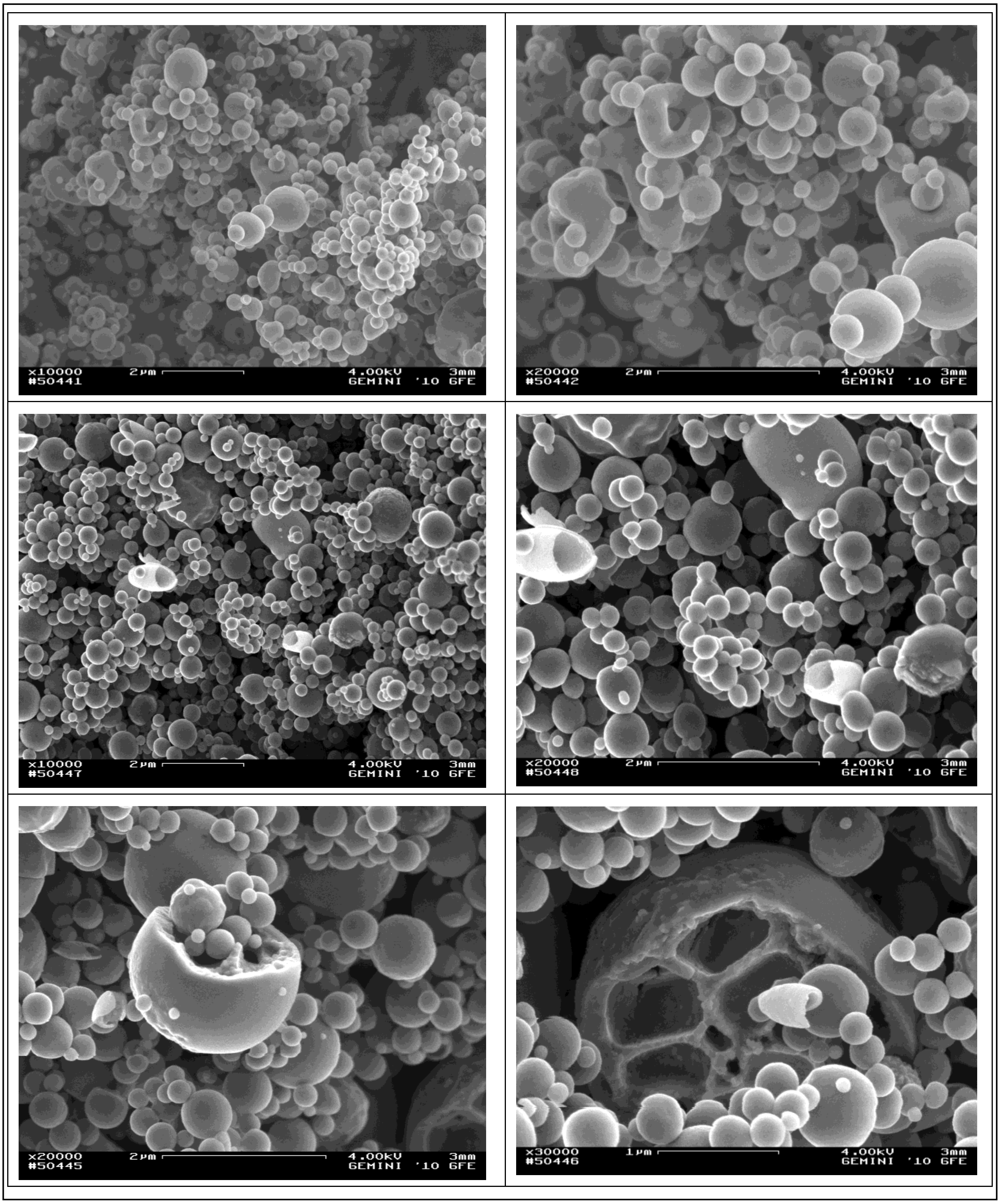

Figure 3: SEM analysis form titanium dioxide nanopowder obtained in experiments 1-3 (left and right are SEM images of same experiment)

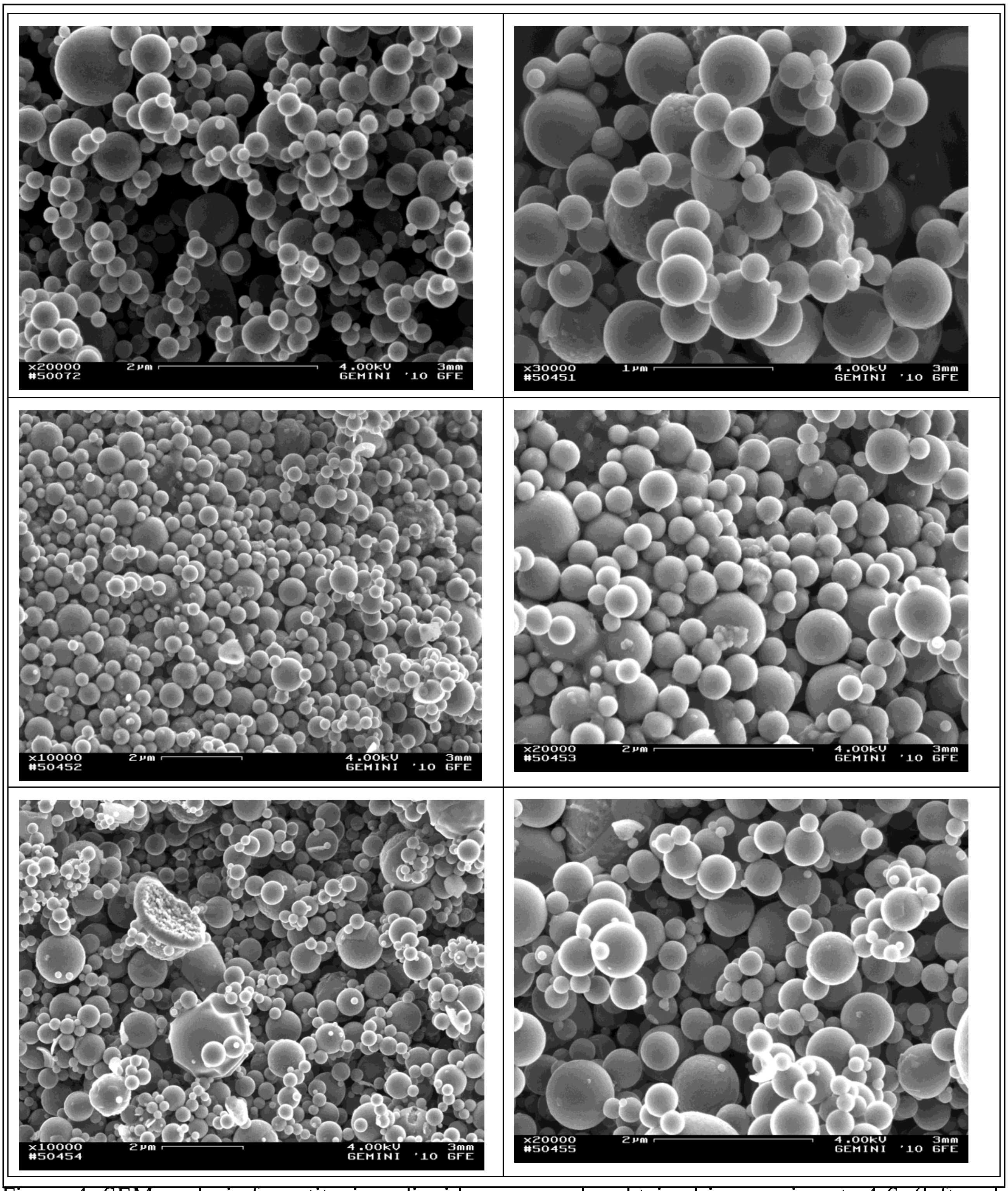

Figure 4: SEM analysis form titanium dioxide nanopowder obtained in experiments 4-6, (left and right are SEM images of same experiment)

From presented results it can be concluded that produced nanopowder in first three experiments (Fig. 3, temperature in first heating zone is regulated to be 800°C) is consisting mainly of spherical particles and certain number of particles in irregular form. In first experiment, image left, we can se "settle" like particles with whole in the middle. In second and third experiment with higher flow rate of carrier gas we can see broken, "exploded" nanoparticle with "caves inside its structure. As shown at Fig. 3 where are presented results of experiments with temperature in the first heating zone of 300°, we can see that most of the particles in obtained powder are spherical shape. Few examples of destroyed particles can be seen in last experiment, with higher flow rate. It is assumed that by high flow rate particle come to reaction zone and high temperature before evaporation and precipitation steps are finished, and this might be reason for particle destruction.

Since in is obvious that temperature plays important part in particle formation, temperature profile for both temperature regulations are measured. They are presented in Fig.5.

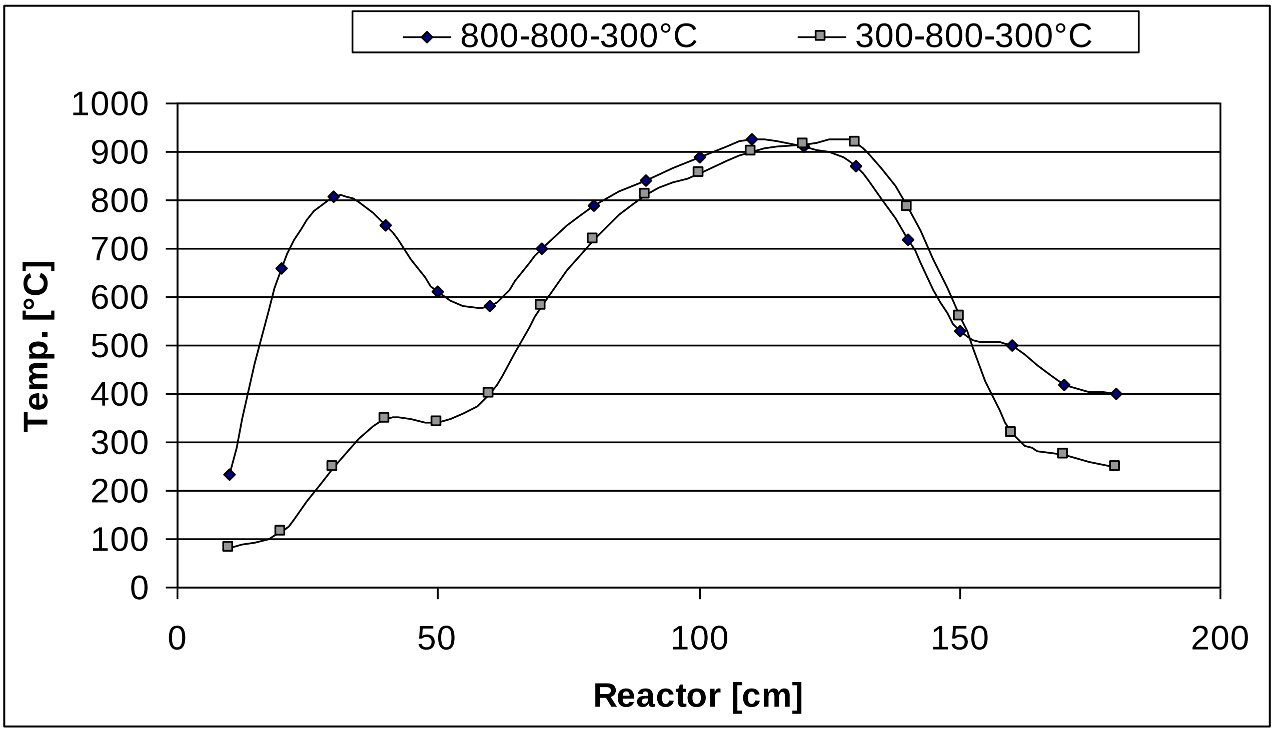

Figure 5: Measured temperature profile in reactor for different flow rates and temperature regulation in heating zones 800-800-300°C

From Fig. 5 it can be concluded that temperature profile in reactor in middle heating zone for both regimes looks similar. The difference is only in first heating zone. If we look at the model of particle formation, presented at Fig.6, we can see that in first heating zone evaporation and precipitation take place. Since process parameter (temperature) in this area is significantly different, we assume that problems in evaporation and precipitation stage are responsible for formation of non spherical particle.

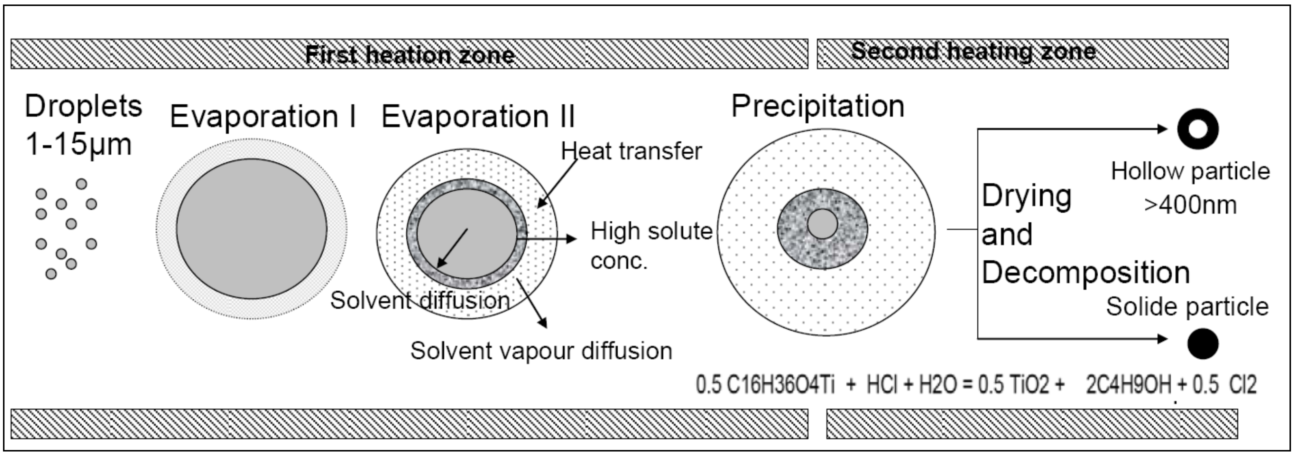

Figure 6: Proposed mechanisms of particle formation and decomposition reaction

In further discussion evaporation stage is going to be analyzed and its influence on obtained powder is going to be explained. One of proposed explanations for formation of hollow, “settle” and “cave” like particles is that by experimental conditions where temperature in the first heating zone is 800°C, rate of evaporation is much higher than rate of solute diffusion from centre of a droplet to a surface. From this reason, concentration of precursor in surface area rapidly increases and surface precipitation occurs. Trapped solute in the centre of droplet boils, pressure increase and particle is destroyed or deformed. From presented results it can be concluded that most non-spherical particle are the bigger ones. That leads to conclusion that size of primer droplet is also one of parameter that influence on final particle morphology, if we assume that bigger particle are created from bigger droplets. In bigger droplets formation of bubble inside a droplet in evaporation stage is possible and also distance dependent processes like diffusion last longer. Unwanted effect of high evaporation rate was determined by experiment number 3, where was applied maximal carrier gas flow rate. By increscent carrier gas flow rate droplet velocity through reactor is increased, and it comes faster in area of high temperature, which increases evaporation rate on surface of droplet and leads to surface precipitation.

In experiments number 4 and 5 (temperature in reactor 300-800-300°C) powder with spherical morphology was obtained and it was further characterized with a goal to determine particle size distribution. Particle size was measured on-line with SMPS system and after collection of a powder by image analyze with software ImageJ and Origine programme. Results are presented in Fig.7.

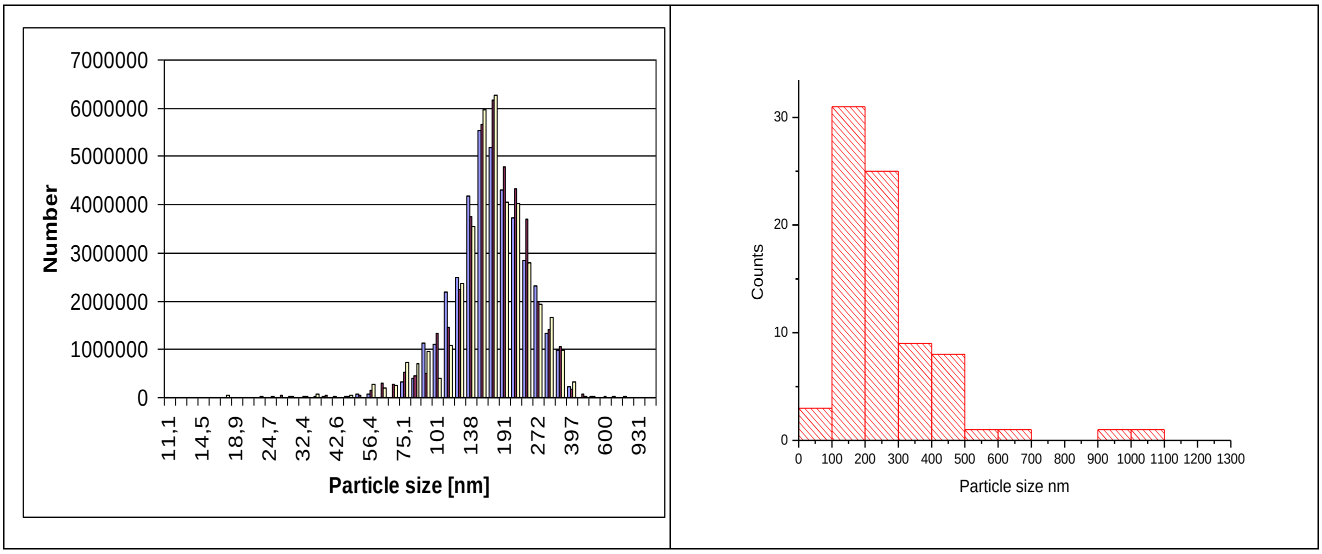

Figure 7: SMPS on-line measurement of particle size and particle size distribution after collection of powder

SMPS on-line measurement was done at exit of second heating zone. After that carrier gas with powder was cooled down in third zone of reactor and powder was collected in electrostatic precipitator. If we compare particle size distribution at exit of second reaction zone and after collection, we can see that most of the particle in both distribution are in size range 100-400nm. In analyze of powder after collection group of particle has diameter bigger than 400nm. It is possible that that number is so small that by online measurement bigger particles were not detected. For obtaining narrower particle size distribution, it is necessary to produce aerosol droplets in more narrow range. Qualitative EDS analysis of obtained powder has confirmed that titanium dioxide was obtained in all experiments. Characteristic result is shown in Fig.8.

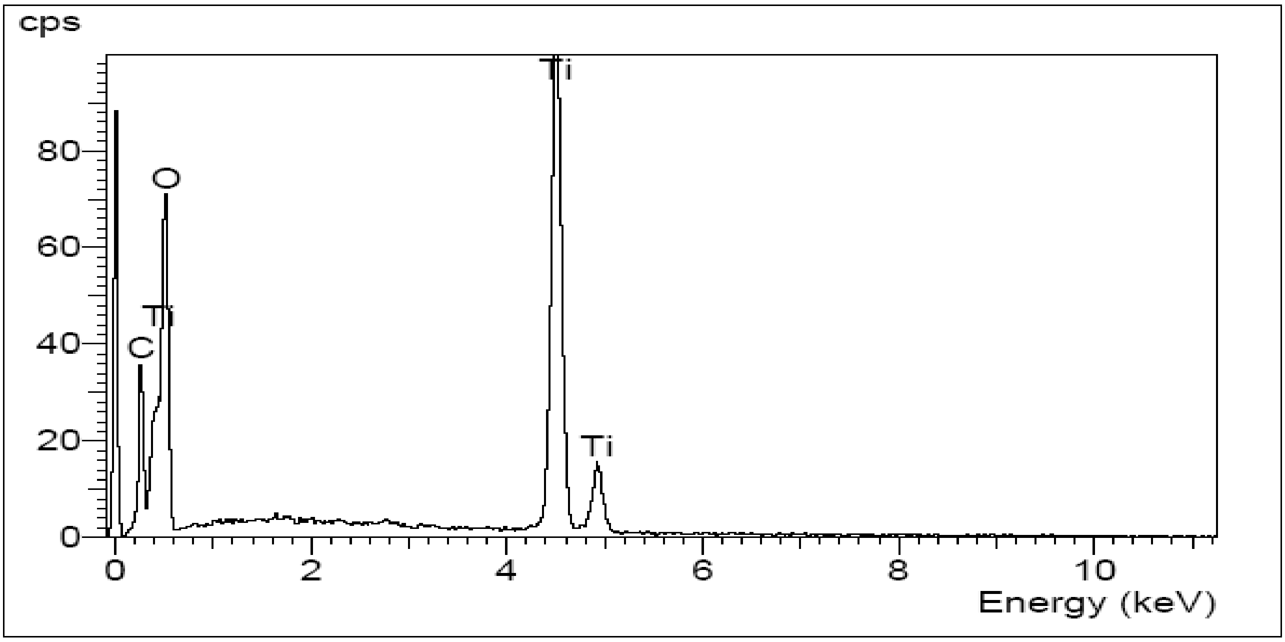

Figure 8: EDS analyze of titanium dioxide nano powder

This way it is confirmed that even by higher flow rate, and lower retention time in reactor there was enough time for decomposition reaction to occur. If we look at the model of process steps presented at Fig.6, we can see that most sensitive process steps in those experiments were first two process steps: evaporation and precipitation stage, since all other steps occurred with no problem by all tested experimental conditions.

4 Conclusions

From obtained results it can be concluded that it is possible to produce nanosized titanium dioxide with ultrasonic spray pyrolysis. This method can produce spherical nanoparticles with narrow particle size distribution. Final particle sizes depend on generated precursor droplet size distribution, if we assume that every droplet undergoes same process steps and transform to a particle. Influence of coagulation of aerosol droplets, and influence of process parameters on coagulation rate wasn't tested in this work, but it is filed of interest for further investigation.

Evaporation of solute and precipitation stages were determined as most sensible and with high influence on final particle morphology. It is proved that high evaporation rate lead to surface precipitation, which means that precipitation occurs in the surface region of the droplet. This results with deformed, destroyed, non spherical particle. Reason for this is rapid solvent evaporation and solvent vapour diffusion, compared to slow diffusion process inside droplet.

Higher temperature and higher carrier gas flow rate lead to production of deformed particles. These phenomena are much more present by droplets with bigger radius. To avoid formation of non spherical particles it is recommended to have reactor with slowly increasing temperature profile.

Measurements of temperature profile showed that separate temperature regulated zones with good temperature regulation can provide slowly increasing temperature profile, where first two process steps are going to take place on lower temperature and in further process enough energy is going to be provide for decomposition and particle formation process. On this way it is possible to optimise process parameters in the way to produce spherical nanopowder.

In experiments in which nanopowder with satisfying morphology was obtained, further analysis of powder was done. Particle size distribution was determined and qualitative analyze on powder was done. It is proved that titanium dioxide nanopowder with spherical particles and particle size distribution in main range of 100-400nm was present.

In further work, next to analyse of theoretical models, simulation of all process parameters on all process steps is going to be conducted with a goal to modify theoretical model. Detailed understanding of all parts of process is of great importance for further modelling of process. By knowing these details about each process step, specific process parameters can be controlled with a goal to produce nanoparticles with different morphology. Those morphology modifications are going to be demanded by various applications of nano powder.

5 Acknowledgments

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