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SYNTHESIS OF NANOSIZED METALLIC AND CORE-SHELL PARTICLES BY ULTRASONIC SPRAY PYROLYSIS

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Abstract: Ultrasonic spray pyrolysis is a versatile method for preparation of powders of metals, oxides and composites. Nanoparticles of silver were prepared by ultrasonic spray pyrolysis in a horizontal and vertical reactor. Direct synthesis of RuO_2-TiO_2 nanoparticles with core and shell structure was investigated in a vertical reactor. An influence of reaction parameters (the temperature, the residence time, the concentration of solution, and the ultrasonic frequency) on the morphological characteristics of prepared nanoparticles was studied. Using the ultrasonic spray pyrolysis, the ideally spherical metallic particles were obtained at temperatures below the melting point of metals. Scale up of the ultrasonic spray pyrolysis was applied for the synthesis of nanosized silver. The coating of titanium anode was successfully performed using ultrasonic spray pyrolysis method in an electrostatic field.

Keywords: ultrasonic spray pyrolysis, synthesis, metals, core-shell.

1. INTRODUCTION

This paper includes my previous research studies describing the synthesis of metallic and core-shell particles from the precursor solution such as metal nitrates, tetra-n-butilorthotitanat, and ruthenium (III) chloride hydrate using the ultrasonic spray pyrolysis method [1]. Owing to the control of used process parameters (the ultrasonic frequency, the concentration of the solution, the residence time of aerosol, the gas flow rate, and the reaction temperature), it is possible to guide the process of producing powders with a desired morphology that satisfies more complex requirements for the properties of advanced engineering materials [2−6]. Collection of nanosized metallic particles in an electrostatic field as final step represents the highest challenge in order to improve a small production rate of ultrasonic spray pyrolysis method [7−10]. Ultrasonic spray pyrolysis was carried out using an action of powerful ultrasound on the corresponding water solution of metallic salts forming the aerosol with constant droplet size, which depends on the liquid characteristics (surface tension, density and viscosity) and the frequency of ultrasound. The produced aerosols were transported into the hot wall tubular reactor, thus enabling the chemical reaction in a very small volume of a particle preparing submicron and nanosized powder. As reported by Bang and Suslick [11], powder synthesis through aerosol routes enable the generation of submicronic to nanoscaled oxidic powders from a variety of water solutions of salts such as nitrate, chloride, sulfates and acetate (as shown in Figure 1).

Spherical, non-agglomerated, nanosized particles of metals (Cu, Ag, Au), and mixed metal/oxides particles (Ru/TiO_2) were produced with new and improved physical and chemical characteristics [1]. The high costs associated with small producing large quantities of uniform, nanosized (submicron) particles using ultrasonic spray pyrolysis limit the use of prepared nanoparticles in many practical applications. Synthesis of metallic and core–shell particles will be presented in this work.

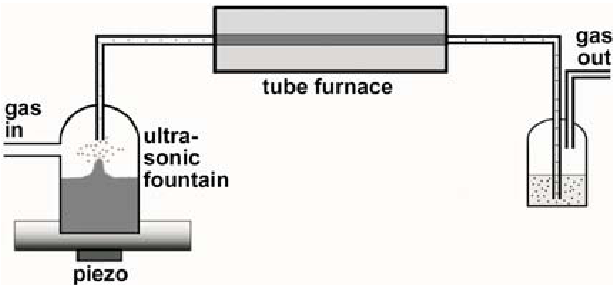

Figure 1. Ultrasonic spray pyrolysis synthesis in a single step

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2. SYNTHESIS OF SILVER PARTICLES IN A HORIZONTAL REACTOR

Firstly the ultrasonic spray pyrolysis (USP) is successfully introduced for the preparation of nanosized silver particles from silver nitrate using a horizontal reactor. The ultrasonic spray pyrolysis of $AgNO_3$-solutions was performed in a small horizontal reactor with a quartz tube (diameter 0.021 m, length 0.3 m) in hydrogen and nitrogen atmosphere (as shown at Figure 2). Calculated residence time in tube was about few seconds. It is confirmed that in the absence of hydrogen at 600°C (only nitrogen atmosphere) is also suitable for the synthesis of spherical, dense, non-agglomerated nanoparticles of silver.

The particle size of silver was increased with higher concentration. At a 0.05 mol/l $AgNO_3$, the powder is composed of non-agglomerated and rarely spherical nanoparticles between 144.5 nm and 1000 nm. At a concentration of 0.1 mol/l $AgNO_3$, the powder is composed of non-agglomerated, spherical nanoparticles of sizes between 83.6 nm and 190.2 nm . Cylindrical and prismatic forms were observed in this powder (as shown at Figure 3).

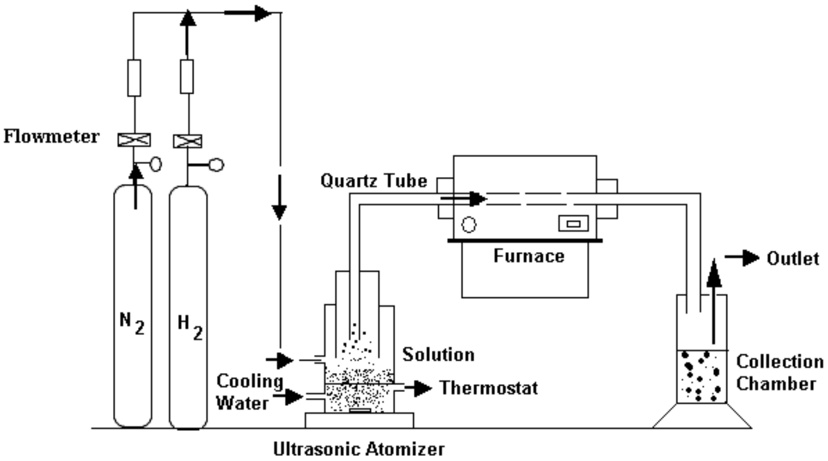

Figure 2. Experimental apparatus for the USP-synthesis of silver particles [8, 9]

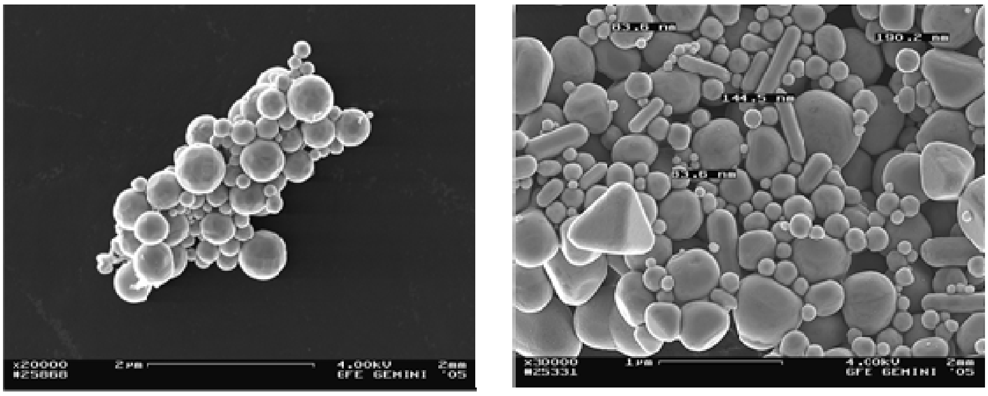

Figure 3. Reduction of silver nitrate in nitrogen (left), and in hydrogen (right)

An increase of the concentration to 0.2 mol/l leads to more spherical and dense particles of sizes between 83.6 nm and 433.6 nm without the presence of cylindrical and prismatic particle forms. The ultrasonic spray pyrolysis of $AgNO_3$-solutions followed by a hydrogen reduction is suitable for the synthesis of spherical, dense, non-agglomerated of silver at 1000°C (as shown at Figure 4). Because of the reaction temperature of 1000°C was higher than the melting point of silver (962 °C), the required conditions for the formation of fully-reacted and ideally spherical silver particles were ensured.

A decrease of the hydrogen reduction temperature from 1000°C to 150°C leads the amount of spherical, but not dense particles in the Ag-powder structure obtained from silver nitrate (as shown at Figure 5).

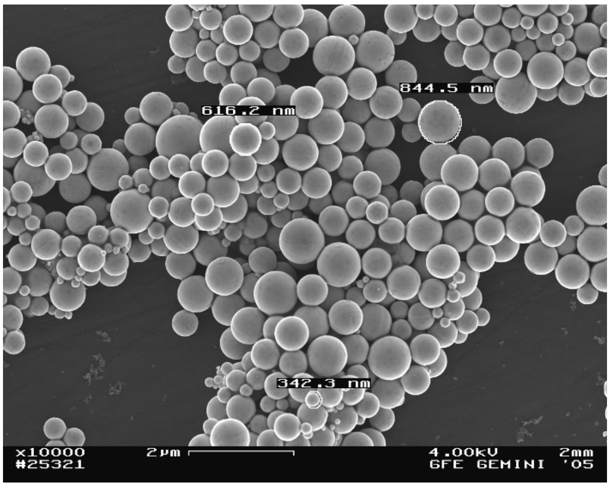

*Figure **4**. Silver nanoparticles obtained at 1000°C [10]*

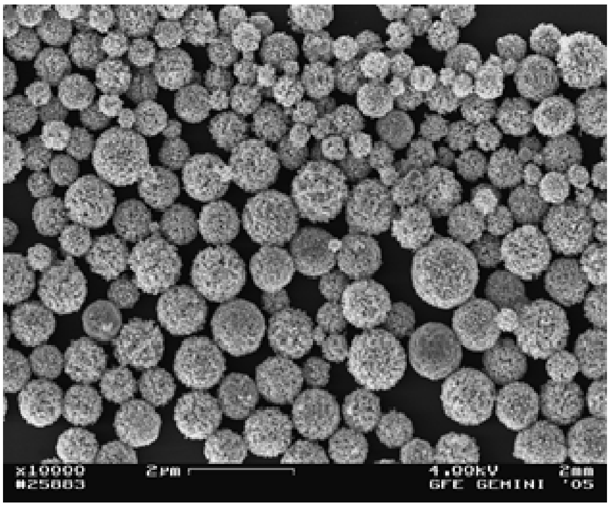

Figure 5. Silver nanoparticles obtained at 150°C

The preheating of the $AgNO_3$-solution at 45°C in an ultrasonic atomizer has no influence on the particle morphology. But the preheating has a big influence on the destruction on an ultrasonic transducer. Because of this behavior, the temperature in an ultrasonic chamber has to remain constant (about 23°C).

The connection between the mean diameter of aerosol droplets and the frequency of the ultrasonic atomizer was earlier studied by Rajan and Pandit [12]. Assuming that the characteristics of water are close to those of the used diluted precursor solution, the parameters of our experiments $\gamma = 72.9\ 10^{-3}\ Nm^{-1}$, $\rho = 1.0\ g\ cm^{-3}$, f = 800 kHz lead to a calculated value of the ultrasonically dispersed droplet diameter of D = 4.79 µm. An increase of the operating frequency decreases the aerosol droplet size. Using the parameters of previous experiments using transducers (assuming that characteristics of water are closed ones of water solution of precursors): $\gamma = 72.9 \times 10^{-3}\ Nm^{-1}$, $\rho = 1.0\ g \cdot cm^{-3}$ and f = 2.5 MHz. The calculated value of the ultrasonically dispersed droplet diameter amounts to D= 2.26 µm. The change of the aerosol droplet is a function of the operating frequency of the ultrasonic generator, shown in Figure 6.

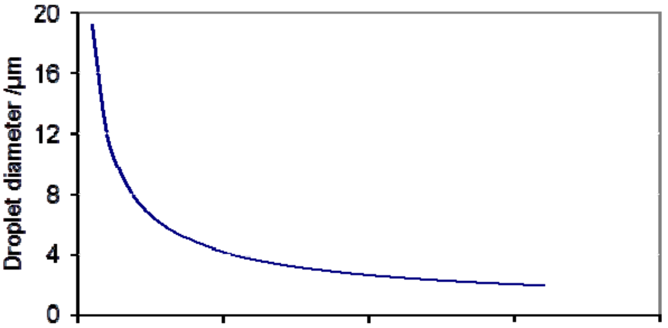

Figure 6. Dependence of aerosol droplet size of the operating frequency

Although the one-particle-per-droplet model fits in many cases, it does not explain the difference between the calculated and the measured particle sizes; thus, a different model should be examined (e.g. gas-to-particle conversion mechanism). During transport of an aerosol to a furnace, the droplets may coalescence due to Brownian motion and electrostatic attraction forming agglomerated and non-uniform particles, which is the reason for this difference in calculation.

Based on obtained values of the aerosol droplets size (in reality a size distribution spectrum) the mean powder particle size can be calculated from the following equation.

$$d_p = d \cdot \left(\frac{c_{pr} \cdot M_p}{\rho_p \cdot M_{pr}} \right)^{1/3} \qquad (2)$$

Where d_p is the powder particle diameter, ρ_p the powder density, M_p the powder molecular mass, c_{pr} the precursor concentration (solution used for spraying when forming powder particles) and M_{pr} the precursor molecular mass. This formula is based on the conventionally accepted one particle per drop mechanism. But a careful comparison of the precursor drop sizes with the product particle sizes reveals that in addition to this model spray pyrolysis may also involve a gas-to-particle conversion mechanism, which creates nanoparticles much smaller. According to the Eq. 2, using the parameters of own experiments (D: 4,79 µm, M_{Ag}: 107,87 g/mol and ρ_{Ag}: 10,50 g/cm^3) the calculated mean particle diameter of Ag develops with the precursor concentration as Figure 7 shows. The experimentally values of the Ag powders in this pre-study show a reasonable agreement with the calculated values by Eq. 2, but the presence of particles below 100 nm is evident. Differences between calculated and experimentally obtained values may be due to the approximate values used for surface tension and density of aqueous solution, micro-porosity of particles, and also due to coalescence/agglomeration of aerosol droplets at a high flow rate for the carrier gas (turbulence effects). As it can be seen, the particle size decreases with dilution of the precursor concentration in the solution as a result of the reaction in a smaller volume.

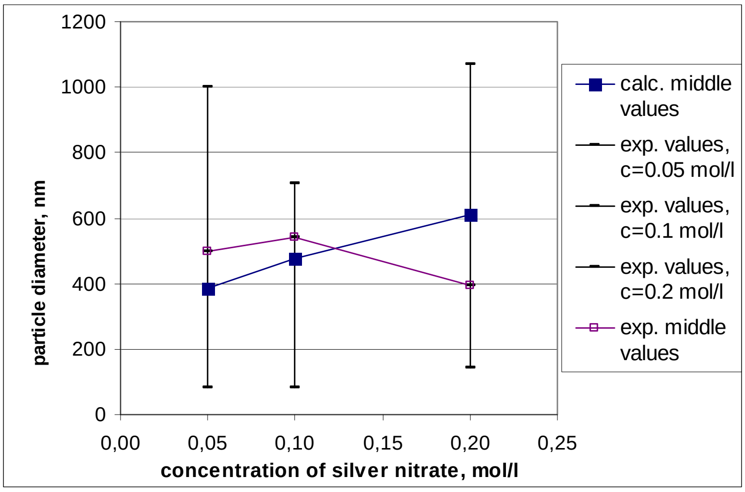

Figure 7. Calculated and experimentally obtained particle size of Ag after aerosol drying and hydrogen reduction/thermal decomposition, depending on the $AgNO_3$ -concentration in solution

After generation of drops from a precursor solution spray pyrolysis involves three major steps: 1) drop size shrinkage due to evaporation, 2) conversion of precursor into metal due to hydrogen reduction and 3) solid particle formation. The vapor diffusion proceeds much faster than the droplet shrinkage and reaches steady state before there is a significant change in droplet size: Some technical limitations of this technique persist at the actual state-of-the-art: a) porous or hollow particles, b) low production rates, c) large off-gas volumes, and d) an agglomeration of particles. Control of the reaction parameters, especially of the flow rate of a carrier gas is one way to prevent the agglomeration of particles. The most important step for study of USP synthesis for production of nanosized silver was the subsequent scaling-up to a prototype production reactor in order to improve very small production rate. Development of a scaled-up vertical reactor technology line was made with improved productivity of powder, the investigation of the chamber characteristics and the hydrodynamic system in order to optimize the injection of the carrier gas and the transport of produced aerosols, and an electrostatic collection system for nanoparticles.

Silver nanoparticles prepared in a vertical reactor were collected in an electrostatic field of new collection system developed at the IME, RWTH Aachen University (as shown at Figure 8). During the synthesis, a new system for particle collection shows an efficiency up to 42 % at U=27 kV and current intensity between 0.08 and 0.14 mA (as shown at. Figure 9.)

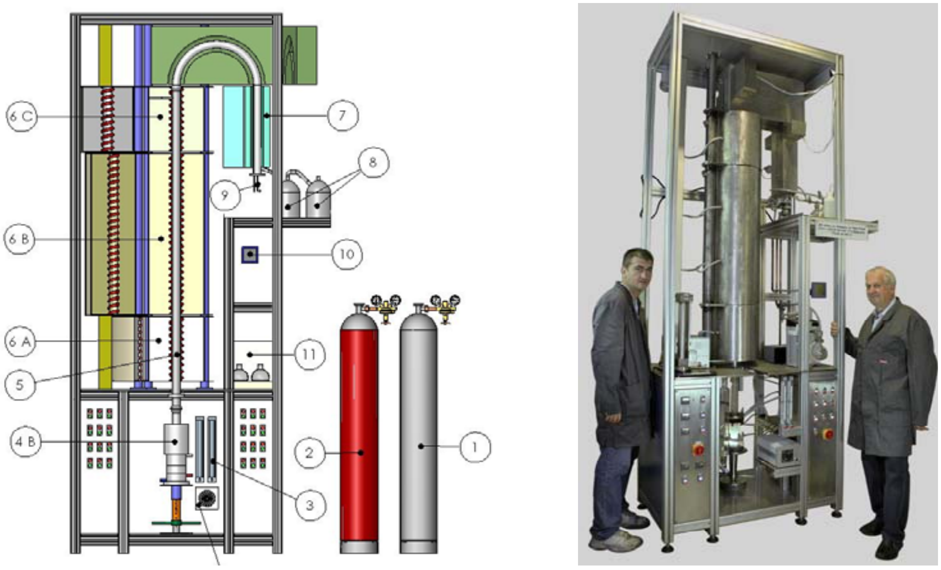

Figure 8. Experimental setup for the USP-synthesis of Ag- nanoparticles in a vertical reactor: 1. bottle with hydrogen, 2. bottle with nitrogen, 3. flow meter, 4A- electronic unit, 4B- ultrasonic generator, 5. quartz tube, 6A-furnace (an evaporation zone up to 300°C), 6B-furnace (a reaction zone up to 1100°C), 6 C- a furnace (a heating up to 500°C), 7. a system for collection of powder, 8. a bottle with water and alcohol, 9.a connection with a high voltage device, 10. a pressure indicator, 11. a vacuum pump.

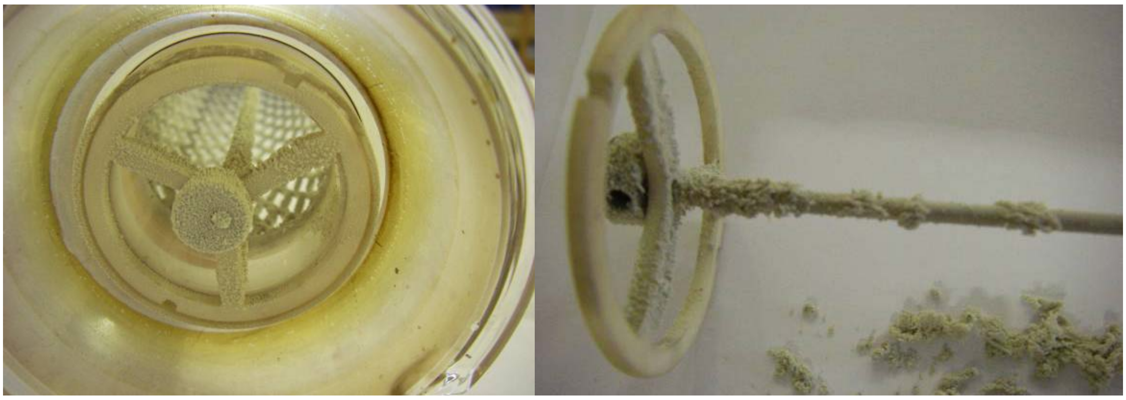

Figure 9. Prepared nanosilver in a vertical reactor shown at Figure 8: on a first electrode (left), on the second electrode (right) [13]

3. SYNTHESIS OF CORE-SHELL PARTICLES

Core-shell particles comprise a core made from one material, and a shell (or coating) made from second material. The core/shell nanoparticles are always made from an inorganic core (i.e. oxide, nitride, carbide, rarely from metal particle). The shell is made from another oxide, which is very active. By clever selection of core and shell materials properties can be combined, or the surface can be functionalized. Tetra-n-butilorthotitanat, ruthenium (III) chloride hydrate, and chloric acid were used as precursor for the synthesis RuO_2/TiO_2 nanoparticles by USP using the equipment shown schematically as shown in Figure 11. The majority of the core consists of TiO_2, while the shell is predominantely composed of RuO_2. Model of core-shell formation in a single step was proposed and shown in Figure 10.

As shown in Figure 10, the core-shell particles are present in a structure, but also the hollow and solid particles were formed. Under new conditions, all reactions were not completed, which is a reason for the formation of hollow particles. Although the solid particles appeared in structure, there is no time for the formation of ideally core- shell structure. Molar fractions of precursors, solvent type and process temperature play crucial roles in the formation of core--shell structures of RuO_2/TiO_2. The ideal core-shell structure was finally obtained in multistep pyrolysis [14], which was not achieved in previous mentioned experiments in a single step synthesis.

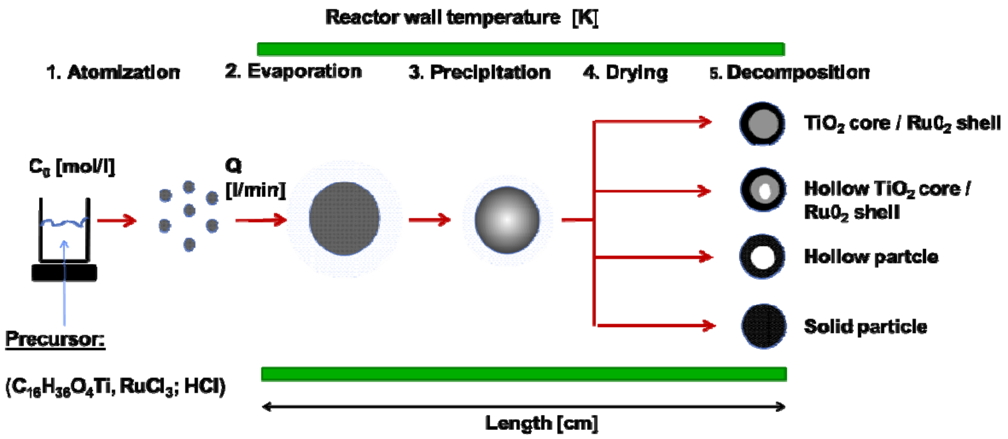

Figure 10. Formation of core-shell structure in single step [1]

The exact mechanism for formation of RuO_2/TiO_2 from aerosol droplet with core- shell structure in the single step USP- process was not yet well understood. Two hypotheses are available based on a) different solubilities of precursors and b) the melting points of the core-shell components. Concerning the first theory, the less soluble components tend to precipitate faster than those with higher solubility. In the case RuO_2/TiO_2, the solubility of tetra-n-butilorthotitanat in water is smaller than ruthenium chloride. Therefore, firstly Tetra-n-butilorthotitanat precipitates forming the core, followed by $RuCl_3$ precipitation on the top of Tetra-n-butilorthotitanat, what leads to the formation of a shell. During a decomposition step, both salts tend to form ruthenium oxide and titanium oxide. Nitrogen as carrier gas prevents oxidation of the metal in the tubular reactor. Therefore, the synthesis of spherical RuO_2-TiO_2 nanoparticles with nearly perfect core-shell structure had a special variant of ultrasonic spray pyrolysis (multistep synthesis), as shown in Figure 11. In contrast to conventional ultrasonic spray pyrolysis, a modified set-up with separated ultrasonic atomizers for each precursor and two horizontal reactors for thermal decomposition was employed. According to the process chart in Figure 11, titania nanoparticles are formed in the first pyrolysis zone from an aerosol containing tetra-n-butylorthotitanate.

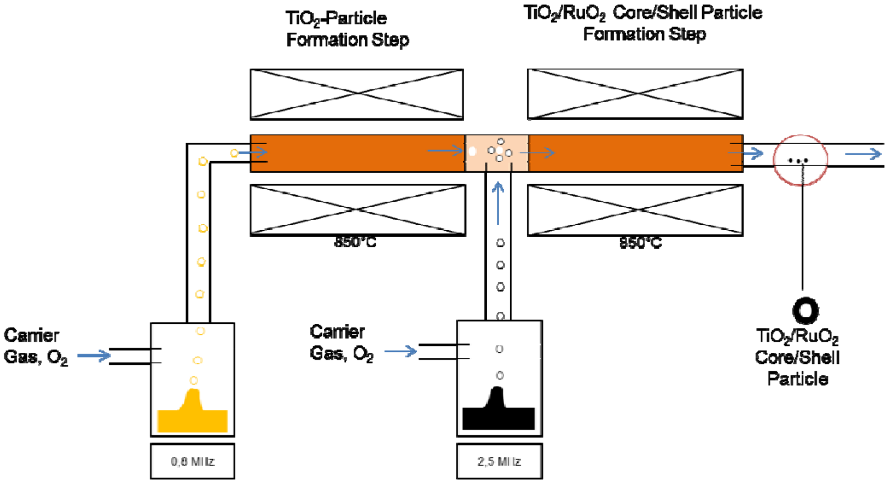

Figure 11. Multistep synthesis of core-shell structure [14]

The aerosol was generated with an ultrasonic frequency of 0.8 MHz. Pure oxygen was used as carrier gas at a flow rate of 1 l/min under atmospheric pressure. The second aerosol stream, generated at f=2.5 MHz using a ruthenium (III) chloride hydrate precursor, was then admixed to the stream of solidified titania particles emerging from the first decomposition zone. This mixture was then piped through the second pyrolysis zone, where the desired core-shell particles were formed. In the last step the nanoparticles are separated from the carrier gas by passing the gas stream through a washing flask filled with water. The experiments were performed at decomposition temperature of 850°C. Initial characterization of the obtained nanoparticles was performed by powder X-ray diffraction (Philips PW1820) with Cu Kα radiation and scanning electron microscopy (LEO1450VP) operated at 20 kV. For further characterization of the samples, we employed high-angle annular dark field (HAADF) scanning transmission electron microscopy (STEM) and energy dispersive spectroscopy (EDS) using a FEI Tecnai F20 operated at 200 kV [14]. In addition to X-ray diffraction, selected area electron diffraction was used for phase identification of small volumes. Diffractograms obtained from the RuO_2/TiO_2 powders showed the presence of RuO_2 and TiO_2 in two different modifications: anatase and rutile. Analysis of the nanoparticles by SEM showed in Figure 12**,** that nearly ideal spheres with mean particle diameters between 200 and 400 nm were formed during the multistep USP process.

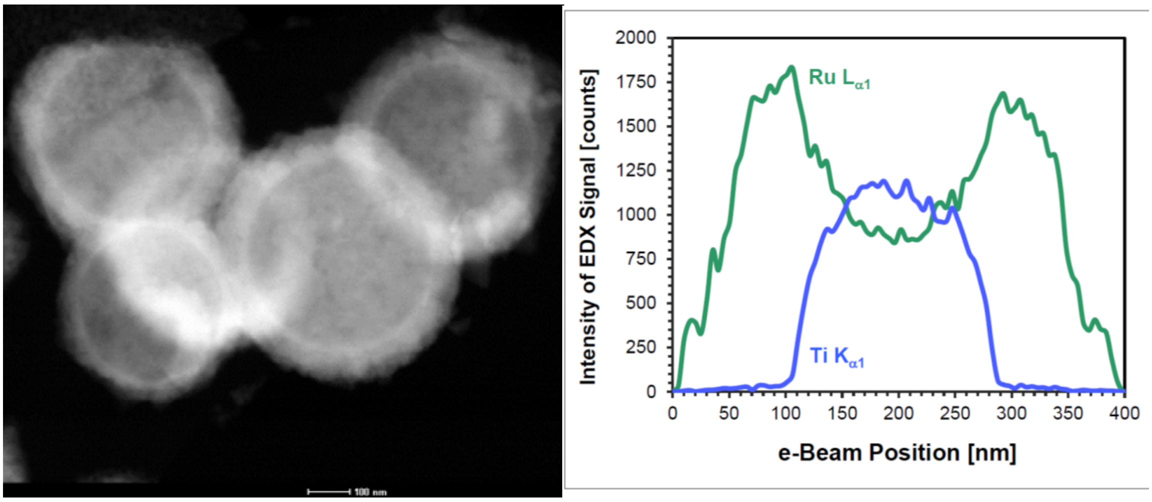

*Figure 12***.** *SEM analysis (left) and EDX line scan across RuO_2/TiO_2 particle (right) [14]*

Analytical results such as EDX line profiles are complex due to the special geometry of spherical nanoparticles. Thus the elemental profiles obtained from EDX (as shown in Figure 12) were compared using a simple core-shell particle model, which is described in detail in [14]. Comparison of these results has confirmed a perfect core-shell structure of the particles of RuO_2/TiO_2. A future development step should be especially focused on the optimization of the mixing device of the solid particle stream with the aerosol, and collection of particles in an electrostatic field.

4. COATING OF ACTIVATED TITANIUM ANODE WITH PARTICLES PRODUCED BY USP-METHOD

Synthesis and coating of sub-micron spherical RuO_2/TiO_2 particles were performed in a new developed continuous process in two connected reactors. Synthesis of particles from organic precursor was achieved by ultrasonic spray pyrolysis method in first reactor. The subsequent coating of previously produced RuO_2/TiO_2 was performed on a titanium anode in a second reactor in a high-voltage electrostatic field at 500 °C.

The most important parts of the equipment for synthesis are the ultrasonic atomizer and the reactor with three separated heating zones. The temperature and pressure control was adjusted using a thermostat and a vacuum pump. Fountainization of the obtained solution after dissolution of precursors took place at room temperature in an ultrasonic atomizer with one transducer to create the aerosol from a mixed solution based on tetra-*n*-butyl orthotitanate, ruthenium (III) chloride hydrate, and hydrochloric acid. With regards to our previous results, the resonant frequency was selected to be 2.5 MHz. Under spray pyrolysis conditions, oxygen overpassed continuously through the quartz tube (at a flow rate of the 3 l/min) in order to oxidize precursors at 800 °C. Then, atomized and pyrolysis droplets containing ruthenium oxide and titanium oxide in an ultrasonic generator were further transported by carrier gas to the horizontal furnace, (Thermostar, Aachen). After formation of RuO_2/TiO_2, the produced particles were used to coat an expanded titanium anode in an electrostatic field at 500 °C with high voltage of 27 kV. RuO_2/TiO_2 particles, which are not deposited on a titanium anode, and were collected in a bottle filled by water.

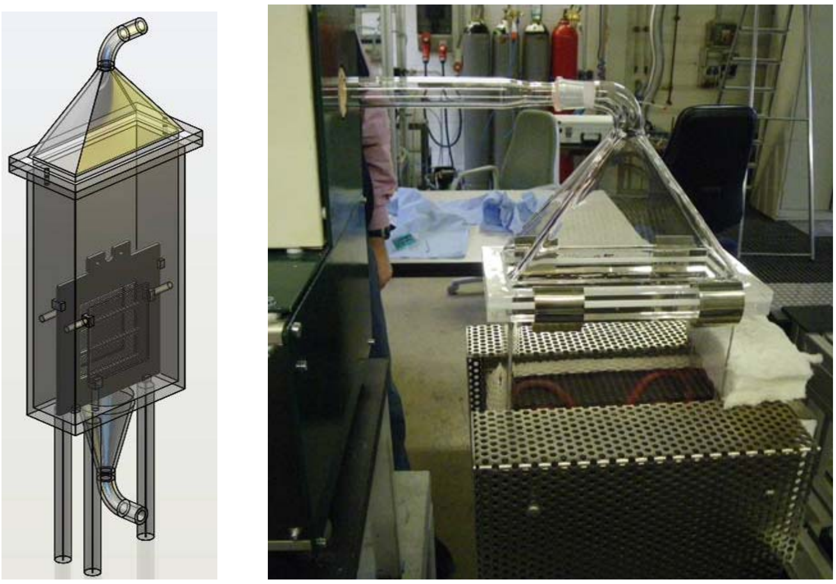

Figure 13. The coating process in a specially constructed quartz equipment in one furnace [15]

As shown Figure 13, a titanium anode was inserted in a specially constructed furnace made of quartz, which contained two electrodes for electric field generation at maximal achievable temperature of 600 °C. A scanning electron microscope (MIRA VP) from Large Chamber Scanning Electron Microscopy, Central Facility for Electron Microscopy GFE, Aachen, Germany, was used for the characterization of the obtained powders at a titanium anode. SEM-images were used to examine the surface morphology of the particles formed at different parameter sets. The qualitative characterization of the impurity level was performed by the energy disperse spectroscopy (EDS) analysis with a Si(Bi) X-ray detector connected to the SEM and a multi-channel analyzer. The electrostatic field was generated by a high voltage device (27 kV, 0.08 mA) from Eltex, Elektrostatik-GmbH, Weil am Rhein, Germany, to enable the coating of the produced submicron particles. A sand-blasted titanium anode (mechanically cleaned) was previously treated with oxalic acid in order to remove passive film and to degrease the surface, which enable a better adhesion of formed particles onto the anode surface [15].

The RuO_2/TiO_2 material electrostatically deposited onto a titanium anode was analyzed by SEM/EDS. The important aim was to check the morphology of obtained RuO_2/TiO_2 coating and its distribution at titanium anode. Figure 13 shows the image of an anode during the electrostatic coating deposition in a quartz furnace, and the surface appearance of the activated anode.

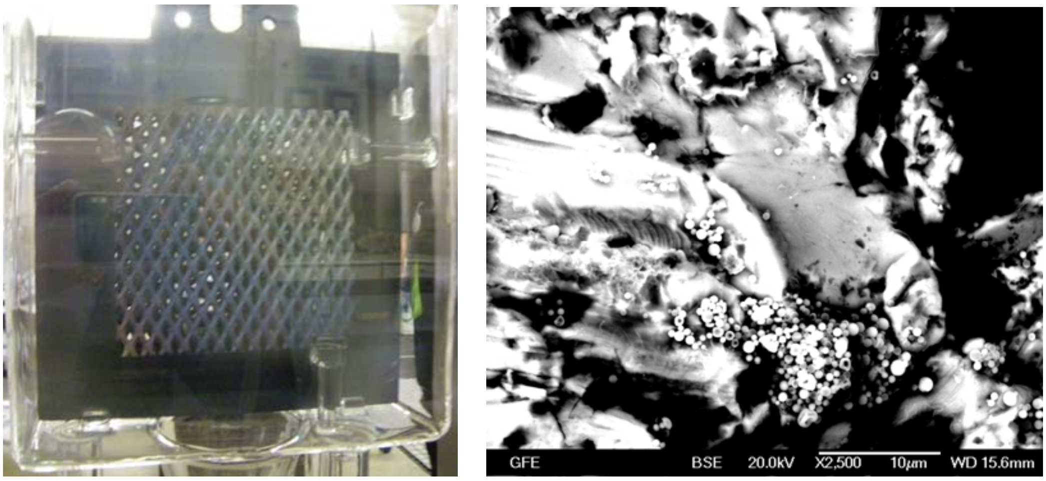

Figure 13. a) Activated titanium anode just after electrostatic deposition of the coating,
b) SEM surface appearance of the coated anode [15]

The sub-µm-sized spherical particles of RuO_2-TiO_2 obtained by a single ultrasonic spray pyrolysis method were confirmed at anode surface after deposition. The particles appear adherent to the surface in clusters without changes in the particle texture. It is indicated that the TiO_2 core of the particles of enables good adhesion of formed mixed TiO_2/RuO_2 particles on a titanium anode surface. The obtained coated anode was investigated in the oxidation process of hydrochloric acid in order to produce gaseous chlorine in the industrial conditions.

5. CONCLUSION

The nanosized particles of silver were prepared in a single step ultrasonic spray pyrolysis. RuO_2/TiO_2 particles with the core and shell structure were successfully prepared using the ultrasonic spray pyrolysis method in multistep ultrasonic spray pyrolysis. Different precursors of metallic and organic salts such as silver nitrates, tetra-n-butilorthotitanat, and ruthenium (III) chloride were successfully used for the synthesis of metallic and core-shell particles. Tetra-n-butilorthotitanat as a precursor was used for the formation of titanium oxide. Spherical RuO_2/TiO_2 particles with mixed core/shell structure have been synthesized by single-step ultrasonic spray pyrolysis and continuously applied as a coating onto expanded titanium substrate in order to prepare an industrial type of activated titanium anode. SEM analysis showed that the coating appears adherent to the surface, arranged in clusters without changes in the initial particle texture.

6. ACKNOWLEDGMENT

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СИНТЕЗА НАНОЧЕСТИЦА МЕТАЛА И ЧЕСТИЦА ОД ЈЕЗГРА СА ПРЕВЛАКОМ КОРИШЋЕЊЕМ УЛТРАЗВУЧНЕ ПИРОЛИЗЕ

Сажетак: Распршивање ултразвучном пиролизом је разноврсна метода за припрему прахова метала, оксида и композита. Наночестице сребра су синтетизоване ултразвучном пиролизом у хоризонталном и вертикалном реактору. Испитивана је директна синтеза честица на бази коре од RuO_2 и језгра од TiO_2 у вертикалном реактору. Утицај реакционих параметара (температуре, време задржавања честица, концентрација раствора и ултразвучне фреквенце) на морфологију припремљених честица је испитиван. Коришћењем распршивања ултразвучном пиролизом, идеално сферне честице су добијене на температурама испод температуре топљења метала. Увећана производња распршивањем ултразвучном пиролизом изведена је за синтезу сребра. Превлачење аноде од титана са честицама RuO_2, добијених ултразвучном пиролизом је изведено у електростатичком пољу.

Кључне ријечи: распршивање ултразвучном пиролизом, синтеза, метали, језгро-кора.

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