Synthesis of spherical nanosized silver powder by ultrasonic spray pyrolysis

Stopic, S. (1); Dvorak, P. (2); Friedrich, B. (1)

Spherical, non-agglomerated nanosized particles of silver were prepared by the ultrasonic dispersion of solutions from silver nitrate in a hydrogen and nitrogen atmosphere. A controlled particle size was realized through the choice of the solution concentration as well as by changing the aerosol decomposition parameters. The experimental investigations were performed by an ultrasonic source of 800 kHz, acting on the water solution of the silver nitrate-forming aerosols with constant droplet sizes. This size depends on the characteristics of the solution and the frequency of the ultrasound. The subsequent thermal decomposition of the aerosol droplets was performed in a hydrogen atmosphere between 150 °C-1000 °C, and in a nitrogen atmosphere between 600 °C and 800 °C. The paper presents the ways to control this synthesis over the choice of the reaction parameters and compares the experimental results with a calculation of the average diameter of particles of Ag-powder.

Important applications for silver particles can be found in the catalyst and electronic industry [1-4]. For example, the production of formaldexyde and ethylene oxide can benefit from the use of silver comprising nanoscale catalysts. Silver dissociates molecular oxygen from the air and weakly holds the separated oxygen atoms until an alkene, such as ethylene, reacts with them to form respective alkene oxide. Silver comprising nanoparticles prepared by the ultrasonic spray pyrolysis method offer the potential to reach a number of surprising and unique advantages. Especially, the unique interaction between silver in nanoparticle form and oxygen is high interest for the catalytic industry.

Chemical bonds between the Ag-nanoparticles and the organic shell function as a passivation layer that prevents the self-cohesion of the nanoparticles. Fine Ag-particles (average particle size of 100 nm) were used by Ide et al. [2] as a reference material to consider the effect of particle size on bondability. By reducing the metal particle size, the surface energy and the vapour pressure increase proportionately with the inverse of the particle radius, this strongly influence the sintering of particles and the bondabilities to copper.

Solid, spherical, micron-sized silver metal particles were produced from a silver nitrate solution. Plum at al. [1] show effects of reaction temperature, carrier gas type, solution concentration, and aerosol droplet size on the characteristics of the resultant silver particles. Pure, dense unagglomerated particles obtained using an ultrasonic generator at and above 600 °C under N_2-carrier gas, and above 900 °C using air as the carrier gas. Solid particle formation at temperatures below the melting point of silver (962 °C) was attributed to sufficiently long residence times up to 4 s, which allowed the aerosol-phase densification of the porous silver particles resulting from the reaction of the precursor. As the precursor solution concentration was increased from 0.5 to 4.0 M, the particle size increased from 1.03 to 1.68 µm. But that when particles are reduced in size to less than 100 nm, their characteristics are different from those of the bulk state [3]. For example, the melting point and the sintering temperature are detectably lower.

The ultrasonic spray pyrolysis (USP) is an innovative and powerful tool for the synthesis of nanoparticles with controlled and uniform particle size [5-8]. In the USP-process, a metal-containing solution is cold-atomized and form an aerosol (Fig.1) and enables an easy control of the powder morphology and the excellent availability of cheap precursors at acceptable costs. This technology has a great potential to be the future solution for the synthesis of silver nanopowder.

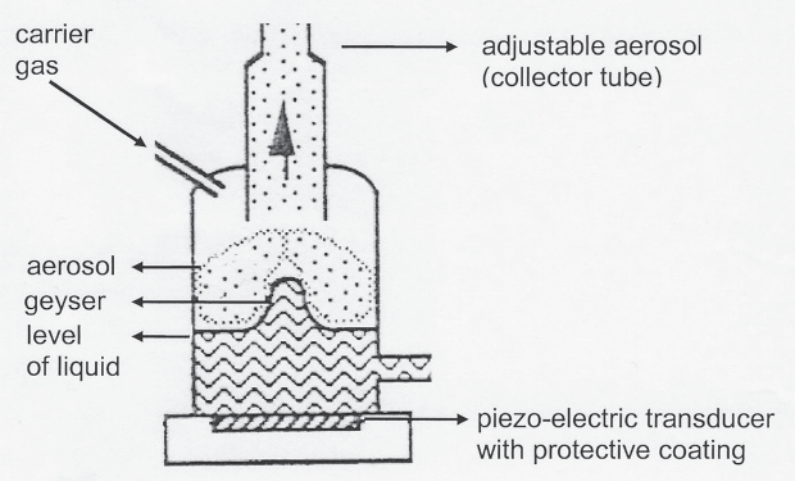


Fig. 1: The principle of the aerosol production

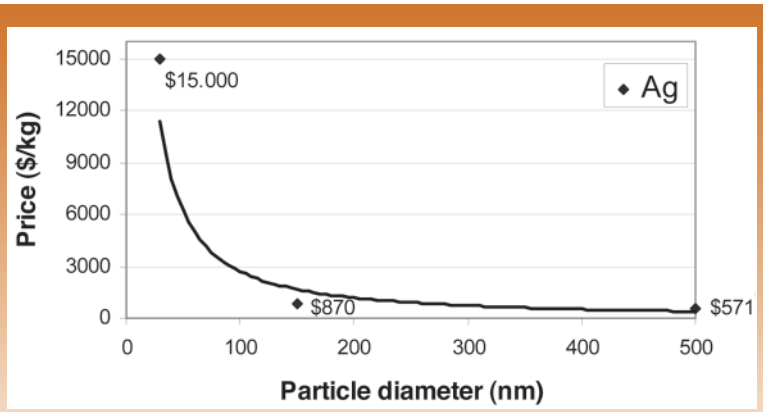


Fig. 2: Price of nanopowder of silver depending on the particle size

The piezo-electric ceramic $Pb(Zr,Ti)O_3$ transforms the alternating tension of an ultrasonic source into mechanical vibrations, which influence the formation of the geyser and aerosol. The transducer type influence the gas-liquid interface forming an aerosol of constant droplet sizes of D= 2.3 - 4.9 µm at ultrasonic frequencies of 0.8 - 2.5 MHz. This aerosol is transported by a carrier, mostly a reduction gas, into a hot reactor, where the aerosol droplets undergo drying, droplet shrinkage, solute precipitation, thermolysis and sintering to form spherical particles. Very short residence times of several seconds are mostly sufficient to ensure the formation of the desired spherical nanoproduct.

Using the prices of Ag-nanopowder from the USA, the benefit of this research and the potential economic impact on nanocatalyst industry of this research are shown in Fig. 2. The decrease of the particle size of silver nanopowder from 500 nm to 30 nm leads to a price increase from 571 $ per kg to 15.000 $ per kg. The shown values were obtained by INFRAMAT, Advanced Materials, USA, and NANOTECNOLOGIES Inc., USA [9].

The aim of this paper is to present the investigations concerning the synthesis of spherical nanoparticles of silver by the ultrasonic spray pyrolysis method. The study explains the influence of the different parameters of the synthesis (different concentration of the initial solution, reaction temperature, atmosphere) on the morphological characteristics of the powders and is based on both thermochemical and experimental studies.

Thermochemical analysis of the decomposition of silver nitrate

In order to model the reaction system the following decomposition chemical reactions are considered:

$$AgNO_3 \rightarrow Ag + NO_2 + 1/2\ O_2 \quad (1)$$
$$AgNO_3 + H_2 \rightarrow Ag + NO_2 + H_2O \quad (2)$$

A FactSage®- thermochemical analysis of the hydrogen reaction with silver nitrate (Eq. 2) and the decomposition of silver nitrate Eq. (1) showed in the temperature range between 0 and 1000 °C that the thermodynamic equilibrium is present at 400°C for the decomposition. In the presence of hydrogen, the thermodynamic equilibrium is already present at room temperature.

The decomposition behaviour of silver nitrate was investigated using thermogravimetric (TGA) and differential thermal analysis (DTA). This study was conducted under an argon atmosphere in a temperature range between 25 °C and 1000 °C using Derivatograph NETZSCH STA 409 with α-Al_2O_3. The heating rate amounts to 10 °C/min. The DTA and TGA analyses of the decomposition of silver nitrate in argon have confirmed the mechanism expressed in Eq. (1). The decomposition temperature of silver nitrate amounts to 485°C at the heating rate of 10 °C/min. Weiping and Lide [3] concluded that the decomposition of silver nitrate in argon starts at temperatures above 300°C, according to Eq. (1).

Experimental

Material and procedure

Silver nitrate (Merck, Darmstadt, Germany) was used as the precursor

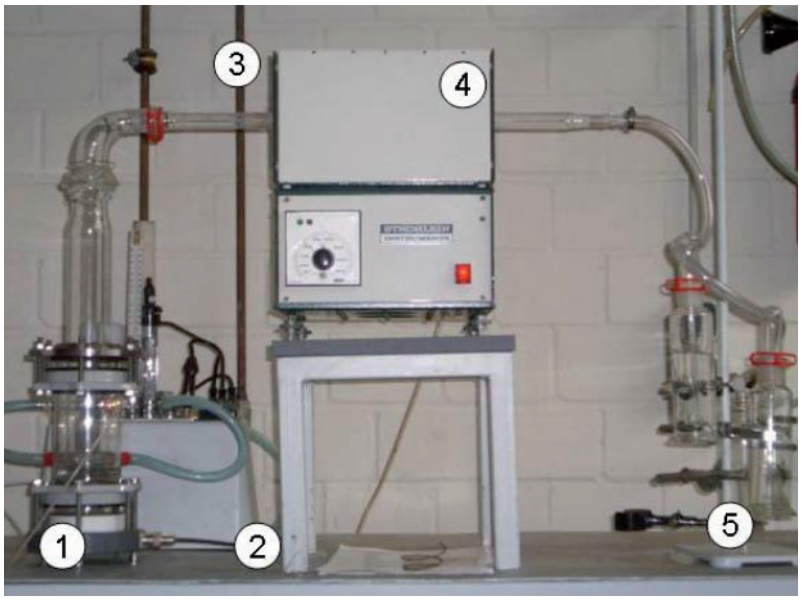


Fig. 3: Experimental apparatus for the USP-synthesis of silver particles (1. ultrasonic generator, 2. thermostat, 3. quartz glass tube, 4. furnace, 5. collection of powder)

Exp. No.	$T_{furnace}$ (°C)	c $AgNO_3$ (mol/l)	dV/dt H_2 (l/min)	dV/dt N_2 (l/min)	$T_{precursor}$ (°C)
1	1000	0.1	1	-	25
2	800	0.1	1	-	25
3	600	0.1	1	-	25
4	600	0.2	1	-	25
5	600	0.05	1	-	25
6	600	0.1	-	1	25
7	600	0.1	-	1	45
8	600	0.1	1	-	45
9	300	0.1	1	-	25
10	150	0.1	1	-	25

Table 1: Experimental plan for the preparation of nanosized Ag-powder

material for the preparation of silver powders by ultrasonic spray pyrolysis, using the equipment shown in Fig. 3. The apparatus consists of an aerosol generator, an electrically heated reac-tion furnace carrying a quartz tube (670 mm in length and 20 mm inner diameter), and a powder collection chamber. The experiments were carried out in the temperature range of 150 °C and 1000 °C in a H_2-atmosphere, and of 600 °C and 800 °C in a nitrogen atmosphere. Ten experiments were performed (Table 1). The first six experiments were connected with the reduction of silver nitrate by hydrogen. The experiments 6 and 7 were associated with the decomposition of silver nitrate in a nitrogen atmosphere. In order to investigate the influence of a reduced temperature on the morphological characteristics of particles, the experiments 8 - 10 were additionally performed in a hydrogen atmosphere.

The atomization of the silver nitrate solutions took place in an ultrasonic atomizer (Pyrosol 7901, RBI, France). Only one transducer was implemented to create the aerosol. For this ultrasonic atomizing system, the resonant frequency was selected to 0.8 MHz. Nitrogen with a flow rate of 1 l/min was used for oxygen removal. Under spray pyrolysis conditions, a hydrogen atmosphere at a flow rate of 1 l/min continuously passed the quartz tube. The calculated retention time of droplets in the reaction zone was calculated to be about 1 s. An X-ray diffractometer (Siemens D 5000) and a scanning electron micro-scope (ZEISS DSM 982 Gemini) were used for the characterization of the obtained silver powders. SEM-images were used to observe 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.

Results and discussion

Hydrogen reduction of silver nitrate

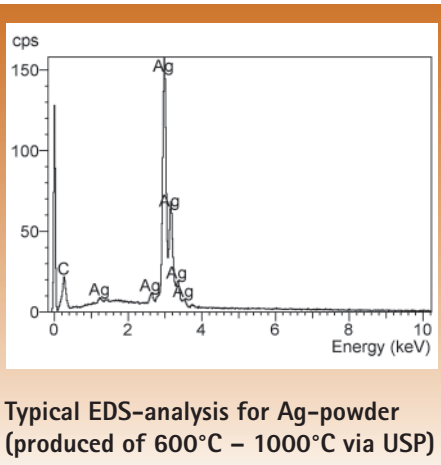
Effect of temperature

The influence of temperature was investigated in a range of 150 °C and 1000 °C. EDS-analysis of silver powder prepared at 600 °C and 1000 °C proved the full transformation to elementary Ag (Fig. 4), and did not reveal any differences in chemical composition with temperature. In contrast to the EDS-analysis, the SEM-analysis (Fig. 5a - 5d) of the obtained powder shows significant variations.

Fig. 5.d reveals that fully-reacted, ideally spherical, completely dense silver particles can be produced at temperatures close to the melting point of silver. Spherical, but not completely dense are obtained at 150°C by hydrogen reduction (Fig. 5a). This is probably due to the short residence time in this experiment. A sufficient time for the aerosol phase densification resulted even at lower temperatures to a complete reaction [1]. The experiments at 300 °C and 600 °C produce the agglomerated and irregularly shaped Ag-particles (Figs. 5b and 5c)

Effect of silver nitrate concentration

Three different concentration levels of silver nitrate (0.05, 0.1 and 0.2 mol/l) were used for the synthesis (experiments 3, 4 and 5) at 600 °C. Fig. 6a, 6b and 6c show the resulting morphologies of the obtained silver powder. At a 0,05 mol/l $AgNO_3$-concentration, the powder is composed of non-agglomerated and rarely spherical nanoparticles of sizes between 144.5 nm and 1000 nm. At a 0.1 mol/l $AgNO_3$-concentration, the powder is composed of non-agglomerated, spherical nanoparticles of sizes between between 83.6 nm and 190.2 nm. Cylindrical and prismatic shapes are also present. 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. Nevertheless, big particles and satellites are always present. It is most likely that a coalescence of droplets occurs during the spray, the drying and/or the pyrolysis



Typical EDS-analysis for Ag-powder (produced of 600°C – 1000°C via USP)

Fig. 4 coatin on re % Si using (440

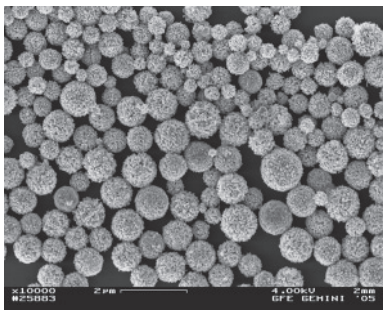


Fig. 5a: Experiment at 150 °C (Exp. 10)

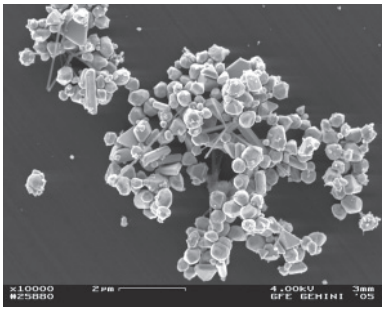


Fig. 5b. Experiment at 300 °C (Exp. 9)

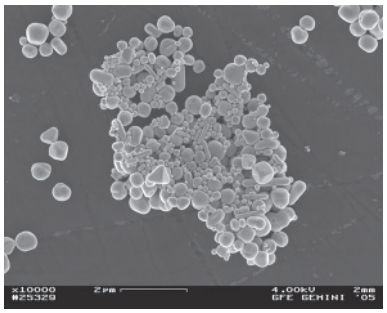


Fig. 5c. Experiment at 600 °C (Exp. 3)

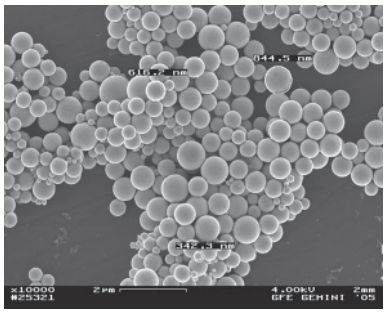


Fig. 5d. Experiment at 1000 °C (Exp. 1)

Fig. 5. Morphologies of the obtained Ag-nanopowder

steps. The agglomeration of aerosol droplets is especially enhanced at elevated flow rates of the carrier gas due to turbulence effects leading to larger particles.

Thermal decomposition of silver nitrate in nitrogen atmosphere

Pluym et al. [1] have reported that silver powder particles made via the spray pyrolysis of $AgNO_3$-solutions at and above 600 °C in N_2 were pure, dense, unagglomerated, spherical, micron-sized or smaller in diameter. The melting of silver was not required for aerosol-phase densification of the particles when nitrogen was used as a carrier gas. This is based on the fact that the residence times were sufficient for densification in the aerosol phase. According to these results, the decomposition of silver nitrate was performed at 600 °C using gaseous nitrogen atmosphere (Fig. 7a), and additionally by the preheating of solution (Fig. 7b).

Spherical particles of sizes between 102.7 nm and 650.5 nm with a small amount of satellites were obtained. Unlike the results reported in [1], the particle sizes were in the nano- and submicron-range. The preheating of the solution of silver nitrate in Exp.7 had no influence on the morphological characteristics of particle.

The particle size of the obtained powder

The connection between the mean diameter of aerosol droplets and the frequency of the ultrasonic atomizer were studied by Peskin and Raco and used by many authors [10-12]. They identified the following relationship:

$$D = 0.34 \cdot (8 \cdot \pi \cdot \gamma / \rho \cdot f^2)^{1/3} \qquad (3)$$

Where D is the mean droplet diameter, γ is the surface tension, ρ the density of the atomized solution and f the frequency of the ultrasound. Assuming that the characteristics of water are close to those of the used diluted precursor solution, the parameters of our experiments ($g = 72.9 \cdot 10^{-3}$ 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 could decrease the aerosol droplet size further.

The expected mean particle diameter of the Ag-powder finally obtained after the hydrogen reduction and the thermal decomposition in nitrogen can be calculated from the value of the aerosol droplet size. Depending on the initial concentration of the solution and assuming that each droplet is transformed into one particle and that during atomization no

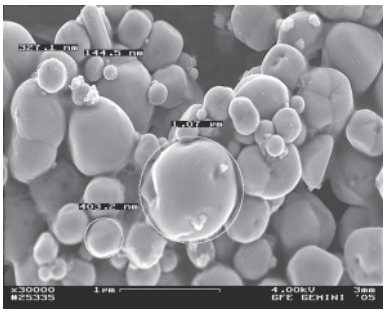


Fig. 6a: SEM-micrograph of Ag-powder using an $AgNO_3$-concentration of 0.05 mol/l (Exp. 5, 600 °C)

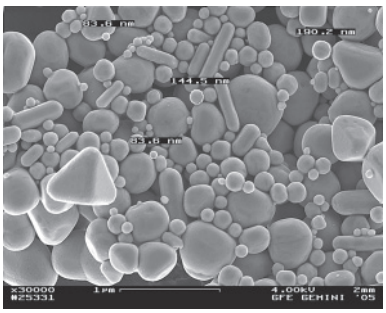


Fig. 6b: SEM-micrograph of Ag-powder using an $AgNO_3$ concentration of 0.1 mol/l (Exp. 3, 600 °C)

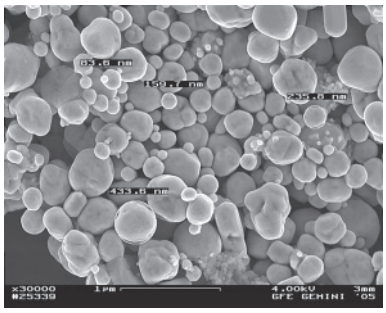


Fig. 6c: SEM-micrograph of Ag-powder using the $AgNO_3$-concentration of 0.2 mol/l (Exp. 4, 600 °C)

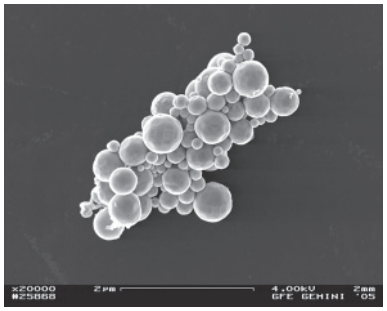


Fig. 7a: SEM-micrograph of silver powder obtained at 600 °C from 0.1 mol/l $AgNO_3$ (Exp. 6, precursor temperature: 25°C)

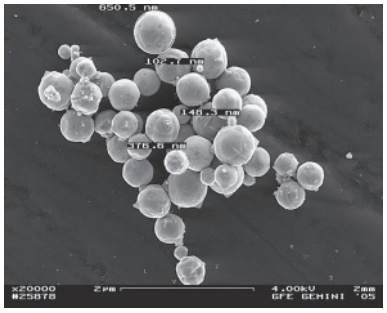


Fig. 7b: SEM-micrograph of silver powder obtained at 600 °C from 0.1 mol/l $AgNO_3$ (Exp. 7, precursor temperature: 45°C)

coalescence occurs, the final particle diameter can be calculated by using the formula (4) that have previously been presented by Messing [12]:

$$D_p = D \cdot (C_p \cdot M_{Ag}/\rho_{Ag}\, M_P)^{1/3} \quad (4)$$

Where D_p is the mean particle diameter, D is the mean droplet diameter, M_P and C_p are the molar mass and the concentration of the precursor (here: $AgNO_3$), and ρ_{Ag} represents the density of silver. Using the parameters of our 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 silver develops with the precursor concentration, as shown in Fig. 8.

Fig. 8 reveals that the increase of the concentration of silver nitrate did not increase the particle size significantly as the calculation request. The calculated values of the particle diameters of Ag range between 384 and 609 nm for the used solution of silver nitrate of 0.05 and 0.2 mol/l. The experimentally obtained values are in range of 84 and 1070 nm. The experimental values of the Ag-powders show very little correlation to the calculated values. In contrast to the calculated values, the presence of particles below 100 nm (satellite nanoparticles) is evident. The differences between the calculated and the ex-perimentally obtained values may be a consequence of the approximate values used for the surface tension and the density of aqueous solutions, the microporosity of particles, and the coalescence/agglomeration of the aerosol droplets at a high flow rate for the carrier gas (turbulence effects). As can be seen, the particle size decreases with the dilution of the precursor concentration in the solution as the result of the reaction in a smaller volume. After the generation of drops from a precursor, the solution spray pyrolysis involves three major steps: 1) the drop size shrinkage due to evaporation, 2) the conversion of the precursor into metal due to hydrogen reduction and 3) the solid particle formation. The vapor diffusion proceeds much faster than the droplet shrinkage and reaches a steady state before the droplet size changes significantly [12].

In the equation (4), too, which is based on the assumption of one particle per one droplet, the influence of temperature on the process mechanism and the mean particle size was not taken into account. For seriously considering this relationship, the aerosol droplet size and the particle size should be precisely measured and matched, and the model has to be modified accordingly.

Conclusion and scale up steps

The ultrasonic spray pyrolysis (USP) was successfully used for the preparation of nanosized silver particles. The results of the thermodynamic analysis of the decomposition of silver nitrate revealed that the equilibrium in presence of hydrogen is already present at room temperature, in difference to 400 °C in the absence of hydrogen.

The investigation regarding the influence of the reaction parameters on the decomposition of the initial solution of silver nitrate showed the following results:

- The ultrasonic spray pyrolysis of $AgNO_3$-solutions in pure nitrogen atmos-phere at 600°C (Fig. 7a and 7b) is suitable for the synthesis of spherical, non-agglomerated nanopowders of silver.
- The increase of the hydrogen reduction temperature from 150 °C to 1000 °C increases the amount of spherical, dense particles in the Ag-powder structure, but there is no influence on the purity of the obtained powder of silver.

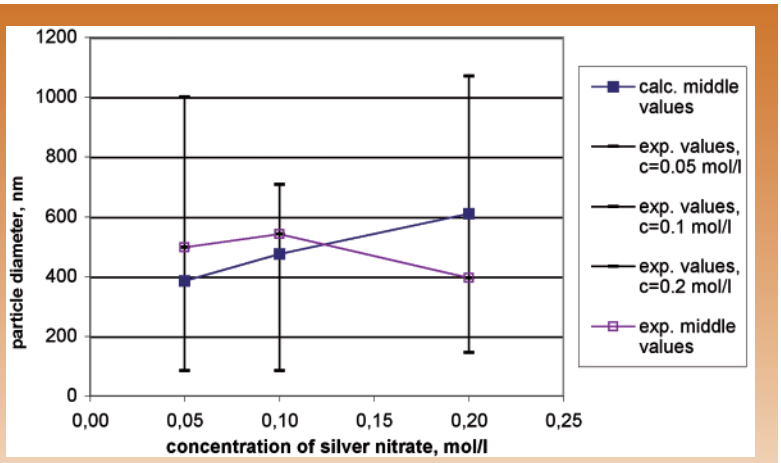


Fig. 8: Calculated and experimental particle size of Ag after aerosol drying and hydrogen reduction/thermal decomposition, depending on the $AgNO_3$ -concentration in the solution

- The ultrasonic spray pyrolysis of $AgNO_3$-solutions followed by a hydrogen reduction lead to fully dense, perfect spherical and non-agglomerated nano-powders of silver at 1000 °C furnace temperature.
- The preheating of the $AgNO_3$-solution to 45 °C has no influence on the particle morphology.
- 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 must be examined (e.g. gas-to-particle conversion mechanism). The most important step to commercialize this process is the scale-up, which will be done to a prototype production reactor at IME in Aachen in 2006.

The most important aims are:

- The development of a scaled-up vertical reactor technology line up to improved productivity of powder, based on project results (chamber with 20 transducers), serving a minimum output of 100 g/h instead of the published data of few grams/hour.
- The investigation of the chamber characteristics and the hydrodynamic system in order to optimize the injection of the carrier gas and the transport of aerosols
- The development of an electrostatic collection system for nanoparticles

The new equipment is shown in Fig. 9.

Acknowledgments

We would like to thank the DAAD for its 2005 research fellowships for Dipl.-Ing. Petr Dvorak during 10 month at IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany. We would also like to thank Mr. Dieter Leimbach for his highly motivated assistance in our experimental part.

Fig. 9a: Furnace with three different heating zones

Fig. 9b: Electrostatic collection powder

Fig. 9: Scale-up of the USP system for the synthesis of nanopowder at IME, Aachen

References

[1] Pluym, T.C., Powell, Q.H., Gurav, A.S., Ward, T.L., Kodas, T.T., Wang, L.M., Glicks-man, H.D. (1993): Solid silver particle production by spray pyrolysis, Journal Aero-sol Science 24, 3, pp. 383-392.
[2] Ide, E, Angata, S, Hirose, A, Kobayashi, K (2005): Metal-metal bonding process using Ag metallo-organic nanoparticles, Acta Materialia 53, pp.2385-2393.
[3] Majumdar, D, Glicksmann, H, Kodas, T (2000): Generation and sintering char-terisics of silver-copper (II) oxide composite powders by spray pyrolysis, Powder Technology 110, pp. 76-81.
[4] Weiping, C and Lide, Z (1997): Synthesis and structural and optical properties of mesoporous silica containing silver nanoparticles, J. Phus.:Condens. Matter. 9, pp. 7257-7267.
[5] Jokanovic, V. (2006): Structures and substructures in spray pyrolyis process: Nan-odesigning, Surfactant science Series 130, ed. Spasic, A.M and Hsu, J.P, pp. 513-533.
[6] Stopic, S., Dvorak, P., Friedrich, B. (2005):Synthesis of nanopowder of copper by ultrasonic spray pyrolysis method, World of Metallurgy Erzmetall 58, 4, pp. 191-197.
[7] Stopic, S., Gürmen, S., Friedrich, B. (2005): Mechanism of synthesis of nano-sized spherical cobalt powder by ultrasonic spray pyrolysis, Journal of metallurgy 11, pp. 65-73.
[8] Marinkovic, Z., Mancic, L., Maric, R, Milosevic, O, (2001): Preparation of nanostructured Zn-Cr-O spinel powder by ultrasonic spray pyrolysis, J.Europ. Ceramic Soc., 21 pp. 2051-2055.
[9] http://environmentalchemistry.com/yogi/periodic/Ag.html
[10] Xia, B., Lengorro, W. & Okyama, K. (2001): Preparation of nickel powders by of nickel formate, J.Am.Ceram.Soc. 84, pp. 1425-1432
[11] Peskin, R & Raco, R (1963) Ultrasonic atomization of Liquids, Journal of the acous-tical society of America 35, pp. 1378-1381.
[12] Messing, G, Zhang, S, & Jayanthi, G (1993), Ceramic powder synthesis by spray pyrolysis, Journal American Ceramic Society 76, pp. 2707-2726.

(1) Dr.-Ing. Srecko Stopic, Prof. Dr.-Ing. Bernd Friedrich, IME Process Metallurgy and Metal Recycling, RWTH University Aachen, Germany
(2) Ing. Petr Dvorak, Department of Metals and Corrosion Engineering, Institute of Chemical Technology, Prague, Czech Republic