

# Mechanism and kinetics of nanosilver formation by ultrasonic spray pyrolysis - progress report after successful up-scaling (Part 2)

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In 2006 the authors presented in Metall [Vol. 60, No. 6, pp. 377-382] first results on this promising new technology for nano-powder synthesis. Since then a significant improvement and up-scaling took place at IME Aachen and this article present the first results in the unique vertical tube reactor. Spherical, non-agglomerated nanosized particles of silver were prepared by ultrasonic dispersion of solutions from silver nitrate in 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 2.5 MHz, acting on the water solution of the silver nitrate forming aerosols with constant droplet sizes. The droplet size depends on the characteristics of the solution and the frequency of the ultrasound. Subsequent thermal decomposition of the aerosol droplets was performed in nitrogen atmosphere between 300 °C and 600 °C. During synthesis the particle sizes of nanosized silver are measured using SMPS. The residence time and time for nanoparticle formation was calculated using a new mathematical model proposed in this work. Silver nanoparticles were collected in an electrostatic field. The paper presents also ways to control synthesis over the choice of the reaction parameters and compares the experimental results with a model.

## Size of nanoparticles

The final Ag particle size can be predicted by knowing the droplet size and the concentration of solution. Assuming that water evaporation and the reaction go to completion and the particles reaches theoretical density ( $\rho=10.46 \text{ g/cm}^3$ ), an Ag mass balance for each spherical particle amounts to

$$\frac{4 \cdot \pi \cdot r_{Ag}^3 \cdot \rho_{Ag}}{3 \cdot M_{Ag}} = \frac{4 \cdot \pi \cdot r_{droplet}^3 \cdot [AgNO_3]^{1/3}}{3 \cdot 1000} \quad (5)$$

Where:  $[AgNO_3]$  is the concentration in mol/l and  $M_{Ag}$  is the atomic weight of silver. This reduces to:

$$\frac{d_{Ag}}{d_{droplet}} = 0.2174 \cdot [AgNO_3]^{1/3} \quad (6)$$

The most probable droplet size is proportional to the halfwave-length of the most rapidly growing wave and can be predicted by the following relationship (7)[1]:

$$d_{droplet} = 0.34 \cdot \left( \frac{8 \cdot \pi \cdot \gamma}{\rho \cdot f^2} \right)^{1/3} \quad (7)$$

Where  $d$  is the mean droplet diameter,  $\gamma$  is the surface tension,  $\rho$  is the density of the atomized solution and  $f$  is the frequency of the ultrasound. Using the physical values of the atomized silver nitrate solution (density ranges from 1,003 - 1,032 g/cm<sup>3</sup> and surface tension from 72.3 - 73.3 mN/m and the ultrasonic frequency of 2.5 MHz the calculated value of the ultrasonically dispersed droplet diameter amount to approx. 2.26  $\mu\text{m}$ . The comparative analysis of theoretical calculation using Eq. (6), and our SMPS measurement are shown in the Table 2.

As shown at Fig. 6.a and 6.b obtained results via a formula (5) confirm that an increase in concentration of silver nitrate leads to larger particles size of silver.

In comparison to traditional particle size measurement using SEM-pictures a SMPS

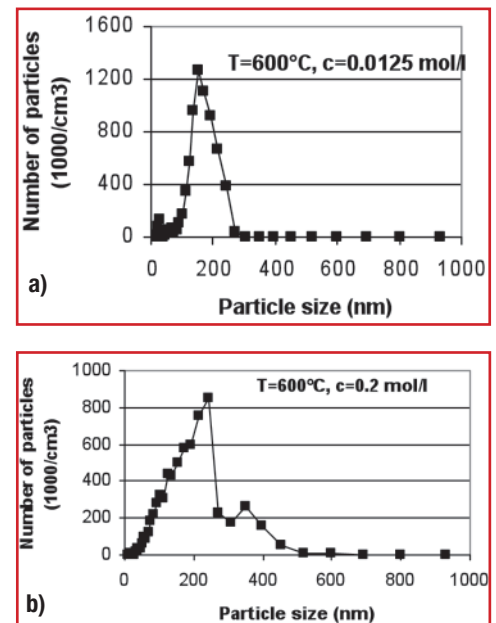


Fig. 6: SMPS during the synthesis of nanoparticles (a:  $d_{Ag} = 136 \text{ nm}$ ; b:  $d_{Ag} = 241 \text{ nm}$ )

analysis offers the information about particle size ranged between 7 and 930 nm in 43 different channels. The measured particles contain the values of million particles in comparison to 150 - 250 particles measured from SEM picture using software for picture analysis. The obtained differences between values shown via SMPS and SEM analysis are expected concerning the different number of particles and online measurement. The both analysis are focused on spherical particles.

## Formation of nanoparticles

The mechanism for the synthesis of nanosized particles by USP is proposed at Fig. 7. According to a model proposed by Pluym et al [1] the most important steps for the synthesis of silver nanoparticles from silver nitrate droplet are evaporation of water followed by calcination forming

Concentration of silver nitrate (mol/l)	Experimental result by SMPS	Predicted by Model (Eq. 6)
0.0125	136	114
0.025	168	143
0.05	172	181
0.10	190	228
0.2	241	287

Table 2: Comparative analyses of theoretical and experimental mean particle size ( $f = 2.5 \text{ MHz}$ ,  $T = 600 \text{ }^\circ\text{C}$ ,  $AgNO_3$  solution)

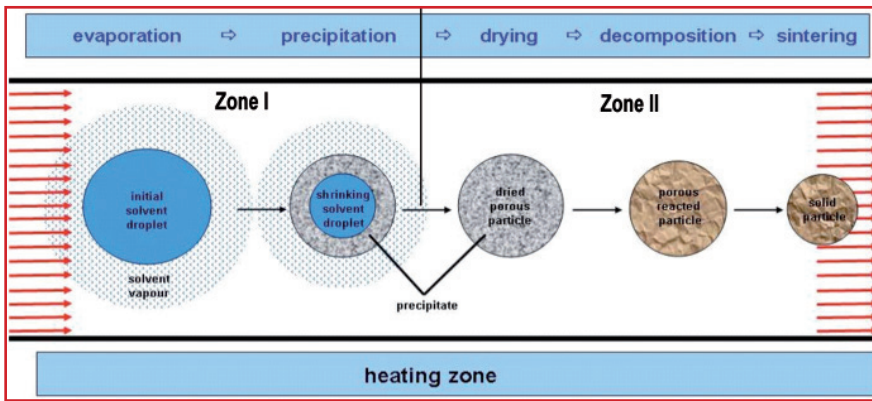


Fig. 7: The model of nanoparticle formation with two major reaction zones

a dry and porous silver nitrate particle, decomposition to silver oxide and reduction to solid silver. The short life of silver nitrate was reported by Plum [1] and Yang [12] based on TGA and DTA analysis. At 600 °C and above only the metallic silver was detected.

However, the intraparticle reaction chemistry regarding to formation of nanosized silver in nitrogen atmosphere is poorly understood at this time and no general conclusions can be drawn. Based on this general view a model of nanoparticle formation is presented in Fig. 7 assuming the processes in two phases, which need different retention times, as shown in the following calculations.

- Phase 1: evaporation of droplet with strongly decreasing radius
- Phase 2: transformation of droplet to final products: solid particles and gases

*Necessary retention time in zone I (Thermal balance concept)*

When a liquid sphere enters zone I, a thermal boundary characterized by a temperature gradient ( $\Delta T$ ) will form around it. This gradient may exhibit strong deviation from chemical and kinetic equilibrium. The heat transfer coefficient ( $h$ ) towards the sphere may be calculated from the well known correlation (when  $Re_{D(n)} \approx 0$ ):

$$Nu = hD/k = 2 \quad \text{or} \quad h = k/r \quad (\text{with } r = D_s/2 \text{ (} r^* < r < r_1)) \quad (8)$$

$Nu$  represents hereby the Nusselt number and  $k$  thermal conductivity. As a consequence, the difference of heat approaching the sphere is:

$$dQ = -4\pi r^2(k/r)(\Delta T)dt \quad (9)$$

Using  $L$  as the latent heat of water evaporation and  $\rho_l$  as density of the liquid substance, the appropriate mass  $G$  leaving the sphere is expressed by:

$$dG = dQ/L = -4\pi r^2 dr \rho_l \quad (10)$$

The balance gives the time for the particle decrease from  $r^*$  to  $r_1$  (11) and also the radius of the final condensed droplet (12).

$$tI = [(L\rho_l)/(2k\Delta T)](r^{*2} - r_1^2) \quad (11)$$

$$r_1 = [r^{*2} - (2k\Delta T)t/(L\rho_s)]^{1/2} \quad (12)$$

Using the process values ( $L = 25.1 \text{ MJ/kg}$ ,  $k = 23.7 \cdot 10^{-3} \text{ W/mK}$ ,  $\rho_l = 103 \text{ kg/m}^3$ ,  $\Delta T = 101 - 100 \text{ °C}$  as a minimum for evaporation,  $r^* = 1.14 \cdot 10^{-6} \text{ m}$  and  $r_1 = 10^{-6} \text{ m}$  as estimated value) the calculated value for evaporation time in first zone amounts to  $t_1 = 0.5 \text{ s}$ .

Tsai et al.[22] have predicted of water evaporation rates of precursor droplets during ultrasonic spray pyrolysis. The weight of water evaporated was calculated from the water balance for two cases: (1) when the precursor drop reaches saturation and (2) when the drop is completely dehydrated at 650 °C for 20, 25, and 31 l/min. The results

show that the water evaporation rates for drops of diameter smaller than 9  $\mu\text{m}$  at all carrier airflow rates are very low ( $< 1.56 \cdot 10^{-6} \text{ cm}^3/\text{s}$ ). Due to this fact we expect very short time for an evaporation of aerosol droplet of 2.26  $\mu\text{m}$  in our case. The calculated value for evaporation time in first zone of 0.5 s corresponds with the results reported by Tsai [22].

*Necessary retention time in zone II (Mass balance concept)*

After entry of the almost dewatered particle into zone II complete drying, calcining, reduction as well as sintering takes place. In the following the necessary time for particle formation is calculated using a mass balance. During drying a liquid layer is formed around the sphere with  $r_1$ , produced by surface chemical reactions, which lead to:

$$d(\rho_s \frac{4}{3} r^3 \pi) = K_s 4\pi r^2 dt \quad (13)$$

and after following transformation to

$$\frac{dr}{dt} = \frac{K_s}{\rho_s} \quad (14)$$

In (14)  $K_s$  represents the overall rate of gas layer formation around the particle ( $\text{kg/m}^2\text{s}$ ) and  $\rho_s$  is the density of the quasi solid particle.  $K_s$  is defined as:

$$K_s = \xi \frac{\beta k}{\beta + k} C_o \quad \text{or} \quad K_s = \xi \frac{1}{\frac{1}{\beta} (\frac{2r}{Sh} + \frac{D}{k})} C_o \quad (15)$$

using “ $\xi$ ” as stoichiometric coefficient of the homogeneous reaction of solid surface formation from volume, “ $C_o$ ” as local bulk concentration of characteristic gas constituent at temperature  $T_0$ , “ $k = \eta k(o)$ ” as the real heterogeneous chemical reaction rate coefficient at  $T_0$ , “ $k(o)$ ” as the pure heterogeneous chemical reaction rate coefficient at  $T_0$ ,  $\eta$  for the internal effectiveness, “ $\beta = a\beta(o)$ ” as the real interphase mass transport

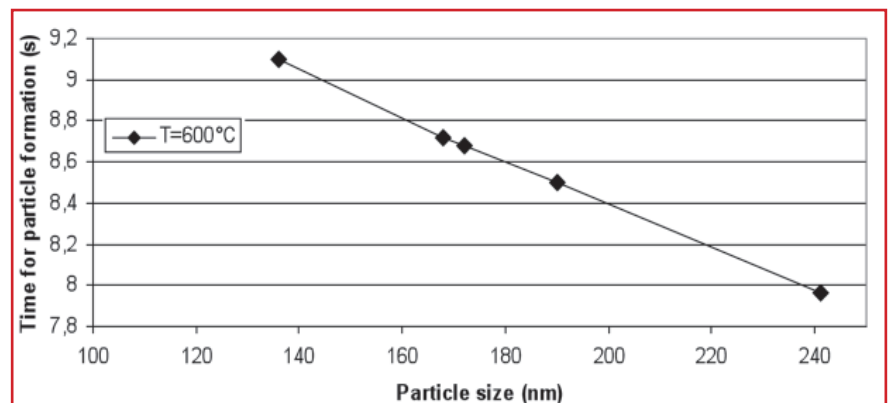


Fig. 8: Calculated time for Ag-particle formation

coefficient ( $\beta = ShD/D_s$ ),  $\beta(o)$  as the pure interphase mass transport coefficient and  $a$  for the external (superficial) surface to volume ratio. So, the time for the particle growth from  $r_1$  to  $r(\text{end})$  amounts:

$$t = \rho_s \int_{r_1}^{r(\text{end})} \frac{dr}{K_s} \quad (16)$$

We suppose that the final particle  $r(\text{end})$  was formed during complete drying, calcination, reduction as well as sintering. If  $r(\text{end})$  tends to reach "0" (nano dimension) and the Sherwood number assumed to be "2" in case of small velocities, the formula gets simplified to:

$$t_{II} = \frac{\rho_s (r_1 - r(\text{end}))}{K_s} \quad (17)$$

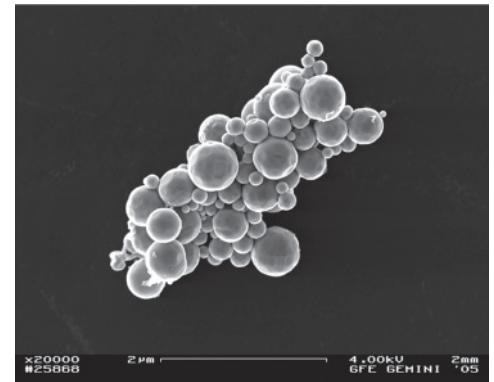
With (17) the calculation the necessary time for the particle formation with shrinkage from  $r_1$  to  $r(\text{end})$  can be calculated. In the present case using  $\rho_s = 10.49 \cdot 10^3 \text{ kg/m}^3$ ,  $r_1 = 10^{-6} \text{ m}$  (estimated),  $r(\text{end}) = 120 \cdot 10^{-9} \text{ m}$  and  $K_s = 10^{-3} \text{ kg/m}^2\text{s}$  (estimated) the necessary time of particle formation in the second zone amounts to  $t_{II} = 9.1 \text{ s}$ . Together with a previous estimated preheating time of 0.3 s and the necessary retention time in zone I (11) of 0.5 s the overall reaction time of this process amounts to 9.9 s. This value

is smaller than the residence time (about 14 s) as shown at figure 5, what is enough for complete particle transformation. Different results of time for particle formation are calculated via (17) and shown in Fig. 8. The long residence time in furnace provided sufficient time for aerosol-nanoparticle transformation at 600 °C as well as at 300 °C from silver nitrate in nitrogen, what is also at Figs. 3 and 4 confirmed.

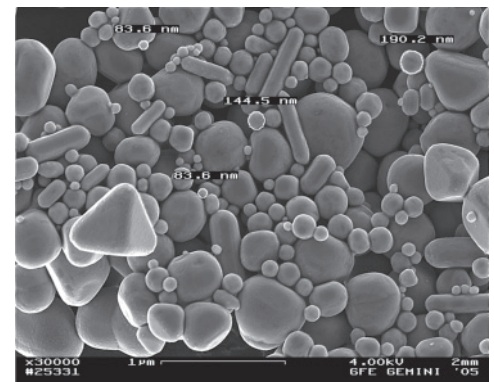
**Comparison with previous results in a lab scale horizontal reactor**

Previously obtained and published[14] results received from a 600°C USP treatment of 0.1 mol/l precursor using a small lab scale horizontal reactor have shown partly different particle morphologies, as can be seen fig. 4 and fig. 9. Table 3 compares the main characteristics received during this first "scale up" procedure.

The results from the Table 3 confirm the positive influence of longer residence time on the particle morphology. Regarding to experiments in big reactor the particle form is spherical in contrast to mixed of cylindrical, prismatic and spherical in small reactor. The obtained results will be used for the following scale up of available equipment. Re-



**Fig. 9.a: Lab scale experiment in nitrogen atmosphere**



**Fig. 9.b: Lab scale experiment in hydrogen atmosphere**

Parameter	Lab-Scale [14]		Technical scale	
Frequency (MHz)	0.8		2.5	
Concentration of silver nitrate (mol/l)	0,05; 0.1 and 0.2		0.0125; 0,025; 0.05; 0.1; 0.2	
Length of reaction zone (m)	0.3		1.5	
Gas flow (l/min)	1		3	
Tube diameter (mm)	21		42	
Residence time (s)	< 1		17	
Collection of particles	In a glass bottle with alcohol		an electrostatic field (U=27 kV)	
Type of reactor	horizontal		vertical	
Maximal consumption of solution (ml/hour)	60		90	
Carrier gas	hydrogen	nitrogen	hydrogen	nitrogen
Mean particle size				
Size range 90 %	84-190	100-650	-	136 - 241
Particles morphology	Mixed of cylindrical, prismatic and spherical	Very spherical and dense	-	Very spherical and dense
Figure No.:	9.a	9.b	-	4
Agglomeration degree	partly	partly	-	partly

**Table 3: Comparison of particle characteristics obtained in lab-scale (horizontal) and technical (vertical) scale experiments at 600 °C**

garding to particle size of silver, Yang and Kim in Powder Technology [12] reported that mean diameter of the particles was almost independent of the residence time as well as from the temperature. They found that the reduction to silver and densification through sintering took place fast and simultaneously, and that crystallization, formation and growth of silver crystallites followed with some lag of time.

**Summary and general assessment**

Thermodynamic considerations have shown that the thermal decomposition of silver nitrate starts at 400 °C in neutral atmosphere. Thermalgravimetrical analysis of this reaction in nitrogen was performed at different heating rates (5, 10, 20, 40 °C). The calculated value of the activation energy amounts to EA= 137 kJ/mol, what confirms that the decomposition of AgNO3 is a chemical rate controlled process depending on reaction temperature.

Silver nanoparticles were prepared by ultrasonic spray pyrolysis of aqueous solutions of silver nitrate using a new vertical reactor technology with on line measurement of nanoparticles. The reduction of silver ni-



trate and subsequent intraparticle sintering of silver nuclei took place almost instantly at 600°C. The silver nanoparticles obtained at 600°C were spherical and dense, and thus the average particle size ranged from 136 to 241 nm for aqueous solutions between 0.0125 and 0.20 mol/l. The SMPS-online data (168 nm) showed acceptable agreement with theoretical calculations as well as with SEM analyses.

Based on one droplet-one particle model for the synthesis of nanosized silver particle from silver nitrate by USP method is proposed comprising the main steps evaporation of porous silver nitrate, decomposition of dried silver nitrate to silver oxide and final reduction of dried silver oxide through a porous solid silver layer. These steps can be assumed to take place in two main reactor zones determined by thermal balance (zone I) and mass balance (Zone II). The calculated value for time of particle formation amounts 9.1 s (nitrogen flow rate of 3l/min at 600°C). This value is smaller than the calculated residence time (about 17 s), showing that the chosen parameter set is sufficient for densification of formed particles.

The comparison between nanoparticles obtained in a large scale horizontal and a lab scale vertical tube reactor has shown similar spherical morphology in nitrogen in contrast to irregular particles obtained in hydrogen atmosphere. The experiments revealed that the average particle size is almost independent from the residence time at 600°C in nitrogen atmosphere.

In all experiments silver nanoparticles were collected in a new dry and filterless electrostatic field reactor. During the synthesis the system was capable for particle collection with efficiencies up to 42 %. A future development step will be focused on an improvement of collection efficiency.

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