Synthesis of Spherical Nanosized Copper Powder by Ultrasonic Spray Pyrolysis

Srećko Stopić, Petr Dvorak, Bernd Friedrich

Spherical, non-agglomerated nanosized particles of copper were prepared by ultrasonic dispersion of solutions from copper sulphate and copper acetate. A controlled particle size was realized through the choice of precursor and solution concentration as well as by changing the aerosol decomposition parameters. The experimental investigations were performed by ultrasonic sources of 800 kHz, acting on water solution of the metal salts (sulphate and acetate) 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 800 and 1000 °C. The choice of reaction parameters (different precursors and reducing agents, concentration of the initial solution and reaction temperature) is very important for the synthesis of uniform spherical metal particles. The paper presents the ways to control this synthesis through the choice of the reaction parameters and compares the experimental results with a calculation of the average diameter of particles of Cu powder.

Keywords:

Copper – Synthesis – Ultrasonic spray pyrolysis – Nanometer

Synthese von kugelförmigem Kupfer-Nanopulver mittels Ultraschallpyrolyse

Kugelförmige, nicht agglomerierte Kupfer-Nanopartikel wurden mittels Ultraschallsprühpyrolyse aus Kupfersulfat- und Kupferacetat-Lösungen hergestellt. Die Partikelgröße wird über die Auswahl der Vorläufer, die Konzentration der Lösung sowie die Reaktionsparameter kontrolliert. Die experimentellen Untersuchungen wurden mittels eine Ultraschallquelle von 800 kHz durchgeführt. Dabei wurden aus den Kupfersulfat und Kupferacetat Aerosole mit einem konstanten Tropfendurchmesser gebildet. Die Größe der Tropfen hängt von den Eigenschaften der Lösungen und von der Ultraschallfrequenz ab. Die nächste Spaltung von Aerosoltropfen wird mit Wasserstoff zwischen 800 und 1000 °C durchgeführt. Die Wahl der Reaktionsparameter Vorläufer, Reduktionsmittel, Konzentration der untersuchten Lösung und Temperatur ist sehr wichtig für die Synthese der einheitlich kugelförmigen Metallpartikel. Die Synthese wurde über die Wahl der Reaktionsparameter kontrolliert. Die experimentellen Ergebnisse der Durchmesser der Kupferpartikel wurden mit den berechneten Werten verglichen.

Schlüsselwörter:

Kupfer – Synthese – Ultraschallsprühpyrolyse – Nanometer

Synthèse de nanopoudre sphérique de cuivre par pyrolyse avec tuyère ultrasonique

Síntesis de polvos esféricos de cobre de tamaño nanométrico mediante pirólisis ultrasónica

Paper presented on the occasion of the conference of the GDMB Copper Committee, April 15, 2005, in Hamburg, Germany.

1 Introduction

Submicron and micron particles of copper are today industrially produced either from copper sulphate solutions by electrolytic recovery [1] or from hydrogen reduction in an autoclave under high pressure [2]. In the HydroCopper process the copper sulphate is reduced by hydrogen at the temperature of 175 °C and hydrogen pressure of 25 bar [2]. Early experimental and theoretical studies have revealed that nanostructured copper particles show interesting and improved mechanical and catalytic properties [3]. In many applications, they are found to be much better than commonly used bulk copper materials, because of their very fine grain size and enhanced specific surface. Of course, the nanoscale and the related high specific surface have also some drawbacks. Such it is very difficult to prepare the powders without a thin oxide layer which is formed immediately by any exposure to air or even when traces of oxygen are present by fabrication.

The biggest use of copper nanopowders represents the area of catalysis. This is the typical benefit coming along when using fine powders instead of bulk material. Chemical reactions catalyzed by fine powders exhibit faster kinetics and can be often carried out at lower temperatures in comparison to reactions catalyzed by bulk material or coarse particles. Copper nanoparticles have been used in organic synthesis reactions such as oxidation of phenol with molecular oxygen [4], oxydation of alkanethiols [5], coupling of epoxyalkylhalides [6], and in the Ullmann reaction [7]. Furthermore, nanoparticles enhance the catalytic activity and selectivity of ZnO in hydration and dehydration reactions, and hydrogenation reactions such as methanol synthesis [8].

The ultrasonic spray pyrolysis (USP) is an innovative and powerful tool for synthesis of particles with controlled and uniform particle size [9], because of the easy control of the powder morphology and the excellent availability of cheap precursors and the small operative costs. This technology has a great potential to be the future solution for the synthesis of copper nanopowder. In the USP-process, a metal-containing solution is cold atomized forming an aerosol. 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.

The aim of this paper is to present investigations concerning the synthesis of spherical nanoparticles of copper by the ultrasonic spray pyrolysis method. The investigation explains the influence of the different parameters of synthesis (different precursors and reducing agents, concentration of initial solution, reaction temperature) on the morphological characteristics of powders based on thermochemical as well on experimental studies.

2 Thermochemical analysis of hydrogen reduction

2.1 Hydrogen reduction of copper sulphate

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

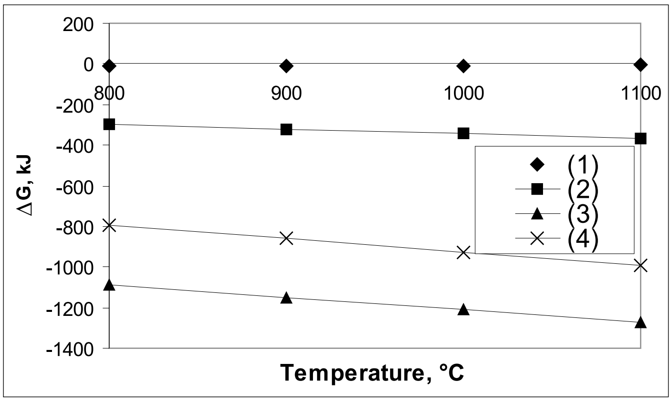

Fig. 1: Thermochemical FactSage®-analysis of hydrogen reactions with $CuSO_4$ between 800 °C and 1100 °C

$$CuSO_{4(aq)} + H_{2(g)} \rightarrow Cu_{(s)} + H_2SO_{4(aq)} \tag{1}$$

$$CuSO_{4(aq)} + 2\,H_{2(g)} \rightarrow Cu_{(s)} + SO_{2(g)} + 2\,H_2O_{(g)} \tag{2}$$

$$3\,CuSO_{4(aq)} + 8\,H_{2(g)} \rightarrow Cu_{(s)} + Cu_2S_{(s)} + 2\,SO_{2(g)} + 8\,H_2O_{(g)} \tag{3}$$

$$3\,CuSO_{4(aq)} + 8\,H_{2(g)} \rightarrow Cu_{(s)} + Cu_2O_{(s)} + 3\,SO_{2(g)} + 5\,H_2O_{(g)} \tag{4}$$

The FactSage®-thermochemical analysis of hydrogen reacting with $CuSO_4$ showed the following free reaction enthalpies for the four above mentioned reactions (Figure 1).

The thermochemical analysis in the temperature range between 800 and 1100 °C showed that all four reactions of reduction are possible. Besides reaction (1) an increase of the reaction temperature increases the possibility of hydrogen reduction in all investigated cases. Reactions (3) and (4) seem to be favorised, reaction (3) has the most negative value of free Gibbs energy. Unfortunately reactions (3) und (4) promote the formation of undesirabled Cu_2S und Cu_2O. An additional thermochemical analysis was performed in order to determine the reaction conditions concerning the excess of hydrogen with the aim to identify a process window suppressing the formation of copper sulphide and copper (I) oxide. (Figures 2a and 2b).

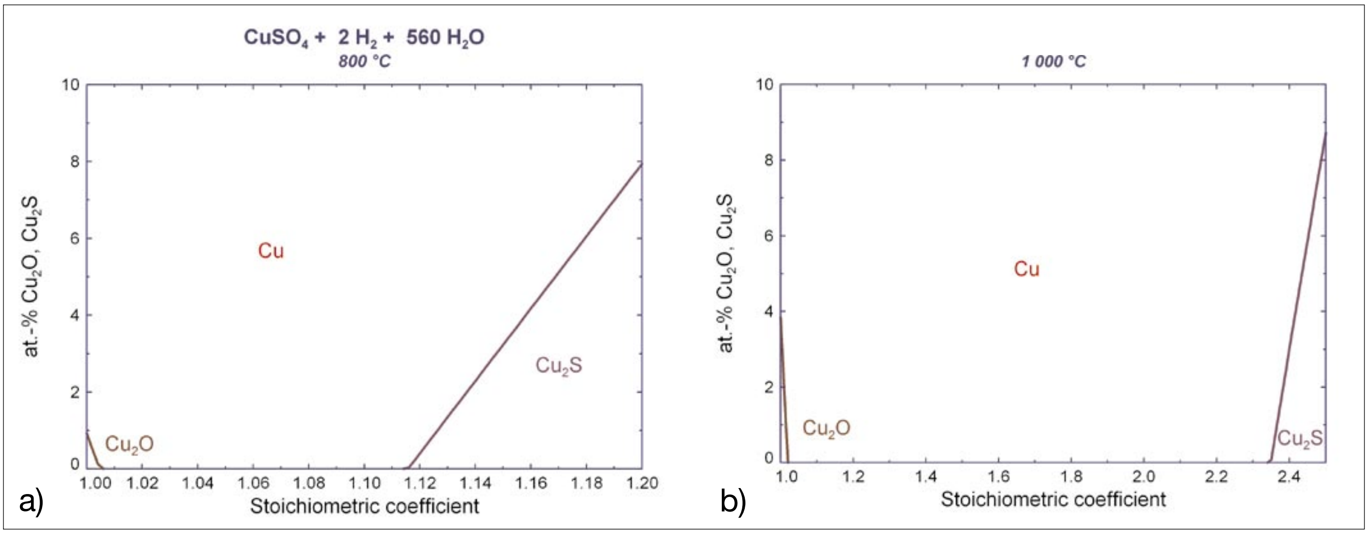

Fig. 2: Phase areas of Cu, Cu_2O and Cu_2S depending on the stoichiometric coefficient of H_2 at a) 800 °C and at b) 1000 °C

Concerning the synthesis of copper without the presence of copper oxide and copper sulphide the calculated stoichiometric coefficient of hydrogen should amount 1.00 and 1.12 at 800 °C (Figure 2a). An increase of the temperature from 800 °C to 1000 °C increases the necessary value of the calculated stoichiometric coefficient of hydrogen to 2.35 (Figure 2b). Because of this fact it is very important to ensure the required quantity of hydrogen for the planned reduction.

2.2 Thermal analysis of decomposition of copper acetate (CuAc), $(CH_3COO)_2Cu$

As thermodynamical data of copper acetate is not available in the present FactSage®-database, a similar thermochemical analysis could not be performed. Such, the decomposition behaviour of $(CH_3COO)_2Cu$ was investigated using thermogravimetric TGA and differential thermal analysis DTA. This study was conducted under 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 10 °C/min.

The first step of decomposition of CuAc was noticed at 164.2 °C (Figure 3) and may be assigned to the reaction:

$$(CH_3COO)_2Cu \cdot H_2O \rightarrow (CH_3COO)_2Cu + H_2O \tag{5}$$

The second step of CuAc decomposition of was noticed at 296.4 °C, most probably related to the two reactions:

$$(CH_3COO)_2Cu \rightarrow CuCO_3 + (CH_3)_2CO \tag{6}$$

$$CuCO_3 \rightarrow CuO + CO_2 \tag{7}$$

It can be supposed from the thermochemical results, that under the experimental conditions the hydrogen reduction of CuAc is possible at temperatures above 600 °C following Eq. (8):

$$CuO + H_2 \rightarrow Cu + H_2O \tag{8}$$

3 Experimental – Material and procedure

$CuSO_4$ and CuAc (Merck, Darmstadt, Germany) was used as precursor materials for the preparation of copper powders by ultrasonic spray pyrolysis, using the equipment shown in Figure 4. The apparatus consists of an aerosol generator, a electrical heated reaction furnace carrying a quartz tube (670 mm length and 20 mm diameter) and a powder collection chamber. The experiments were carried out in the temperature range between 800 °C and 1000 °C in H_2 atmosphere. Two sets of experiments are performed (Table 1). The first five experiments are connected with the reduction of copper sulphate by hydrogen. The experiments from 6 to 11 build up the second set concerning the reduction of CuAc by hydrogen.

Atomization of the copper sulphate and CuAc solutions took place in an ultrasonic atomizer (Pyrosol 7901, RBI,

Fig 4: Experimental apparatus for the USP-synthesis of copper particles (bottles with H_2 and N_2, flowmeter, thermostat, aerosol generator, quarz tube, tube furnace, collection of powders)

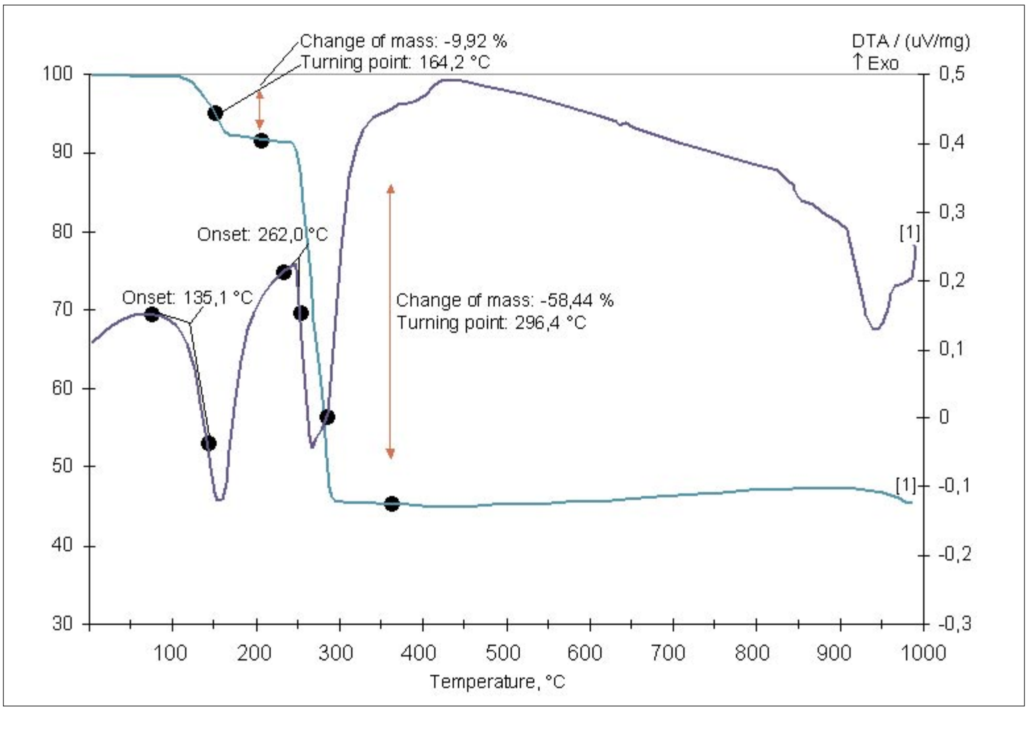

Fig. 3: DTA and TGA analysis of decomposition of copper acetate in argon

Tab. 1: Experimental conditions for the preparation of nanosized Cu powder from aqueous solutions of $CuSO_4$ and CuAc

No.	solution	T [°C]	c [mol/l]	gas reduction agent	c_{HCOOH} [mol/l]
1	$CuSO_4$	800	0.1	H_2	
2	$CuSO_4$	1000	0.1	H_2	
3	$CuSO_4$	1000	0.05	H_2	
4	$CuSO_4$	1000	0.2	H_2	
5	$CuSO_4$	1000	0.1	H_2	
6	CuAc	800	0.1	H_2	
7	CuAc	1000	0.1	H_2	
8	CuAc	1000	0.05	H_2	
9	CuAc	1000	0.2	H_2	
10	CuAc	800	0.1	N_2,HCOOH	3
11	CuAc	800	0.2	N_2,HCOOH	6

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 passed continuously the quartz tube. The calculated retention time of droplets in the reaction zone was calculated to be about 1 s [9]. An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (Zeiss DSM 982 Gemini) were used for the characterization of the obtained copper powders. SEM images were used to observe the surface morphology of particles formed at different parameter sets. The qualitative characterization of the impurity level was performed by energy disperse spectroscopy (EDS) analysis with a Si(Bi) X-ray detector, connected with the SEM and a multi-channel analyzer.

4 Results and discussion

4.1 Hydrogen reduction of copper sulphate

4.1.1 Effect of temperature

The influence of temperature was investigated at 800 °C, 1000 °C and 1083 °C. The EDS analysis of copper powder prepared at 800 °C revealed the presence of Cu, S and O. This indicates an incomplete reduction of the precursor at 800 °C (Exp. 1, Figure 3a), what was already supposed by the thermochemical analysis in chapter 2.1 The disappearance of S and O in the obtained copper powder synthesized at 1000 °C (Exp. 2, Figure 5b) can be assigned to an almost complete reduction. A further temperature increase to 1083 °C leads to presence of small traces of oxygen (Exp. 5, Figure 5c).

Champion et al. [3] reported that due to high pyrophoricity, nanoparticles need to be passivated by soft oxidation, which leads to the formation of a 3 to 5 nm thin layer of cuprite on their surface. The passivation step is of importance, since it allows to handle the powder in air during the following steps in powder processing. However, this oxide layer has a strong effect on the sintering ability of the nanopowder and the quality of the sintered object because of the oxide reduction with hydrogen occurs for nanoparticles at lower temperature than for micron range particles.

4.1.2 Effect of copper sulphate concentration

Three concentration levels of copper sulphate (0.05, 0.1 and 0.2 mol/l) were used for synthesis (experiments 3, 2 and 4) at 1000 °C, Figures 6a, 6b and 6c show the resulted SEM micrographs of the obtained copper powder. At 0.05 mol/l $CuSO_4$-concentration the powder is composed of non-agglomerated and almost spherical nanoparticles

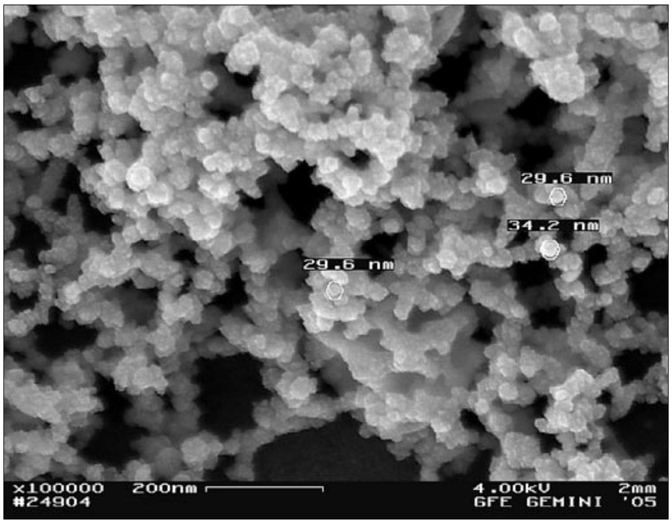

Fig. 6a: SEM micrograph of Cu powder using a $CuSO_4$ concentration of 0.05 mol/l (Exp. 3, 1000 °C)

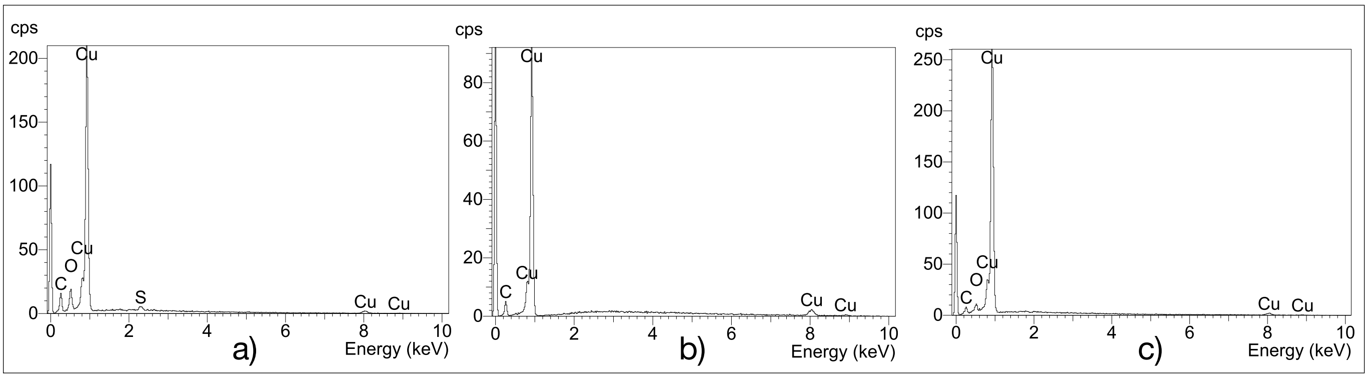

Fig. 5: a) EDS analysis for copper powder obtained in experiment (1) at 800 °C from a $CuSO_4$ solution, b) EDS analysis for copper powder obtained in experiment (2) at 1000 °C from a $CuSO_4$ solution, c) EDS analysis for copper powder obtained in experiment (5) at 1083 °C from a $CuSO_4$ solution

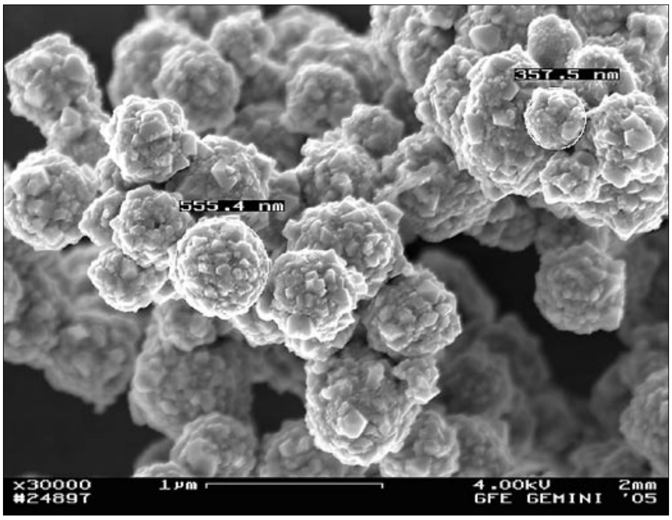

Fig. 6b: SEM micrograph of Cu powder using a $CuSO_4$ concentration of 0.1 mol/l (Exp. 2, 1000 °C)

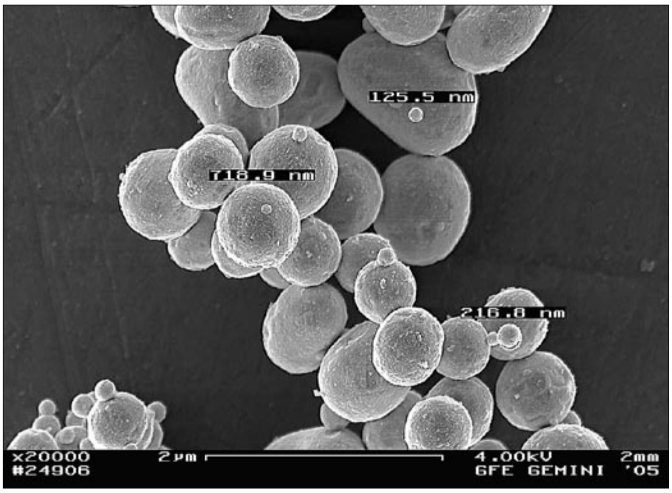

Fig. 6c: SEM micrograph of Cu powder using a $CuSO_4$ concentration of 0.2 mol/l (Exp. 4, 1000 °C)

between 30 nm and 35 nm. An increase of the concentration to 0.2 mol/l leads to fully spherical and dense particles of sizes between 125 nm and 720 nm.

Nevertheless always big particles and satellites are present in the obtained powders. It is most likely that a coalescence of droplets occur during the spray, drying and/or pyrolysis steps,. The agglomeration of aerosol droplets is especially enhanced at high flow rates of the carrier gas due to turbulence effects.

4.2 Hydrogen reduction of copper acetate (CuAc)

4.2.1 Effect of the hydrogen source

The reduction of copper acetate was performed using gaseous hydrogen from the bottle supply (Figure 7a) as well as using in situ hydrogen, generated from the decomposition of formic acid HCOOH (Figure 7b).

In both cases spherical particles of sizes between 380 nm and 490 nm with small amount of satellites were obtained. A strong surface adhesion was seen due to the presence of carbon based organic derivates from HCOOH. Using formic acid and nitrogen gas flow for the reduction of copper acetate in nitrogen showed similar results to a pure hydrogen flow. Xia et al. [10] already mentioned that formic acid decomposes below 100 °C by simultaneous reactions, but with different kinetics:

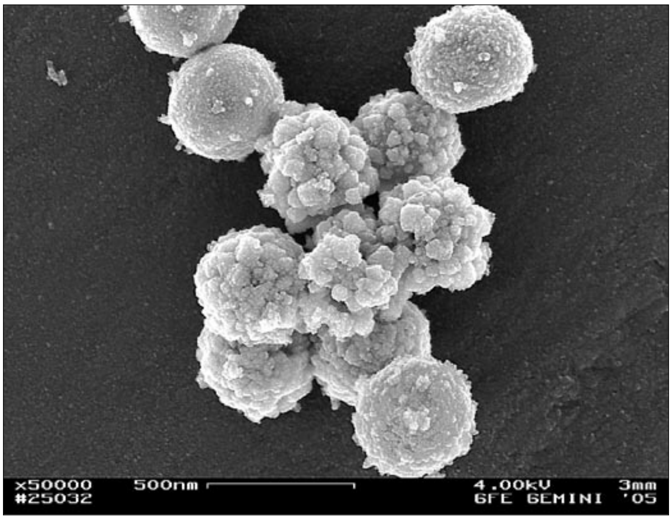

Fig. 7a: SEM micrograph of copper powder obtained at 800 °C from 0.1 mol/l CuAc (Exp. 6) by direct hydrogen gas reduction

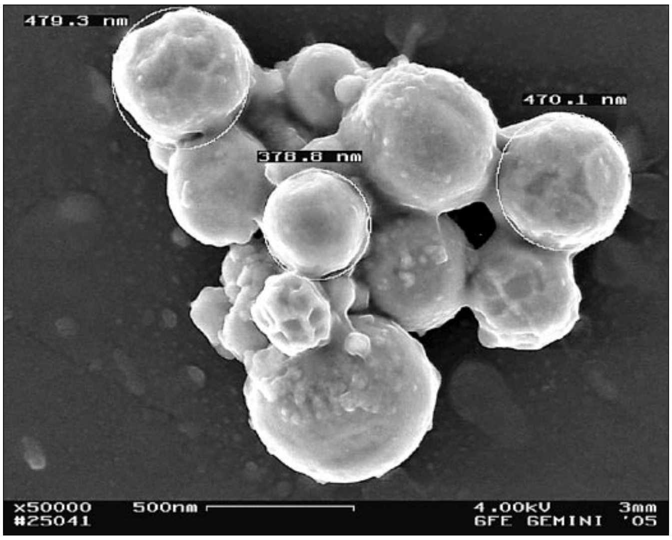

Fig. 7b: SEM micrograph of copper powder obtained at 800 °C from 0.1 mol/l CuAc (Exp. 10) by reduction using formic acid

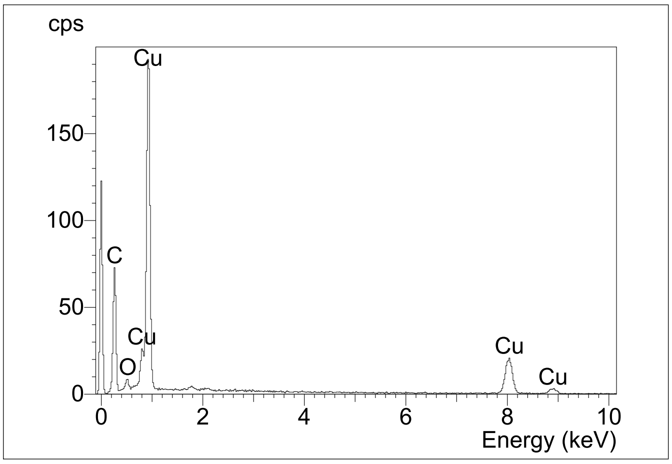

Fig. 7c: EDS analysis for copper powder obtained by reduction of CuAc using formic acid as hydrogen source

$$HCOOH \rightarrow CO_2 + H_2 \qquad (9)$$

$$HCOOH \rightarrow CO + H_2O \qquad (10)$$

The formic acid decomposes to reducing gases such as H_2 and CO, which also protect the copper powder like "bottle"-hydrogen does. Similar EDS analysis confirmed the above-mentioned results (Figure 7c). On the powder surface only a small amount of oxygen (probably a layer of Cu_2O) can be detected.

4.2.2 Effect of copper acetate concentration

The influence of different concentration of copper acetate (0.05, 0.1 and 0.2 mol/l) was considered at 1000 °C. The obtained micrographs are presented in Figures 8a, 8b and 8c.

The increase of the CuAc concentration lead to spherical particles of almost similar morphology, but also to increased particle size as expected. In all cases spherical particles of sizes between 240 nm and 650 nm were synthesized. Especially in the case of 0.2 mol/l the powder reveals high uniformity and a small amount of satellites (Figure 8c).

4.3 Particle size of obtained powder

The connection between the mean diameter of aerosol droplets and the frequency of the ultrasonic atomizer was earlier studied by PESKIN and RACO [11]. They identified the following relationship:

$$D = 0.34 \cdot (8 \cdot \pi \cdot \gamma / \rho \cdot f^2)^{1/3} \qquad (11)$$

where D is the mean droplet diameter, γ 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 $\gamma = 72.9 \cdot 10^{-3}$ Nm^{-1}, $\rho = 1.0$ g cm^{-3}, f = 800 MHz 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.

The expected mean particle diameter of the finally obtained Cu powder after hydrogen reduction can be calculated from the value of the aerosol droplet size. Depending on the initial concentration of the solution, assuming that each droplet is transformed into one particle and that during atomization no coalescence occurs, the final particle diameter can be calculated using formula (12), which was previous presented by MESSING [12]:

$$D_\rho = D \cdot (C_\rho \cdot M_{Cu} / \rho_{Cu} \, M_P)^{1/3} \qquad (12)$$

where D_ρ is the mean particle diameter, D the mean droplet diameter, M_ρ and C_ρ are the molar mass and concentration of the precursor (here $CuSO_4$ or CuAc) and ρ_{Cu} is the density of copper. Using the parameters of our experiments: D: 4.79 µm, M_{Cu}: 63.55 g/mol and ρ_{Cu}: 8.960 g/cm^3 the calculated mean particle diameter of copper developes with the precursor concentration as Figure 9 shows.

As 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. 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

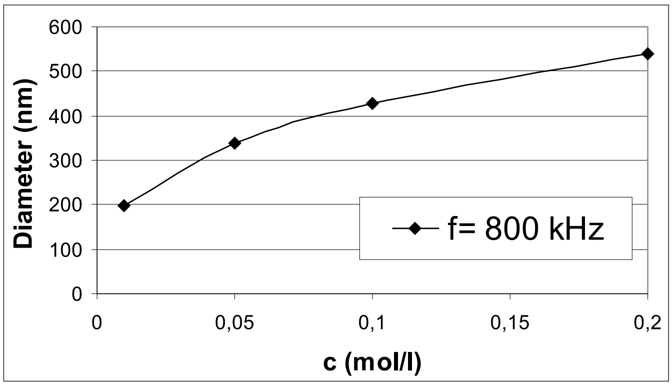

Fig. 9: Calculated particle size of copper after aerosol drying and hydrogen reduction, depending on the $CuSO_4$ concentration in solution

Tab. 2: Experimental and theoretical diameters of particles of copper obtained at 1000 °C with 800 MHz ultrasound frequency

Particle size [nm]	Concentration of precursor solution [mol/l]		
	0.05	0.1	0.2
Calculated value according to Eq. 12	339	427	538
Experimental results obtained from $CuSO_4$	30-34	350-560	125-710
Experimental results obtained from $(CH_3COO)_2Cu$	240-559	not measured	285-651

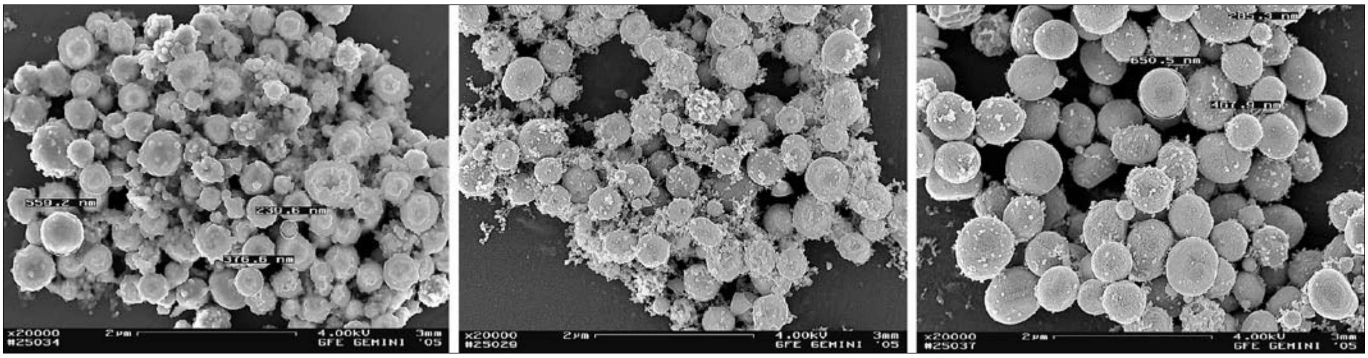

Fig. 8: SEM micrographs of hydrogen reduced Cu powder using a CuAc concentration of a) 0.05 mol/l (Exp. 8, 1000 °C), b) 0.1 mol/l (Exp. 7, 1000 °C), c) 0.2 mol/l (Exp. 9, 1000 °C)

reaches steady state before there is a significant change in droplet size [12].

The calculated and experimentally obtained values of the Cu powders are presented in Table 2.

Differences between calculated and experimentally obtained values may be due to the approximate values used for surface tension and density of aqueous solution, microporosity of particles, and also due to coalescence/agglomeration of aerosol droplets at a high flow rate for the carrier gas (turbulence effects). Also in the equation (12), based on the assumption of one particle per one droplet, the influence of temperature on the mean particle size was not taken into account. For serious consideration of this relationship the aerosol droplet size and particle size should be precisely measured and matched and the model has to be modified.

5 Conclusion

The ultrasonic spray pyrolysis (USP) is successfully introduced for the preparation of nanosized copper particles. The investigation regarding the influence of reaction parameters on the reduction of initial solution showed:

- Aerosol generation by ultrasonic spray of Cu solutions followed by hydrogen reduction pyrolysis is suitable for the synthesis of spherical, non-agglomerated and uniform nanopowders of copper with particle sizes from D = 30 nm to 700 nm.
- Copper sulphate and copper acetate were both suitable to prepare copper powder by ultrasonic spray pyrolysis method. In both cases optimal morphology was reached at 1000 °C, 0.2 mol/l Cu. Comparing the results in Exp. 4 (Figure 6.c) and Exp. 9 (Figure 8c) both precursor materials allow to produce fully spherical and dense particles of a size between 100 nm and 700 nm. In comparison to copper sulphate the use of copper acetate enables the complete reduction even at 800 °C. HCOOH can be used to provide a reductive atmosphere in situ during spray pyrolysis and thus make it unnecessary to use gaseous H_2.
- The use of $CuSO_4$ may result in a sulphur contamination, the risk of CuAc is the formation of sticky surfaces due to derivates from the organics. The increase of the reaction temperature from 800 to 1000 °C leads to a complete hydrogen reduction of solution of copper sulphate. The increase of the precursor concentration increases the final particle size and uniformity of the obtained Cu powder. On the powder surface a thin oxide film is present (protective layer of Cu_2O).
- Although the one particle per droplet model fits in many cases, it does not explain the difference between calculated and measured particle sizes. A different model should be investigated (e.g. gas to-particle conversion mechanism).

Acknowledgments

We would like to thank the DAAD for its 2004 research fellowships for Dipl.-Ing. Petr Dvorak during ten month at IME Process Metallurgy and Metal Recycling, RWTH Aachen University, Germany. Also we would like to thank Mr. Dieter Leimbach for his highly motivated assistance in our experimental part.

Literature

[1] Owais, A. & Friedrich, B. (2003): Packed bed electrolysis for production of copper powder. – ERZMETALL, **56**: 668-677.

[2] Jääskeläinen, E., Hyvärinen, O. & Hämäläinen, M. (2004): Hydrogen reduction of copper (I) oxide in an autoclave. – In: Collins, M.J. & Papangelakis, V.G. (Eds.): Pressure Hydrometallurgy 2004; Banff, Alberta, Canada (Canadian Institute of Mining, Metallurgy and Petroleum): 119-125.

[3] Champion et al. (2003): Sintering of copper nanopowders under hydrogen: an in situ X-Ray diffraction analysis. – Materials Science and Engineering, A 360: 258-263.

[4] Vitulli, G. et al. (2002): Nanoscale copper particles derived from solvated Cu atoms in the activation of molecular oxygen. – Chemistry of Materials, **14**, 3: 1183-1186.

[5] Chen, T. et al. (2002): Reactivity of Laser-Prepared Copper Nanoparticles: Oxidation of Thiols to Disulfides. – Journal of Physical Chemistry, B 106, 38: 9717-9722.

[6] Rieke, R.D. et al. (1989): New organocopper reagents prepared utilizing highly reactive copper. – Tetrahedron, **45**, 2: 443-454.

[7] Ponce, A.A. & Klabunde, K.J. (2005): Chemical and catalytic activity of copper nanoparticles prepared via metal vapor synthesis. – Journal of Molecular Catalysis A: Chemical **225**, 1: 1-6.

[8] Park, S., Gorte & R.J., Vohs, J.M. (2000): Applications of heterogeneous catalysis in the direct oxidation of hydrocarbons in a solid-oxide fuel cell. – Applied Catalysis, A: General 200, 1-2: 55-61.

[9] Stopic, S., Gürmen, S. & Friedrich, B. (2005): Mechanism of synthesis of nanosized spherical cobalt powder by ultrasonic spray pyrolysis. – Journal of Metallurgy, **11**: 65-73.

[10] Xia, B., Lengorro, W. & Okyama, K. (2001): Preparation of nickel powders by **((???))** of nickel formate. – J.Am.Ceram.Soc., **84**: 1425-1432 **((???))**

[11] Peskin, R. & Raco, R (1963) Ultrasonic atomization of Liquids. – Journal of the Acoustical Society of America, **35**: 1378-1381.

[12] Messing, G., Zhang, S., & Jayanthi, G. (1993): Ceramic powder synthesis by spray pyrolysis. – J.Am.Cer.Soc., **76**: 2707-2726.

Dr.-Ing. Srećko Stopić
Prof. Dr.-Ing. Bernd Friedrich
Both:
IME Process Metallurgy and Metal Recycling
RWTH Aachen
Intzestr. 3
D-52056 Aachen

Ing. Petr Dvorak
Department of Metals and Corrosion Engineering
Institute of Chemical Technology, Prague
Technicka 5
16828 Prague 6
Czech Republic