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CHARACTERISATION OF NANO-POWDER MORPHOLOGY OBTAINED BY ULTRASONIC SPRAY PYROLYSIS

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ABSTRACT

Spherical nanosized particles of copper were synthesized by ultrasonic dispersion of solutions from copper sulphate in the temperature range of 800-900°C in hydrogen atmosphere. A controlled particle size was realized through the choice solution concentration as well as by changing the aerosol decomposition parameters. The experimental investigations were performed by ultrasonic sources of 2.5 MHz, acting on water solution of the copper sulphate forming aerosols with constant droplet sizes. This size depends on the characteristics of the solution and the frequency of the ultrasound. The morphological characteristics of copper nanosized powders are investigated.

Key words: Morphology, copper, powder, ultrasonic spray pyrolysis, nanotechnology

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 drawbacks. Such it is very difficult to prepare the powders without a thin oxide layer which is formed immediately by 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], oxidation 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, 10, 11, 12], because of easy powder morphology control and the availability of cheap precursors. This technology has a great potential to be a 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 career, 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 main aim of this work was to prepare and characterize spherical nanosized particles using SEM, EDS and TEM analysis. Using our previous experience the copper powder was chosen for the synthesis from copper sulphate in a hydrogen atmosphere.

2. PREVIOUS RESEARCH REGARDING TO USP-SYNTHESIS OF Cu-NANOPOWDER

A coo-solvent-assisted spray pyrolysis process was developed by Kim et al. [13] for the formation of phase-pure copper particles from metal salt precursors without the direct addition of hydrogen or other reducing gas. Generation of phase-pure copper particles from aqueous solutions of copper acetate and copper nitrate over the temperature range of 450°C and 1000°C was demonstrated. Addition of ethanol as a coo-solvent plays a crucial role in producing phase –pure metal powders. The addition of coo-solvent, selection of precursors, and reaction temperature in spray pyrolysis were the main factors in determining final product composition. However, copper acetate is less soluble than copper nitrate in water, so the use of copper nitrate as a precursor would be more desirable for industrial application.

In our previous work [14] the ultrasonic spray pyrolysis (frequency f=800 kHz, length of reaction zone l=28 cm) was successfully introduced for the preparation of nanosized copper particles from copper sulphate and copper acetate. In both cases optimal morphology was reached at 1000 °C and solution concentration 0,2 mol/l Cu. Comparison the results 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 H2 . The use of $CuSO_4$ may result in a S-contamination, the risk of CuAc is the formation of sticky surfaces due to derivates from the organics.

In this work the ultrasonic spray pyrolysis of copper sulphate solution was applied using the new equipment for the synthesis of nanopowder at the IME of the RWTH Aachen University (f=2.5 MHz, length of reaction zone l=150 cm, electrostatic precipitator with U= 30kV)

3. EXPERIMENTAL

3.1. Material and procedure

Copper sulphate $CuSO_4$ x $5H_2O$ (Merck, Darmstadt, Germany) was used as precursor for the synthesis of copper powder by ultrasonic spray pyrolysis, using the equipment shown in Figure 1. The most important part of the set up are the ultrasonic atomizer, the reactor with three separated heating zones and an electrostatic precipitator. The temperature and pressure control was adjusted using a thermostat and a vacuum pump. Atomization of the copper sulphate solution took place in an ultrasonic atomizer (Gapusol 9001, RBI/ France) with one transducer to create the aerosol. The resonant frequency was selected to 2.5 MHz. Nitrogen was flushed for 1 to remove air from the system. Under spray pyrolysis conditions hydrogen at a flow rate of 5 l/min passed continuously through the quartz tube (l= 1.5 m, b= 42 mm). The calculated retention time of droplets in the reaction zone was calculated to be about 100 s. The performed experiments are shown in Table 1.

Table 1: Experimental conditions for the preparation of nanosized Cu-powder from aqueous solutions of $CuSO_4$ in a hydrogen atmosphere, flow rate of 5 l/min

Test No.	Potential in collection chamber (kV)	T (°C)	C (mol/l)
1	21	800	0,3
2	24	800	0,3
3	0	900	0.3
4	27	900	0,3
5	27	900	0,1
6	27	900	0,05

A scanning electron microscope **ZEISS DSM 962** (1994) with W-cathode (lateral resolution 2.5 nm at 30 kV) was 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. An estimation 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. An EDX-System Oxford Link ISIS with HPGe-Detector and UT-Window was used for chemical analysis of microscopic volumes for all elements with atomic number > 4. The imaging and analysis of very fine particles was performed by transmission electron microscopy analysis using FEI Tecnai F20. The electrostatic precipitator used a high voltage device by Eltex, Elektrostatik-GmbH, Weil am Rhein, Germany to enable the collection of the nanopowder in a special constructed quartz tube (Fig. 2).

Fig. 1: Experimental apparatus for the USP-synthesis of copper particles at IME, Aachen

a) grid for powder collection *b) high voltage device*

Fig. 2. ESP-system for collection of nanosized powder

3.2. Results and discussion

3.2.1. The influence of temperature and precursor concentration

The influence of temperature was investigated at 800° and 900 °C. An increase of temperature leads to the removal of small traces of sulphur and oxygen in the powder. As shown in Fig. 3b versus 3d the decomposition of copper sulphate in hydrogen atmosphere was not complete at 800°C and the given retention time. The powder shows a substructure based of copper particles below 100 nm. The increase of temperature from 800°C to 900°C leads to the complete decomposition of $CuSO_4$ to Cu. Always big particles and satellites are present in the obtained powder (Fig. 3c). It is most likely that a coalescence of droplets occur during the spray, drying and/or pyrolysis steps. It can be expected that agglomeration of aerosol droplets is especially enhanced at high flow rates of the carrier gas due to turbulence effects.

Champion et al.[3] reported that due to their high pyrophoricity nanoparticles need to be passivated by soft oxidation, which leads to the formation of a 3-5 nm thin layer of cuprite on their surface. The passivation step is of big 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 its sintering ability and the quality of the finished object, oxide reduction with hydrogen occurs for nanoparticles at lower temperatures than for micron range particles, which can be used in the powder processing steps, e.g. sintering.

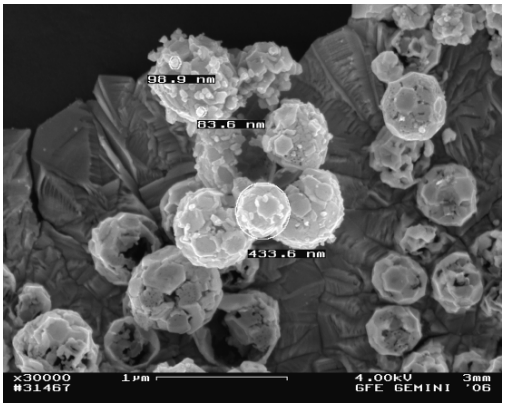

Fig. 3a: Cu particles produced at 800°C, 0.3 mol/l, Exp. 1

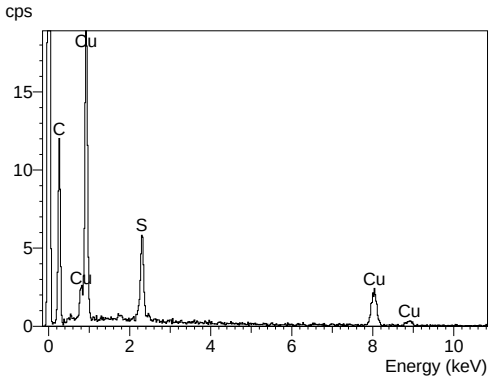

Fig. 3b: EDS analysis of Cu particles produced at 800°C, Exp. 1

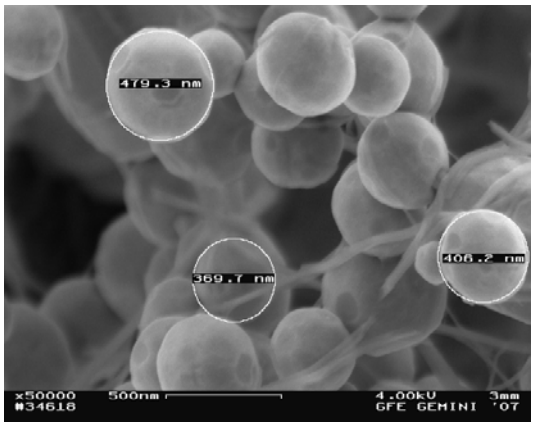

Fig. 3c: Cu particles produced at 900°C, 0.3 mol/l, Exp. 4

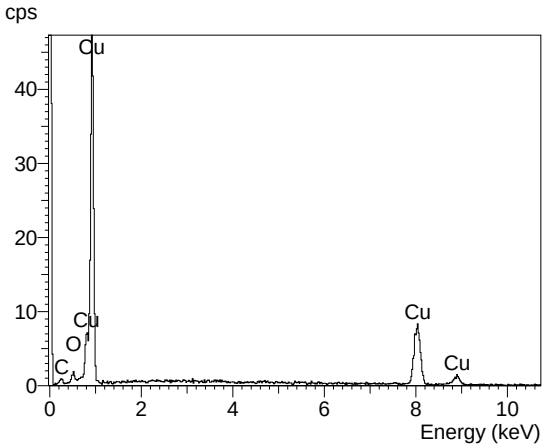

Fig. 3d: EDS analysis of Cu particles produced at 900°C, Exp. 4

Three concentration levels of copper sulphate (0.05, 0.1 and 0.3 mol/l) were used for synthesis (experiments 3, 2 and 4) at 900 °C, Figures 3c, 4a and 4c show the corresponding SEM micrographs of the obtained copper powder. With the concentration decrease from 0,3 to 0.05 to 0.3 also the particle sizes decreased. The TEM analysis confirms the spherical shape of the collected nanosized particles (Fig. 5).

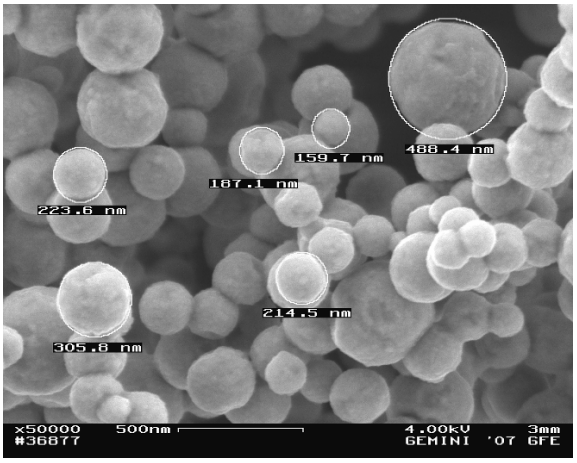

Fig. 4a: Cu particles produced at 900°C, 0.1 mol/l, Exp. 5

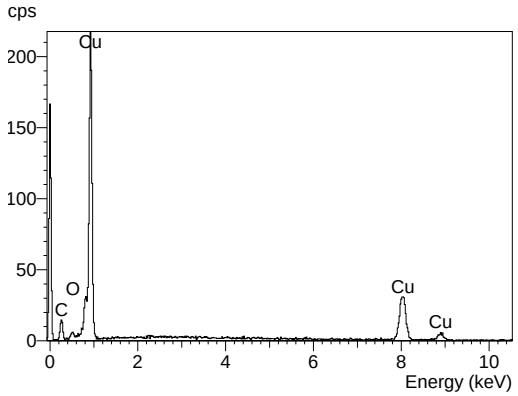

Fig. 4b: EDS analysis of Cu particles produced at 900°C, Exp. 5

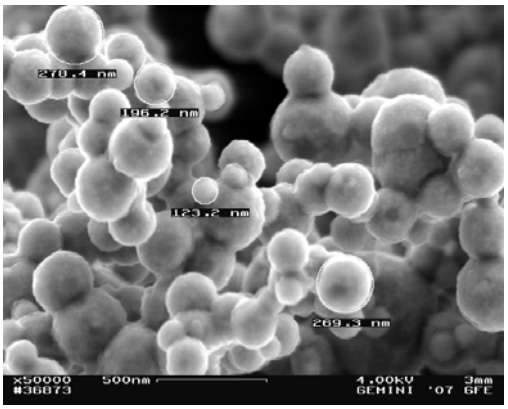

Fig. 4c: Cu particles produced at 900°C, 0.05 mol/l, Exp. 6

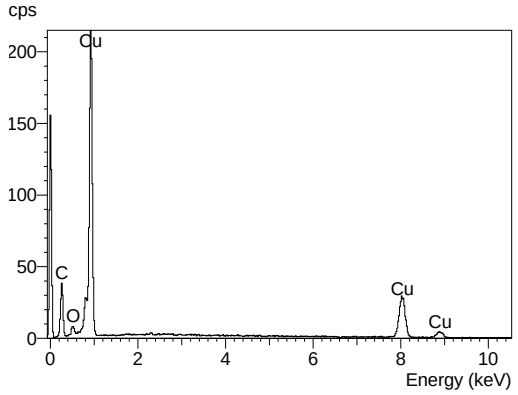

Fig. 4d: EDS analysis of Cu particles produced at 900°C, Exp. 6

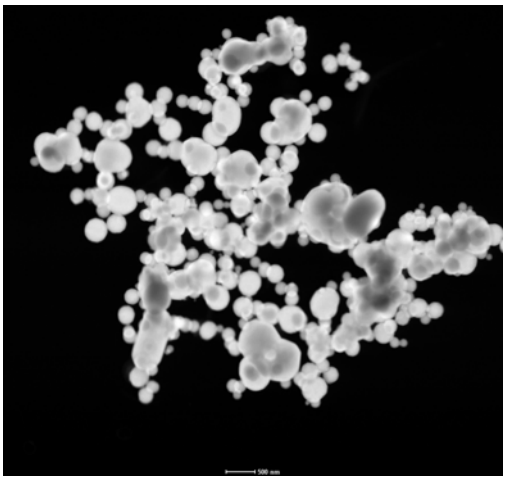

Fig. 5. TEM analysis of USP particles in Exp. 5 (900°C, 0.1 mol/l)

3.2.2. Theoretical model of particle size design

The possibility of generating a cloud of droplets by means of ultrasonic waves was studied by many researchers [15-19] The mean size of the generated aerosol droplets was estimated in accordance with the Lang's equation:

$$d = 0.34 \cdot \left(\frac{8 \cdot \pi \cdot \sigma}{\rho \cdot f^2} \right)^{1/3} \qquad (1)$$

where γ is the surface tension and ρ is the density of the atomized solution and f is the frequency of the ultrasound. Assuming that the characteristics of water ($\sigma = 72.9 \cdot 10^{-3}$ Nm^{-1}, $\rho = 1.0$ g cm^{-3}) are close to those of the used precursor solution, and using different values of frequencies up to 3 MHz the values of the ultrasonically dispersed droplet diameters can be calculated (Fig. 6).

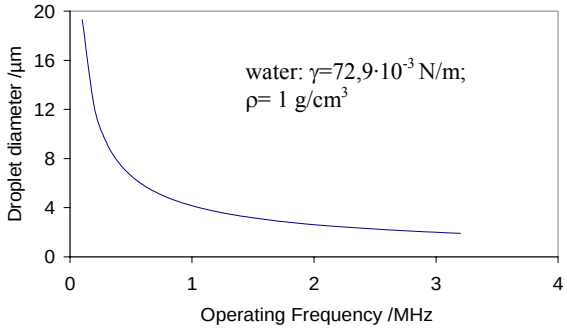

Fig. 6: Calculated aerosol droplet size dependent on the ultrasonic frequency

The exponential growth of the surface disturbances ultimately leads to the formation of liquid drops, which diameters are proportional to the wavelength of the most rapidly growing initial disturbance. The mean droplet size d is proportional to the half-wavelength of the most rapidly growing capillary waves.

Using the experimental frequency value of 2.5 MHz the mean aerosol droplet size d can be expected to be 2.3 μm. The final mean particle diameter of the dried and reacted Cu-particle after hydrogen reduction can be further calculated from this value. Depending on the initial concentration of the solution, assuming that each droplet is transformed into one particle and that during atomization no coalescence or disintegration occurs, the final particle diameter can be calculated using equation (2), developed by Messing [20]

$$D_p = d \cdot \left(\frac{C_p \cdot M_{Cu}}{\rho_{Cu} \cdot M_p}\right)^{1/3} \qquad (2)$$

Where D_p is the mean aerosol particle diameter, d is the mean droplet diameter (equation 1), M_P and C_p are the molar mass and concentration of the precursor ($CuSO_4$), and ρ_{Cu} is the density of copper.

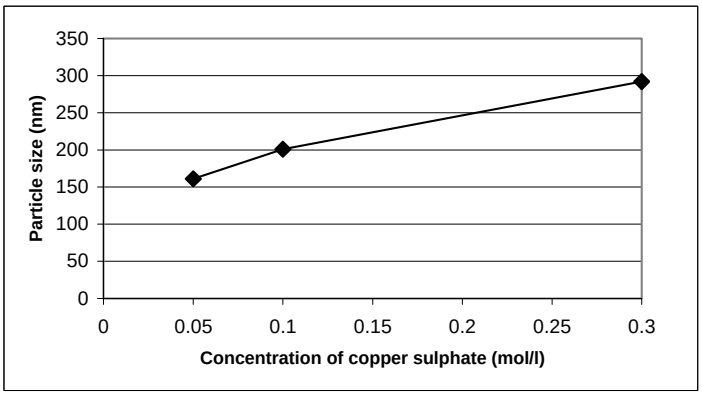

Fig. 7. Calculated solid particle size after USP dependent on the precursor concentration

The obtained particle sizes from the individual experiments are determined using the image analyzing Software Image Pro Plus based on SEM results (example shown in Fig. 7).

The obtained results for copper particle size from experiments 1 and 4 (temperature dependence) are presented at Fig. 8. With increase of temperature from 800°C to 900°C the particle size decreases slightly from 0.453 μm to 0.436 μm. The enhanced sintering conditions are the reason for this change of particle size what was also evident comparing Figures 3a and 3c.

A decrease of the copper sulphate solution concentration from 0.3 mol/l via 0.1 mol/l to 0.05 mol/l leads to the decrease of particle size from 0.435 via 0.234 μm to 0.201 μm, as shown in Fig. 8(right).c and 9. This can be easily explained by the reduced

mass present in a given volume. After generation of droplets from the precursor solution spray pyrolysis involves three major steps: 1) drop size shrinkage due to evaporation, 2) conversion of salt into metal due to hydrogen reduction and 3) solid particle formation and sintering. The vapour diffusion proceeds much faster than the droplet shrinkage and reaches steady state before there is a significant change in droplet size

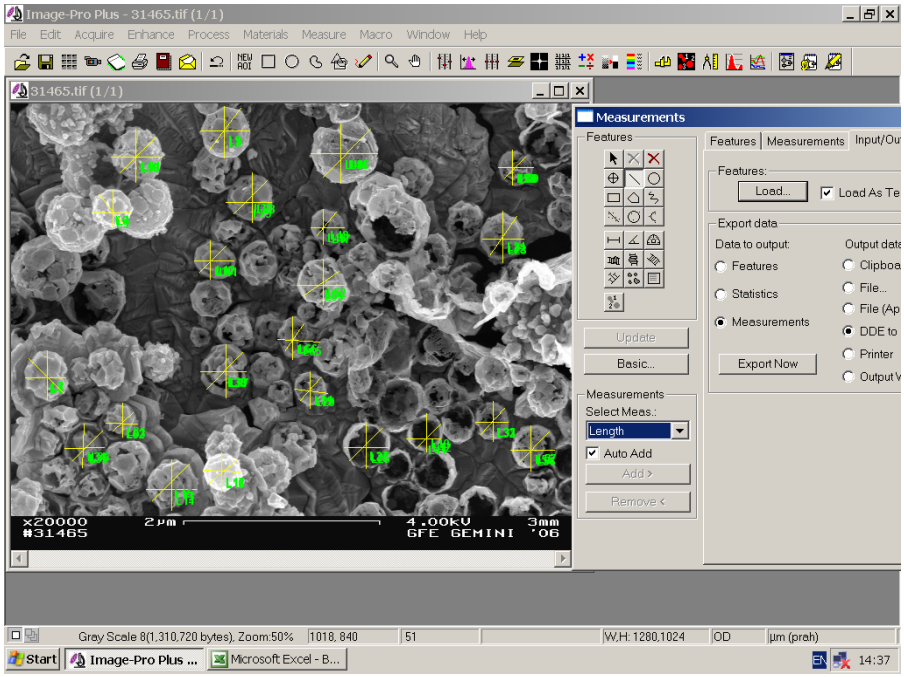

Fig. 8. Image analysis of SEM results for particle size measurement (Exp. 1)

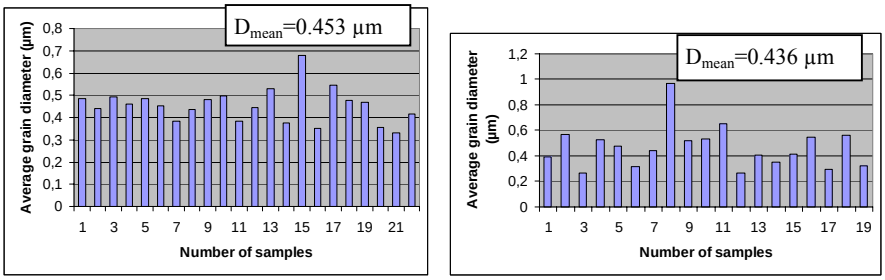

Fig. 9: Mean diameters from particles; left Exp. 1 (T=800°C, c=0.3 mol/l), right Exp. 4 (T=900°C, c=0.3 mol/l)

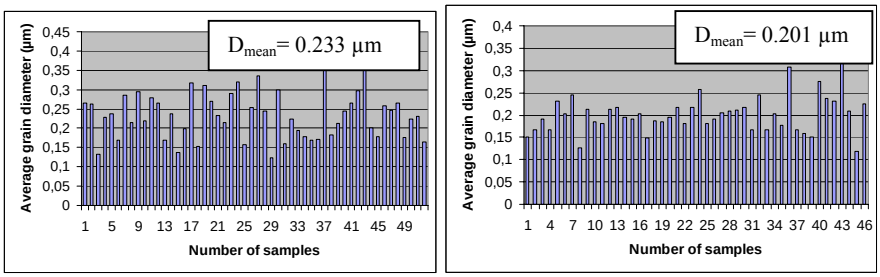

Fig. 10: Mean diameters from particles; left Exp. 5 (T=900°C, c=0.1 mol/l), right Exp. 6 (T=900°C, c=0.05 mol/l)

Using the parameters of our experiments (d: 2,28 µm, M_{Cu}: 63,55 g/mol and ρ_{Cu}: 8,960 g/cm^3) and the concentration values of the used of copper sulphate solution (0.05; 0.1 and 0.3 mol/l) in equation 2. the calculated mean particle diameter of copper can be compared with the experimental data (Fig. 11).

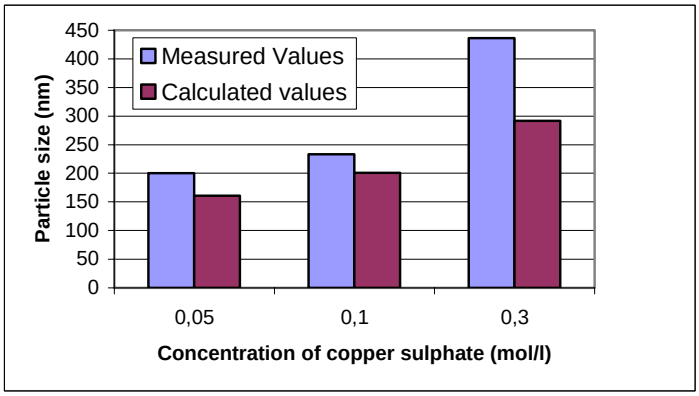

Fig. 11. Experimental and theoretical diameters of particles of copper obtained at 900°C with 2.5 MHz ultrasound frequency and three precursor concentrations

The differences between calculated and experimentally obtained values may be due to coalescence/agglomeration of aerosol droplets at the high flow rate for the carrier gas (turbulence effects). The values of the surface tension, viscosity and density of used solution should be measured in order to the determine their influence. Also in the equation (2), based on the assumption of one particle per one droplet, the influence of temperature on the mean particle size was not taken into account.

4.CONCLUSION

The ultrasonic spray pyrolysis (USP) can be successfully used for the preparation of nanosized powder 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 nano-powders of copper with particle sizes from 200-500 nm
- The use of $CuSO_4$ resulted in a S-contamination at 800°C, as the reaction was not complete.The increase of the reaction temperature to 900 °C leads to a complete sulfur removal in hydrogen atmosphere. An increase of the precursor concentration increases the final particle size of the obtained Cu-powder. On the powder-surface a small oxide film is present (protective layer of Cu_2O)

Although the one particle per droplet model fits in some cases, it does not explain the difference between calculated and measured particle sizes. A different new model should be considered.

5. Acknowledgments

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