Preparation and characterization of cobalt (Co) and silver (Ag) nanoparticles synthesized by ultrasonic spray pyrolysis (USP)

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The aim of this paper is to present the investigations concerning the synthesis of spherical nanoparticles of cobalt and silver by the ultrasonic spray pyrolysis method.

1. RATIONALE OF THE RESEARCH

The field of "Nano-technology" highlights the inter-disciplinary collaboration and is considered as the technology of the future. Nano-sized metal particles are the indispensable assets of high-technology materials and their fields of use are remarkably widespread.

Target:

- synthesis of metal nano particles
- very fine grain size, high uniformity and big specific surface
- better in many applications than commonly used Co and Ag powders

2. INTRODUCTION

Nanoscale particle research has recently become a very important field in materials science. Such metal nanoparticles often exhibit very interesting electronic, magnetic, optical, and chemical properties. The reactivity of nanoparticles depends on its size, shape, surface composition, and surface atomic arrangement. Their high surface-to-volume ratios have large fractions of metal atoms at surface available for catalysis. In the case of cobalt nanoparticles, they are expected to possess exceptionally hihg-density magnetic property, sintering reactivity, hardness levels and improved catalytic properties [1-4]. Silver nanoparticles, as one of nanomaterials of noble metals, have extensive applications in many fields. For example, they can be used for antibacterial materials, antistatic materials, cryogenic uperconducting materials, and biosensor materials, catalytic materials, microelectronic materilas and so on [5]. Nanoparticles are produced by numerous different methods:such as sol–gel, chemical and physical vapor deposition, inert gas condensation and ultrasonic spray pyrolysis (USP) have been employed for synthesis of nanoparticles. USP is a useful tool for large-scale or small-scale production of particles with controlled particle size because the final product properties can be controlled through the choice of precursor and solution concentration or by changing flow rate of carrier/reduction gas. Spray pyrolysis involves four major steps: (a) generation of drops from a precursor solution, (b) drop size shrinkage due to evaporation, (c) conversion of precursor, and (d) solid particle formation [6].

2.1 PRINCIPLE OF USP

Fig. 1a and 1b show the principle of the aerosol production. In the USP process, a metal-containing solution is cold-atomized and form an aerosol.

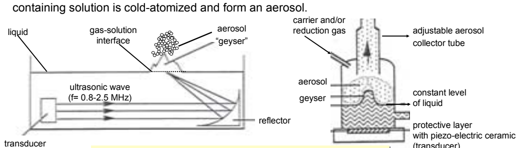
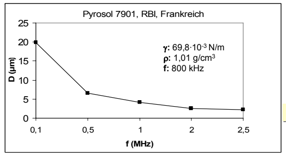


Fig. 1.a. USP-Method



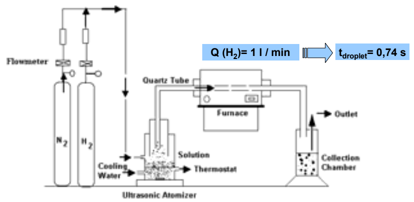
$$d = 0.34 \cdot \left(\frac{8 \cdot \pi \cdot \gamma}{\rho \cdot f^2} \right)^{1/3}$$

d: diameter of aerosol droplets
γ : surface tension of the liquid
ρ : density of liquid
f : frequency

Fig. 1.b. The diameter of the aerosol droplets

3. APPROACH AND EXPERIMENTAL METHODS:

The nanostructured particles were synthesized by USP, using $CoNO_3$ and $AgNO_3$ as precursor. Fig. 2 shows the scheme of the apparatus. Very fine droplets of the aerosol were obtained in an ultrasonic atomizer Pyrosol 7901 (R.B.I.). The aerosol was transported by H_2-carrier/reduction gas via a quartz tube (0.7 m length and 0.02 m diameter) to an electrical heated furnace with a temperature control ± 1 °C. Nitrogen with a flow rate of 1 l/min was used prior for the air removal before the reduction process. Under spray pyrolysis conditions in hydrogen atmosphere and at a flow rate of 1 l/min, the dynamic (continuous) reduction took place in the quartz tube reactor. Regarding the above -mentioned dimensions of the quartz tube and flow rate of hydrogen the calculated retention time of the droplets in the reduction zone was about 1 s. An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (ZEISS Gemini) were used for the characterization of the obtained cobalt particles.



Parameters:
260 ml solution
800-1000 °C
1.0 l / min H_2
2 h
800 kHz

Fig. 2. Experimental apparatus for the synthesis of Co and Ag nanoparticles.

These parameters affect the morphology and the efficiency of Co, and Ag particles production.

4. RESULTS & DISCUSSIONS

4.1 Characterization of Co - particles

The reaction for the formation of Co metal from cobalt nitrate can be described as in Eq. 1.

$Co(NO_3)_2 + 2\ H_2 \rightarrow Co + 2\ NO_2 + 2H_2O$ (1)

XRD patterns of cobalt nanoparticles are shown in Fig. 3. The X-ray analysis of the particles, produced at 800 °C from $CoNO_3$ solution in H_2 atmosphere by USP, indicated the presence of pure cubic cobalt particles. SEM micrographs and particle size distrubitions of the obtained cobalt particles are shown in Fig. 4a and 4b.

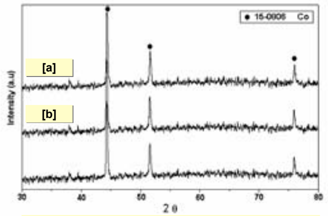
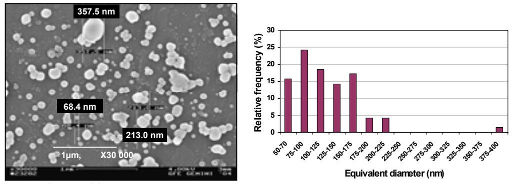
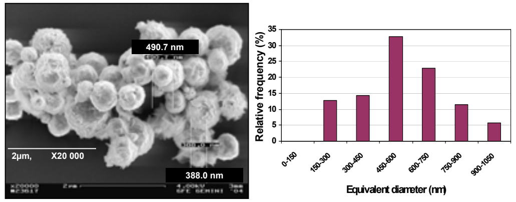


Fig. 3. X-ray analysis of the cobalt particles at 800 °C



2,5 g/l Co, 800 °C, 2h, 1l/min H_2

4.a.



5 g/l Co, 800°C, 2h, 1 l/min H_2

4.b.

Fig. 4.a/b. SEM micrographs and particle size distrubitions of the nano cobalt particles

4.2 Characterization of Ag-particles

$AgNO_3 \rightarrow Ag + NO_2 + ½\ O_2$ (2)
$AgNO_3 + H_2 \rightarrow Ag + NO_2 + H_2O$ (3)

A FactSage®- thermochemical analysis of the hydrogen reaction with silver nitrate (Eq. 3) and the decomposition of silver nitrate Eq. (2) 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. SEM analyses (Fig. 5) of silver showed that fully-reacted, ideally spherical, completely dense particles were produced at furnace temperatures slightly above the melting point of silver.

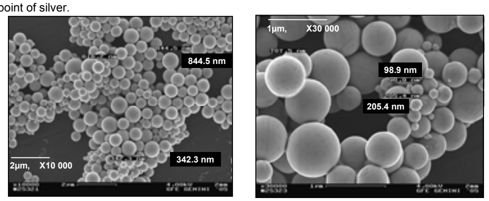


Fig. 5. SEM micrographs of Ag particles at 1000°C (0.1 M $AgNO_3$, 1000°C, 2h, 1 l/min H_2)

EDS-analysis of nano Ag particles prepared at 1000 °C proved the full transformation to elementary Ag (Fig. 6).

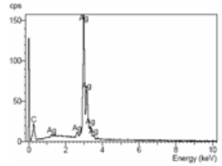


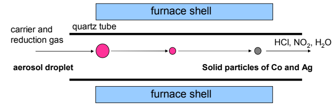
Fig. 6. EDS analysis of the Ag particles at 1000 °C via USP

4.3 Transformation of aerosol droplets

Ultrasonic atomisation is a very effective way of generating small droplets. *The size and shape of primary particles depends on the temperature/time history and materials properties.*

The reaction model: one particle per one droplet

Steps from aerosol to powder:
1. Evaporation 2. Conversion of precursor into metal due to H_2-Reduction
3. Solid particle formation



5. CONCLUSIONS

The USP method is a good choice for the production of the particles with controlled morphology.

The most important results of this study:

1. The average particle size of cobalt particles decreases with decrease of the initial concentration of cobalt chloride.
2. Hydrogen gas played a significant role in a pyrolysis reactor as carrier and reducing gas.
3. Throughout present experiments, spherical cobalt nanoparticles showing nearly uniform size were produced and the crystal structure was cubic.
4. The nanosized Co particles can be used for the production of new nano-structured thermoelectric materials, and hard metals.
5. The nanosized particles have reduced melting and sintering temperatures compared to micron-sized particles and open new applications and processing alternatives.
6. The USP was successfully used for the preparation of nanosized silver particles.
7. The USP of $AgNO_3$-solutions followed by a hydrogen reduction lead to fully dense, perfect spherical and non-agglomerated nanoparticles of silver at 1000°C.
8. 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.
9. The Ag nanoparticles can be used for antibacterial materials in medical textiles, biosensor materials, catalytic materials, and microelectronic materials.
10. 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).

- in the future applications of metal nanoparticles is expected also in environmental protection.

6. REFERENCES

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7. ACKNOWLEDGEMENTS

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