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Synthesis of nanosized spherical cobalt powder by ultrasonic spray pyrolysis

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Abstract

The ultrasonic spray pyrolysis (USP) method has been used to prepare nanosized powders of metallic, intermetallic compounds and ceramic materials. Spherical nanosized cobalt powders were obtained by USP of aqueous solutions of cobalt nitrate followed by thermal decomposition of generated aerosols in hydrogen atmosphere. Particle sizes of the produced cobalt powder can be controlled by the change of the concentration of an initial solution. Non-agglomerated spherical nanosized cobalt particles in the range of 158–1001 nm were obtained at 800 °C. A decrease of the concentration of cobalt nitrate decreases the mean particle diameter from 596 to 480 nm. The discrepancy between the experimentally and theoretically obtained values indicates that the partial coalescence of the droplets occur during the formation of aerosol.

Keywords: A. Nanostructures; A. Metals

1. Introduction

Metal particles smaller than 100 nm in primary particle diameter are generally considered as nanoparticles. 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 improved catalytic properties [1–4]. Spherical non-agglomerated submicron particles of complex composition and controlled phase content, suitable for direct application or fabrication of high technology sintered materials, can be prepared by the spray pyrolysis method [5]. The ultrasonic spray pyrolysis (USP) is a versatile technique for producing various materials in a wide range of composition, size and morphology. Suh and Suslick [6] applied the USP technique to synthesize silica-encapsulated metal nanoparticles. USP of solutions is performed by applying a powerful source of ultrasound to the corresponding solution forming an aerosol with constant droplet size, which depends on the characteristic of the liquid and the frequency of the ultrasound. At a resonance frequency of the order of 2 MHz, the droplet size is approximately 2 μm [7–9]. Stopić et al. [7,8] prepared the nickel

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powder by ultrasonic spray pyrolysis method. The authors state that powders had a spherical morphology and were substantially crystalline. Ultrasonic spray pyrolysis enables the subsequent reactions to occur in a very small volume leading to an ultra fine powder. The different form of produced particles is present due to the process conditions leading to either volume or surface precipitation within the droplet and the subsequent conversion to a dense, solid particle or one hollow, shell-like particle. From the viewpoint of the application of the as-generated particles for advanced materials synthesis, particle morphology is of great interest. It is presumed that certain particle morphology is formed during the evaporation/drying stage that encountered processes of evaporation and diffusion of both the solvent and solute, changing in droplet temperature and crust formation [8]. Messing et al. [10] mentioned that developments in process control, atomisation, and system design are required for wider commercialisation of spray pyrolysis process. USP is a useful tool for large-scale or small-scale production of particles with controlled particle size. The fabrication of cobalt nanosized powder in this way has not yet been investigated. And only a few studies for the synthesis of cobalt particles by gas phase chemical reaction have been reported in the literature [11]. Cobalt nanoparticles were produced by the hydrogen reduction of cobalt chloride in a multistage tubular aerosol flow reactor by Jang et al. [11]. Reaction zone temperature, preheating temperature, mole fraction of $CoCl_2$ and H_2, and residence time were considered as key process variables for the control of particle size and size distribution. Ranging from 50 to 78 nm in average diameter, cobalt nanoparticles with narrow size distribution were synthesized throughout the above-mentioned experiments.

A novel route to prepare spherical nanopowders of cobalt using ultrasonic spray pyrolysis (USP) will be investigated. A controlled particle size will be realized through the choice of precursor obtained from cemented tungsten carbide scrap and solution concentration as well as by changing the aerosol decomposition parameters. Because of a higher surface to volume ratio and an enhanced reactivity the prepared nanopowder should be ideally effective in catalysis in order to accelerate chemical reactions. This hydrometallurgical method will utilize hydrogen reduction of a produced aerosol under dynamic conditions.

2. Experimental

2.1. Materials

A purified leach solution from co-extraction experiments from cemented tungsten carbide scrap using nitric acid was used as starting material for this research (for details, see Refs. [12,13]). The chemical composition of the cemented tungsten carbide scrap used in our experiments is mainly as follows (wt.%): 75.86 W, 8.14 Co, and 6.07 C. The concentration of the obtained final Co solution is between 0.08 and 0.04 mol/l.

2.2. Experimental procedure

The nanostructured materials were synthesized using the ultrasonic spray pyrolysis method. Fig. 1 shows the schematics of the apparatus. The experiments were done at 700–900 °C starting from cobalt nitrate solutions with concentrations of 0.08 mol Co/l and 0.04 mol/l. Very fine droplets of the aerosol were obtained in an ultrasonic atomizer Pyrosol 7901 (Ramine Baghai Instrumentation, with a frequency of 800 kHz). The liquid feed rate amounted between 12 and 14 ml per hour. 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 (Ströhlein, Germany) with a temperature control of ± 1 °C. Because of the safety reasons and to create an inert atmosphere, nitrogen with a flow rate of 1 l/min was used prior to 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 (heated zone 280 mm). The residence time, calculated from the ratio of the volume of the reaction zone and the carried gas flow, was about 1 s with the assumption that the rate of droplets and the carried gas are equal. According to model one particle from one droplet [9] we supposed that this short reaction time is sufficient for the transformation of droplets to metal particle in the hydrogen atmosphere. An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (Zeiss DSM 982 Gemini) were used for the characterization of the obtained cobalt powders. SEM images were used to observe the surface morphology of particles formed at different reaction temperatures. The powders were first dispersed in ethanol and inserted in ultrasonic bath for 30 min and then the suspension was dispersed dropwise onto a glassy carbon slide to make a thick film, which later coated by palladium for SEM characterization. The particle size was examined using the

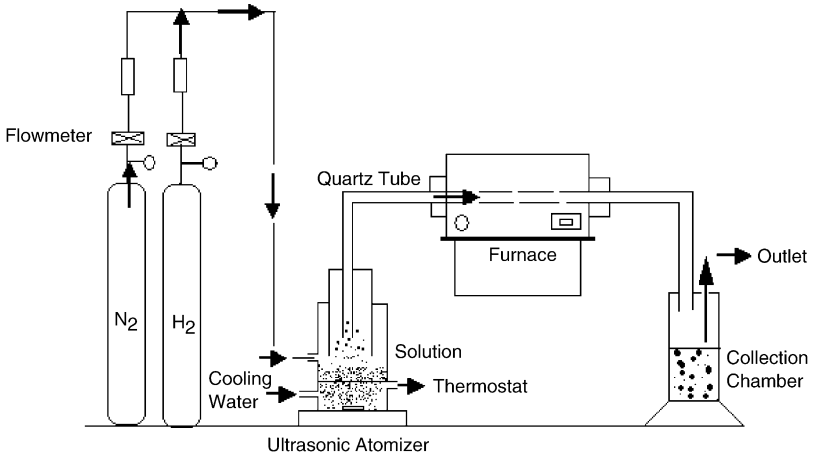


Fig. 1. Schematic drawing of experimental apparatus for the synthesis of cobalt nanoparticles from Co-nitrate-solutions.

Table 1
Composition of precursor solutions, conditions of the process, and descriptions of the obtained powders (test period = 2 h, volume of used solution = 260 ml)

No.	Concentration of precursor solution (mol/l)	Temperature (°C)	Flow rate of H_2 (l/min)	Characteristic of the product
1	$Co(NO_3)_2$, 0.08 M	700	1	Spherical, nanostructured cobalt powder
2	$Co(NO_3)_2$, 0.08 M	800	1	Spherical, nanostructured cobalt powder
3	$Co(NO_3)_2$, 0.08 M	900	1	Spherical, nanostructured cobalt powder
4	$Co(NO_3)_2$, 0.04 M	800	1	Spherical, nanostructured cobalt powder

areal analysis method with a semi-automatic image analyzer (Videoplan, Kontron). ICP (Spectroflame Modula EOP) analysis was used for quantitative chemical composition.

Table 1 contains data for chemical composition of the applied solutions, conditions of the production process, and a short description of the obtained powders.

3. Results and discussion

3.1. X-ray analysis of cobalt powder

Fig. 2 shows X-ray diffraction (XRD) patterns of the cobalt powders. The X-ray analysis of the powders, produced at 700, 800 and 900 °C from $Co(NO_3)_2$ solution in H_2 atmosphere by ultrasonic spray pyrolysis, indicated the presence of pure cobalt powders.

The final product (Co particles) contains no impurities such as tungsten.

3.2. Thermodynamic analysis of hydrogen reduction

The reaction for the formation of Co metal from cobalt nitrate can be described as in Eq. (1). The thermodynamic analysis is done using Fact Sage Software and in the temperature range of 25–1000 °C (Fig. 3).

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

The values of Gibb's free energy (ΔG^0) for the reaction 1 in the temperature range up to 1000 °C confirm the probability for formation of Co from $Co(NO_3)_2$ by hydrogen reduction. This probability for formation of Co increases at elevated temperatures.

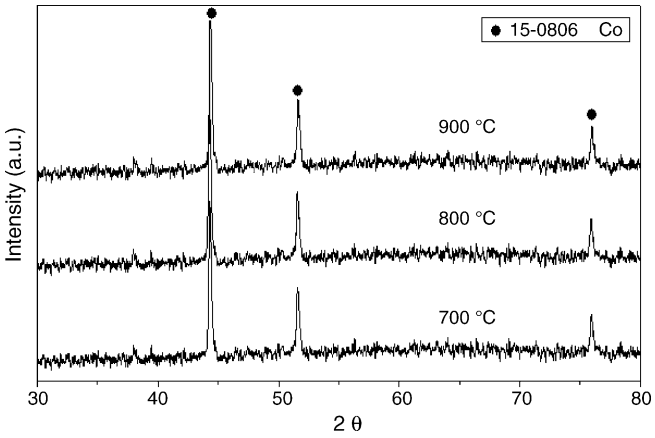


Fig. 2. X-ray analysis of the USP cobalt powders (700, 800 and 900 °C).

3.3. The effect of precursor solution concentration

The effects of the precursor drop size on size distribution of the particles and their morphology after spray pyrolysis have been reported by Tsai et al. [14]. This study examines the effect of the precursor concentration in the range of 0.04–0.08 M under the conditions of 2 h run time, 800 °C reduction temperature, and 1 l/min H_2 volumetric flow rate. SEM micrographs of the obtained cobalt powders are shown in Fig. 4a and b, respectively.

In both cases the cobalt powders are almost spherical with comparable particle morphology. Under the same conditions the reduced concentration of cobalt in the precursor solution decreases the particle size and the uniformity of the powder. Some agglomeration of particles is particularly present in both cases the surface morphology seems to be smoother at low Co concentration. The increase in the number of larger particles with cobalt concentration appears to indicate that they are produced by the coagulation, surface reaction, and sintering. However, smaller particles that seemed to be grown by the coagulation and surface reaction are observed at low cobalt concentrations. In difference to non-agglomerated particles by ultrasonic spray pyrolysis nanosized primary particles prepared in the gas phase [14] form aggregates because of interactive forces between particles. Such aggregates change into large particles when the temperature in the gas phase is high enough to sinter the aggregates.

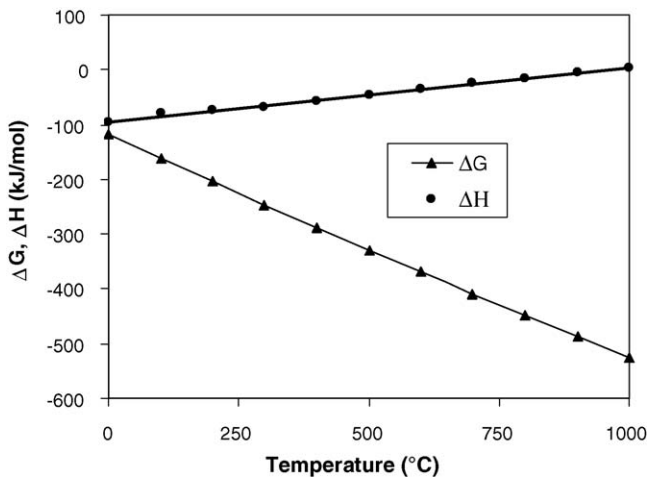
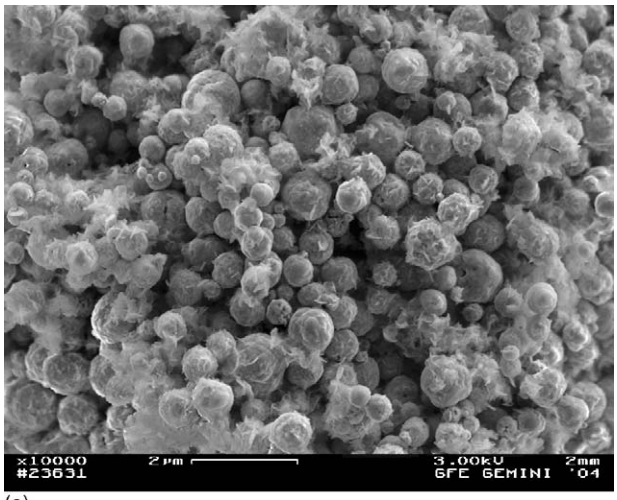
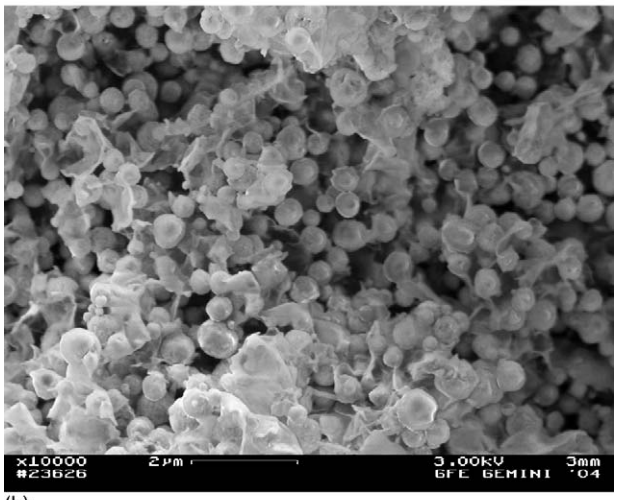


Fig. 3. Dependence of the Gibb's energy on the temperature.



(a)



(b)

Fig. 4. (a) SEM micrograph of the cobalt powder obtained at 800 °C with cobalt concentration of 0.08 M Co/l. (b) SEM micrograph of the cobalt powder obtained at 800 °C with cobalt concentration 0.04 M Co/l.

3.4. Comparative analysis of powders obtained under static and dynamic conditions

In a previous investigation cobalt powders were produced from a similar solution by chemical precipitation, and the calcination and reduction were performed under static conditions [13]. The cobalt hydroxide precipitates were placed in a quartz tube without any displacement for 2 h. Micron size particles started to agglomerate at increased temperatures of 800 °C. Also particles with irregular shapes have been produced (Fig. 5).

Compared to the static conditions the droplets in this paper were reduced in the reaction furnace by hydrogen in a very short time, leaving the quartz tube after approximately 1 s.

The difference between the results in dynamic and static conditions using the same furnace, the same temperature, and the initial concentration of solution is a consequence of different retention times and fluid dynamics in the reaction zone. Under static conditions the retention time of 2 h is long enough for an agglomeration and growth of particles. Due to these reasons an ultrasonic atomizer produces spherical droplets of $Co(NO_3)_2$. It can be presumed that in the first stage water is removed from the surface of the droplets and that the solution is being concentrated. Such the concentration of the solution at the droplet's surface is much higher than in the inner part of the droplets. When the solution reaches its saturation point, compounds crystallize, decompose thermally, and form a product shell. This is the reason why ideally spherical non-agglomerated powders can be produced using the ultrasonic spray pyrolysis.

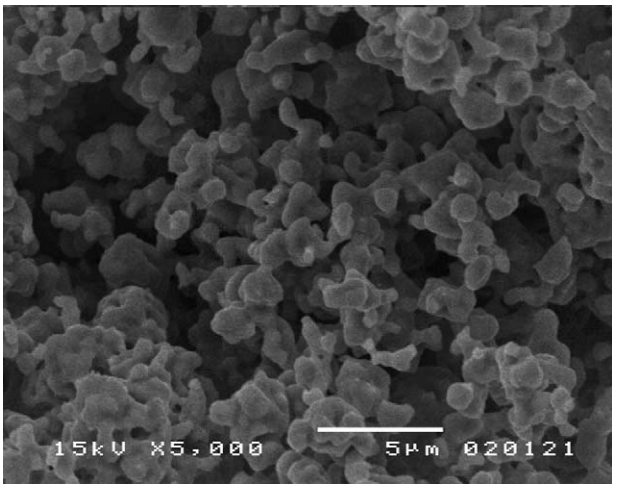


Fig. 5. SEM micrograph of a cobalt powder obtained under static conditions at 800 °C [13].

3.5. Comparative analysis of theoretically expected particle diameter and the experimentally obtained values

The relation between the droplet diameter of the atomized solution and the frequency of the ultrasound source was studied by Tsai et al. [14]. It was shown that the mean diameter of the aerosol droplets develops according to the relationship:

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

where D is the mean droplet diameter, γ is the surface tension of the solution, ρ is the density of the solution and f is the frequency.

Using the parameters of this study (γ, 72.9×10^{-3} N m^{-1}; ρ, 1 g cm^{-3}; f, 800 kHz) the calculated droplet diameter amounts to $D = 4.26$ μm.

The dependence of the mean droplet diameter by the frequency of the used ultrasonic atomizer is shown in Fig. 6. It can be seen that the mean droplet diameter decreases with increasing frequency of the ultrasonic atomizer.

Using this rule for the droplet size the expected value of the mean particle diameter of the cobalt powder can be calculated depending on the initial concentration of the $Co(NO_3)_2$ solution. It is assumed that each droplet is transformed into a particle and that during the atomisation no coalescence occurs. If D_p is the particle diameter; D is the droplet diameter; $C_{precursor}$ is the concentration of the water of $Co(NO_3)_2$-solution and ρ_{Co} is the density of cobalt, the following equation can be developed:

$$D_p = D(C_{precursor}M_{Co}/M_{precursor}\rho_{Co})^{1/3} \tag{3}$$

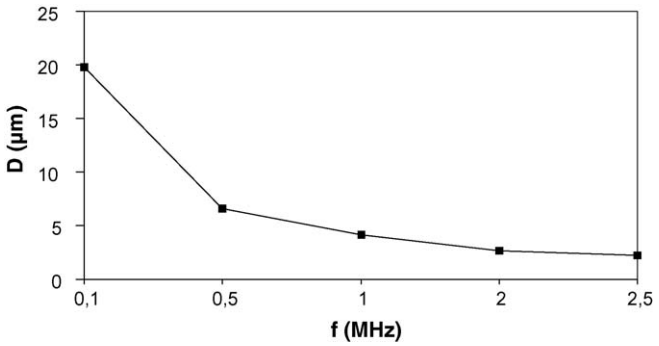


Fig. 6. Dependence of the mean droplet diameter by the frequency of ultrasonic atomizer.

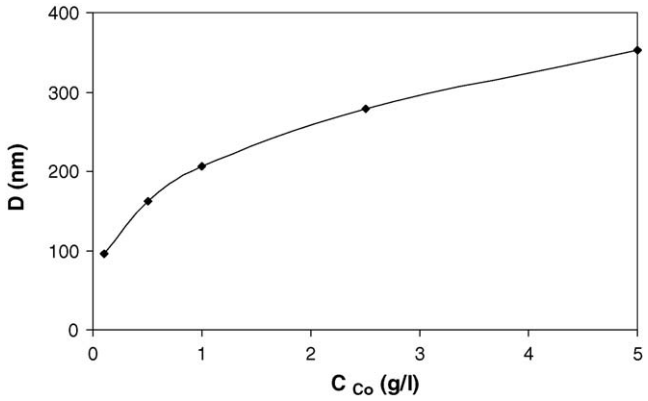


Fig. 7. Dependence of particle diameter by the concentration of cobalt in solution.

The calculated particle diameter of Co (D_p) varies from 352 to 274 nm, by changing the precursor concentration from 0.08 to 0.04 mol/l, while keeping the following data constant: D, 4.26 μm; M_{Co}, 58.93 g/mol; $M_{precursor}$, 182.93 g/mol; ρ_{Co}, 7.84 g/cm^3. The fact is clearly seen in Fig. 7.

Experimental values of the minimal, maximal and mean particle diameters and theoretical calculated values of the particle diameter of cobalt are given in Table 2.

The experimental results confirmed that the decrease of the concentration of cobalt nitrate decreases the particle size. In both cases the calculated values of particle diameter of cobalt are between the minimal and mean experimental obtained values (157.97 nm < 352 nm (calculated value for 0.08 M of cobalt nitrate) < 595.88 nm and 143.94 nm < 274 nm (calculated value for 0.04 M of cobalt nitrate) < 479.83 nm, respectively). The maximal experimental values of particle diameters of cobalt of 766.27 and 1001.00 nm are consequence of the coalescence of droplets during the transport by hydrogen. We have supposed that different sized droplets produced by an ultrasonic generator have different rising velocities. Larger droplets can catch smaller ones along their way into the furnace. Also the droplet collisions could be caused by the turbulent velocity of hydrogen.

This calculation is done by the conventionally accepted one particle drop mechanism [14]. The principle of the proposed mechanism is based on a single-step high temperature aerosol decomposition (one droplet/one particle), ultrasonically generated from precursor solutions of cobalt nitrate. A careful comparison of precursor drop sizes with the product particle sizes reveals that in addition to the conventionally accepted one particle per drop mechanism, spray pyrolysis may also involve the gas to particle conversion mechanism, which creates nanoparticles much smaller than those predicted by the one particle per drop mechanism alone according to Tsai et al. [14]. Thus, uniform nanoparticles can be produced by spray pyrolysis at proper conditions using uniform drops of precursor salts with low vapour pressure. Fig. 8 presents scaled SEM picture of particles received from 700 °C, 0.08 mol/l cobalt nitrate solution USP tests. The particles between 50.2 and 73 nm seen in Fig. 8 constitute one big spherical particle of cobalt powder.

In contrast to ideally spherical particles by ultrasonic spray pyrolysis method Jang et al. [11] prepared the spherical cobalt nanoparticles in a range between 55 and 78 nm by hydrogen reduction of cobalt chloride in the gas phase at 900 °C. Primary particles looked like single spherical crystals of nearly uniform size and the directional linkage of particles was observed. The production rate of Co nanoparticles was 1 g/h at 0.0862% of $CoCl_2$, that was the same in ultrasonic pyrolysis method.

Table 2
Experimental and theoretical values of diameter of cobalt particles

	Concentration (mol/l)					
	0.08			0.04		
	Maximum	Minimum	Mean	Maximum	Minimum	Mean
Experimental values (nm)	1001.00	157.97	595.88	766.27	143.94	479.83
Theoretical values (nm)	352.0			274.0		

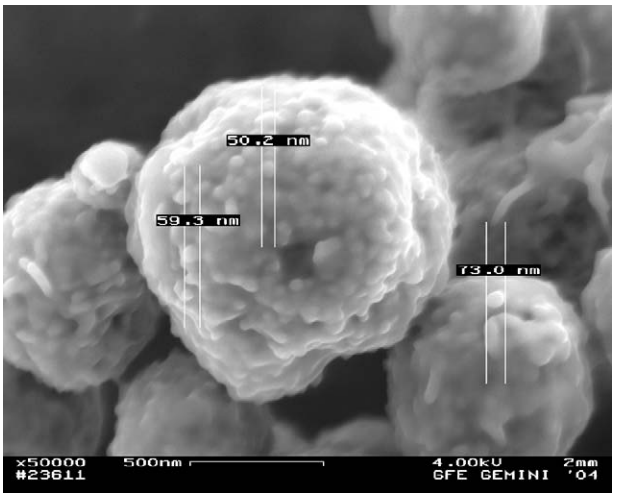


Fig. 8. SEM micrograph of USP cobalt powder obtained at 700 °C with a precursor cobalt concentration of 0.08 mol/l (magnification 50,000×).

The results, presented here, are very promising and further detailed investigations including the physical properties have been started.

4. Conclusion

Ultrasonic spray pyrolysis (USP) is used for the synthesis of fine, spherical, nanosized cobalt particles from a dispersed cobalt nitrate solution formed during the recycling of waste cemented carbide. In the temperature range between 700 and 900 °C the aerosol droplets of 4 μm were decomposed by hydrogen reduction in order to produce cobalt powder. The experimental results confirmed that the decrease of the concentration of cobalt nitrate decreases the particle size. In both cases the calculated values of particle diameter of cobalt ranged between the minimal and mean experimental obtained values (157.97 nm < 352 nm (calculated value for 0.08 M of cobalt nitrate) < 595.88 nm and 143.94 nm < 274 nm (calculated value for 0.04 M of cobalt nitrate) < 479.83 nm, respectively). The maximal experimental values of particle diameters of cobalt of 766.27 and 1001.00 nm are consequence of the coalescence of droplets during the transport by hydrogen into the furnace. One comparison between the powder morphology of cobalt obtained in static and dynamic conditions emphasizes that the ultrasonic spray pyrolysis method is a good choice for the production of the particles with controlled morphology.

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