Mechanism of synthesis of nanosized spherical cobalt powder by ultrasonic spray pyrolysis

Mehanizam sinteze sfernih nanoprahova kobalta rasprsivanjem ultrazvucnom pirolizom

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Abstract

The mechanism of synthesis of nanosized spherical cobalt (Co) powders by the ultrasonic spray pyrolysis of $Co(NO_3)_2$ was presented. Phase-pure cobalt powder was obtained at 800 °C at a residence time as short as 1.0 s. The leach solution [$Co(NO_3)_2$] of cemented carbide scrap was investigated in the hydrogen atmosphere using of horizontal and vertical experimental construction variant. The final characteristics of Co-powder depend on the concentration of precursor solution and the working parameters.

Keywords: Cobalt Powder, Spray, Ultrasonic Pyrolysis, Nanoparticles

1. Introduction

Micrometer- or nanometer- size metal particles have various applications such as electrode materials for electronic products, electromagnetic interference shielding materials for electronic packaging, and catalysts for synthesing nanotubes. The ultrasonic spray pyrolysis is a useful tool for large-scale or small-scale production of particles with controlled particle size [1]. The ultrasonic spray pyrolysis (USP) is a powerful tool for preparing powders and films, because of the easy control of target composition, the excellent availability of the precursors, and the high quality of the products. In the preperation of a powder by USP, a solution atomized into a hot reactor, where the aerosol droplets undergo drying, droplet shrinkage, solute precipitation, thermolysis, and sintering to form final particles. Residence times from several seconds to tens of seconds are most frequently used to ensure the formation of the desired product. Metals, metal oxides, and non-oxides can be readily produced by spray pyrolysis [2, 3]. 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 proporties. In the case of cobalt (Co) nanoparticles, they are expected to possess exceptionally high-density magnetic property, sintering reactivity, hardness levels, excellent impact resistance properties, etc. [4-9]. Many studies on synthesis and magnetic properties of nanoscale metal particles such as Fe, Au, Pd and composites have been reported. But only a few studies for the preparation of cobalt particles from the cobalt chloride ($CoCl_2$) both by gas-solid reaction and by gas-gas reaction [8].

The main aim of this paper was to present the first investigation concerning the synthesis of nanosized cobalt powder at the new built equipment at the IME Process Metallurgy and Metal Recycling, RWTH Aachen University. The mechanism of the formation of cobalt nanosized powders under ultrasonic spray pyrolysis conditions will be explained.

2. Experimental

2.1. Materials

A purified leach solution from Co-extraction experiments from cemented carbide scrap using nitric acid leaching used as the starting material for this research. The final concentration of cobalt amounted 0.08 mol Co/l.

2. 2. Experimental procedure

The equipment for powder synthesis is shown in Figure 1a. (horizontal variant) and 1b (vertical variant). The experimental conditions are given in Table 1. The apparatus consists of an aerosol generator, a reaction furnace (Stroehlein, Germany) with a quartz tube (0.7 m length and 0.02 m diameter) and a powder collection chamber. Experiments were carried out at 800 °C using 0.04 M and 0.08 M of $Co(NO_3)_2$ solution in a N_2/H_2 atmosphere. Atomization of the initial salt solutions was done in an ultrasonic atomizer (Pyrosol 7901, RBI, France) with one transducer for making an aerosol. For this ultrasonic atomizing system, the resonant frequency is 800 kHz. For cobalt production N_2/H_2 atmosphere is used. Nitrogen with a flow rate of 1 l/min was used for the samples evacuation before the reduction process. Under spray pyrolysis conditions in hydrogen atmosphere and at a flow rate of 1 l/min, took place in a furnace with quartz tube. The calculated residence of droplets in the reaction zone was about 1 s. An X-ray diffractometer (Siemens D 5000) and a scanning electron microscope (ZEISS DSM 982 Gemini) was used for the characterization of an obtained cobalt powders. SEM images were used to observe the surface morphology of particles formed at different mole fractions.

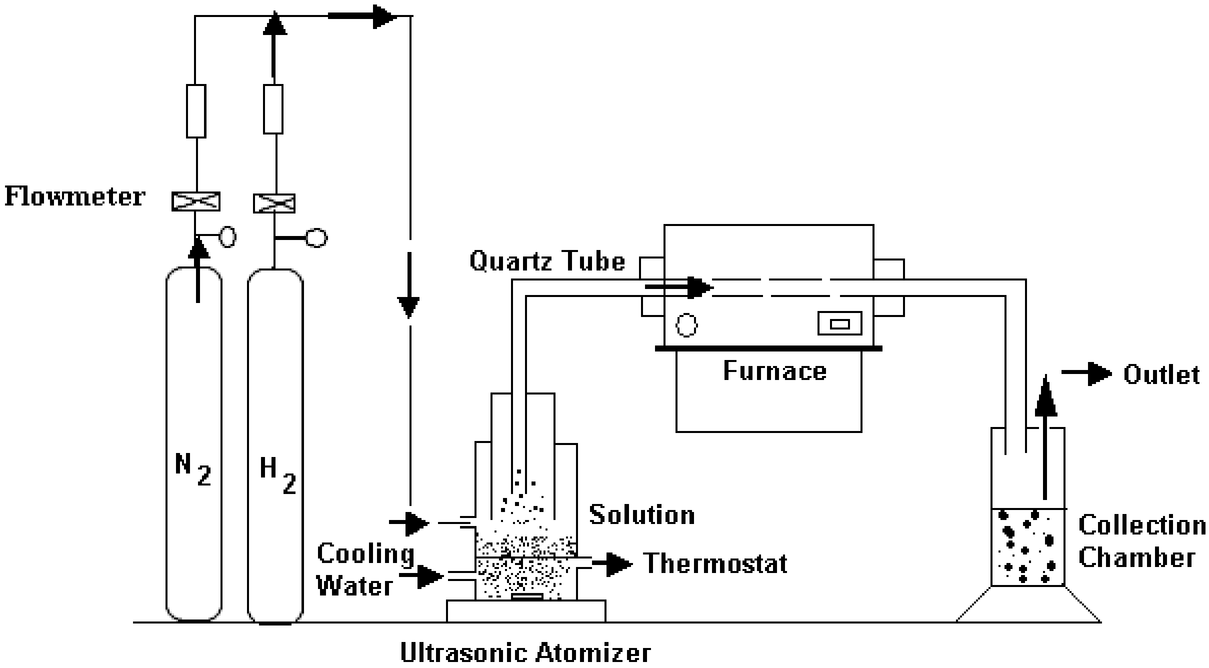

Fig. 1. Schematic drawing of experimental apparatus for the synthesis of cobalt nanoparticles .1.a Horizontal variant for the USP method

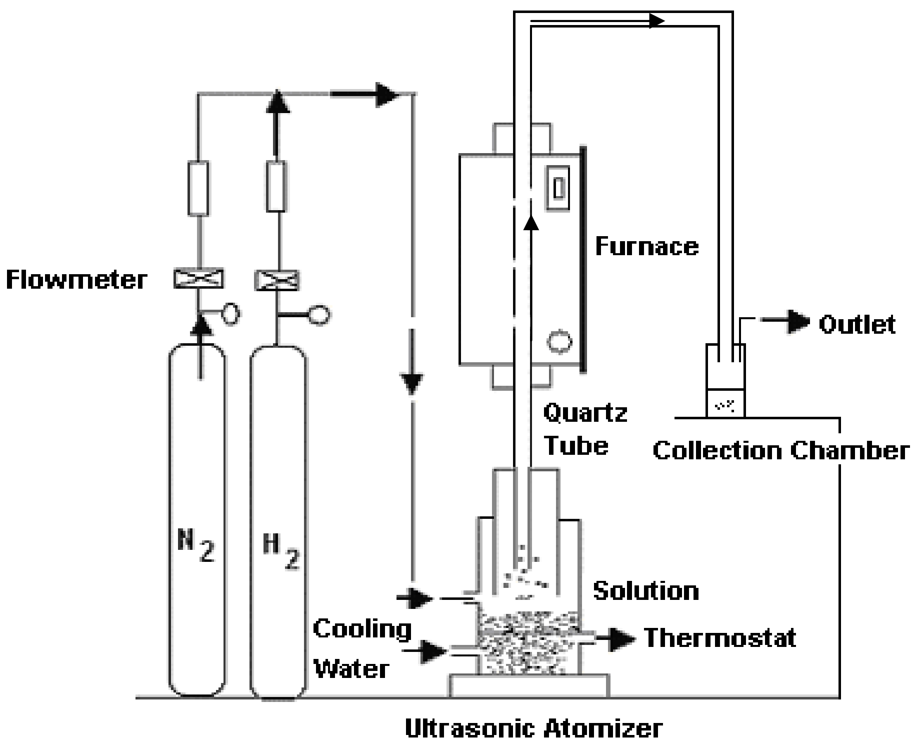

Fig. 1.b. Vertical variant for the USP method

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

Table 1. Composition of precursor solutions, conditions of the process, and descriptions of the obtained products

No	Concentration of $Co(NO_3)_2$ (mol/l)	Temperature (°C)	H_2-Flow (l/min)	Characteristic of the product
1 (a)	0.04 (Horizontal variant)	800	1	Spherical, nanostructured cobalt powder (reduction in H_2, 2 h)
2 (a)	0.08 (Horizontal variant)	800	1	Spherical, nanostructured cobalt powder (reduction in H_2, 2 h)
3 (b)	0.04 (Vertical variant)	800	1	Spherical, nanostructured cobalt powder (reduction in H_2, 2 h)
4 (b)	0.08 (Vertical variant)	800	1	Spherical, nanostructured cobalt powder (reduction in H_2, 2 h)

3. Results and discussion

3. 1. X-ray analysis of cobalt powder

Fig. 2 shows X-ray Diffraction (XRD) patterns of the cobalt powders from $Co(NO_3)_2$ solution in H_2 atmosphere at 800 °C by ultrasonic spray pyrolysis, indicated the pure typical cobalt powders.

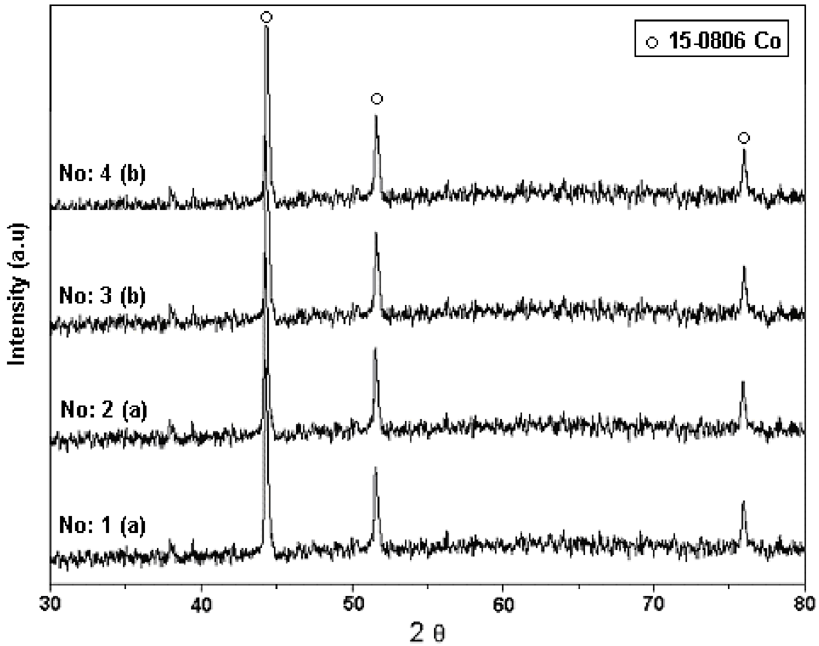

Fig. 2. Typical X-ray analysis of the cobalt powders (800 °C)

3.2. SEM Analysis of the obtained powders

Using the horizontal variant of USP method (Exp. 1a) the spherical nanosized particles of cobalt were obtained (Fig. 3).

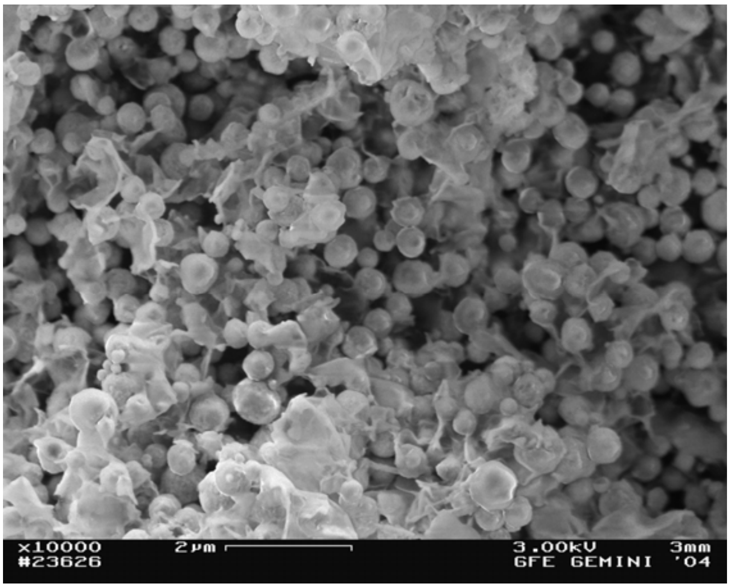

Fig. 3. Typical micrograph for the cobalt powders (Exp. 1.a)

Using the vertical variant of USP method (Exp. 1a) the spherical nanosized particles of cobalt were also obtained (Fig. 4).

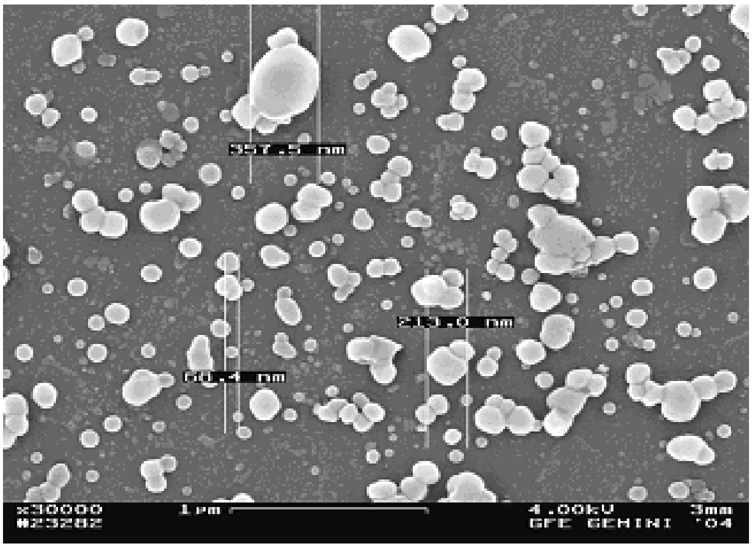

Fig. 4. Typical micrograph for the cobalt powders (Exp. 3.a)

In case of using of the vertical variant for USP Method the particles are smaller than in the case of ones obtained with horizontal variant.

Morphological characteristics of obtained powders from 0.08 mol/L of cobalt nitrate were presented in [10].

3.3. Morphological characteristics of obtained powders

The ultrasonic irradiation of a liquid above a certain excitation power threshold leads to the atomization of fine droplets forming a spray. Better insight into the influence of additives on particle size can be gained by a comparison of experimentally obtained and theoretically expected values for the mean particle diameter. The relationship between the mean diameter of aerosol droplets and the frequency of ultrasonic atomizer was studied by Peskin and Raco [11]. The existence of a correlation between the capillary wave lengths (λ_c) at the liquid surface and the mean diameter of the atomized droplets (D) is one of the fundamental principles of the ultrasonic atomization.

$$D=\alpha\ \lambda_c \qquad (1)$$

Where ‘α’ is a constant.

It was shown that the mean diameter of the aerosol droplets decreases with increase in the ultrasound frequency according to the relationship.

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

Where,

- D Mean droplet diameter
- γ The surface tension of the dilute solution
- ρ Density of the aqueous solution
- f Frequency of the ultrasound

Using the parameters of our experiments:

- γ= 75,9·10^{-3} Nm^{-1}
- ρ= 1,073 g cm^{-3}
- f= 800 KHz.

The calculated value of droplet diameter amounts D= 4,75 µm. Using this value for the droplet size we can also calculate the expected value of the mean particle diameter of the Co powder depending on the initial concentration of the Co $(NO_3)_2$ solution, assuming that each droplet is transformed into the particle and that during the atomization no coalescence occurs.

$$D_p= D(C_{Co\,(NO3)2} \cdot M_{Co}/\rho_{Co}\, M_{Co\,(NO3)2})^{1/3} \qquad (3)$$

Where,

- D_p particle diameter
- D droplet diameter
- $C_{Co(NO3)2}$ the concentration of the water solution of Co $(NO_3)_2$
- ρ_{Co} density of cobalt

Using the parameters of our experiments: D- 4,75 µm, $C_{Co(NO3)2}$ - 0.08 mol/l (14,58 g/l); $M_{Co(NO3)2}$ -182,93 g/mol; M_{Co}- 58,93 g/mol; ρ_{Co}- 8,89 g/mol the calculated particle diameter of cobalt amounts 384 nm. Under same conditions but for the concentration of cobalt nitrate $C_{Co(NO3)2}$- 0.04 mol/l (7,29 g/l) the calculated particle diameter of cobalt is 304 nm. Because of one decrease of concentration of the used solution the particle size was decreased.

The experimental obtained values of particle diameter for concentration of cobalt nitrate are in interval between 60.4 and 357.5 nm (Fig. 4). The value of 357.5 nm is closed to one calculated with the equation (3). Because of the coalescence of droplet before the reduction the particle size of cobalt is different. The new experiments and analysis will offer one reliable explanation this difference between experimental and theoretical values.

A careful comparison of precursor drop sizes to product particle sizes (Fig. 3 and 4) 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.

Mechanism of the formation of nanosized cobalt powders

The possible mechanism of the formation of cobalt powder was shown on Eq. 4.

$$Co(NO_3)_2 + 2\ H_2 = Co + 2\ NO_2 + 2H_2O \quad (4)$$

We suggest the mechanism of formation the nanosized cobalt powder from the droplet of 4,75 μm produced by ultrasonic atomizer during the next operations: 1. Evaporation of droplets with cobalt nitrate solution, 2. Reduction of cobalt nitrate with hydrogen and 3. Sintering of the obtained cobalt particles. The short residence time of droplet in furnace could cause that the above-mentioned steps are not completely finished. The consequence of this behaviour is one difference in particle size of obtained powders.

4. Conclusion

The ultrasonic spray pyrolysis (USP) is used for the synthesis of ideally fine, spherical, nanosized cobalt particles from the corresponding cobalt nitrate solution with the mean aerosol droplet size of around 4,75 μm. The nanosized cobalt powder was produced at 800°C in the hydrogen atmosphere from cobalt nitrate of concentration of 0.04 mol/l. The average particle size of cobalt powder decreases with decrease of the initial concentration of cobalt nitrate between 0.04 and 0.08 l/min. Hydrogen gas played a significant role in a pyrolysis reactor as carrier and reduction gas. The both variants (horizontal and vertical) of USP method are suitable for the production of nanosized particles. The proposed mechanism of formation of nanosized cobalt powder contains: 1. Evaporation of droplets with cobalt nitrate solution, 2. Reduction of cobalt nitrate with hydrogen and 3. Sintering of the obtained cobalt particles.

5. Acknowledgments

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6. References

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