Synthesis of particles of Ni- and Co- powders by ultrasonic spray of $NiCl_2$ and $Co(NO_3)_2$ and hydrogen reduction pyrolysis

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Abstract

Spherical, non-agglomerated nanosized particles of nickel and cobalt, suitable for direct application in e.g high technology sintered materials, were prepared by ultrasonic dispersion of corresponding salt solutions. The actual increase in the interest for nanometer metal powders with well defined characteristics is the consequence of the need for metallic materials with improved properties and better reliability. In the last decades it became obvious that the full control of synthesis parameters is essential to develop nanometer metal particles with novel functional properties leading to new applications. The ultrasonic spray pyrolysis method was used in this investigation as a useful tool for small-scale preparation of nanosized nickel and cobalt particles. 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 0.80 –2.50 MHz, acting on water solution of the metal salts (chloride and nitrate) forming aerosols with constant droplet sizes. This size depends on the characteristic of the solution and the frequency of the ultrasound. The subsequent thermal decomposition of the aerosol droplets was performed in hydrogen atmosphere between 800-1000°C. The choice of reaction parameters (frequency of ultrasonic atomizer, concentration of an initial solution, hydrogen-nitrogen ratio, flow rate and different additives) is very important for the synthesis of uniform spherical metal particles. The paper presents the ways to control this synthesis over the choice of the reaction parameters and compares the experimental results with a calculation of the average diameter of particles of Ni- and Co- powder.

1 Introduction

Submicron- and nanometer-sized metal particles have high potentials to improve 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 (USP) is an innovative and powerful tool for synthesis of particles with controlled particle size [1], because of the easy control of target composition, the excellent availability of cheap precursors, as well as the high and reproducible quality of the products. In the preparation of a powder by USP, a metal-containing solution is cold atomized forming an aerosol. This aerosol is transported by career and/or 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 product. Metals, metal oxides, and non-oxides as well as their compounds can be readily produced

by spray pyrolysis [2, 3]. Nanometer 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 [4]. 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. 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 [5].

The aim of this paper is to present investigations concerning the synthesis of nickel and cobalt powder by ultrasonic spray pyrolysis method jointly conducted at University of Serbia and at IME Process Metallurgy and Metal Recycling, RWTH Aachen University. The investigation explains the influence of the different parameter of synthesis (frequency of ultrasonic atomizer, concentration of initial solution, presence of additives, type of precursor) on the final powder characteristics (particle sizes, spheroidity and particle size distribution).

2. Thermochemical analysis of hydrogen reduction

The next reactions are considered:

$$NiCl_2 + H_2 = Ni + 2HCl \quad (1)$$

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

Thermodynamic analysis of hydrogen reduction of the investigated $NiCl_2$ and $Co(NO_3)_2$ is shown in Figure 1.

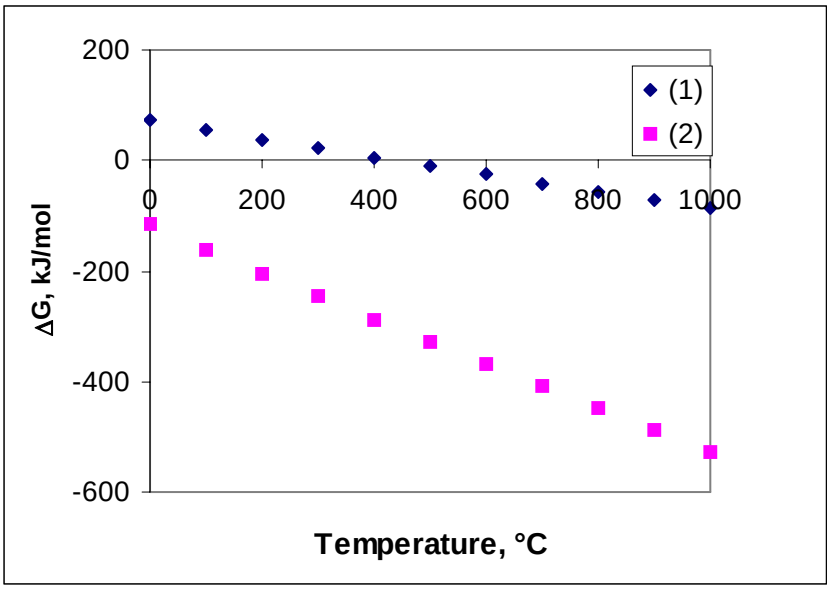

Figure 1. Thermodynamic analysis of hydrogen reduction of $NiCl_2$ and $Co(NO_3)_2$

The thermodynamic analysis showed that the both reactions of reduction are possible in planned temperature range between 800-1000°C.

3. Experimental

3.1. Synthesis of nickel powder by ultrasonic spray pyrolysis

3.1.1. Material and procedure

$NiCl_2 \cdot 6\ H_2O$ (Merck, Darmstadt, Germany) was used for preparation of nickel powders by reduction in an hydrogen- nitrogen atmosphere at 900 ^oC and 1000 °C by ultrasonic spray pyrolysis, using the apparatus shown in Figure 2.

Figure 2. Experimental apparatus for the USP-synthesis of Co/Ni-particles
(bottles with H_2 and N_2, flowmeter, thermostate, aerosol generator, quarz tube, tubular furnace, bottles for collection of powders)

$PdCl_2$ and $CuCl_2$ were particularly added in order to accelerate the hydrogen reduction of nickel chloride. After the addition of appropriate amount of this additive (0.1 mass % Pd or Cu) the aqueous solution was excited in an ultrasonic atomizer (GAPUSOL 9001, RBI, France) operating at a frequency of 2.5 MHz [6-7]. Very fine aerosol droplets were created and transported into in a quartz tube (1.0 m length and 0.02 m diameter), placed in a tube furnace. Nitrogen with a flow rate of 1.0 $dm^3\ min^{-1}$ was used as carrier gas, hydrogen with a flow rate of 3.0 $dm^3\ min^{-1}$ was used as reduction

gas. Assuming these flow rates the retention time of the aerosol droplets in the reaction zone amounts 5 s.

Table 1: Experimental conditions for preparation of Ni from aqueous solutions of $NiCl_2$

Exp.	Concentration of $NiCl_2$ (mol/l)	Temperature (°C)	Additives (mass %)	H_2: N_2- Ratio
1	0.5	900		0.33
2	0.5	1000		0.33
3	0.5	900	0.1 Pd	0.33
4	0.5	900	0.1 Cu	0.33
5	1.0	900		0.20
6	1.0	1000		0.20

A scanning electron microscope (SEM JEOL-5300) was used to study the size and shape of Ni particles. The powders were dispersed in ethanol and treated in an ultrasonic bath for half an hour. Stereological analysis of the powders was made by measuring surface area using a semiautomatic video analyser (VIDEOPLAN, Kontron) connected with the scanning electron microscope. For each sample, about 70-300 particles were examined.

Hydriding of Ni powders, prepared by ultrasonic spray pyrolysis, under nonisoterhmal conditions was studies by differential scanning calorimetry (Thermal Analyser 1090, Du Pont, Wilmington). The heating rate was 10°C/min.

X-ray analysis of the prepared Ni powders was made using a diffractometer (PW 1710, Philips, Eindhoven, Netherlands) with CuKα radiation and a graphic monohromator.

3.1.2. Results

3.1.2.1 X-ray analysis of Ni powders

X-ray analysis of nickel powders prepared at 900°C and 1000°C revealed the presence of $NiCl_2$ and $NiCl_2$x 2 H_2O phases, indicating an incomplete reduction of the starting material at these temperatures (Fig. 3a). Disappearance of precursor phases and appearance of crystalline Ni phase were observed on the addition of 0.1 mass % Pd and Cu (Fig. 3b). At 900°C with H_2-N_2 ratio of 0.2 and 0.33 from 0.5 and 1.0 mol solution of $NiCl_2$ does not happen the complete transformation into nickel because these experimental conditions did not give enough time for this reduction process. The formation of nickel is increased by increasing temperature up to 1000°C with H_2-N_2 ratio of 0.33, because the chloride ions are more strongly connected to the hydroxide ions. Hydrolysis is more complete and additional energy is needed to break this bond. The complete reduction from $NiCl_2$ into Ni took place in the presence of additives of Pd and Cu. The positive effect of Pd is a consequence of the dissociation and spillover of hydrogen. In case of copper it is manifested in a decrease in energy of the bonds in the nickel lattice, because of good Cu-solubility.

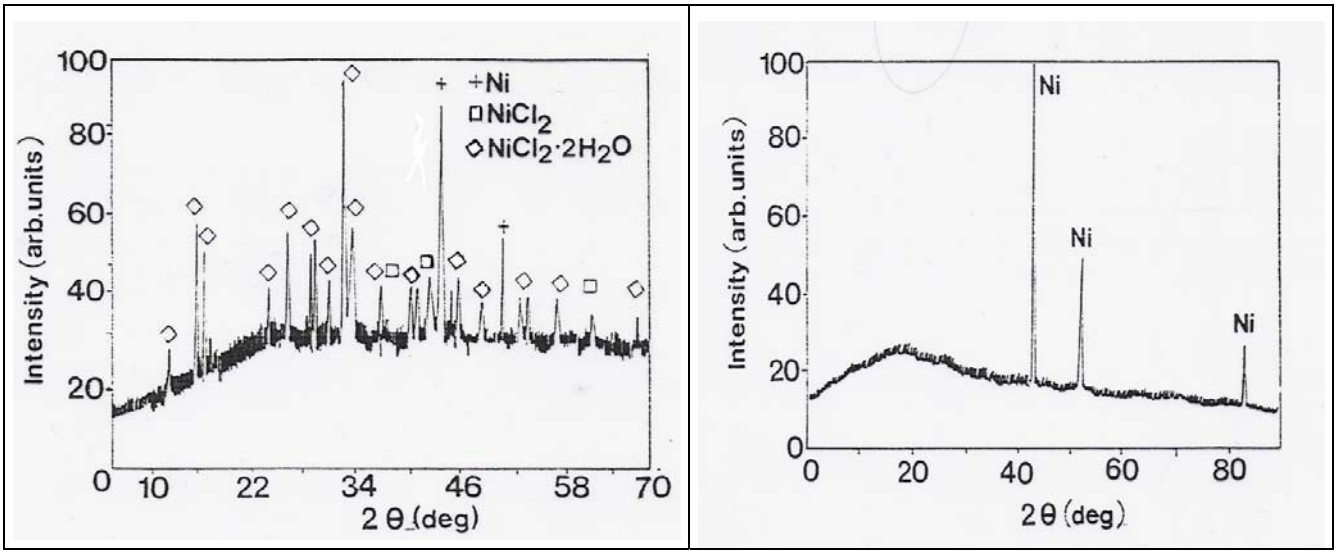

Fig. 3.a. Fig. 3b.

Figure 3. X-ray diffractograms of Ni powders prepared by ultrasonic spray pyrolysis: a) No additives (Exp. 1, 5, 6), b) with 0.1 mass % Pd and 0.1 mass % Cu added (Exp. 2, 3, 4)

3.1.2.2 Particle size of nickel powders

Fig. 4 shows SEM micrographs of the dehydrated $NiCl_2$ powder at 200°C and 60 min and nickel prepared by ultrasonic spray pyrolysis at 900 °C from 0.5 mol/l $NiCl_2$ without added Pd and Cu.

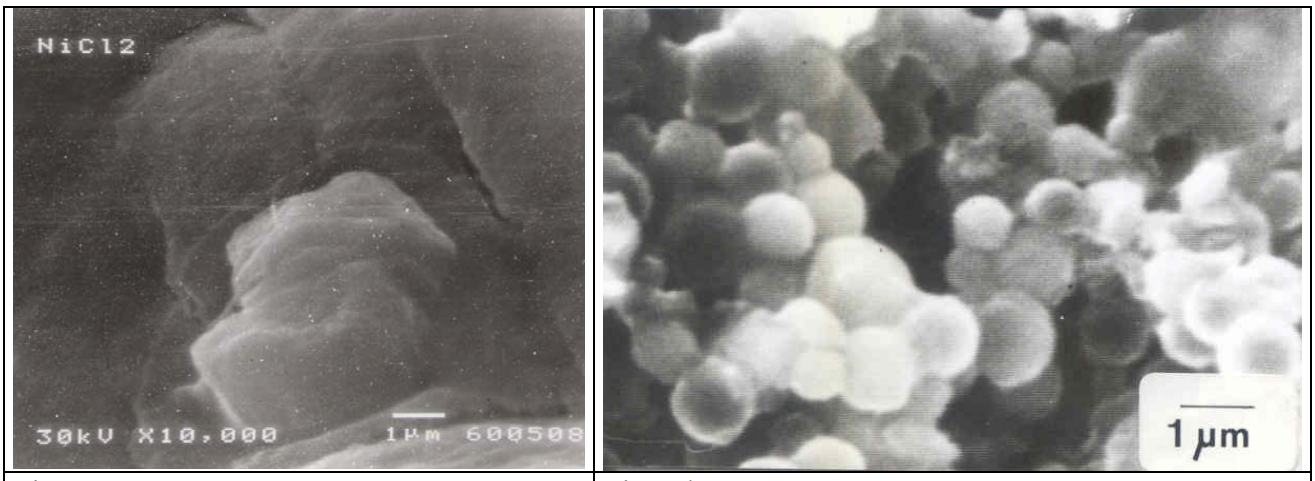

Fig. 4.a. Fig. 4.b.

Figure 4. SEM micrographs of: 4.a) of the dehydrated $NiCl_2$ powder and 4.b) Ni powder prepared by ultrasonic spray pyrolysis

The sample of $NiCl_2$ is composed of non-agglomerated particles of irregular shape. Ni powder in Fig. 4.b is characterized by agglomerated spherical Ni particles due to incomplete reduction leading to the presence of precursor phases. On the other hand ideal spherical non-agglomerated Ni particles were obtained by ultrasonic spray pyrolysis of $NiCl_2$ aqueous solution, if 0.1 mass percent of Pd and Cu was added. The presence of Pd catalysts/accelerates the reduction of $NiCl_2$ and formation of ideally spherical non-agglomerated Ni particle due to the hydrogen spillover effect [8] .

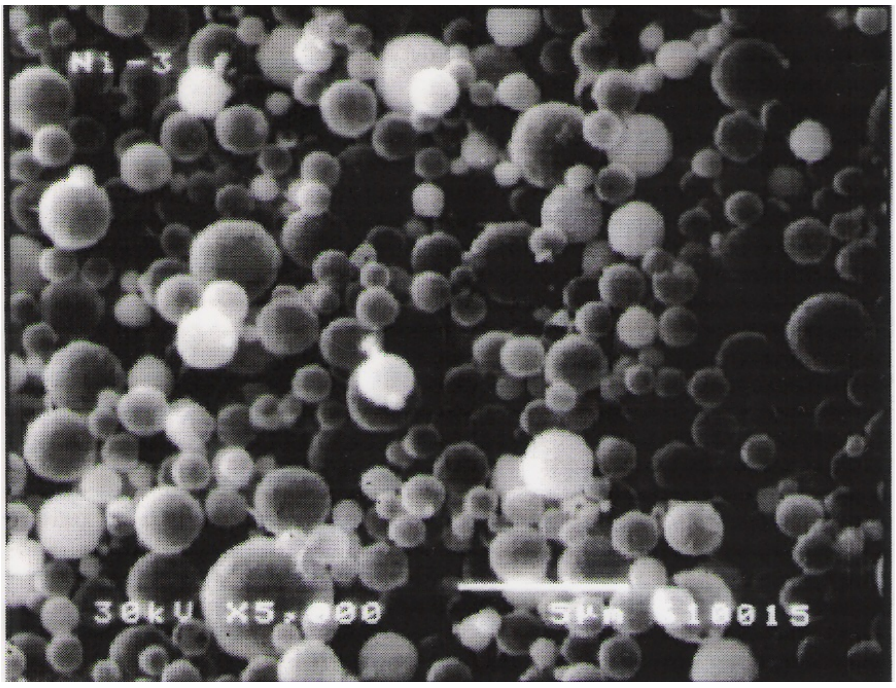

Figure 4.c. SEM micrograph of nickel particle prepared by ultrasonic spray pyrolysis in the presence of 0.1 mass % Pd added

It is known pure nickel belongs to a group of metals which are poor absorbents for hydrogen, but in the presence of Pd nickel can absorb hydrogen easily. The hydriding enthalpies of Ni (Pd-doted and Pd free) are ΔH= -8390 J/g resp. ΔH= -108 J/g) indicate the significant improvement of the hydrogen absorption properties in the presence of palladium [8].

3.1.2.3 Particle size of obtained Ni-powders

The ultrasonic irradiation of a liquid above a certain excitation power threshold leads to the atomization of fine droplets forming an aerosol spray. A better understanding of the influence of the atomisation parameters on the particle size can be gained by 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 earlier studied by Peskin and Raco [9]. The existence of a correlation (Eq. 3) between the capillary wave length (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.

$$D = \alpha \lambda_c \tag{3}$$

'α' is a constant, determined by Peskin´s formula (4) show that the mean diameter of the aerosol droplets decreases by a 2/3 root rule with increase of the ultrasound frequency:

$$D= 0.34 \cdot (8 \cdot \pi \cdot \gamma / \rho \cdot f^2)^{1/3} \tag{4}$$

Where D is the mean droplet diameter, γ is the surface tension of the dilute solution, ρ is the density of the aqueous solution and f is the frequency of the ultrasound. Using the parameters of our experiments (assuming that characteristics of water are closed ones of water solution of nickel chloride)

- $\gamma = 72.9 \cdot 10^{-3}$ Nm^{-1}
- $\rho = 1.0$ g cm^{-3}
- f= 2.5 MHz.

the calculated value of the ultrasonically dispersed droplet diameter amounts to D= 2.26 μm. The change of aerosol droplet is function of an operating frequency of ultrasonic generator.

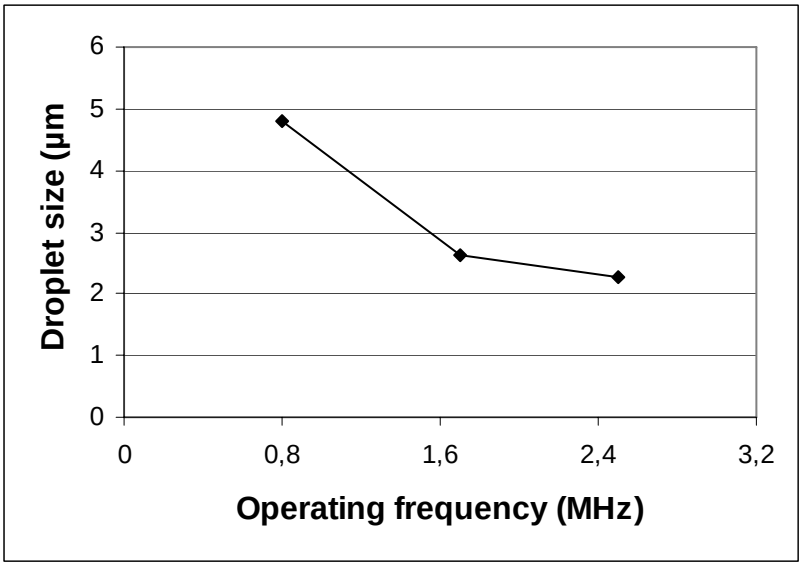

Figure 5. Dependence of aerosol droplet size by the operating frequency

The increase of the operating frequency decreases the aerosol droplet size. Using this value of 2.26 μm for the droplet size the expected value of the mean particle diameter of the finally obtained Ni powder can be calculated. Depending on the initial concentration of the $NiCl_2$ solution, assuming that each droplet is transformed into a particle and that during the atomization no coalescence occurs, the final particle diameter can be calculated using formula (5):

$$D_p = D(C_{NiCl2} \cdot M_{Ni} / \rho_{Ni} M_{NiCl2})^{1/3} \quad (5)$$

Where D_p is the mean particle diameter, D is the mean droplet diameter, C_{NiCl2} is the $NiCl_2$-concentration of the water solution of and ρ_{Ni} is the density of nickel.

Using the parameters of our experiments: D- 2.26 μm, C_{NiCl2}- 0.5 and 1.0 mol/l; M_{NiCl2}-129.62 g/mol; M_{Ni}- 58.74 g/mol; ρ_{Ni}- 8.90 g/cm^3 the calculated mean particle diameter of nickel amounts between 550 and 680 nm. The experimentally obtained values of the mean nickel particle diameter amounted to about 1000 nm (see picture 4.c). Particle size decreases with diminution in the initial concentration of the solution as the results of the reaction in a smaller volume. The spherical factor is 0.997-0.998 which is near to the ideal sphere. Differences 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 (turbulance effects).

3.2. Synthesis of cobalt powder by ultrasonic spray pyrolysis

3.2.1. Materials

A purified leach solution from Co-extraction experiments treating cemented carbide scrap [10] using nitric acid leaching used as the starting material for this research. The final concentration of cobalt amounted 0.08 mol Co/l.

3.2.2. Experimental procedure

The equipment for powder synthesis is shown in Figure 2. The apparatus consists of an aerosol generator, a reaction furnace with a quartz tube (0.67 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 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 0.8 MHz. For cobalt powder preparation H_2 atmosphere is only 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.

3.2.3. X-ray analysis of cobalt powder

Fig. 6 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.

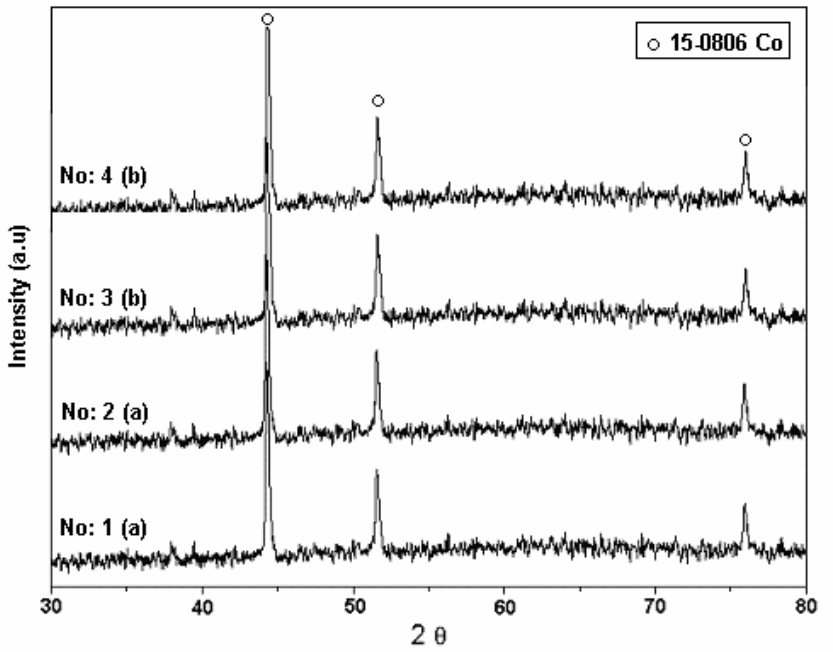

Fig. 6. Typical X-ray analysis of the prepared cobalt powders (800 °C)

3.2.4 Particle size of obtained Co-powders

Using the parameters of our experiments concerning the measured characteristics of water solution of $Co(NO_3)_2$:

- $\gamma = 75.9 \cdot 10^{-3}$ Nm^{-1}
- $\rho = 1.073$ g cm^{-3}
- f= 800 KHz.

The calculated value of aerosol droplet diameter amounts D= 4.75 μm. Using this value in Eq. 6 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.

$$D_p = D(C_{Co\,(NO3)2} \cdot M_{Co}/\rho_{Co}\, M_{Co\,(NO3)2})^{1/3} \quad (6)$$

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; $M_{Co(NO3)2}$ -182.93 g/mol; M_{Co}- 58.93 g/mol; ρ_{Co}- 8.86 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 the calculated particle diameter of cobalt is 304 nm. Because of one decrease of concentration of the used solution the particle size was decreased (Fig. 7).

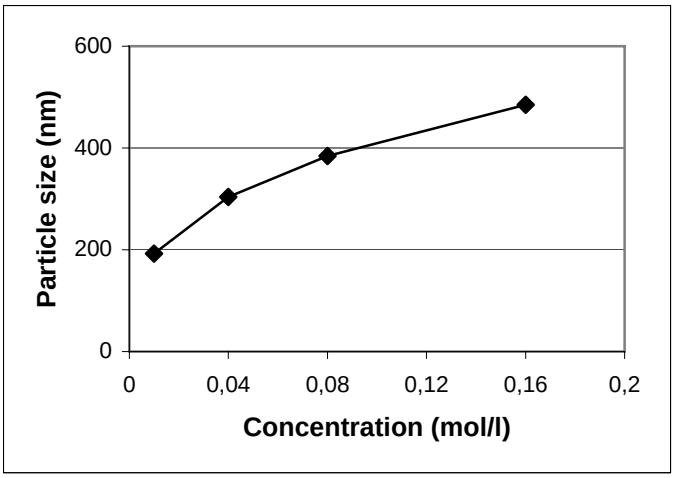

Fig. 7. Calculated values of particle size of cobalt

The obtained particles of cobalt are spherical and non-aglomerated (Fig. 8a. and 8.b.)

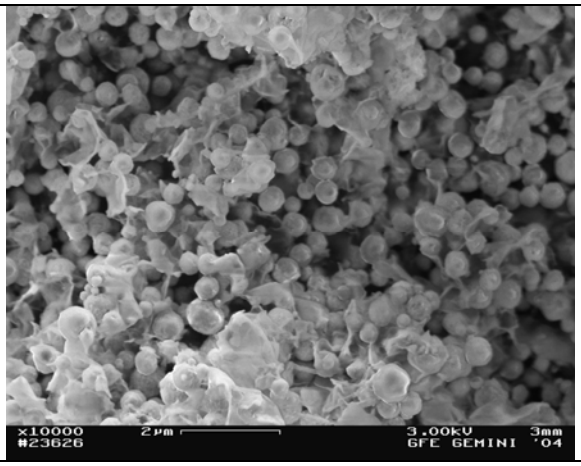

Fig. 8.a. SEM micrograph of Co-powder (T=800°C, $c_{Co(NO3)2}$= 0.04 mol/l)

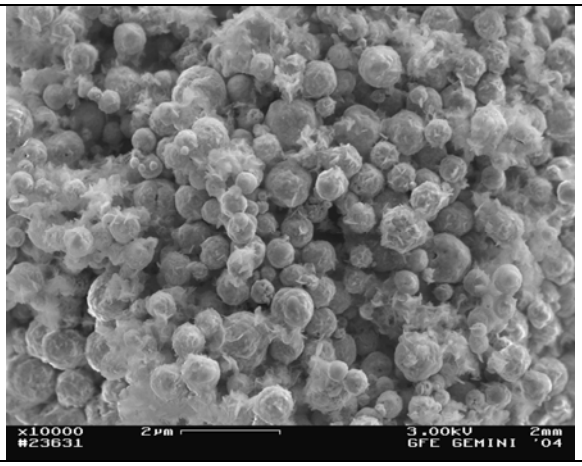

Fig. 8.b. SEM micrograph of Co-powder (T=800°C, $c_{Co(NO3)2}$= 0.08 mol/l)

The stereological analysis of the obtained powders (Fig. 9a. and 9.b) ensures the results for the comparison to the calculated particle size of Co-powders (Fig. 8.a and 8.b)

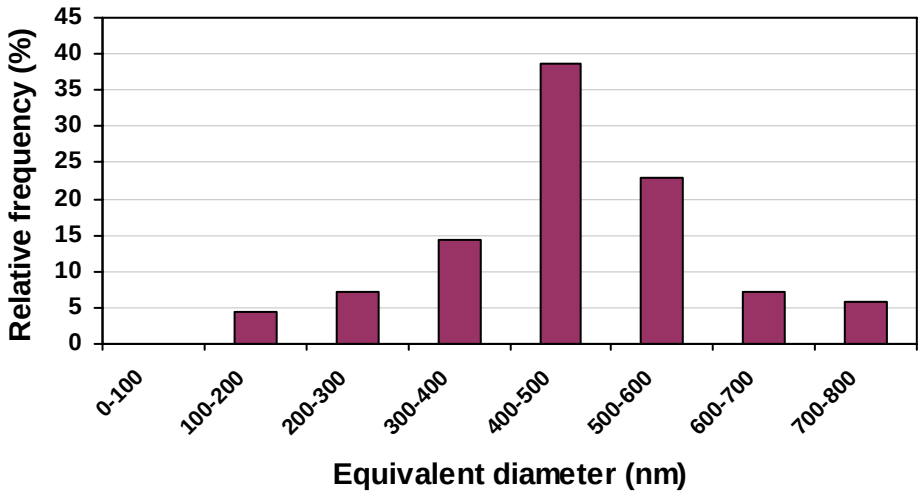

Fig. 9.a. Stereological analysis of Co-Powder prepared by ultrasonic spray pyrolysis (see Fig. 8.a)

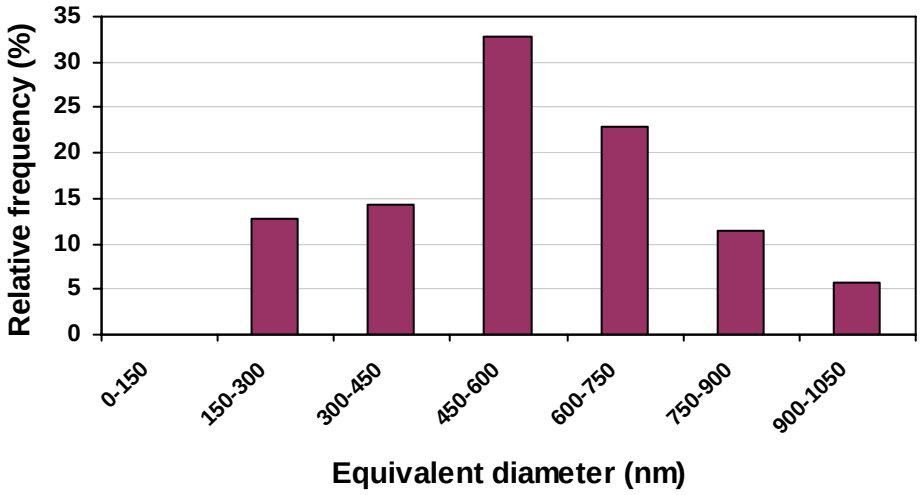

Fig. 9.b. Stereological analysis of Co-Powder prepared by ultrasonic spray pyrolysis (see Fig. 8.b)

Comparative analysis of theoretically expected particle diameter of cobalt and experimentally obtained values was shown in Table 2.

Table 2: Experimental and theoretical diameters of Co-Powders

Diameter (nm)	Experimentally obtained values			Calculated values
	max	min	mean	mean
Exp. (T=800°C; c $Co(NO_3)_2$ =0.04 mol/l	766	144	480	304 nm
Exp. (T=800°C; c $Co(NO_3)_2$ =0.08 mol/l	1000	158	596	384 nm

Decrease of concentration of an initial solution of $Co(NO_3)_2$ from 0.08 mol/l to 0.04 mol/l decreases the mean particle size of obtained powder of Co from 596 nm to 480 nm. The calculated values are

in relative agreement with the experimentally obtained ones. Differences may be also due to coalescence of aerosol droplets at a high flow rate for the carrier gas.

4.Conclusions

The ultrasonic spray pyrolysis (USP) is successfully used for the synthesis of ideally fine, spherical, uniform nanosized nickel and cobalt particles from the corresponding nickel chloride and cobalt nitrate solution. Powder particles were prepared from aerosol droplets. The investigation regarding the influence of reaction parameters on the reduction of initial solution showed:

- Increase of the working frequency of an ultrasonic generator from 0.80 MHz up to 2.5 MHz decreases the aerosol droplet sizes from 4.75 μm to 2.26 μm
- Decrease of concentration of an initial solution of $NiCl_2$ from 1.0 mol/l to 0.5 mol/l decreases the final particle size of obtained Ni-powder from 680 nm to 550 nm
- Using pure hydrogen instead of the mixture of hydrogen and nitrogen leads more easy to the complete reduction of initial solution, even at 800°C in case of cobalt
- The presence of Pd accelerates the reduction of $NiCl_2$ and the formation of ideally spherical particles
- Decrease of concentration of an initial solution of $Co(NO_3)_2$ from 0.08 mol/l to 0.04 mol/l decreases the mean particle size of obtained powder of Co from 596 nm to 480 nm
- Nickel chloride and cobalt nitrate precursors were successfully used for the synthesis of nanosized nickel and cobalt powder in hydrogen atmosphere

5. Acknowledgments

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6. References

[1] TSAI, S. C., SONG, Y. L., TSAI, C. S., YANG. C., CHIU, W. Y., LIN, H. M. (2004), Ultrasonic spray pyrolysis for nanoparticles synthesis, Journal of materials science 39, 3647-3657.

[2] STRIEMER, C.C, KRISHNAN, R., B., FAUCHET, P.M (2004): The development of nanocrystalline silicon for emerging microelectronic and nanoelectronic applications, JOM 8, 20-25.

[3] STOPIĆ, S., NEDELJKOVIĆ, J., RAKOČEVIĆ, Z., AND USKOKOVIĆ, D. (1999): Influence of additives on the properties of spherical Ni particles obtained by ultrasonic spray pyrolysis, Journal of Materials Research 14, 3059-3065.

[4] SRIVASTAVA and BANERJE, K. (2004): Interconnect challenges for nanoscale electronic circuits, Journal of Metals 8, 30-31.

[5] JANG, D. H., HWANG, W.D, ET al, (2004): Preparation of cobalt nanoparticles by hydrogen reduction of cobalt chloride in the gas phase, Materials Research Bulletin 39, 63-70.

[6] STOPIĆ, S., (1997): Kinetics and Mechanism of the Reduction Process from an Aqueous Nickel-chloride Solution, Ph Thesis, Faculty of Technology and Metallurgy, Belgrade, 148.

[7] STOPIĆ, S., ILIĆ, I., USKOKOVIĆ, D. (1995): Structural and morphological transformations during NiO and Ni particles generations from chloride precursor by ultrasonic spray pyrolysis. Materials Letters 24, 369.

[8] STOPIĆ, S., ILIĆ, I., NEDELJKOVIĆ, J., RAKOČEVIĆ, Z., ŠUŠIĆ, M., USKOKOVIĆ, D. (1997): Influence of hydrogen spillover effect on the properties of submicrometer Ni-powder obtained by ultrasonic spray pyrolysis, Studies in Surface Science and Catalysis 112, 103-110.

[9] PESKIN, R. L., RACO, R. J. (1963): Ultrasonic atomization of liquids, J. Acoust. Soc. Am. 35, 1378-1379.

[10] GÜRMEN, S., STOPIC, S., FRIEDRICH, B., (2004): Recovery of cobalt powder and WC from cemented carbide srap-Part II, Erzmetall-World of metallurgy 57 (6), 341-346.