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A comparative study on the influence of heating modes on the properties of cobalt and nickel nanopowders produced by the chemical-metallurgy method

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The effect of heating modes on the properties of Co and Ni nanopowders obtained by the chemical-metallurgy method was compared. It was shown that all established heating modes (isothermal, non-isothermal and mixed) ensure the production of Co and Ni nanopowders with an average size of less than 100 nm, while the mixed regime makes it possible to obtain reduction products with the best characteristics in terms of dispersion and morphology.

Keywords: *cobalt, nickel, nanopowder, nanoparticle, chemical-metallurgy method, heating modes.*

Introduction. At present, materials based on Co and Ni, in particular nanomaterials based on them, have found an increasing practical application in various fields of science, technology and industry. Co nanopowders (NP) can be used to obtain magnetically hard, superhard, heat-resistant, tool and wear-resistant alloys, which are used in mechanical engineering, especially in aviation and space technology, electrical and nuclear industries [1–7]. On the other hand, Ni nanopowders are primarily used to create new-generation magnetic materials, to obtain highly efficient catalysts and adsorbents, as multifunctional additives and additives to various oils, lubricants, paints and composite materials (conductive rubbers, polymers, adhesives, etc.); in the electronic industry, Ni NP are used in the manufacture of capacitors, high-efficiency electrodes, etc. [1, 8–12].

At present, the production and application of Co and Ni NP with desired properties, which are determined primarily by the morphology and fineness of particles, are of particular scientific and practical interest [5, 12]. The production of Co and Ni NP is carried out in various ways, most of which are characterized by a number of disadvantages, such as reduced productivity, high energy costs, and a negative impact on the environment [13]. The chemical-metallurgy method, which includes the stages of chemical precipitation of oxygen-containing metal compounds and hydrogen reduction of the resulting compounds, is an environmentally friendly and highly efficient method in terms of energy savings, the ability

to control the dimensional and morphology characteristics of the formed metal nanoparticles (NPs) during their production [13, 14].

A big disadvantage of the chemical-metallurgy method for obtaining metal NP is low productivity due to the low rate of hydrogen reduction processes under the condition of holding at low temperatures [13, 15]. Nevertheless, carrying out the reduction stage at elevated temperatures very sensitively has a significant effect on the quality of the formed nanomaterials (NM).

The authors in [16, 17] also obtained NP of the Fe, Co, Ni groups, however, they used other methods for the synthesis of NP, such as plasma-chemical synthesis, IR-pyrolysis, chemical dispersion, and hydrogen reduction, and studied only the effect of the method of preparation, crystallization patterns, in while no research has been carried out to study the effect of heating modes on the efficiency, as well as the properties of the metal NP.

Thus, the study and establishment of the optimal time-temperature and the establishment of the optimal time-temperature regimes of the hydrogen reduction process while guaranteeing the necessary properties of the obtained NM is a scientific and practical task.

The purpose of this work is to study the effect of temperature regimes of hydrogen reduction processes on the properties of Co and Ni NP obtained by the chemical-metallurgy method.

Materials and methods. $Co(OH)_2$ and $Ni(OH)_2$ NP, previously synthesized by chemical precipitation from aqueous solutions of oxygen-containing compounds of cobalt and nickel nitrate (10 wt. %) and NaOH alkali (10 wt. %) at room temperature, pH = 9, under continuous stirring. Precipitation of hydroxide compounds was carried out according to the reactions:

$$Co(NO_3)_2 + 2NaOH = Co(OH)_2\downarrow + 2NaNO_3 \quad (1)$$

$$Ni(NO_3)_2 + 2NaOH = Ni(OH)_2\downarrow + 2NaNO_3 \quad (2)$$

The acidity pH of the solution mixture was recorded using a “Mettler Toledo MP 230” pH meter (Switzerland), the accuracy of which is 0.03. The deposition temperature was controlled using a “Lauda E 300” thermostat (Germany).

The synthesized precipitates of $Co(OH)_2$ and $Ni(OH)_2$ were washed with distilled water using a “Buchner funnel” (Germany). Complete purification of the precipitate from nitrate salt ions was achieved when the pH value of the water above the precipitate was 7. After that, the resulting precipitates were dried at 40 ± 5 °C for 48 h.

The dried hydroxides were ground in a “Fritsch Pulverisette 2” mortar mill (Germany) and then subjected to thermogravimetric analysis (TGA) using an SDT Q600 thermal analyzer (USA).

The process of obtaining metal NP from hydroxides by hydrogen reduction was carried out in three modes: in non-isothermal (I^{st}), isothermal condition (II^{nd}) and mixed mode (III^{rd}), combining non-isothermal and isothermal conditions. The chemical reactions occurring in hydrogen reduction processes were as follows:

$$Co(OH)_2 + H_2 = Co + 2H_2O \quad (3)$$

$$Ni(OH)_2 + H_2 = Ni + 2H_2O \quad (4)$$

Analysis of the crystal structure and composition of powder samples was carried out by X-ray phase analysis using a "Difrey-401" diffractometer (Russia) using CrKα radiation.

The specific surface area S_a (m^2/g) of the samples was measured by the BET method (measurement accuracy is ± 5 %) using low-temperature nitrogen adsorption utilizing a "NOVA 1200e" analyzer (USA). The average particle size of powders D_{BET} (nm) was determined from the measurement data of the specific surface area S_a according to the expression

$$D_{BET} = \frac{6}{\rho \cdot S_a}, \quad (5)$$

where, ρ is the pycnometric density of the material, g/m^3.

The size and morphology of the metal NPs were studied by the SEM method using a "Tescan Vega 3" device (Czech Republic).

Results and discussion. Figure 1 shows thermogravimetric (TG) curves obtained by the TGA method under non-isothermal conditions (linear heating). The result of the TG curves analysis shows that both processes of reduction of $Co(OH)_2$ and $Ni(OH)_2$ NP pass through two stages corresponding to two peaks on the specific reduction rate curves. The 1^{st} stage is the processes of thermal decomposition of $Co(OH)_2$ and $Ni(OH)_2$ into CoO and NiO oxides, respectively. At the 2^{nd} stage, the processes of reduction of CoO and NiO oxides to metal phases proceed.

The study of TG curves makes it possible to determine the temperatures for carrying out the reduction processes of $Co(OH)_2$ and $Ni(OH)_2$ NP in the hydrogen flow. As shown in the TG curves, the temperatures of the maximum hydrogen reduction rate are 280 ± 5 °C and 285 ± 5 °C for $Co(OH)_2$ and $Ni(OH)_2$, respectively. These temperatures fully correspond to the established temperature ranges for the reduction of Co and Ni NP, which was shown in [6, 12, 16].

For a comprehensive and varied study, experiments were carried out to obtain Co and Ni NP by hydrogen reduction of their hydroxide compounds at three different heating modes. The scheme of the experiments is shown on fig. 2.

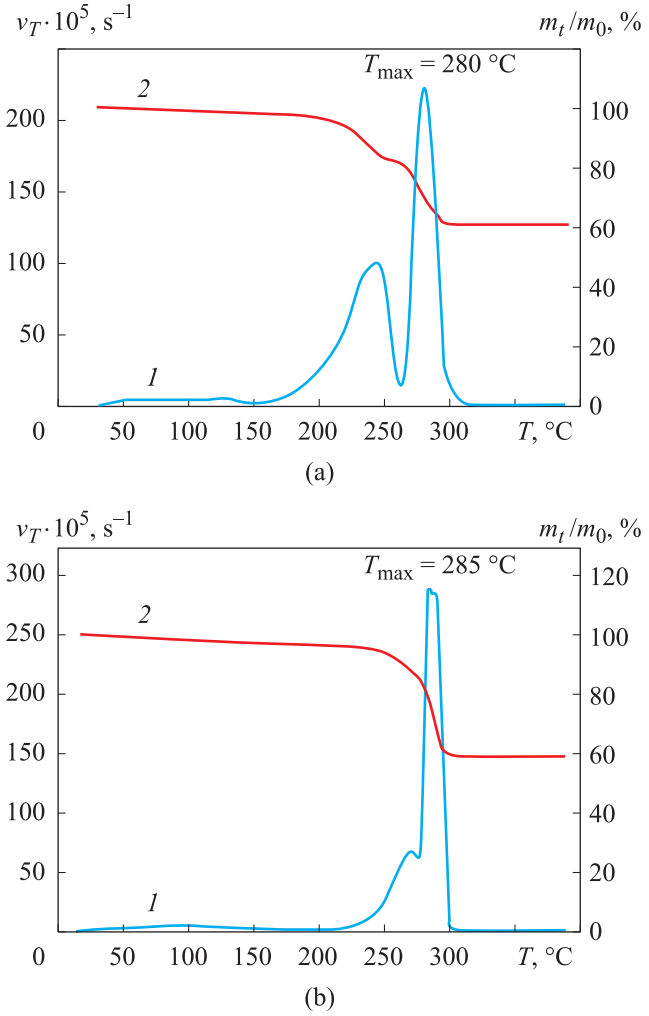

Figure 1. Thermogravimetric curves of hydrogen reduction processes of $Co(OH)_2$ (a) and $Ni(OH)_2$ (b) NP: *1* — specific speed, s^{-1}; *2* — total weight loss, %

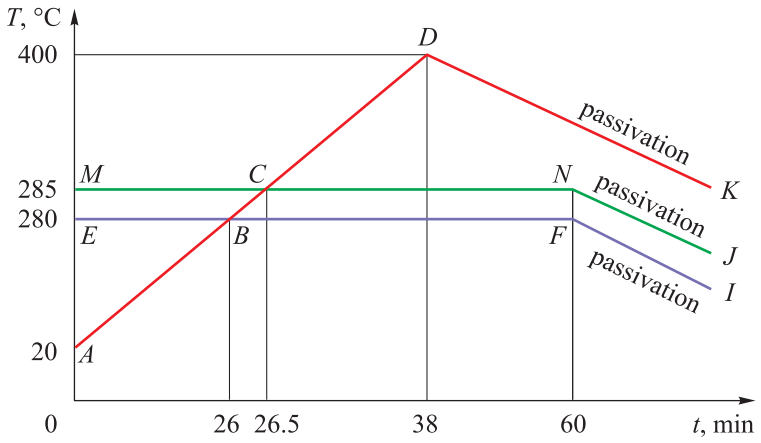

Figure 2. Scheme of experiments for obtaining Co and Ni NP at different heating modes

The Ist mode corresponds to the process of reduction in a non-isothermal condition (line *ABCD*) with linear heating at a rate of 0.167 K/s in the temperature range 20…400 °C for both cases of reduction of cobalt and nickel hydroxides. The IInd mode corresponds to the reduction process under isothermal conditions (lines *EBF* and *MCN* for the cases of reduction of $Co(OH)_2$ and $Ni(OH)_2$ NP, respectively). The IIIrd mode is mixed, combining non-isothermal and isothermal conditions (lines *ABF* in the case of reduction of $Co(OH)_2$ and *ACN* in the case of reduction of $Ni(OH)_2$, respectively).

At the end of the reduction processes, in order to prevent the resulting metal NP from igniting in air, their surfaces were passivated in a stream of nitrogen supplied from a liquid nitrogen balloon (lines *DK*, *NJ*, and *FI*) for 12 h.

For the obtained Co and Ni NP, the structures, sizes, and shapes were studied. The result of X-ray phase analysis of the reduction products (fig. 3) revealed that the samples under study are single-phase, consisting only of particles of metallic cobalt (with an *hcp* crystal lattice) and nickel (with an *fcc* crystal lattice).

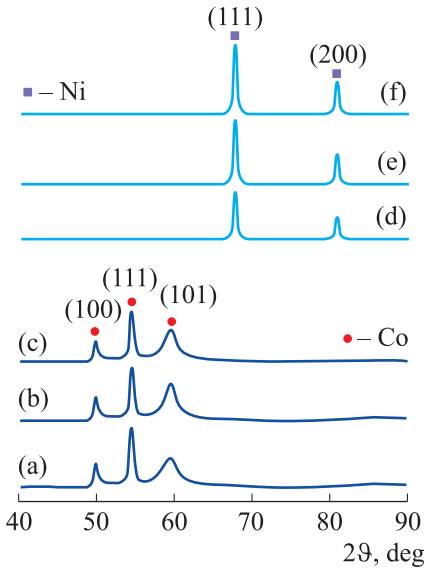

Figure 3. X-ray patterns of cobalt (a, b, c) and nickel (d, e, f) hydroxides reduction products at different heating modes: Ist mode (a, d); IInd mode (b, e); IIIrd mode (c, f)

The results of measuring the specific surface area S_a and studying the morphology and fineness of the obtained metal NPs are shown in fig. 4 and in table 1. In this case, the calculation of the sizes of Co and Ni NPs is carried out both from the measurement data of the S_a and from the analysis of SEM images.

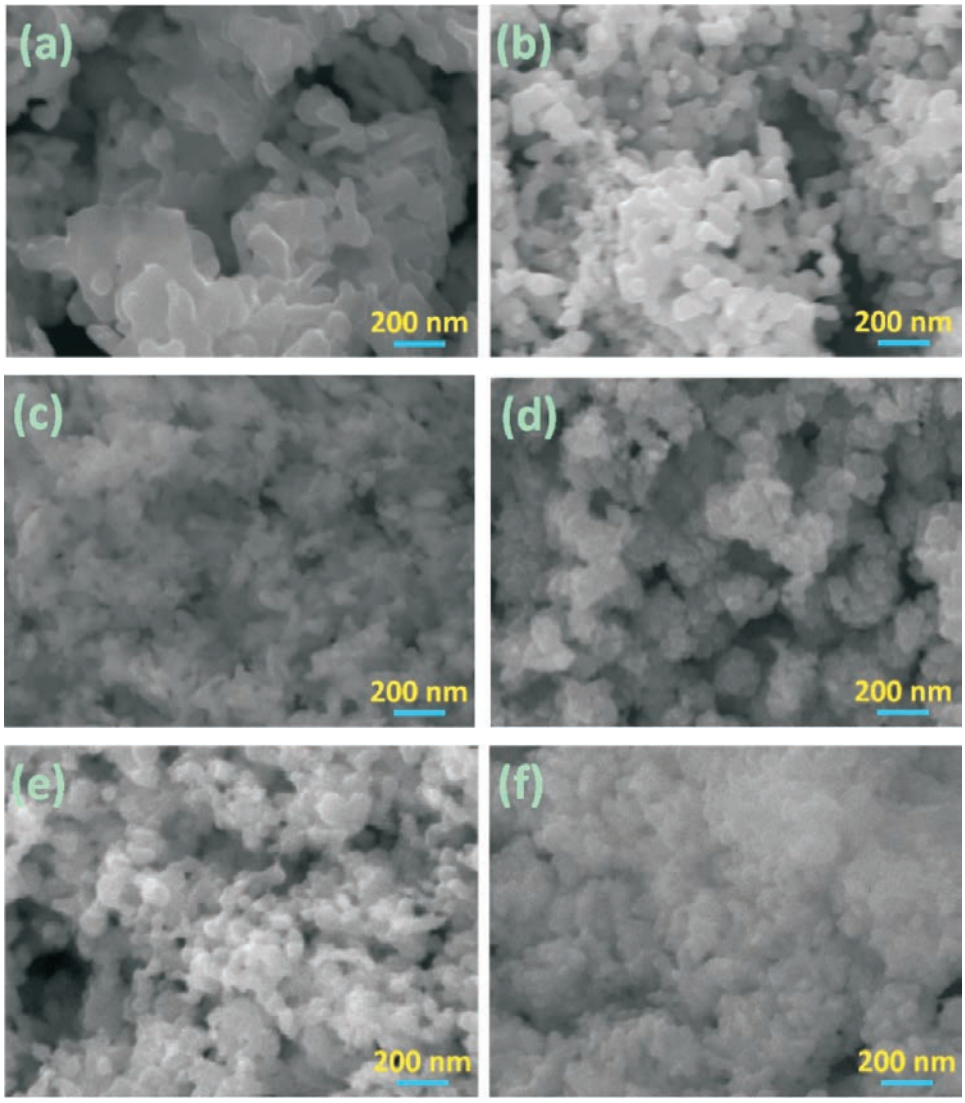

Figure 4. SEM images of the products of hydrogen reduction of cobalt (a, b, c) and nickel (d, e, f) hydroxides at different heating modes: Ist mode (a, d); IInd mode (b, e); IIIrd mode (c, f)

Table 1

The result of measuring the specific surface area S_a of obtained Co and Ni NP

Nanopowders	Heating modes (fig. 2)	S_a, m^2/g
Co	Ist (*ABCD* line)	11.6 ± 0.6
	IInd (*EBF* line)	9.8 ± 0.5
	IIIrd (*ABF* line)	17.3 ± 0.9
Ni	Ist (*ABCD* line)	13.6 ± 0.7
	IInd (*MCN* line)	8.3 ± 0.4
	IIIrd (*ACN* line)	18.5 ± 0.9

Analysis of SEM images (see fig. 4) of the reduction products shows that the obtained of Co and Ni NPs are mainly spherical with a size of less than 100 nm. Co and Ni NPs are mainly in the sintered state, each of which is connected to neighboring particles by connecting necks.

Comparison of the heating modes in the preparation of Co and Ni NP by hydrogen reduction revealed that the mixed regime (IIIrd mode) provides a condition for obtaining high-quality Co and Ni NPs with the smallest average size while maintaining a good round shape.

When using both the Ist and IInd heating modes, in both cases, the resulting Co and Ni NP agglomerate into small aggregates consisting of several tens of interconnected NPs. This can be explained by the fact that in both of these heating modes, raising the temperature to high (up to 400 °C) in Ist non-isothermal mode and maintaining the reduction process at an elevated temperature from the very beginning in IInd isothermal mode creates an advantageous time-temperature condition for intensification the process of agglomeration and sintering of formed metal NPs. At that time, in mixed heating IIIrd mode, the reduction temperature rises from room temperature to the value of the maximum process rate, and then a relatively short exposure to reduction at this temperature makes it possible to significantly eliminate the aggregation and sintering of NPs compared to the cases of reduction at Ist and IInd heating modes.

Figure 5 shows the result of calculating the average size of Co and Ni NPs (according to measurements of the S_a and analysis of SEM images) depending on the technology modes of reduction.

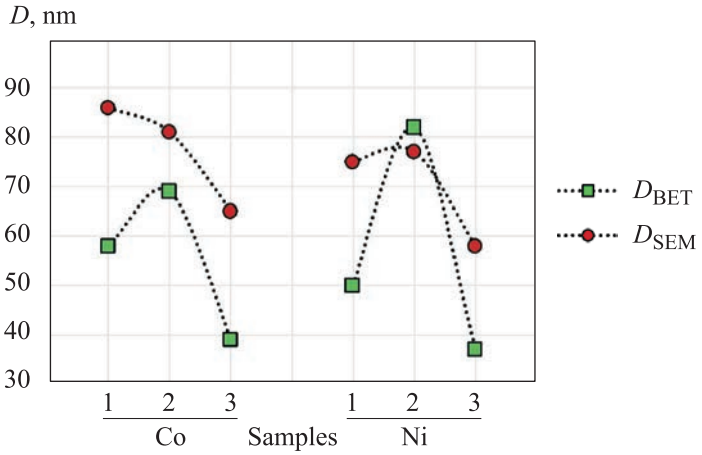

Figure 5. Average sizes of Co and Ni NPs calculated by the BET method and SEM images

The result of calculating the value of the average particle size of Co and Ni NP according to the value of S_a is in good agreement with the result of the analysis of dispersity by SEM images. It is shown that the

IIIrd mode provides a condition for obtaining metal NPs with a higher dispersity compared to the case of reduction at the Ist and IInd heating modes.

Thus, the mixed heating mode is the most rational way of hydrogen reduction, which provides the condition for obtaining Co and Ni NPs with high quality in terms of morphology and dispersion.

Conclusion. Three different heating modes for the reduction of $Co(OH)_2$ and $Ni(OH)_2$ nanopowders have been established and carried out: non-isothermal, isothermal, and mixed.

It was revealed that all three technology modes allow obtaining Co and Ni nanoparticles smaller than 100 nm in size with a spherical shape. In this case, the mixed mode provides the most desirable condition for obtaining nanoparticles with the best quality in terms of dispersion and morphology.

It was shown that Co and Ni nanoparticles were mainly in the sintered state, each of which was connected to neighboring particles by connecting necks.

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