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Research article
Научная статья

Production of nickel and cobalt metal powders under autoclave conditions

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Abstract: This paper presents the results of studies on the reduction of dispersed cobalt and nickel metal powders from their salts in ammonia-alkaline aqueous solutions under hydrothermal autoclave conditions. A unified and environmentally friendly method for producing these powders has been developed. Hydrazine hydrate, with a 25–50 % excess of the stoichiometric ratio, was used as a reducing agent. This choice allows for obtaining metal phases that are chemically uncontaminated by decomposition products. The experiments determined the conditions for the quantitative reduction of cobalt (II) and nickel (II) ions from ammonia-alkaline aqueous solutions. The synthesis temperature for the dispersed phases ranged from 110 to 155 °C. It has been demonstrated that under the conditions used, the process is completed quantitatively within 60 min. Metal concentrations in the solutions were determined using atomic absorption spectroscopy. The results of the *X*-ray phase analysis confirm that cobalt forms in the HCP lattice, while nickel forms in the FCC lattice. No other phases, including *X*-ray amorphous phases, were observed. It was found that with an increase in the hydrothermal synthesis temperature from 110 to 155 °C, the specific surface area of cobalt increased by more than 1.5 times, and that of nickel black powders increased by approximately 2 times. Scanning electron microscopy revealed that cobalt is formed in the shape of lamellar particles with a lateral size of about 500 nm and a thickness of 50 nm, which aggregate into fractal structures. Nickel is represented by spherical particles arranged in chain-like structures. Using *X*-ray photoelectron spectroscopy, it was determined that the surface of the materials is covered with oxidized forms. The surface atomic concentration of cobalt (0) was approximately 2 %, while that of nickel (0) was about 25 %.

Keywords: nickel, cobalt, autoclaves, hydrothermal conditions, nanopowders, surface.

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Получение металлических порошков никеля и кобальта в автоклавных условиях

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Аннотация: Представлены результаты исследований восстановления дисперсных металлических порошков кобальта и никеля из аммиачно-щелочных водных растворов их солей в гидротермальных автоклавных условиях. Отработана унифицированная, экологически безопасная методика получения этих порошков. В качестве восстановителя применяли гидрат гидразина с 25–50 %-ным избытком от стехиометрического соотношения, который позволяет получать металлические фазы, химически не загрязненные продуктами разложения. В результате экспериментов установлены условия количественного восстановления ионов кобальта (II) и никеля (II) из аммиачно-щелочных водных растворов. Температуру синтеза дисперсных фаз варьировали в диапазоне от 110 до 155 °С. Показано, что в использованных режимах проведения процесс количественно завершается в течение 60 мин. Концентрации металлов в растворах определяли методами атомно-абсорбционной спектроскопии. Результаты рентгенофазового анализа подтвердили, что кобальт формируется в ГПУ-, а никель – в ГЦК-решетке, другие фазы, включая рентгеноаморфные, отсутствуют. Установлено, что с ростом температуры гидротермального синтеза от 110 до 155 °С удельная площадь поверхности кобальта увеличивается более чем в 1,5 раза, а порошков никелевой черни – примерно в 2 раза. Сканирующей электронной микроскопией показано, что кобальт формируется в виде пластинчатых частиц латеральным размером около 500 нм и толщиной 50 нм, которые агрегированы во фрактальные структуры. Никель представлен частицами сферической формы, упорядоченными в цепочкоподобные структуры. Методом рентгеновской фотоэлектронной спектроскопии установлено, что поверхность материалов покрыта окисленными формами. Поверхностная атомная концентрация кобальта (0) составила порядка 2 %, а никеля (0) – около 25 %.

Ключевые слова: никель, кобальт, автоклавы, гидротермальные условия, нанопорошки, поверхность.

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Introduction

Serious attention to dispersed materials based on non-ferrous metals is warranted due to their properties, which are primarily of practical interest. Powders of nickel, cobalt, and their alloys have been and continue to be widely used in numerous vital areas of human activity, including metallurgy [1], heterogeneous catalysis [2; 3], materials science [4—6], medicine and biology [7], electronic and electrical engineering [6; 8], among others. In the paper [9], magnetic carbon materials containing nickel and cobalt are described for addressing environmental issues. Furthermore, the authors of the article [4] have presented information on the production of corrosion-resistant coatings based on these metals.

The specific requirements for the composition, dispersion ability, morphology, and other essential characteristics of functional materials are largely determined by their application spheres. Consequently, methods for producing these materials are actively under development and improvement. The body of research dedicated to addressing these issues is extensive. Classical approaches for obtaining highly dispersed nickel and cobalt powders, such as thermal decomposition or exposure to reducing gases like hydrogen, are well-established [6; 8; 10]. However, they come with a set of challenges, primarily associated with the difficulty of controlling the powders' dispersion ability due to the potential sintering of materials driven by diffusion processes. Maintaining the required temperature is a significant challenge in heterogeneous reduction to metal powders. This difficulty may arise from the heat generated during the reduction reaction, leading to localized overheating of specific surface areas and, consequently, the sintering of particles.

Enlargement processes in hydrothermal systems can be observed at lower temperatures, but spontaneous heating does not occur, especially with conventional convection heating methods [11].

Chemical precipitation of dispersed Ni and Co metal powders from aqueous solutions under the influence of potent reducing agents has been the focus of numerous studies. In the article [12], the potential for separating nickel and cobalt metal phases from their hot salt solutions using sodium hypophosphite is demonstrated. Several investigations have been dedicated to the reduction of Ni(II) and Co(II) salts from aqueous solutions using sodium tetrahydridoborate [13—15]. However, in these cases, it is essential to consider the possibility of metal powder contamination with decomposition products of sodium hypophosphite and sodium tetrahydridoborate, respectively. Such contamination is entirely unacceptable in various practical applications, such as heterogeneous catalysis.

The use of hydrazine hydrate as a reducing agent is highly appealing, as it guarantees the purity of the materials obtained. It's not surprising that occasional instances of using this reagent for producing dispersed metal powders, including nickel and cobalt, can be found in the literature [16—19]. In [19], it was demonstrated that the reduction of mixtures of difficult-to-solubilize nickel and cobalt carbonates with hydrazine hydrate at 80—95 °C resulted in the formation of nanocrystalline powders of the respective metals.

The use of hydrometallurgical processes in open systems, despite their simplicity, is accompanied by several challenges, including inefficient reagent utilization and environmental pollution. The development of environmentally sustainable and efficient methods for producing dispersed materials based on non-ferrous metals with the necessary structural characteristics and properties is an urgent objective. This challenge can be addressed through autoclave technologies [17; 18].

The objective of this study is to develop a unified, environmentally friendly technique for obtaining dispersed cobalt and nickel metal powders and to investigate the structural parameters of the resulting materials.

Research methodology

In this study, we used high-purity aqueous ammonia (special purity grade 23-5; GOST 24147-80), $NiCl_2 \cdot 6H_2O$ (reagent grade), $CoCl_2 \cdot 6H_2O$ (reagent grade), potassium hydroxide (reagent grade), 64 % $N_2H_4 \cdot H_2O$ (reagent grade), and gaseous argon (Grade-3). Deionized water was prepared using the Direct-Q3 purification system (Millipore, USA). The experiments were conducted in laboratory fluoroplastic autoclaves with volumes ranging from 30 to 200 cm^3, the design of which is detailed in [17; 20; 21].

The synthesis of dispersed cobalt and nickel magnetic powders was carried out within a temperature range of 110 to 155 °C, following the procedure outlined in [17]. The choice of this temperature range is based on the consideration that at lower temperatures, the reduction processes may be hindered due to the possible formation of stable hydrazine complexes, while at higher temperatures, the system's pressure significantly increases.

The procedure involved placing a measured quantity of $CoCl_2 \cdot 6H_2O$ (or $NiCl_2 \cdot 6H_2O$) in a fluoroplastic liner and dissolving it in an aqueous solution of ammonium hydroxide. Subsequently, a 10 % sodium hydroxide solution and hydrazine hydrate (in excess of 30 % of the stoichiometry ratio) were added and stirred. Argon purging was used to remove air oxygen. Following this, the autoclave was sealed by securing it within a stainless-steel casing and then placed in a thermostat, where it was heated to the required temperature for a specified duration (60 min). The thermostat design allowed for vertical plane stirring. After the experiment, the autoclave was disassembled, the liquid phase was collected for analysis, and the solid phase was thoroughly washed with distilled water, dried at a temperature of 100 °C, and weighed. The residual concentration of cobalt or nickel ions in the solution was used to calculate the extent of metal reduction. Additionally, the obtained mass of the precipitate was compared to the calculated mass. The excess of the mass of synthesized powder over the calculated mass served as an indicator of the formation of oxidized forms of the metal (oxide, hydroxide).

The electron-microscopic analysis of materials was conducted using a scanning electron microscope TM4000 (Hitachi, Japan) equipped with a microanalysis system Quantax 70 (Bruker, Germany) operating in backscattered electrons mode, with an accelerating voltage of 20 keV. High-resolution electron microphotographs were obtained using a scanning electron microscope S5500 (Hitachi, Japan) in secondary electrons mode, with an accelerating voltage of 3 keV.

The specific surface area of the powders was determined through low-temperature nitrogen adsorption using an analyzer ASAP-2420 (Micromeritics, USA), at a $t = -195.75$ °C, applying the BET model.

X-ray diffractograms were recorded using a desktop diffractometer Proto AXRD (Proto Manufacturing, Canada) and CuK_α radiation. The recording was conducted in the angle range of $2\theta = 15°\div100°$, with a spacing of 0.02° and accumulation time at 2 sec point.

X-ray photoelectron spectra were registered using a spectrometer SPECS (SPECS GmbH — Surface Analysis and Computer Technology, Germany), equipped with a hemispherical energy analyzer PHOIBOS 150 MCD9 (SPECS GmbH). Monochromatic AlK_α radiation (1253.6 eV) from the anode of the *X*-ray tube was used for excitation. The transmittance energy of the energy analyzer was set at 20 eV for panoramic spectra or 10 eV for high-resolution spectra. Spectra data were processed using the CasaXPS software package. To correct for electrostatic charging, the maximum of the C 1s spectrum (285.0 eV) arising from hydrocarbon contaminants was utilized. High-resolution spectra were approximated using doublets of the asymmetric Gaussian—Lorentzian form, following Shirley subtraction of the nonlinear background.

The content of nickel and cobalt ions in the solutions was determined by atomic absorption spectroscopy using a spectrometer AAnalyst-400 (Perkin Elmer, USA).

Research results and discussion

The reduction process of nickel and cobalt salts by hydrazine hydrate, as demonstrated earlier [17], can be thermodynamically described by the following equations:

$$2CoCl_2 \cdot 6H_2O + N_2H_4 \cdot H_2O + 4NaOH = \\ = 2Co + 4NaCl + N_2 + 17H_2O, \quad (1)$$

$$2NiCl_2 \cdot 6H_2O + N_2H_4 \cdot H_2O + 4NaOH = \\ = 2Ni + 4NaCl + N_2 + 17H_2O. \quad (2)$$

According to the assumption proposed in [18; 22], the reduction of nickel and cobalt proceeds through the stage of formation of stable hydrazine complexes of the respective metals. These complexes are stable under normal conditions, and precipitation into the metallic state occurs at elevated temperatures.

Despite the use of closed systems, the quantitative progress processes (1) and (2) requires an excess of reducing agent, approximately 20 % above the stoichiometric ratio. This excess is necessary due to the potential oxidation of the reducing agent, which may occur because of the presence of oxygen in both the gas phase of the autoclave (owing to incomplete removal) and oxygen dissolved in the liquid phase.

It was observed that in ammonia-alkaline media, the reduction of nickel and cobalt at a temperature of 110 °C is completed within 1 h, while, as per [18], cobalt metal separation does not occur below $t = 120$ °C.

Specific surfaces of nickel and cobalt powders

Удельные поверхности порошков никеля и кобальта

Sample No.	Metal	t, °C	S_{surf}, m^2/g
1	Co	110	5.1
2		125	5.8
3		140	6.5
4		155	8.0
5	Ni	110	10.2
6		125	15.1
7		140	21.3
8		155	21.6

Under hydrothermal conditions in a closed system at $t = 110$ °C, it was found that the precipitation depth of cobalt metal is not less than 95 % with a 20 % excess of hydrazine hydrate from the stoichiometric ratio. With a 50 % excess of the reducing agent, the concentration of cobalt ions in the solution after metal precipitation, as determined by atomic absorption spectroscopy, is less than < 0.1 mg/L.

A similar situation is observed in the reduction process of nickel chloride (2). Increasing the synthesis temperature does not result in significant changes in product output, but it does influence the structural characteristics of the powders (see the table). The specific surface area of cobalt synthesized at $t = 155$ °C is nearly twice

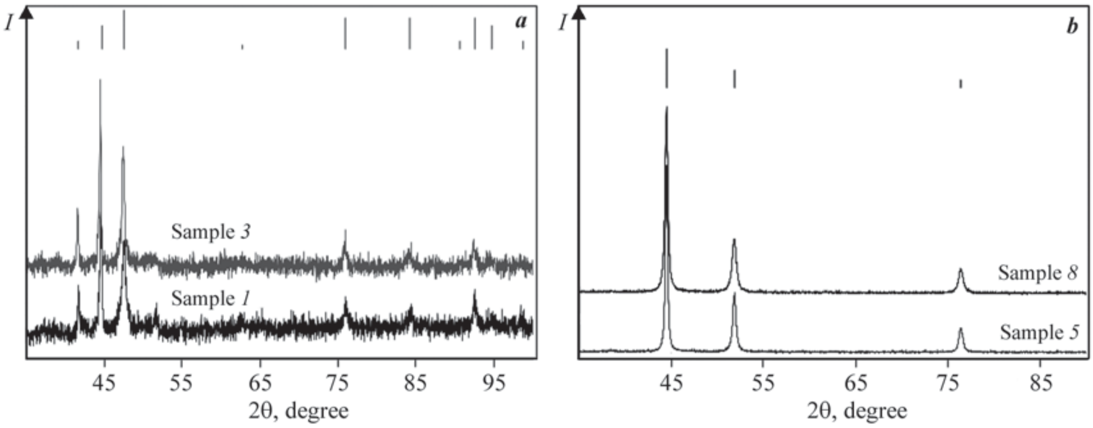

Fig. 1. Fragments of *X*-ray diffractograms of cobalt (***a***) and nickel (***b***) powders (see the table)

The stick diagrams of cobalt JCPDS 05-0727 (P63/mmc, $a = 0.25031$ nm, $c = 0.40605$ nm) and nickel JCPDS 65-2865 (FCC, $a = 0.35240$ nm) are shown above

Рис. 1. Фрагменты рентгеновских дифрактограмм порошков кобальта (***a***) и никеля (***b***) (см. таблицу)

Сверху показаны штрих-диаграммы кобальта JCPDS 05-0727 (P63/mmc, $a = 0{,}25031$ нм, $c = 0{,}40605$ нм)
и никеля JCPDS 65-2865 (ГЦК, $a = 0{,}35240$ нм)

that of the material obtained at t = 110 °C. In the case of nickel, a similar situation arises: the surface areas of powders synthesized at 110 and 155 °C differ by approximately a factor of 2. This phenomenon is likely linked to the formation of a higher number of nuclei at higher temperatures due to an increased rate of reduction. This situation has been discussed in [23] concerning the preparation of noble metal nanoparticles for catalytic processes.

Based on the *X*-ray phase analysis of the precipitates, the material is composed of a single phase corresponding to the respective metal (see Fig. 1). Cobalt *X*-ray diffractograms exhibit metal reflections (JCPDS 05-0727) in the HCP modification, which is characteristic for the considered temperature range. The parameters for this phase are a = 0.25031 nm and c = 0.40605 nm. However, it's worth noting that [18] suggests that cobalt is formed from alkaline media with a metastable FCC lattice. In contrast, nickel adopts an FCC lattice with a cell parameter of a = 0.35240 nm. The *X*-ray diffractograms display peak broadening, which could be attributed, in part, to the material's dispersion.

It's worth noting that as a result of reactions (1) and (2), cobalt and nickel are generated in the modifications that are stable within these temperature ranges, specifically HCP and FCC, respectively.

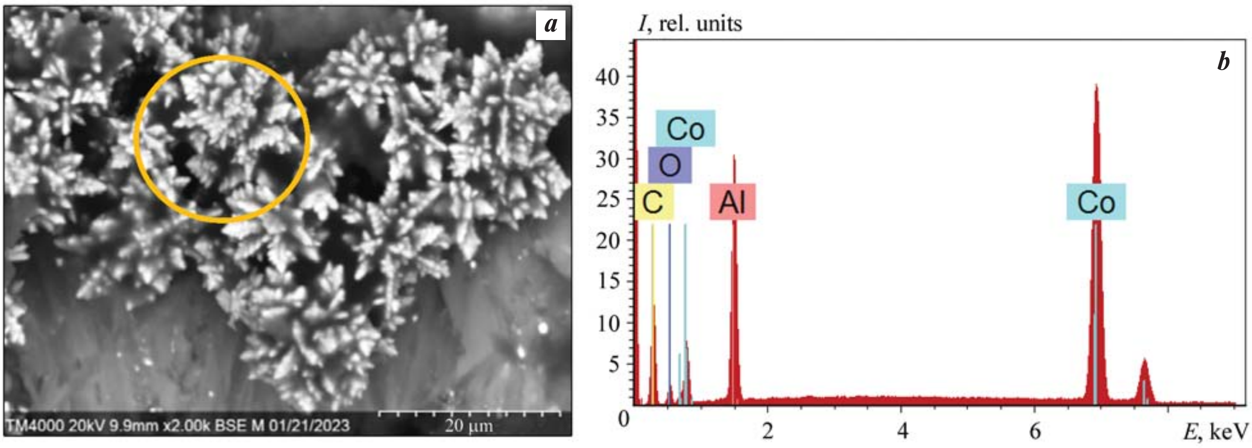

Fig. 2. SEM image (***a***) and energy dispersive spectrum for the imaged area (***b***) for cobalt (sample *3*, see the table)

Рис. 2. СЭМ-изображение (***a***) и энергодисперсионный спектр по отображаемой области (***b***) для кобальта (обр. *3*, см. таблицу)

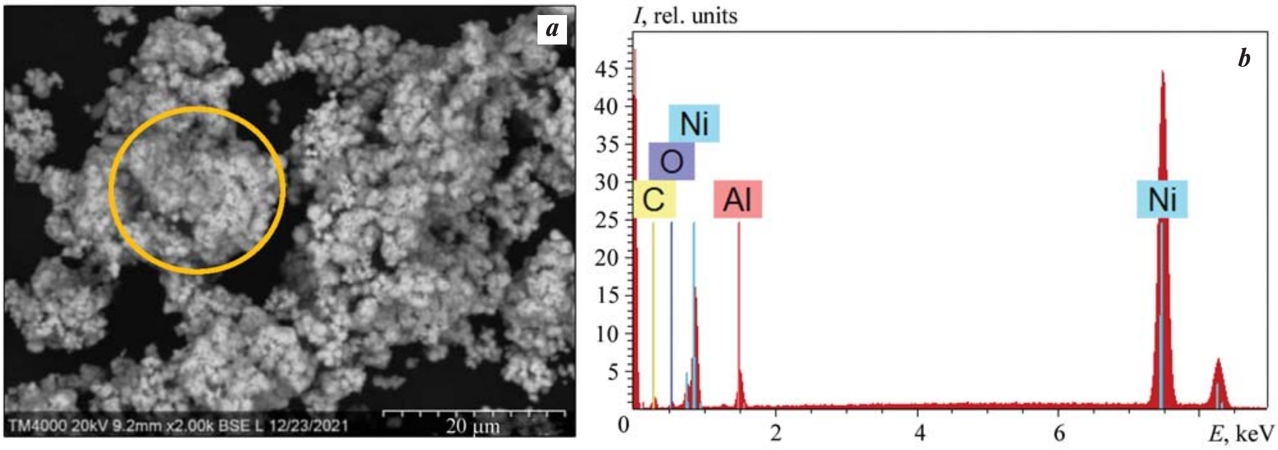

Fig. 3. SEM image (***a***) and energy dispersive spectrum for the imaged area (***b***) for nickel (sample *7*, see the table)

Рис. 3. СЭМ-изображение (***a***) и энергодисперсионный спектр по отображаемой области (***b***) для никеля (обр. *7*, см. таблицу)

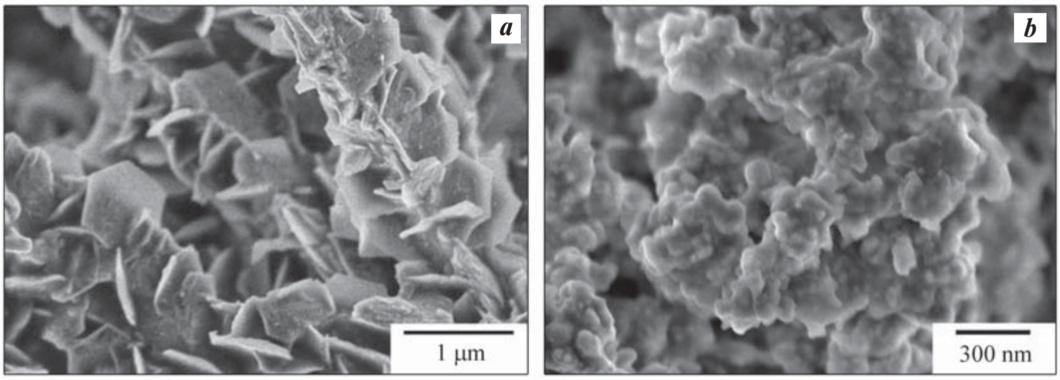

Fig. 4. SEM image of cobalt (***a***, sample *3*) and nickel (***b***, sample *7*)

Рис. 4. СЭМ-изображения кобальта (***a***, обр. *3*) и никеля (***b***, обр. *7*)

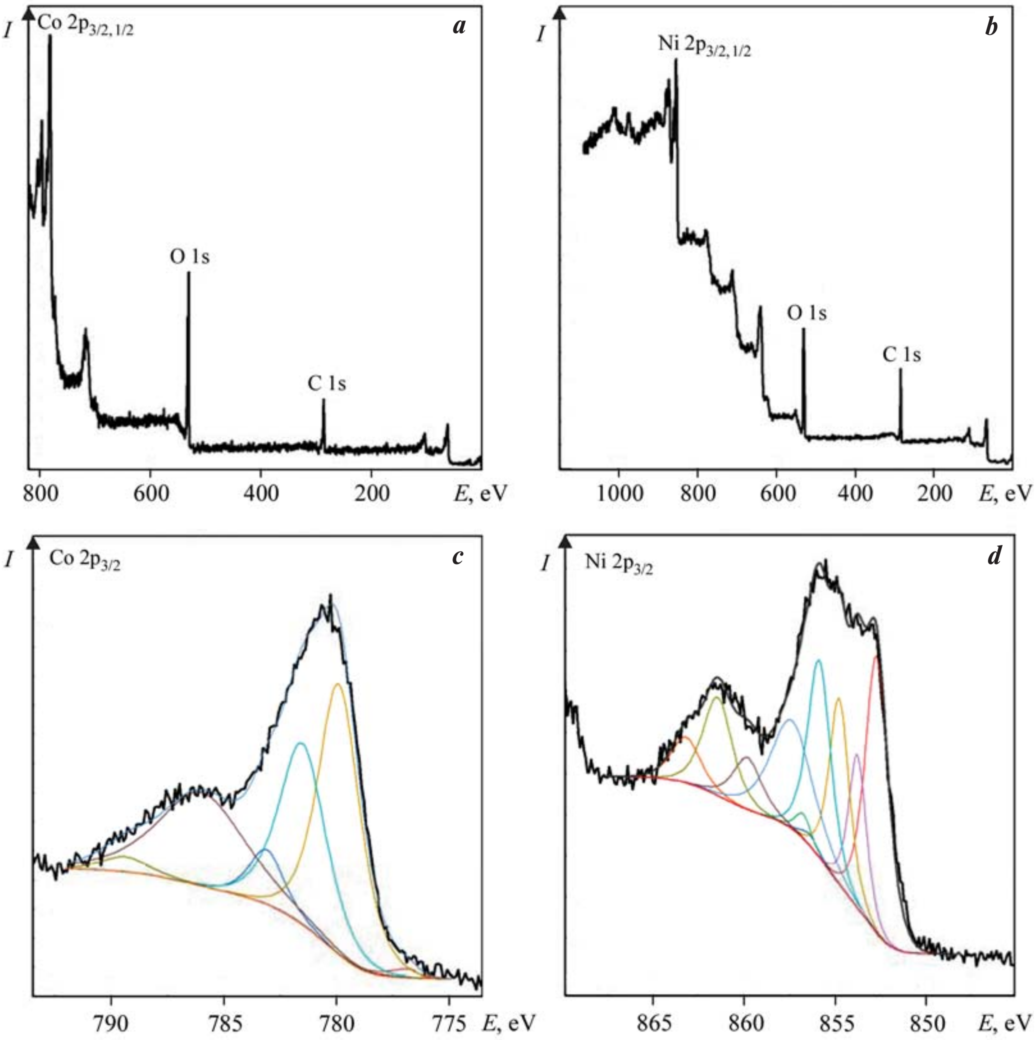

Fig. 5. *X*-ray photoelectron spectra after etching with argon ions for 3 min – panoramic spectra for cobalt (***a***) and nickel (***b***) and high-resolution spectra of Co $2p_{3/2}$ (***c***, sample *3*) and Ni $2p_{3/2}$ (***d***, sample *7*) lines

Рис. 5. Рентгеновские фотоэлектронные спектры после травления ионами аргона в течение 3 мин – обзорные для кобальта (***a***) и никеля (***b***), а также спектры высокого разрешения линий Co $2p_{3/2}$ (***c***, обр. *3*) и Ni $2p_{3/2}$ (***d***, обр. *7*)

Electron microscopic investigations have revealed that during reduction, cobalt forms fractal structures with dimensions of up to 10 μm (see Fig. 2). Upon closer examination, it becomes evident that these fractal agglomerates are composed of lamellar particles, including regular hexagonal shapes, with lateral dimensions of approximately 500 nm and a thickness of about 50 nm. Based on the *X*-ray spectral analysis (see Fig. 2), the material primarily consists of cobalt (94—98 at.% at various points) and oxygen (2—6 at.%), potentially indicating the presence of oxidized forms of the metal on the surface, likely in an amorphous state.

The morphology of nickel as revealed by scanning electron microscopy (Fig. 3), is markedly distinct. The particles have a shape closely resembling spheres and are arranged in chain structures, which become more distinguishable upon closer inspection (Fig. 4). According to the *X*-ray spectrometry analysis, the material primarily consists of nickel (97—100 at.% at various points) with a minimal oxygen content (up to 3 at.%).

The extent of oxidized products formed on the surface of nickel and cobalt metal, within a layer up to ~5 nm thick, can be estimated using *X*-ray photoelectron spectroscopy. Panoramic *X*-ray photoelectron spectra (Fig. 5, *a*, *b*) clearly exhibit the 1S lines of oxygen and carbon, as well as the 2p lines of cobalt and nickel, respectively. High-resolution spectra were subjected to decomposition (Fig. 5, *c*) using parameters and line shapes as presented in [24]. This decomposition identified components with energies of 780 eV or higher, corresponding to oxidized forms of Co(II), along with a component corresponding to the cobalt metal (778.1 eV). Calculations indicated that the total fraction of oxidized forms of cobalt on the surface is approximately 98 at.%. The nickel line, when scanned within the narrow $2p_{3/2}$ range (Fig. 5, *d*), can be decomposed into 8 components [24]. The peak at $E = 852.9$ eV corresponds to the nickel metal, while the other components align with the Ni(II)–OH multiplet set [25]. According to calculations, the fraction of nickel metal on the surface is 25 at.%.

Conclusion

1. A unified and environmentally friendly methodology for producing dispersed cobalt and nickel metal powders has been successfully developed.

2. It has been demonstrated that under autoclave hydrothermal conditions, cobalt and nickel are quantitatively reduced from their ammonia-alkaline salt solutions when hydrazine hydrate is used in excess of 50 % of the stoichiometric ratio.

3. XRF data confirm that cobalt adopts the HCP lattice, while nickel takes on the FCC lattice; no other phases were detected.

4. The *X*-ray photoelectron spectroscopy method revealed that the materials' surfaces are covered with oxidized forms of the metals.

5. Furthermore, it has been observed that as the temperature increases from 110 to 155 °C, the specific surface area of nickel increases by a factor of 2, and that of cobalt increases by 1.6 times.

References

1. Bolshakova O.V., Bolshakov S.V., Belousova N.V., Sinko A.V. Variations in cemenation reactions for different active Ni powders. *Tsvetnye Metally*. 2018;6:77—83. (In Russ.).
https://doi.org/10.17580/tsm.2018.06.11
Большакова О.В., Большаков С.В., Белоусова Н.В., Синько А.В. Изучение кинетики процесса цементации меди активным никелевым порошком. *Цветные металлы*. 2018;6:77—83.
https://doi.org/10.17580/tsm.2018.06.11
2. Yin W., Alekseeva M.V., Venderbosch R.H., Yakovlev V.A. Heeres H.J. Catalytic hydrotreatment of the pyrolytic sugar and pyrolytic lignin fractions of fast pyrolysis liquids using nickel based catalysts. *Energies*. 2020; 13(1):285.
https://doi.org/10.3390/en13010285
3. Lapidus A.L., Tsapkina M.V., Krylova A.Yu., Tonkonogov B.P. Bimetallic cobalt catalysts for the synthesis of hydrocarbons from CO and H_2. *Russian Chemical Reviews*. 2005;74(6):577—58.
https://doi.org/10.1070/RC2005v074n06ABEH001170
4. Li W., Hao J., Liu W., Mu S. Electrodeposition of nano Ni—Co alloy with (220) preferred orientation from choline chloride-urea: Electrochemical behavior and nucleation mechanism. *Journal of Alloys and Compounds*. 2021;853(5): 157158.
https://doi.org/10.1016/j.jallcom.2020.157158
5. Gürmen S., Stopić S., Friedrich B. Synthesis of nanosized spherical cobalt powder by ultrasonic spray pyrolysis materials. *Research Bulletin*. 2006;41(10):1882.
https://doi.org/10.1016/j.materresbull.2006.03.006
6. Khokhlacheva N.M., Lyushinskii A.V., Paderno V.N., Khokhlacheva T.G., Gryunval'd M.P., Bel'chikova M.E. Preparation of the mixtures of ultrafine powders of nickel, cobalt, and copper. *Soviet Powder Metallurgy and Metal Ceramics*. 1992;31(7):555—558.
https://doi.org/10.1007/BF00793429

7. Zakharov Yu.A., Eremenko N.K., Dodonov V.G., Obraztsova I.I., Eremenko A.N. Synthesis and properties of Co/Au and Ni/Au nanoparticles with core/shell structure. *Chemistry for Sustainable Development*. 2015;2: 177—182.
https://doi.org/10.15372/KhUR20150212
8. Huang Z., Liu F., Makuza B., Yu D., Guo X., Tian Q. Metal reclamation from spent lithium-ion battery cathode materials: directional conversion of metals based on hydrogen reduction. *ACS Sustainable Chemistry and Engineering*. 2022;10(2):756—765.
https://pubs.acs.org/doi/10.1021/acssuschemeng.1c05721
9. Kang J., Zhang H., Duan X., Sun H., Tan X., Liu S., Wang S. Magnetic Ni—Co alloy encapsulated N-doped carbon nanotubes for catalytic membrane degradation of emerging contaminants. *Chemical Engineering Journal*. 2019;362:251—261.
https://doi.org/10.1016/j.cej.2019.01.035
10. Nguyen T.H. Study on the kinetics of process for obtaining cobalt nanopowder by hydrogen reduction under isothermal conditions. *Izvestiya. Non-Ferrous Metallurgy*. 2021;27(1):49—56. (In Russ.).
https://doi.org/10.17073/0021-3438-2021-1-49-56
Нгуен Т.Х. Исследование кинетики процесса получения нанопорошка кобальта водородным восстановлением в изотермических условиях. *Известия вузов. Цветная металлургия*. 2021;27(1):49—56.
https://doi.org/10.17073/0021-3438-2021-1-49-56
11. Belousov O.V., Belousova N.V., Sirotina A.V. Solovyov L.A., Zhyzhaev A.M., Zharkov S. M., Mikhlin Y.L. Formation of bimetallic Au—Pd and Au—Pt nanoparticles under hydrothermal conditions and microwave irradiation. *Langmuir*. 2011;27:11697—11703.
https://doi.org/10.1021/la202686x
12. Brenner A., Riddell G.E. Deposition of nickel and cobalt by chemical reduction. *Journal of Research of the National Bureau of Standards*. 1947;39:385—395.
13. Zaharov Yu.A., Pugachev V.M., Dodonov V.G., Popova A.N., Kolmykov R.P., Rostovtsev G.A., Vasiljeva O.V., Zyuzyukina E.N., Ivanov A.V., Prosvirin I.P. Nanosize powders of transition metals binary systems. *Journal of Physics: Conference Series*. 2012;345:012024.
https://doi:10.1088/1742-6596/345/1/012024
14. Solov'eva A.Yu., Eremenko N.K., Obraztsova I.I., Eremenko A.N., Gubin S.P., Synthesis and optical properties of Fe@Au, Ni@Au bimetallic core—shell nanoparticles. *Russian Journal of Inorganic Chemistry*. 2018;63(4): 444—448.
https://doi.org/10.1134/S0036023618040204
Соловьева А.Ю., Еременко Н.К., Образцова И.И., Еременко А.Н., Губин С.П. Синтез и оптические свойства биметаллических наночастиц ядро—оболочка Fe@Au, Ni@Au. *Журнал неорганической химии*. 2018;63(4):416—420.
https://doi.org/10.1134/S0036023618040204
15. Zaharov Yu.A., Pugachev V.M., Bogomyakov A.S., Ovcharenko V.I., Korchuganova K.A., Russakov D.M., Kolmykov R.P. Influence of NicoreAushell nanoparticles' morphology on their magnetic properties. *Journal of Physical Chemistry C*. 2020;124(1):1008—1019.
https://doi.org/10.1021/acs.jpcc.9b07897
16. Logutenko O.A., Titkov A.I., Vorob'ev A.M. Shundrina I.K., Yukhin Yu.M. Lyakhov N.Z. Synthesis of nickel nanoparticles by the reduction of its salts using the modified polyol method in the presence of sodium polyacrylates with various molecular weights. *Russian Journal of General Chemistry*. 2018;88(2):288—294.
https://doi.org/10.1134/S1070363218020160
Логутенко О.А., Титков А.И., Воробьев А.Ю., Шундрина И.К., Юхин Ю.М., Ляхов Н.З. Синтез наночастиц никеля восстановлением его солей модифицированным полиольным методом в присутствии полиакрилатов натрия с различной молекулярной массой. *Журнал общей химии*. 2018;88(2): 311—318.
https://doi.org/10.1134/S1070363218020160
17. Belousov O.V., Borisov R.V., Romanchenko A.S., Belousova N.V., Zeer G.M. Autoclave synthesis of finely divided nickel powders. *Russian Journal of Inorganic Chemistry*. 2021;66(10):1463—1468.
https://doi.org/ 10.31857/S0044457X21100032
Белоусов О.В., Борисов Р.В., Белоусова Н.В., Зеер Г.М., Романченко А.С. Автоклавный синтез высокодисперсных порошков никеля. *Журнал неорганической химии*. 2021;66(10):1380—1386.
https://doi.org/ 10.31857/S0044457X21100032
18. Li Y.D., Li L.Q., Liao H.W., Wang H.R. Preparation of pure nickel, cobalt, nickel—cobalt and nickel—copper alloys by hydrothermal reduction. *Journal of Materials Chemistry*. 1999;9:2675—2677.
https://doi.org/10.1039/A904686K
19. Lapsina P., Popova A., Vladimirov A., Kagakin E., Sachkov V. Effect of synthesis conditions on size characteristics of nickel and cobalt nanostructured powders. *Key Engineering Materials*. 2016;683: 181—186.
https://doi.org/10.4028/www.scientific.net/KEM.683.181
20. Belousova N.V., Belousov O.V., Borisov R.V., Akimenko A.A. Autoclave dissolution of platinum metals in hydrochloric acid oxidizing media. *Russian Journal of Non-Ferrous Metals*. 2021;62:668—674.
https://doi.org/10.3103/S1067821221060043
Белоусова Н.В., Белоусов О.В., Борисов Р.В., Акименко А.А. Автоклавное растворение платиновых ме-

таллов в солянокислых окислительных средах. *Известия вузов. Цветная металлургия.* 2021;27(5):50—57. https://doi.org/10.17073/0021-3438-2021-5-50-57

21. Belousova N.V., Belousov O.V., Borisov R.V. Dissolution of metallic iridium powders in hydrochloric acid oxidizing media. *Tsvetnye Metally.* 2022;(8):40—45. (In Russ). https://doi.org/10.17580/tsm.2022.08.05
Белоусова Н.В., Белоусов О.В., Борисов Р.В. Растворение порошков металлического иридия в кислых окислительных средах. *Цветные металлы.* 2022;8:40—45.
https://doi.org/10.17580/tsm.2022.08.05
22. Li Y.D., Li C.W., Wang H.R., Li L. Q., Qian Y.T. Preparation of nickel ultrafine powder and crystalline film by chemical control reduction. *Materials Chemistry and Physics.* 1999;59(1):88—90.
https://doi.org/10.1016/S0254-0584(99)00015-2
23. Xia X., Xie S., Liu M., Pen, H.C., Lu N., Wang J., Kim M.J., Xia Y. On the role of surface diffusion in determining the shape or morphology of noble-metal nanocrystals. *Proceedings of the National Academy of Sciences.* 2013;110:6669—6673.
https://doi.org/10.1073/pnas.1222109110
24. Biesinger M.C., Payne B.P., Grosvenor A.P., Lau L.W., Gerson A.R., Smart R.S.C. Resolving surface chemical states in XPS analysis of first row transition metals, oxides and hydroxides: Cr, Mn, Fe, Co and Ni. *Applied Surface Science.* 2011;257(7):2717—2730.
https://doi.org/10.1016/j.apsusc.2010.10.051
25. Payne B.P., Biesinger M.C., McIntyre N.S. Use of oxygen/nickel ratios in the XPS characterisation of oxide phases on nickel metal and nickel alloy surfaces. *Journal of Electron Spectroscopy and Related Phenomena.* 2012;185(5-7): 159—166. https://doi.org/10.1016/j.elspec.2012.06.008

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