Application of nickel nanopowders of different morphology for the synthesis of highly porous materials by powder metallurgy

V A Zelensky¹, A B Ankudinov¹, M I Alymov¹², N M Rubtsov² and I V Tregubova¹

¹Baikov Institute of Metallurgy and Materials Science, RAS, Moscow, Russia
²Merzhanov Institute of Structural Macrokinetics and Materials Science, RAS, Chernogolovka, Russia

Abstract. In this work, we studied the morphology of nickel nanopowders synthesized in various ways: by chemical-metallurgical method, by decomposition of nickel formate and by electroexplosive technology. A comparative analysis of the characteristics of these nanopowders has been carried out. A sample carrier was made from the powder synthesized by electroexplosive technology. A porous material with a gradient structure was created by modifying the pore surface of a sample carrier with catalytically active centers of copper oxide.

1. Introduction

At present, of interest are the studies of gas-phase heterogeneous catalytic reactions in membrane reactors, in which, compared with traditional reactors having a bulk catalyst layer, mass and heat transfer has been significantly improved. To intensify endothermic catalytic reactions (for example, steam reforming of methane), accelerated heat transfer from an external source to the reaction zone is necessary. Therefore, the use of catalysts on porous metal supports is promising.

Methods are known for producing highly porous metal and ceramic materials by self-propagating high-temperature synthesis, casting, gas melting, rolling, electrochemical processing, deposition, and others. Methods of producing porous metal materials using powder metallurgy methods using temporary pore-forming agent are being actively developed [1–3]. Research is being conducted in the field of creating highly porous metallic materials (they are also called metal foams, sponges, or cellular materials).

Materials having a bimodal pore size distribution, otherwise materials with a gradient porosity [4, 5] are very interesting. Improved transport properties in such materials due to the presence of large pores (macropores). Pores of small sizes (micro- and nanopores) together with the micro-relief provide a large specific surface, which is important for practical use, since adsorption, desorption and chemical transformations of reagents occur on the surface. The technology of powder metallurgy allows to obtain macropores due to large particles of a pore-forming agent, while micro- and nanopores are created through the use of highly dispersed metal powders.

Another interesting direction is the modification of the surface of the pore space with catalytically active oxide or metal centers of nanometer size [6, 7]. Such centers can be created by the methods of precipitation from solutions, by the sol-gel method, by recondensation, etc.
In the present work, nickel nanopowders were used in the manufacture of porous materials. It is known that the size of powder particles, their morphology and tendency to form agglomerates depend on the method of preparation.

The purpose of this work is the study of nickel powders of various origin: obtained by chemical-metallurgical method [8], by decomposition of nickel-containing salts [9] and by the method of wire explosion. On the basis of a comparative analysis of powders for the manufacture of porous carrier samples, preference was given to a powder produced by an electroexplosive method. Additionally, copper oxide particles, which are catalytically active centers, were deposited on the surface of the porous carrier.

2. Synthesis of nickel nanopowders and their characterization

2.1. Chemical-metallurgical method of obtaining nanopowders

Production of powders by chemical-metallurgical method is carried out in two stages. First, low-water nickel hydroxide is synthesized. For the synthesis, a portion of the solid salt of nickel chloride was treated with 6 mol/l alkali solution of NaOH at a constant pH = 9 and kept for 45 min. The alkali solution was taken 2.5 times the amount required by stoichiometry. The washed powders were dried in air at room temperature for a day before dusting. The nickel hydroxide obtained as a result of precipitation has the structural formula Ni(OH)\(_2\) \cdot H\(_2\)O. The specific surface of the hydroxide obtained is 154 m\(^2\)/g.

The resulting hydroxide was reduced in 60 min in hydrogen at 180°C to the metal. The recovery mode was selected on the basis of the balance: complete recovery of the hydroxide to the metal while maintaining the minimum particle size. The crystallite size of the obtained nickel nanopowder calculated by the Selyakov-Scherer formula is about 30 nm. The particle size determined by the BET method is about 70 nm. Electron microscopy of the reduced nickel nanopowder is shown in figure 1. It is seen that the powder consists of dense agglomerates, in which the particles are strongly burned together.

![Figure 1. Electron microscopy of reduced nickel nanopowder.](image)

2.2. Production of nanopowders by decomposing unstable compounds

This method is one of the easily implemented and low-cost. To obtain nickel nanopowder, nickel formate Ni(HCOO)\(_2\) \cdot 2H\(_2\)O was used, which tends to decompose when heated to pure nickel and exhaust gases. The decomposition reaction was carried out in a quartz reactor in a stream of argon at a temperature of 210°C for 70 min. Electron microscopy of the obtained nanopowder is shown in figure 2. The size of the powder particles is about 70 nm. Particles form large-scale agglomerates.

![Figure 2. Electron microscopy of nickel nanopowder.](image)

2.3. Electroexplosive technology of nanopowders

When an electrical explosion of conductors occurs, the wire material, when a powerful current pulse passes through it, is destroyed to form particles from 5 nm to 1 mm, as a result, the wire material partially evaporates or scatters as liquid droplets. From the evaporated phase, due to the condensation process, very small particles are formed in a stream of rapidly expanding vapor. The technology is quite...
productive, although not without flaws. The main disadvantage is the presence in the nanopowders of this type of a small amount of powder of a large fraction. Figure 3 presents electron microscopy of a commercial nickel powder with an average particle size of 68 nm obtained by this technology. It can be seen that along with the smallest nanoparticles, it contains rather large round particles of submicron size.

Figure 2. Electron microscopy of nickel nanopowder obtained by decomposition of nickel formate.

Figure 3. Electron microscopy of nickel nanopowder obtained by electroexplosive technology.

3. Fabrication of highly porous nanopowder samples

Porous metal samples of the carrier for deposition on the surface of the through channels of catalytically active nanostructured copper oxide layers were made using SDP (sintering-dissolution process). When conducting preliminary experiments, it was found that the use of an electroexplosive nickel nanopowder was preferred. The use of an electroexplosive powder is explained by the fact that, as compared with powders obtained by a chemical-metallurgical method and by the method of decomposition of nickel formate, the highest porosity of carrier samples is achieved. Cylindrical samples were prepared using sodium chloride as a pore former. The ratio of Ni/NaCl by volume in the compacts was 30/70. Samples were sintered for 120 min at a temperature of 800°C in a stream of hydrogen. Their diameter is 26 mm, height 8 mm; porosity of about 70%.

4. Copper oxide precipitation

The deposition of copper oxide was as follows:
1. Samples were soaked with 0.02 M aqueous solution of copper sulfate hydrate CuSO₄·5H₂O.
2. Samples were pre-evacuated.
3. Samples were dried.
4. Samples were treated with 7M aqueous NaOH solution for 20 min. Samples were pre-evacuated. The treatment with alkali is necessary in order for the product to transform to the hydroxide Cu(OH)₂: CuSO₄ + 2NaOH = Cu(OH)₂ + Na₂SO₄. Cu(OH)₂ precipitates; Na₂SO₄ remains in solution and is removed during subsequent washing.
5. Samples were calcined at a temperature of 150–180°C for 30 min. When heated, the hydroxide goes into oxide: Cu(OH)₂ => CuO + H₂O.

On several samples, the salt deposition procedure (operations 1 and 2) was repeated three times. After treatment with an aqueous solution of alkali, washing and calcining (steps 3–5) with an initial mass of samples of 10.3–10.6 g, the mass of precipitated copper oxide was 0.8–1.0 g.

An energy dispersive analysis (EDA) was performed on a TESCAN VEGA II SBU scanning electron microscope. The surface-normalized distribution of Ni/Cu/O elements was 80.60/12.75/6.65%. The results of EDA indicate a relatively uniform deposition of a layer of copper oxide on the pore walls.

The appearance of a porous nickel tablet modified with copper oxide, micrographs of the surface area of its cleavage and the results of EDA are presented in figures 4–6. In contrast to existing industrial
technologies, nickel nanopowders were used as a starting material for creating highly porous samples. This allowed, along with micron-sized macropores created by the pore-forming agent, to obtain a developed surface of the pore walls formed by agglomerates of Ni nanoparticles and having their own nanoporosity.

![Image](image.png)

**Figure 4.** Porous nickel tablet modified with copper oxide.

![Image](image.png)

**Figure 5.** SEM images at different magnifications of the surface area of the cleaved porous Ni modified with copper oxide.

![Image](image.png)

**Figure 6.** The distribution of elements over the surface of porous Ni, modified with copper oxide.
Thus, it was shown that powder metallurgy can create volumetric highly porous nickel catalyst carriers with a developed surface and a gradient structure of the pore space based on preliminary pressing of mixtures of metal nanopowders and blowing agents, followed by sintering metal particles and removing the blowing agent. The experiments on the deposition of catalytically active centers (oxides) on the pore walls allow the creation of a porous membrane-catalytic converter based on copper oxide powders.

Acknowledgements
This work was supported by the Russian Foundation for Basic Research, grant no. 17-03-00867, and the Presidium of the Russian Academy of Sciences, the Program of Basic Research of the Russian Academy of Sciences 34P. Investigations by electron microscopy and X-ray phase analysis were carried out with the involvement of government funds no. 007-00129-18-00.

References
[1] Kränzlin N and Niederberger M 2015 Mater. Horiz. 2 359–377
[2] Stanev L, Kolev M, Drenchev B and Drenchev L 2017 Rev. J. Manuf. Sci. Eng. 139 050801
[3] Stanev L, Kolev M, Drenchev B and Drenchev L 2017 Rev. J. Manuf. Sci. Eng. 139 050802
[4] Singh S and Bhatnagar N 2017 J. Porous Mater. 24 1–18
[5] Izaak T I and Vodyankina O V 2009 Uspekhi khimii 78 80–92
[6] Zhang F, Yuan C, Lu X, Zhang L, Che Q and Zhang X 2012 J. Power Sour. 203 250–256
[7] Danilova M M, Fedorova Z A, Zaikovskii V I, Porsin A V, Kirillov V A and Krieger T A 2014 Appl. Catal. B: Environ. 147 858–863
[8] Tregubova I V, Alymov M I, Ankudinov A B, Zelenskiy V A and Tikhomirov S A 2011 Tsvetnyye metally 5 47–52
[9] Alymov M I, Rubtsov N M, Seplyarskii B S, Kochetkov R A, Zelensky V A and Ankudinov A B 2017 Mendeleev Commun. 27 631–633