Highly porous, hierarchically structured nickel nanomaterials consolidated by powder metallurgy methods

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Abstract. Highly porous permeable nickel materials with a hierarchical structure were consolidated by powder metallurgy methods in sintering-dissolution and sintering-evaporation processes from nickel nanopowder and micropowders of two different types of space holders – water-soluble sodium chloride NaCl and thermally unstable ammonium bicarbonate NH₄HCO₃, respectively. Nanopowder nickel materials with three levels of hierarchical porosity were obtained using bidisperse micropowders of soluble NaCl space holder.

1. Introduction
The current trend in the creation of highly porous materials is the synthesis of metallic structures with a hierarchical organization containing pores of several length scales. Such materials have found numerous practical applications in heterogeneous catalysis, energy saving technologies, and biomedicine [1]. In recent years, methods for their preparation by powder metallurgy route with the use of temporary pore fillers – space holders – have been actively developed. In the space holder technique, the processes of pressing metal powder and space holder mixtures, sintering and removing the space holder are carried out sequentially. Depending on the type of space holder, it is removed before, during or after sintering. There are two main directions in this technology: the production of porous metals in the sintering-dissolution process (SDP) using soluble space holders washed out by water or other solvents [2] and the sintering-evaporation process (SEP) using thermally unstable space holders [3]. Most of the research on fabrication of metallic materials with high porosity by space holder technique has been performed with micron-sized metal powders [4].

This paper reports on the creation of hierarchically porous nanopowder-based nickel materials by powder metallurgy methods. The synthesis of bulk porous materials based on nickel nanopowders has been previously described only in a few papers, e.g., [5-8], and their properties remain poorly studied.

2. Materials and methods
To fabricate porous metallic samples, commercial nickel nanopowder with an average spherical particle size of ~70 nm and a specific surface area 6 m² g⁻¹ synthesized by the method of the electric explosion of wire in an argon atmosphere was employed. Sodium chloride NaCl and ammonium bicarbonate NH₄HCO₃ powders sieved to fine (40-50 μm) and coarse (315-400 μm) fractions were used as space holders. The choice of these space holders was motivated, respectively, by their water solubility and thermal instability and decomposition upon heating. SEM images of the feedstock powders are shown in figure 1.
Nickel and space holder powders were mixed and compacted on a hydraulic press in a cylindrical steel matrix with an inner diameter of 13.6 mm. The compacts were sintered in a tubular furnace in a gas-tight quartz retort 52 mm in diameter and 80 cm long.

Nanopowders and bulk porous materials were characterized by the following methods: electron microscopy of nanopowders and porous nickel samples on a Cross-Beam 1540EsB (Carl Zeiss, Germany) and TESCAN VEGA II SBU (Tescan, Czech Republic) scanning electron microscopes; specific surface area measurement by the Brunauer–Emmet–Teller (BET) method on a TriStar 3000 analyzer (Micrometrics, United States); mechanical tests on an INSTRON 3382 universal electromechanical machine (Instron Corp., United States). Porosity was measured by hydrostatic weighting. Permeability was determined from the Darcy law by measuring the liquid flow through a porous sample into a Bunsen flask kept under vacuum.

3. Results and discussion

3.1. Biporous nickel consolidated using different types of space holders

In the manufacture of porous samples, we used a nickel nanopowder with an average particle size of 70 nm and two different types of space holders – crushed and sieved to 40-50 μm fraction water-soluble sodium chloride NaCl and thermally unstable ammonium bicarbonate NH4HCO3.

To obtain samples with different porosities, Ni nanopowder and one of the space holders (NaCl or NH4HCO3) micropowders were mixed in a given proportion (40/60, 30/70, and 20/80 by volume) and uniaxially pressed under a pressure of 300 MPa. The height of the compacts was ~20 mm. The green compacts were sintered at a temperature of 750 °C for 120 minutes in a stream of hydrogen to avoid oxidation. Sodium chloride was leached from the sintered samples in heated distilled water.
Ammonium bicarbonate decomposed and was distilled off at the initial heating stage prior to sintering. Under these sintering conditions, porous nickel samples (figure 2) acquired sufficient mechanical strength and remained permeable.

**Figure 2.** Cylindrical samples of porous nickel obtained using different types of space holders: soluble sodium chloride (left) and thermally unstable ammonium bicarbonate (right).

SEM images of fracture surfaces of porous nickel samples obtained using NaCl and NH₄HCO₃ as space holders are presented in figure 3. Analysis of the images showed that porous nickel contains interconnected pores of two spatial scales: macropores (30-50 μm in size) and interparticle micropores (less than 1 μm) in the walls of macropores. These materials are characterized by a network of interpenetrating macropores and a developed surface of their microporous walls consisting of partially sintered nickel nanoparticles that have increased in size during sintering. Neighboring macropores are connected by windows. The windows between the macropores are finally formed in the sintering process at the contact points of the space holder particles with each other in the green compact. In SEM images, they are visible as black "spots" on the surface of the macropores.

**Figure 3.** SEM-images at different magnifications of porous nickel sintered using (a)-(b) sodium chloride and (c)-(d) ammonium bicarbonate space holders: (a), (c) fracture surfaces; (b), (d) macropores with windows.
The fracture surface of the sample produced using the NaCl space holder contains macropores in the form of exact imprints of salt particles that have an irregular shape. The macropores in the sample made with NH₄HCO₃ have a rounded shape due to the convergence of the sintered nickel particles because the space holder was removed during the heating stage and no longer holds the shape. The number of windows per macropore in such a sample is greater than in the case of using NaCl.

The porosity and mechanical characteristics of nickel samples depending on the content of space holders are presented in table 1. The porosity of samples obtained using NaCl is higher than expected (which is given by the volume fraction of space holder in the powder mixture). This is due to the contribution of interparticle microporosity, since the pore former is washed out after sintering. The porosity of the samples obtained using NH₄HCO₃ turned out to be lower than its volume fraction, which is a consequence of the shrinkage of the samples (up to ~20% by volume) during sintering of the bulk structure of metal particles, from which the space holder was removed at the preliminary stage of distillation before sintering.

Table 1. Structural and mechanical properties of porous nanopowder-based nickel materials.

| Space holder | Material | Volume fraction, % | Relative density, % | Porosity, % | Yield strength, MPa | Elastic modulus, GPa |
|--------------|----------|--------------------|---------------------|-------------|--------------------|----------------------|
| Porous nickel| NaCl     | 60                 | 34.7                | 65.3        | 25.5               | 0.63                 |
|              |          | 70                 | 26.7                | 73.3        | 8.1                | 0.35                 |
|              |          | 80                 | 18.3                | 81.7        | 2.4                | 0.13                 |
|              | NH₄HCO₃  | 60                 | 55.7                | 44.3        | 113                | 2.33                 |
|              |          | 70                 | 35.5                | 64.5        | 16.2               | 0.60                 |
|              |          | 80                 | 29.8                | 70.2        | 5.8                | 0.24                 |

The yield strength and modulus of elasticity of the samples decrease with increasing porosity for both space holders. It can be seen that the mechanical characteristics of the samples prepared with ammonium bicarbonate as a space holder, due to their lower porosity and denser macropore walls, are higher than those of the samples prepared with sodium chloride. The same tendency has been observed previously for porous materials from diopside nanoparticles obtained using different types of space holders [9]. Due to the larger number of windows connecting the macropores, the permeability of the porous nickel obtained using ammonium bicarbonate was also higher. In particular, at a volume fraction of space holders of 70%, the permeability was 0.61⋅10⁻¹² m² and 0.066⋅10⁻¹² m² for NH₄HCO₃ and NaCl, respectively.

3.2. Nanopowder nickel with trimodal porosity consolidated in the sintering-dissolution process using a bidisperse space holder

One of the methods for obtaining powder materials with multilevel porosity can be the use of a metallic base powder and several space holders with significantly different particle sizes. In particular, in [10], when sintering micron-sized Ni and Ti powders, a bidispersed space holder was used — mixture of sodium chloride (NaCl) powders with particle sizes of 75-90 µm and 500-600 µm. However, the resulting material was characterized as biporous since the metal particles and the pores appearing between them were rather large with sizes of ~30 µm, comparable to the sizes of particles of the fine fraction of the space holder.

In this work, permeable nickel materials with trimodal porosity were obtained by space holder technique. A series of highly porous cylindrical samples based on nickel nanopowder with spherical particles and an average particle size of 70 nm was fabricated in the sintering-dissolution process. As a space holder, a bidispersed mixture of sodium chloride micropowders of two fractions was used — a
fine fraction with a particle size of 40-50 μm and a coarse fraction of 315-400 μm. The salt particles had an irregular shape, which is typical for crushed materials (figure 1). Powders of the base metal Ni and the space holder NaCl were taken in a constant volume ratio of 20/80. At the same time, in different samples, the composition of a mixture of fine and coarse space holder powders varied. After mixing, the powders were uniaxially pressed at 300 MPa and sintered in a stream of hydrogen at 700 °C for one hour, after that the space holder was washed out in heated water. Samples with volume ratios of coarse (315-400 μm) to fine (40-50 μm) NaCl fractions equal to 0/100, 25/75, 50/50, 75/25 and 100/0 were fabricated. A photograph of the cylindrical sample is shown in figure 4.

Analysis of SEM images (figure 5) showed that the samples contain pores of three spatial scales: large (~ 400 μm), medium (~ 40 μm), and small (<1 μm) pores. Large and medium pores (macropores) are negative replicas of NaCl particles of different dispersion. Medium-sized pores form an interconnected spatial network, some of them emerge on the surface of large pores. The origin of the network of small pores (micropores) in the nickel framework is associated with incomplete sintering of Ni nanoparticles.

The porosity of the samples varied within 81-83% and exceeded the expected porosity (80%) due to the contribution of the microporosity of the nickel scaffold. The BET specific surface area reached ~5.0 m² g⁻¹. The yield stress and elastic modulus were 1.4 MPa, and 35.7 MPa respectively. The permeability of porous nickel was studied on a series of samples made with volume ratios of coarse (315-400 μm) to fine (40-50 μm) salt equal to 0/100, 25/75, 50/50, 75/25 and 100/0. Depending on the volume fraction of finely dispersed NaCl powder in the space holder mixture, the permeability of the obtained materials with a porosity of 81-83% varied within an interval of 0.05⋅10⁻¹² – 0.2⋅10⁻¹² m².

The permeability of nanopowder nickel sintered without a space holder is determined only by micropores in the metal scaffold formed due to incomplete sintering of metal nanoparticles. The
measured experimental value was about $2 \cdot 10^{-16}$ m$^2$, which is significantly lower than the permeability of samples sintered using space holders. Thus, macropores contribute largely to the total permeability and appear to be interconnected, as well as micropores. Therefore, according to the classification [11], the porosity observed in our experiments can be referred to the type II hierarchical porosity.

4. Conclusion
Nanopowder nickel materials with high porosity and hierarchical structure were synthesized by the space holder technique in the sintering-dissolution and sintering-evaporation processes using two types of space holders – soluble NaCl and thermally unstable NH$_4$HCO$_3$, respectively. Porous nickel contains pores of different length scales – macropores and micropores. Macropores are formed as a result of the removal of large space holder particles. The origin of micropores in the nickel scaffold is associated with incomplete sintering of Ni nanoparticles. Permeable nanopowder nickel materials with a high specific surface area and three levels of hierarchical porosity were obtained using a bidisperse micropowders of soluble NaCl space holder.

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