Functional properties of nanopowder nickel materials with trimodal porosity consolidated by sintering-dissolution method

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Abstract. Nanopowder nickel materials with trimodal porosity were consolidated in the sintering-dissolution process using bidispersed NaCl porogen powders. The dependence of the permeability of the fabricated porous nickel materials on the ratio of coarse and fine components of bidisperse porogen was investigated. The studies were carried out on samples made using 80 and 85 vol.% of porogen. It is shown that porous samples synthesized using a bidisperse porogen have lower permeability compared to those with a monodisperse porogen.

1. Introduction

Porous materials with open porosity are used as filters and catalyst carriers. An important functional characteristic of the finished product is the hydraulic permeability of the material. In these two applications, it plays a significant role.

Depending on the purpose of the finished product, a certain porous structure is formed in the material by one of the known methods. In the manufacture of a porous material from metal powders, the method of temporary pore filling is widely used, when a porogen is added to the charge with the base material, and then, after pressing, it is removed during heating or dissolved after sintering. The advantage of this method is the ability to control the pore structure by selecting the appropriate pore-forming particles, i.e. their number and morphology [1, 2].

The classification of pores by type and size in porous materials produced by powder metallurgy methods is given in [3]. Materials obtained by sintering metal powders using porogens contain pores of three types: interparticle micropores formed as a result of partial sintering of base powder, macropores arising after removal of large particles of the porogen, and windows – necks connecting neighboring macropores. The permeability of such materials is determined mainly by the size of the windows and their number. The windows have a well-defined function and are considered to be an independent type of pores, usually two-dimensional [4-8]. The windows between the macropores are finally formed in the sintering process at the contact points of the porogen particles with each other in cold compact. Figure 1(a) shows a schematic representation of the porous material with windows, which are indicated by a dotted line. In SEM images they are visible as black "spots" on the surface of the macropores (figure 1 b).
It was found that materials with high porosity do not always have high permeability, as it was shown in previous studies of the authors [9, 10]. An urgent task is to find ways to increase the permeability of powder materials.

The study of the dependence of the powder material permeability on component ratio of bidisperse porogen was the purpose of this work. A porous material obtained from nickel nanopowder was chosen as the object of study. Samples were synthesized with a sufficient level of mechanical strength at a low sintering temperature due to the use of nanopowder.

![Figure 1. Schematic representation of a porous permeable material in which pores are connected by windows indicated by a dotted line (a) and SEM image of a macropore with a window (b).](image)

2. Materials and methods
A commercial nickel nanopowder with an average particle size of 70 nm obtained by electrical explosion of a wire in an argon atmosphere was used as the base material. NaCl salt powders of two fractions with a particle size of 40-50 μm and 315-400 μm were used as a porogen.

Pressing was performed on a Knuth hydraulic press. Sintering was carried out in a tubular electric furnace in a hydrogen atmosphere. The microstructure was studied using an electron scanning microscope Tescan MIRA 3.

The porosity of the materials was measured by hydrostatic weighting. The permeability of the porous nickel samples was determined by the method based on Darcy’s law by passing distilled water.

The samples were pressed at a pressure of 330 MPa and sintered at a temperature of 700 °C. The salt was washed out from the sintered samples in heated distilled water.

3. Results and discussion
Two series of samples containing 80 and 85 vol.% of porogen were fabricated. The ratio of salt volume fractions of different dispersions was varied. It should be noted that the porosity of the obtained samples was 81.5-83.2 % and 86.1-87.2 % for these two series, respectively. The porosity exceeds the expected value, which is given by the volume fraction of the porogen. This is due to the contribution of microporosity of partially sintered nickel powder. This assumption is confirmed by the study of the porous structure of the materials using a scanning electron microscope. SEM images of the fracture of the sample from the series with 80% of porogen show macropores formed by salt particles, as well as micropores resulting from partial sintering of the nickel nanopowder (figure 2).

The permeability of materials obtained using porogens of different fractional composition was investigated. Dependences of material permeability on the ratio of porogens with particle sizes of 40-
50 μm and 315-400 μm in the initial powder mixtures are shown in figure 3. Confidence intervals in the figure correspond to a confidence level of 0.9.

**Figure 2.** SEM images of a fracture of a sample obtained from a mixture of nickel nanopowder with 80 vol.% of a porogen with a particle size of 40-50 μm.

**Figure 3.** Dependence of material permeability on the ratio of volume fractions of porogen with a particle size of 40-50 μm and 315-400 μm: (a) for material with 80 vol.% of a porogen and (b) for material with 85 vol.% of a porogen.

In the samples sintered with a bidisperse porogen, pores of three sizes are observed: large pores of 315-400 μm and medium-sized pores of 40-50 μm formed from salt particles, and pores in the nanoscale range due to incomplete sintering of metal nanopowder (figures 4, 5). Thus, the manufactured nanopowder nickel materials are characterized by trimodal porosity.

The permeability of nickel nanopowder material made without a porogen is determined only by nanosized pores in the metal matrix formed due to incomplete sintering of metal nanoparticles. We have found experimentally that the permeability of such a material is very low. It has a value of about 2·10^{-16} m^2, which is significantly lower than the permeability of the samples synthesized using the porogen. Therefore, the contribution of this type of permeability to the total permeability can be neglected.
It was found that in the case when only a fine porogen is used, the samples have the maximal permeability. In this case, the macropores have many windows connecting them with the neighboring macropores, and the fluid (liquid or gas) passes through the porous material with minimal resistance.

Figure 4. SEM image of a fracture of a sample obtained from a mixture of nickel nanopowder with 80 vol.% of the porogen, in which the percentage of large particles was 15%.

Figure 5. SEM image of a fracture of a sample obtained from a mixture of nickel nanopowder with 80 vol.% of the porogen, in which the percentage of large particles was 50%.

When a coarse fraction is added to the bidisperse porogen, the content of fine pores in the material decreases (since the percentage of pore former remains unchanged). Small pores cease to be in contact with each other and their contribution to the permeability decreases. At the same time, large pores are not yet formed in sufficient amount so that contact windows appear between them. For this reason, the permeability of samples decreases. Further, when the fraction of coarse salt increases, the number of contacts between small pores becomes even lower. However, windows between large pores begin to appear. In the limiting case, when the fine fraction of porogen is absent at all, the maximum number of windows between large pores is observed, as the concentration of large pores increases. This
determines the growth of permeability with the increase of the coarse powder fraction of the porogen. The minimum value of permeability is established at intermediate ratios of coarse and fine fractions of the porogen (figure 3).

The mechanical properties of porous samples were determined in compression tests. For samples with an equal content of porogen of different dispersions, the offset yield strength and the modulus of elasticity were 1.4 MPa and 35.7 MPa, respectively.

4. Conclusion
Nanopowder nickel materials with trimodal porosity were consolidated in the sintering-dissolution process using bidispersed NaCl porogen powders. Pores of three characteristic sizes were observed: large pores of 315-400 μm and medium-sized pores of 40-50 μm formed by leaching of salt particles, and pores in the nanoscale range formed due to incomplete sintering of metal nanopowder. It was shown that porous powder materials synthesized using a bimodal porogen have a lower permeability compared to those with a monodisperse porogen. The permeability of materials with 85 vol.% of porogen and particle size of 40-50 μm is 2-2.5 times higher than the value for samples with 80 % volume fraction of porogen.

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