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MONOLITHIC CATALYST SUPPORTS WITH FOAM STRUCTURE

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Abstract

The present article considers the production of monolithic catalyst supports with a foam structure. A model of an open cell foam material structure is described. Technological schemes for the production of ceramic and metal foam materials, alongside with the main properties of the latter and control algorithms are presented.

Keywords: Foam, support, cell, porous

INTRODUCTION

The present paper considers the problems of production of highly porous monolithic supports with a foam structure.

RESULTS AND DISCUSSION

In modern practice, monolithic supports with fibrous, knitted, honeycomb and foam structures are widely used especially for converting exhaust gases of engines, power and metallurgical plants. There are some advantages of the foam supports such as simplification of the thermal and mass transfer, more efficient surface use and high turbulence. These advantages are revealed under high catalyst loadings that enable a volumetric gas flow speed up to 10^5 L/h [1-3].

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First of all, we shall define the place of foam materials in the class of porous materials. All porous permeable materials can be divided into three classes: porous powder materials with a porosity of 20 - 45%, porous fibrous materials with a porosity of 30 - 70% and highly porous arched materials (honeycomb, foam materials) with a porosity of 70 - 98%. The difference in the porosity of these materials is qualitative rather than quantitative. It is primarily determined by the average area of interparticle contacts, by the coordination number and density of the structure element packing. Mathematically, it is expressed by Balshin's equation widely used in powder metallurgy [4]:

$$\sigma = \sigma_0 (1 - P)^m \qquad (1)$$

where σ and σ_0 are mechanical strengths (MPa) of a porous and a nonporous material, respectively, P is the material porosity in fractions of unity, index m is 3 - 4 for porous powder materials, 2 - 3 for porous fibrous ones, 1 - 2 for arched ones (1.0 - for honeycomb materials and 1.3 - 1.8 for foam ones).

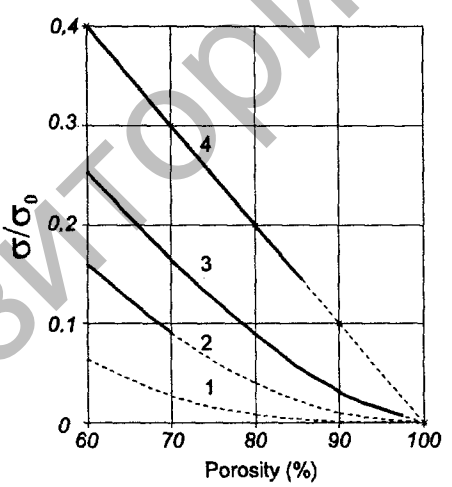

Fig. 1. Dependence of the strength on the porosity for various classes of porous materials (1 - powder materials; 2 - fibrous materials; 3 - foam materials; 4 - honeycomb materials) —— real sphere of existence; ------ hypothetic continuation of the Balshin's formula

For optimization of the technology for production of highly porous materials used as catalyst supports, a compromise must be found between their basic properties - mechanical strength and porosity, which have contrary tendencies in

changing. Figure 1 shows that only arched materials have acceptable mechanical strength when their porosity is higher than 80%. Honeycomb materials have evidently the maximum possible strength at a predetermined porosity level when their permeability is practically equal to that of foam materials. But in practice the production of honeycomb materials with the porosity of 85% is rather problematic.

Privileges of foam materials as initial catalyst supports are predetermined by such properties as their extremely highly porosity and permeability, relatively high mechanical strength, constructional rigidity, relatively low density, capability to be formed into blocks of various configurations.

At present the following methods are used to produce inorganic foam materials: foaming of suspensions, compacting of composite grains and duplicating of polymer foam materials. Foam materials produced by the suspension foaming and foam-like materials produced by compacting of polymer grains coated with a thin layer of an inorganic powder usually have a 70 - 90% porosity and a 0.3 - 10.0 mm cell size. The closed character of the porosity is the main feature of such materials. It predetermines the fields of their applications, *e.g.* low weight constructions and thermal insulations. Unlike the first two methods, the production of foam materials by duplicating of open-cell organic foams enables to produce materials with up to 98% porosity, highly permeability (up to 10^{-7} m^2) and cell size from 0.5 to 10.0 mm. Foam materials produced by this method successfully combine structural and hydrodynamic properties of the organic foam skeleton and thermal, mechanical and physicochemical properties of the base material.

At Powder Metallurgy Research Institute, Minsk, techniques for production of highly-porous foam materials by duplicating the structure of the open-cell polyurethane foam (PF) have been developed.

1. *Metal foam* (MF) is produced by electrochemical deposition. The method is used to produce a nickel foam first and consists of the following main operations: chemical deposition of a thin electrically conductive layer onto a PF structure, electrochemical deposition of the necessary metal quantity from an electrolyte solution (conductive foam serves as a cathode), PF burning-out, sintering. These materials have especially highly porosity (up to 98%) and permeability (10^{-7} m^2), highly thermal shock resistance and plasticity, their tensile strength is 0.5 - 0.6 MPa. The disadvantages of MF are low corrosion resistance and high-temperature strength, which makes it impossible to use them in an oxidizing atmosphere at temperatures higher than 400 C. The material has almost unporous webs and a smooth surface (specific surface area is about 0.01 m^2/g), which impedes the deposition of a highly dispersed secondary support. To improve the working properties of MF, diffusion alloying with Cr, Si, Al may be used. It increases the tensile strength up to 1.2 - 1.5 MPa, rises the temperature

range up to 800°C and creates good prerequisites for the deposition of a secondary support since comparatively highly dispersed oxides form on its surface. A photograph of an MF structure is shown in Fig. 2.

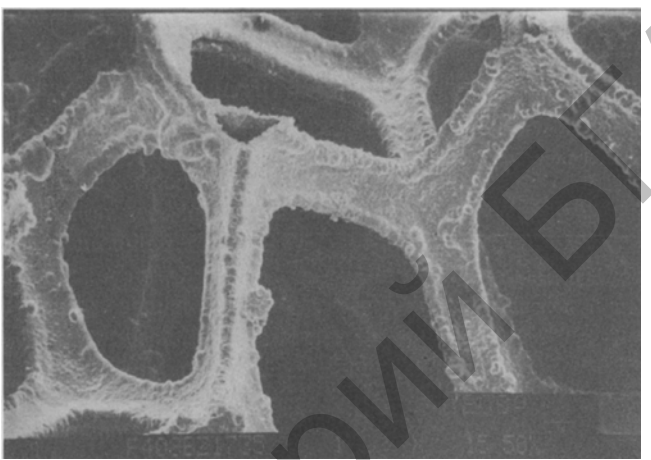

Fig. 2. Metal foam structure

2. *Ceramic foam* (CF) is produced by the PF duplicating with ceramic suspensions. The method involves the following sequence of operations: preparation of a ceramic suspension with the desired complex of rheological characteristics, impregnation of PF blocks with the ceramic suspension and removal of the suspension surplus (forming), drying, PF burning-out and sintering. Centrifugation as a forming method has been developed at Powder Metallurgy Research Institute, Minsk. In comparison with widely used methods (squeezing in rolls, flow-through with compressed air), it allows to fulfill the "impregnation - suspension surplus removal - drying" cycle many times, thus ensuring the possibility to produce a defect-free structure with a desired thickness of the ceramic coating on the CF webs. CF competes with MF in porosity (83 - 87%) and permeability (10^{-8} - 10^{-9} m^2) but exceeds it in the high-temperature strength and corrosion resistance. By changing the ceramics composition (cordierite, mullite, Al_2O_3, SiO_2, ZrO_2 and their combinations), it is possible to produce CF with different strength, operating temperature, thermal shock resistance and crack resistance. The method developed is universal from

this point of view. As a rule, CF have microporous webs (porosity up to 25%) with a rather complicated surface morphology and their specific surface area can reach 0.5 m^2/g. The CF bending strength is 2 - 4 MPa. A photograph of a CF structure is shown in Fig. 3. The cell size is determined by the PF in both cases and usually varies in the range of 0.5 - 10.0 mm.

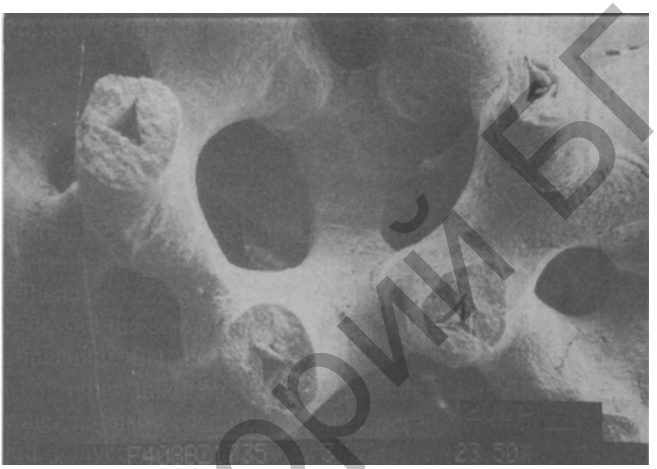

Fig. 3. Ceramic foam structure

To understand the interrelation between mechanical, hydrodynamic and structural properties of foam materials, it is important to have a model of a highly porous open-cell structure. The authors have developed a model capable of forecasting the foam materials properties from their structural characteristics (cell size, thickness of the inorganic coating on the PF structure). It is known that the elementary PF cell is a dodecahedral ellipsoid. The actual foam structure is rather complicated so it was simulated by a cubic structure which simplifies the calculations but preserves special links of the actual structure (Fig. 4). Unlike known similar models of the PF structure [5], this one has inner channels in the webs after sintering. The cell chosen has the following parameters: distance between PF webs (l_0), PF web width (t_0), thickness of the coating on the PF web (δ). An elementary web is a cube with an edge of l_0+t_0, all the edges are limited by hollow webs of a square section. In this model each of 12 hollow webs with

length l_0-2δ and side t_0+2δ belong to 4 allied cells, and each of 8 knots with edge t_0+2δ belong to 8 cells. As a result, we get equations combining the structural parameters with the porosity (2), specific surface area for the material with non-

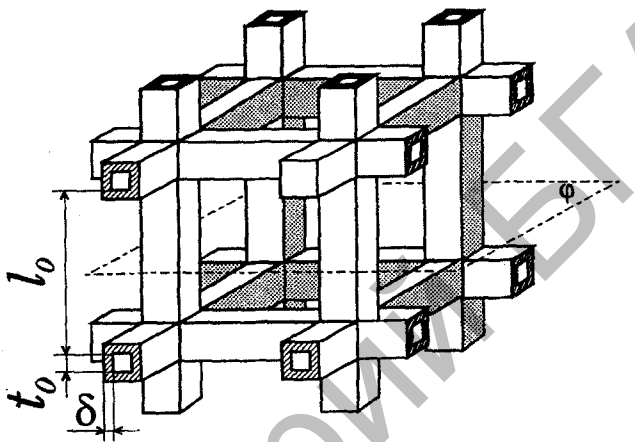

Fig. 4. Model of a foam structure

porous webs (3) and tensile strength (4). It was supposed that destruction takes place along the weakest section φ (Fig. 4).

$$P = 1 - 4\beta \cdot \frac{3\beta_0 + 3\beta(1-\beta_0) - 4\beta^2}{(1+\beta_0)^3} \tag{2}$$

$$S_v = \frac{12}{l_0} \cdot \frac{(\beta_0 + 2\beta)(1-2\beta) + \beta_0}{(1+\beta_0)^3} \tag{3}$$

$$\sigma = \sigma_0 \cdot \frac{4\beta(\beta_0 + \beta)}{(1+\beta_0)^2} \tag{4}$$

where σ_0 is the strength of the nonporous ceramic material, $\beta_0 = t_0/l_0$ and $\beta = \delta/l_0$.

To interpret experimental data, one should note that total porosity (P) of foam materials consists of macroporosity and microporosity. Macroporosity is comprised of open porosity (P_o) and canal porosity (P_c) formed after the PF

burning-out; microporosity (P_m) is determined by the porosity of the web material (P'). P'≈0 for MF.

$$P = P_o + P_c + P_m \quad (5)$$

$$P_m = P' (1 - P_c - P_o) \quad (6)$$

Taking into account (5) and (6), equation (1) can be rewritten as follows:

$$\sigma = \sigma_o \cdot (1 - P')^{m_1 - m_2} \cdot (1 - P)^{m_2} \quad (7)$$

Thus, the model developed allows to calculate the porosity, strength and specific surface area of the produced material on the basis of the cell structural parameters taking into account the "three-porous" character of the foam structure. Experimental data have confirmed that the model developed allows to forecast the properties of foam materials with sufficient accuracy.

As the cell size of an inorganic foam is uniquely determined by the PF cell size, all the main MF and CF properties depend on the thickness of the metal or ceramic coating on the PF structure (it follows from equations 2-4). Thus, it is very important to control this parameter in the course of production.

The MF coating thickness is uniquely and very accurately determined by Faraday's law:

$$M = \frac{k \cdot A \cdot I \cdot t}{z \cdot F} \quad (8)$$

where M is the mass of the deposited material (g), k is the current efficiency coefficient, μ is the molar mass of the material deposited (g/mol), I is the current (A), t is the deposition time (s), z is the charge of the deposited ion and F is Faraday's constant (C/mol). For nickel, A= 58.69 g/mol, z=2, k=0.95 - 0.98, F=94490 C/mol.

To control the process of the coating growth during the multiple PF impregnation with ceramic suspensions, the authors have developed a physical model enabling to produce ceramic coatings with the desired thickness. The thickness of the ceramic coating was evaluated by the dimensionless parameter K_i, which is conveniently and simply obtained in practice:

$$K_i = \frac{M_i}{M_0} \tag{9}$$

where K_i is the relative thickness of the ceramic coating produced in i impregnations, M_0 is the mass of the non-impregnated PF block (g) and M_i is the total mass of the dry ceramics produced on the PF monolithic structure in i impregnations.

It may be shown that the dimensionless parameter K_i is proportional to the true thickness of the ceramic coating:

$$\delta = K_i \cdot t_0 \cdot \frac{\xi \cdot \rho_p}{\rho_c} \tag{10}$$

where t_0 is the PF web side width (cm), ξ is a coefficient taking into account the PF shape (ξ=0.250 for a square section and ξ=1.145 for a triangle one), ρ_p is the pycnometric density of polyurethane - 1.22 g/cm^3, ρ_c is the density of the ceramic coating and δ is the thickness of the ceramic coating (cm).

The model has the following meaning. Let the PF block structure be coated with a ceramics of mass $M_1=M_0K_1$. When this material is dipped into a ceramic suspension with humidity W, water is absorbed into the initial porous coating due to capillary forces. As a result, a layer with humidity W'<W is formed in the vicinity of the webs (*i.e.* when the suspension looses fluidity). The mass of the coating produced in two impregnations is $M_2=M_0K_2$. Water mass in the suspension used to form the new coating is $M_{wo}=(M_2-M_1)/(1/W-1)$ before impregnation. A part of water with mass $M_{w1}=M_1/(1/W'-1)$ is absorbed into the initial layer, and a part of it with mass $M_{w2}=(M_2-M_1)/(1/W'-1)$ remains in the new layer. Then, taking into account that $M_{wo}= M_{w1} +M_{w2}$, we have:

$$1/Z_2 = A \bullet X - 1 \tag{11}$$

where $Z_2 = (K_2 - K_1)/K_1$ is the coefficient of coating thickness increase in the second impregnation, $X = W/(1-W)$, $A = 1/W' - 1$.

A graphic dependence for an alumina-silica ceramics $1/Z = f(X)$ (Fig.5) shows that experimental points coincide with the theoretical dependence within the error limits. A similar coincidence was observed for ceramics with other chemical compositions as well. Therefore, the derived dependence $Z = f(W)$ is universal and can be used to control the kinetics of the ceramic coating growth under multiple impregnations and the mechanical and hydrodynamic CF properties with great accuracy.

Thus, the theoretical and experimental results presented allow to forecast the properties of foam materials and to control the production of highly porous metal and ceramic foam initial supports with a predetermined complex of mechanical and hydrodynamic characteristics and to produce materials with a wide range of operational properties.

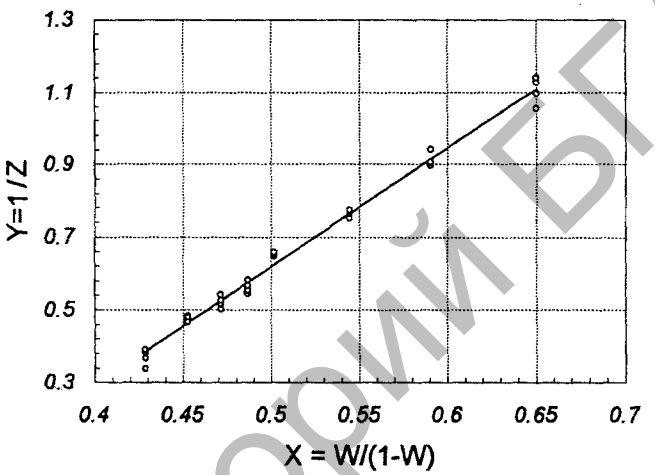

Fig. 5. Dependence of the ceramic coating growth coefficient on humidity. Theoretical dependence - continuous line

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