Titanium carbide based metal-ceramic material with porous layered structure

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Abstract. The method of obtaining a porous material with a layered structure is considered. This method makes it possible to create a finely porous layer on a highly porous base. The method was used to obtain a material based on titanium carbide powders. In the structure of flat samples of such material there were areas with different characteristics of porosity, such as volume and pore size. Creating a layered (or gradient) structure allows to increase the efficiency of membrane filters based on such material. The characteristics of the porous structure are determined. Filters based on titanium carbide powders were synthesized, the isotropic porous structure of which has the following characteristics: filtration fineness is about 460 nm with a total porosity of 39%, gas permeability of $3.3 \times 10^{-19}$ kg/(m²·Pa·s) at a pressure drop of 0.05 MPa. Filters with a gradient structure had a filtration fineness of 320 nm and a gas permeability of $2.4 \times 10^{-19}$ kg/(m²·Pa·s) at a pressure drop of 0.05 MPa.

1. Introduction.

Porous materials occupy one of the most significant places in modern life, due to their wide use in various fields of human activity. Obtaining porous materials in the form of final products with the necessary characteristics and physicomechanical, chemical properties is the key to the development of the economy, technology and science, and would also contribute to the solution of environmental problems.

Membranes are one of the main areas of research and the use of porous materials. The current state of the technology of ceramics and metals allows the manufacture of porous samples from any inorganic raw materials. The composition of the starting material, the porosity and the structure of the material determine the properties of the porous product. The characteristics of the structure are total, open and closed porosity, permeability, shape and size of pores, their size distribution, specific surface area. Of these indicators, the most important structures are porosity and pore size [1]. Depending on the tasks, for which the membrane will be used, it becomes necessary to obtain a porous material with a different value of porosity and pore size, which will be the basis of the membrane. The main task of membrane filters is that it is necessary to make the separation of the components of a liquid or gaseous medium with lower energy costs [2].

It should be noted that currently produced organic polymer filters have significant drawbacks: low strength, corrosion resistance, heat resistance, lack of sorption properties, etc. Most of these shortcomings are absent in filters made of ceramic materials, which are used, for example, when filtration processes, gas separation, various electrochemical processes are carried out at high pressure drops or high temperatures, in aggressive environment.

The membrane consisting of several layers of different materials, each of which has its own structural organization at the micro and nano levels, is a modern and competitive product with a range...
of technological characteristics, such as high transport and separation properties, the ability to regenerate in the process of pollution [2]. In the case of manufacturing porous materials, characterized by a homogeneous and isotropic in volume distribution of porosity and pore size, a rapid decrease in permeability due to clogged pores with colloidal and suspended particles contained in filtered substances is observed [1]. The creation of a fine-pore structure on a highly porous base allows one to increase the cleaning efficiency of technological environment from submicron dispersed contaminants with an insignificant increase in the resistance to the flow of the technological environment in comparison with a single-layer highly porous material. In addition, the advantage of such membrane filters, in addition to the possibility of regeneration by heat treatment, washing with acids or other solvents, is the possibility of regeneration by means of a reverse flow of liquid or gas.

It is known that the performance of a membrane filter increases with decreasing thickness of the membrane layer [3]. However, in the production of membranes of small thickness, difficulties arise in obtaining a defect-free membrane layer.

In this paper, the study was carried out to obtain a metal-ceramic material with a gradient porous structure on the basis of titanium carbide powders with the consolidation of pressing powders and their subsequent sintering. In this case, a material production method was used, including the manufacture of a porous carrier substrate that provides mechanical strength, and the formation of a thin membrane layer on it that determines the filtration fineness.

2. Used materials and research methods

In this work, we used titanium carbide powders obtained by the following methods: calcium-hydride method and a melting method in an electric arc furnace of a consumable electrode in a graphite crucible with subsequent crushing and sieving of the melted ingot. The average particle size of the powder of titanium carbide obtained by the calcium-hydride method was 130 nm. Fraction of crushed titanium carbide powders was less than 56 μm. Commercial highly dispersed powders of carbonyl nickel and molybdenum were also used.

Using scanning electron microscopes LEO 430i and JSM 6480, particles of titanium carbide powders were examined (Figures 1, 2). Sintering was carried out in a shaft electric furnace in a vacuum of 10⁻² Pa. The porosity of the material was determined by hydrostatic weighing. The determination of the pore size in the samples was carried out by the “bubble” method (State standard of Russia R 50516-93. Polymer membranes, the method for determining the bubble point of flat membranes). The method applies to membranes with a maximum pore size of 0.1 to 15 μm and consists in determining the minimum gas pressure required to force a gas bubble through the pores of a flat hydrophilic membrane impregnated with water or through the pores of a flat hydrophobic membrane impregnated with alcohol.

The permeability coefficient \( K \) was calculated by the following equation:

\[
K = \frac{2\mu V P}{S\tau (P_1^2 - P_2^2)}
\]

where \( V \) is the volume of gas passing through the test sample in cm³; \( h \) is the height of the sample in cm; \( S \) is the sample area in cm²; \( \mu \) is the gas viscosity in Pa·s; \( \tau \) is the time in seconds; \( P \) is the pressure at which the volume of gas is determined in dyn/cm²; \( P_1 \) and \( P_2 \) are the gas pressures before the sample and after the sample in dyn/cm², respectively [4].

3. Experiment and results

In the production of such a filter with a gradient (layered) structure, a porous material with a pore size of about 1–10 μm was used as a substrate obtained by pressing of a mixture of crushed titanium carbide powders (Fig. 1), nickel and molybdenum in a cylindrical matrix under a pressure of 75 MPa. A binder, polyvinyl alcohol, was added to the powders, and the compacts were then sintered at a temperature of 1250°C in vacuum. The crushed titanium carbide powder was mixed with 7.5 mass % nickel and 2.5 wt % molybdenum. The good wettability of titanium carbide with Ni–Mo alloy ensures
the formation of the fine-grained structure of alloys, the possibility of reducing the sintering temperature, thereby reducing the degree of overgrowth of pores \[5, 6\].

Selective filtering layer with smaller pores was obtained by sequential deposition of fine-pores layers and heat treatment. This allows creating a structure with high efficiency of trapping highly dispersed pollutants. The front surface of the sample was covered with a thin uniform layer of a suspension of ultrafine powder of titanium carbide, obtained by the calcium hydride method (figure 2), and a solution of a binder with the addition of 50 wt % nickel and 25 mass % molybdenum. Depending on the required efficiency and material resistance to the flow of the substance being filtered, a different number of such layers can be applied. The sintering temperature was chosen to be 1000°C. After sintering the sample on the selective layer, there were no macrocracks and exfoliation.

In figure 3, we can see the presence in the sample volume of a region with a coarse-porous (pore size ~ 10 μm) structure and a surface layer with smaller pores.

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{fig1.png}
\caption{SEM-photograph of crushed titanium carbide powder.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{fig2.png}
\caption{SEM-photograph of titanium carbide powder obtained by the calcium hydride method.}
\end{figure}

\begin{figure}
\centering
\includegraphics[width=0.4\textwidth]{fig3.png}
\caption{Micrograph of the surface region of the sample.}
\end{figure}
The results of the permeability study of the obtained porous samples are presented in table 1. The processing of the experimental data made it possible to determine such characteristics of a sintered sample as porosity, permeability, and filtration fineness. The results of the calculations are presented in table 2.

Table 1. The results of the study of porous samples on permeability.

| Sample                  | Air flow through the sample at a pressure drop of 0.05 MPa, $10^{-3}$ m³/(min×cm²) | Air flow through the sample at a pressure drop of 0.1 MPa, $10^{-3}$ m³/(min×cm²) | Water flow through the sample at a pressure drop of 0.05 MPa, $10^{-3}$ m³/(min×cm²) | Water flow through the sample at a pressure drop of 0.1 MPa, $10^{-3}$ m³/(min×cm²) |
|-------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|-------------------------------------------------------------------------------------|
| before applying the selective layer | 26.2                                                                                | 32.0                                                                                | 0.09                                                                                | 0.18                                                                                |
| with selective layer    | 18.9                                                                                | 26.0                                                                                | 0.05                                                                                | 0.1                                                                                 |

Table 2. Characteristics of the obtained porous material.

| Sample                  | Total porosity, % | Filtration fineness, µm | Permeability at a pressure drop of 0.05 MPa, $10^{-19}$ kg/(m²·Pa·s) |
|-------------------------|-------------------|--------------------------|---------------------------------------------------------------------|
| before applying the selective layer | 39                | 0.46                     | 3.3                                                                 |
| with selective layer    | 39                | 0.32                     | 2.4                                                                 |

As you can see, the application of the selective layer and its sintering at a temperature of 1000°C reduced the filter throughput by almost one and a half times as compared with the sample without such a layer. Filtration fineness also increased by approximately one and a half times. The decrease in the flow of air or liquid indicates that the large pores of the substrate after application of the selective layer were blocked by a fine-pore structure. The application of additional layers will increase and regulate the degree of purification of such a material.

Thus, a porous material based on titanium carbide is obtained, the isotropic porous structure of which has the following characteristics: filtration fineness is about 460 nm with a total porosity of 39%, gas permeability of $3.3 \cdot 10^{-19}$ kg/(m²·Pa·s) at a pressure drop of 0.05 MPa. Filters were also synthesized with a layered (gradient) structure with a filtration fineness of 320 nm and a gas permeability of $2.4 \cdot 10^{-19}$ kg/(m²·Pa·s) at a pressure drop of 0.05 MPa.

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