Technology Obtaining of Highly Efficient Powdered Filtering Materials for Cleaning Liquids and Gases

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Abstract. The work is devoted to development of technology for the production of high-performance powdered filtering materials (FM) on the basis of titanium carbide by dry radial-isostatic pressing (DRIP) method with followed their sintering by self-propagating high-temperature synthesis (SHS). Developed technology of obtaining gradient multilayer filtering materials with uniform and regulated porous structure on volume by method of a stepwise multilayered radial-isostatic pressing of various by nature and composition powder materials (PM) which provides the obtaining FM with variable pore sizes in the direction of filtration. Obtained by us gradient FMs have considerably higher permeability, pollutant capacity and service life in comparison to existing analogues. The developed technology of a step-by-step DRIP of sealing materials also allows receiving high-performance FM new generation with unique operational properties, which today is virtually impossible to obtain by other methods.

Keywords: powder material, dry radial-isostatic pressing, porosity, filtering material.

1 Introduction

In the world, the problems of nature and health protection, issues of industrial wastewater treatment, smoke emissions, household waste disposal, etc. become more and more relevant. Despite this, millions of cubic meters of uncleared industrial waste come to rivers and lakes annually, contaminating the world's oceans and groundwater. In such conditions using of water, the quality of which affects on the health of the population, without additional water treatment can be dangerous. The existing centralized water treatment system does not always ensure compliance with water quality requirements, as water pipes in the form of old pipes are often an independent source of pollution. Therefore, in our opinion, to provide the necessary quality of water it will be more efficient to equip the dwelling houses with individual filtering devices or systems, where contaminated water passes through several porous media and sorbents, which allow providing the necessary mechanical and chemical degree of water purification from pollution.

Traditional filter's constructions involve the use of various porous materials or fillers such as polyurethane foam, felt, paper, mesh, etc., which complicates the construction of the filter or the process of his regeneration, so these filter systems have a short operating time and a narrow spectrum of purification. Low strength and corrosion resistance of such FMs significantly reduces their effectiveness. In this regard, we consider the perspective direction – obtaining of FMs based on powdered metals and ceramics, which due to their structural characteristics will provide a more thorough cleaning. Having a high durability and chemical

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resistance they are relatively easy to process and regenerate and on condition using energy-saving technologies of their production they can become competitive on the market.

2 Literature Review

Analysis of multidisciplinary literary data [1], [2], [3] shows that the basic requirements for FMs at their developing and manufacturing are reduced to the following:

1. FM must have high permeability at a given pore size and high fineness of filtration. When higher the permeability the more efficiently and rationally used of FM and the longer term of service.

2. When creating FM should seek to ensure a uniform distribution of pores throughout the surface of the filtration and to increase its active area. It contributes to the uniform distribution of liquid or gas along the working surface and also provides capture of the pollutant of the required size.

3. FM must have high pollutantcapacity, in other words, must catching and detaining a large amount of pollutant while maintaining high permeability and durability.

4. FM must be corrosionresistant to the environment which is filtering and to the temperature of the process, also it must have the necessary mechanical strength and must be suitable to machining, welding, gluing, etc.

It is easy to see that properties such as permeability, pore distribution by sizes of the filtration surface, pollutantcapacity, the optimallity of which requires the fulfillment of the first three requirements, are entirely determined of the pore structure of the filtering material. These properties of FM can be provided with rational conditions of compaction process.

The process of pressing (forming) the future FM more than any other operation affects the performance characteristics of the finished product. For a wide range of powder materials, preferably with a significant ratio of length to transverse dimensions, the radial compression scheme is optimal [4]. The absence of contact friction between the powder and the elastic shell ensures the uniform distribution of the density by the volume of powder briquette, which ensures after the sintering the required quality of the finished product. Therefore, it is advisable to use the radial compression scheme as a basis for the creation of new technologies of FM forming, since it allows to realize the basic positive features inherent in traditional methods of pressing and also allows receiving various gradient filtering materials in which pore sizes decrease in the direction of filtration [5].

Traditional methods of sintering powder materials require a powerful oven with a protective atmosphere, so the sintering costs can amount up to 50% of the cost of production [1]. Therefore, recently is developing rapidly a new direction of technological combustion - a self-propagating high-temperature synthesis (SHS) [6], [7], which allows to synthesize of powder materials on the basis of carbides, borides, nitrides, silicides, and others without energy consumption for sintering process. The process begins at local influence on the system of a short thermal impulse and proceeds in the future in the form of a combustion wave without the supply of energy from the outside due to the heat of the reaction of combustion and without the use of protective atmospheres.

A promising metal in this respect is titanium, since it has a rare combination of physic-mechanical and anti-corrosion properties. In many cases, thanks to the high corrosion resistance of FM from powders of titanium and its alloys, they have advantages over materials from bronze, stainless steel and nickel powders [1]. Also, we consider is promising direction, the creation of FM based on titanium carbide – a material with a high melting point (3260 ± 150^{o}C), hardness, thermal conductivity, resistance to aggressive environments and abrasive deterioration. It possesses high corrosion resistance both in alkaline and in acidic environments, as well as oxidation resistance [1], [5].

The economic efficiency of filtering powder materials is provided not only due to operational properties, but also at the stage of their production due to the use of cheaper raw materials and energy saving at all stages of the technological process. The largest share in the cost of products production by powder metallurgy methods is the cost of basic materials and electricity (80-90%). Therefore, the use of SHS processes for the consolidation of powder material will reduce the cost of sintering process and protective atmosphere, so the FM based on titanium carbide can successfully compete with traditional ones.

Promising and widespread products with a heterogeneous porous structure are multilayer FM, in which each layer is made of powders of different granulometric composition. Such materials have a permeability, pollutant capacity and service life higher than single-layer [5]. The development of the technology of a step-by-step multilayer DRIP from various by nature sealing materials, will allow producing of high-performance FM of new generation with unique properties. Thus, the purpose of work is developing a technology for obtaining high-performance powdered FM based on titanium carbide by DRIP method with followed sintering in a SHS mode.

3 Research Methodology

3.1 Development of technology for obtaining powdered FM

The reaction of the formation of titanium carbide TiC by the SHS method from the briquetted mixture of titanium and carbon powders due to the high isothermicity of the process belongs to the category of combustion reactions, occurring in narrow zones, moving on the briquettes due to heat transfer after local initiation of reactions in a heated mixture of reagents [6], [7]. The mixture is briquetted, placed in sealed reactors, then vacuumed (or supplied with an inert gas) and ignited. After combustion process and cooling performed a grinding, as result we obtain the titanium carbide powders.

In our case, for the production of powdered filtering materials based on titanium carbide, the technological process should consist of the following operations:

- preparation of a mixture of titanium and carbon powders ($Ti+C$);
- dry isostatic pressing of a given shape and sizes;
- the SHS process - sintering in a protective atmosphere.

The optimal ratio of powders Ti (titanium powder PTS-1) and carbon C (technical carbon PM-16E) was determined experimentally in terms of obtaining quality products (no cracks, warping and obtaining isotropic properties by volume) based on our experimental research the velocity of the process of SHS combustion of powdered briquettes with different amounts of carbon C. The results of the experimental research showed that at ratios Ti and C from $TiC_{0,6}$ to TiC - the rate of combustion increased sharply, leading to cracks, warping of blanks and discontinuities due to intense gas evacuation at high temperature (see **Figure 1*a***). Therefore, due to the apparent reject, there was no need to explore the structure and properties of such carbides ($TiC_{0,6}$ - TiC).

At exploring of SHS combustion process of powdered briquettes with Ti and C ratios from $TiC_{0,4}$ to $TiC_{0,2}$ there was a certain decrease of combustion rate and temperature, which leds to a significant decrease in the strength characteristics of the filtering material (FM disintegrated even under low pressure) (see **Figure *1b***). Thus, in order to obtain qualitative FMs, we have experimentally determined the most rational range of the ratios of Ti and C components – namely from $TiC_{0,4}$ to $TiC_{0,6}$.


a) b)

Fig. 1. General view of sintered powder FMs depending on the ratios *Ti* and *C* (speed of SHS process combustion and temperature): *a)* $TiC_{0.6}$ - TiC; *b)* $TiC_{0.2}$ - $TiC_{0.4}$

3.2 Preparation of a powders mixture

To prepare the powders mixture the starting components are titanium powder PTS-1 (*Ti*-98,18%, *C*-0,03%, N_2-0,08%, H_2-0,32%, *Si*-0,07%, *Ni*- 0,14%, *Fe* -0,10%) obtained by the hydride-calcium method and carbon (*C*) - technical carbon PM-16E with a bulk density of 0,1 g/cm^3. The ratio *Ti* and *C* was determined by their atomic weight. The components were mixed in determined by us the stoichiometric ratio $TiC_{0,5}$ ($8Ti : 1C$) in a mechanical mixer with a volume of 2 dm^3. Mixing was carried out at a speed n = 80-120 rpm. For mixing were used the steel bullets with a diameter 12 mm in quantity 8 pcs. The housing, bullets and main parts of the mixer are made of steel X18H9T. Mixing time is 2 hours. The main monitored technological parameter is the bulk density of the mixture – it is the output parameter for calculating the inner diameter of the shell, which ensures obtaining the sizes of briquette.

3.3 The process of dry radial-isostatic pressing

The filling of a powders mixture into a mold is preceded by the pressing process. After mixing the titanium and carbon powders, on the vibration stand we filled the resulting powders mixture into a form to provide a uniform bulk density along the length (volume) of the product. After filling was performed the DRIP process using the tools and equipment described in [5] to provide the required geometry and the density of the powdered briquette. In order to change the pore size of the filtering material, is possible introducing the filler into the powders mixture (e.g. urotropine). In this case, after DRIP process, during sintering at temperature of 100°C the filler completely burns out with the formation of the required pore structure. On **Figure 2** shows the diagram of DRIP the powders mixture on the mandrel. The optimum pressure in terms of its ability to formation, energy saving and properties of FM was p = 20-40 MPa. The main criterion of the optimal area of DRIP is energy saving, that is, for the manufacture of FM based on $TiC_{0.5}$ needs much less energy consumption (p = 20-40 MPa) than is required for production pure titanium FM *Ti* (PTS-1) (p = 80-100 MPa). Pressure range (Ti+C) at DRIP provides ability to formation powder briquettes and an additional ability to control the filtering properties of FM due to pressure of pressing.

3.4 The process of SHS sintering of powder briquettes

The basis of proposed sintering technology is the process gas-free combustion of mixtures of powders, known as SHS: $Ti+C_{0,5}=TiC_{0,5}+Q$. SHS process has the following advantages: low synthesis time, the absence of external energy consumption due to using the internal energy of the reaction, relatively simple equipment, the possibility the synthesis of multicomponent systems.

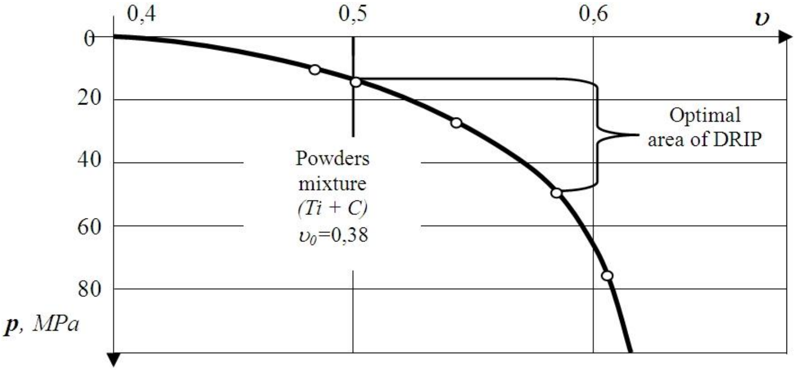

Fig. 2. Dependence of the relative density *υ* of powder briquette from the compression pressure *p*.

Before the SHS process our powder briquettes were dried at 250-300 °C in a drying cabin to remove absorbed vapours from powder briquettes. The SHS process was carried out in the reactors we developed (see **Figure 3**), which represent a vessel of open or closed type cylindrical form from steel (*X18H9T*). The synthesis reaction was initiated by a heated electric tungsten (*W*) spiral.

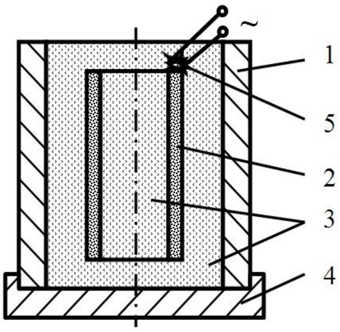

Fig. 3. Scheme of the reactor for SHS-sintering of compositions on the basis of *Ti+C*:
1 - holder (X18H9T); 2 - powder briquette (mixture of powders *Ti+C*); 3 - filling (activated carbon or special gas atmosphere); 4 - base (X18H9T); 5 - electric spiral.

After conduction of SHS reaction (about 20-30 sec) and next cooling the reactor is disassembling and the finished FM is removing. As a result of the synthesis (*Ti+C*) obtained FM has the following chemical composition: $TiC_{0,5}$ - 88%, TiN - 6%, Ti_2N - 1%, Ti_2O – 3,2%, Ti_2O_3 - 0,4%, TiO_2 – 0,1%, C_{free} – 1,3%.

4 Results

4.1 Properties and efficiency

The structure of the obtained powdered FM on the basis of titanium carbide ($TiC_{0,5}$) is homogeneous, in contrast to similar FM obtained from pure titanium powder. In last one is observed the formation of titanium oxinitrides on the outer and inner surfaces of the product. The penetrability by thickness of FM from a pure *Ti* is variable, the inner area is partially melted, while observed a closure of pores, which significantly reduces its performance characteristics [1], [5].

Figure 4 shows the dependence of the coefficient of permeability K of powdered FM from the relative density υ. On this figure you can see that the coefficient of permeability K of powdered FM based on $TiC_{0,5}$ is significantly higher.

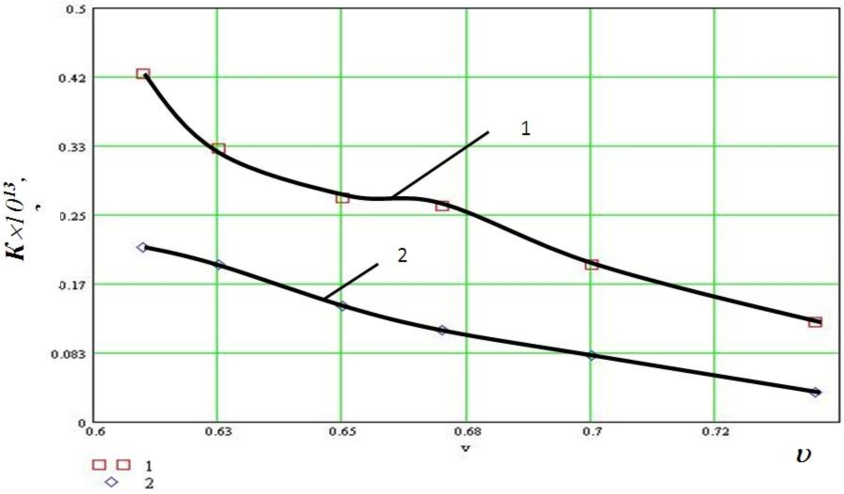

Fig. 4. Experimental dependencies of the coefficient of permeability K from the relative density υ obtained FM: 1 - $TiC_{0,5}$ (SHS-sintering); 2 - Ti (PTS-1) (sintering in vacuum t = 960 °C during 4 hours)

According to our observations, this is directly related with the SHS-sintering processes of a powders mixture ($Ti+C = TiC_{0.5}$), which resulted to an increase the average pore sizes of FM obtained by us, which is d_{cp} ($TiC_{0.5}$)=12÷15 microns in comparison with similar FM whose average pore size does not exceed d_{cp} (Ti)=(6÷8) µm.

Our experimental data shows that the technology developed by us for obtaining powdered FMs based on titanium carbide ($TiC_{0,5}$) allows us to reduce energy consumption at the pressing stage in 2 times and at the stage of sintering in 1,3-1,5 times, which in aggregate can provide the competitiveness of such filtering materials on the market.

Figure 5 shows the FMs based on the $TiC_{0,5}$ powders mixture, which we obtained by the improved DRIP method on the mandrel with followed SHS-sintering of powdered briquettes with an optimal $Ti+C$ ratio.

Fig. 5. General view of obtained single layer filtering materials based on titanium carbide ($TiC_{0,5}$) obtained by the DRIP method on the mandrel.

Figure 6-7 shows the results of experimental researches carried out on the improved by us equipment for DRIP [5]. The conducted researches are in good agreement with the previously obtained theoretical and experimental data [1], [4], [5] and in particular confirm that the developed technology for the production of FM based on $TiC_{0,5}$ provides the obtaining of powdered FMs with a uniform pores distribution by the volume of briquettes compared with similar FMs based on pure titanium powders, obtained by analogous methods.

Figure 6 shows the differential curves of pore distribution by sizes of powdered FM based on titanium carbide $TiC_{0,5}$ and pure titanium *Ti* (PTS-1) obtained by DRIP method. Differential curves of pore distribution by sizes were determined by the method of displacing of fluid from pores [1].

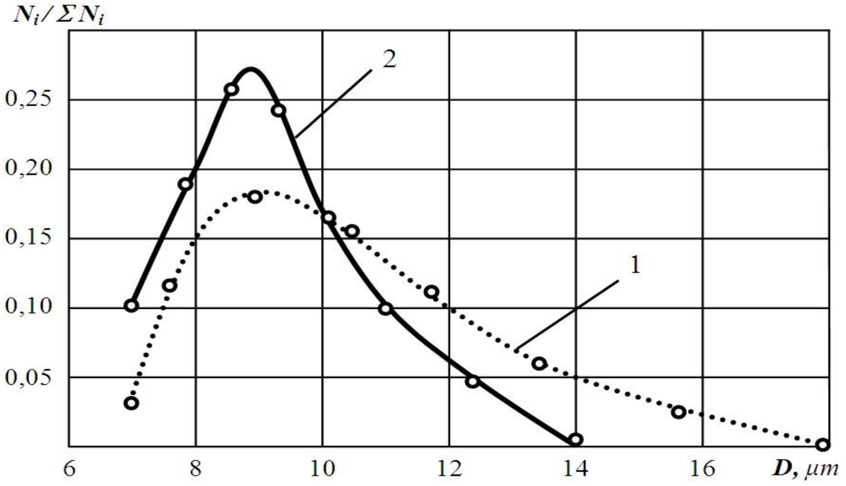

Fig. 6. Differential curves of pore distribution by sizes of powdered FM obtained by DRIP on the mandrel: 1 - *Ti* (PTS-1) traditional technology; 2 - $TiC_{0,5}$ (SHS-sintering) developed technology.

Thus, in the FM based on $TiC_{0,5}$ obtained by the DRIP method, the peak of the curve function of pore distribution by sizes is shifted to a smaller pore sizes area: the relative number of pores of the maximum size decreases on 20-35% due to their transition to a number of averages. Obtaining a more uniform distribution of pore sizes is achieved by obtaining FMs by DRIP method with a more uniform distribution of porosity and, consequently, with a more uniform distribution of local permeability over the filtering area. During of research was used a method for evaluating local permeability based on measuring of air flow volumes through small areas of samples using the measuring head according to the method described in [1].

Figure 7 shows the deviation of the coefficient of local permeability ΔK from its average value K for the FM based on the titanium carbide $TiC_{0,5}$ and pure titanium *Ti* (PTS-1) obtained by the DRIP method on the mandrel. The obtained results indicate that the improved DRIP method with using the developed by us technology provides an increase the uniformity of local permeability by an average on 20-25%.

At the same time, deserves attention the production of multilayer FMs based on metal and ceramic powders. In this case, the inner layer (frame) formed from a large size powder of titanium PTK (-0,63 ... + 0,4) mm, and the outer one - from a mixture of titanium powder of the average fraction PTS (-0,1 ... + 0,063) mm with carbon *C*, according to the technology we developed for producing titanium carbide $TiC_{0,5}$. Keeping whole technology of pressing and SHS-sintering of two-layer powdered briquette in the presence of carbon filler or protective gas atmosphere, it is possible to obtain two-layer FMs with uniform structural characteristics by all volume of product.

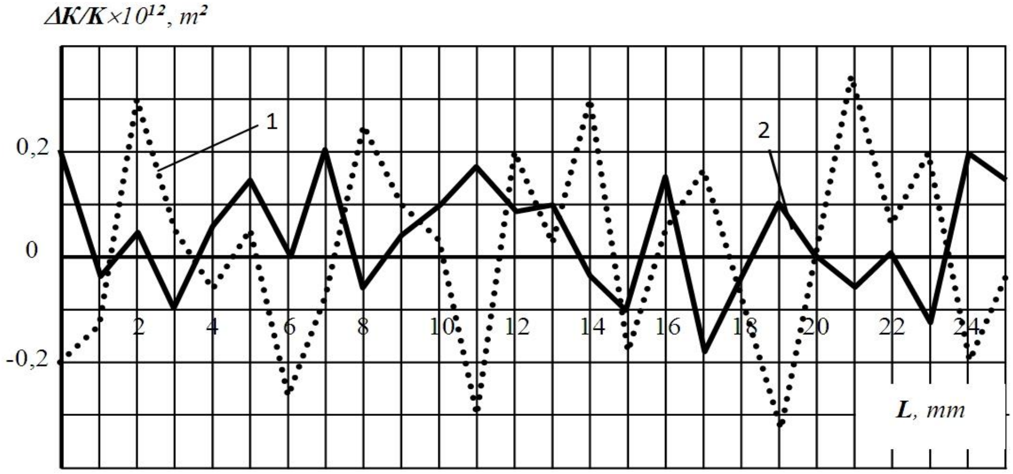

Fig. 7. Dependences of the local permeability deviation ΔK from its average value K by the length of powdered FM: 1 - Ti (PTS-1); 2 - $TiC_{0,5}$ (SHS-sintering).

4.2 Technology of manufacturing multilayer FM based on titanium carbide

The main direction of using powdered FMs based on the above mentioned materials is the purification of liquids and gases in a dead-end filtering mode. Taking into account the environmental situation in Ukraine particular interest has using of such materials for purification from pollution of lubricants, lubricating and cooling liquids and technical waters, which is effectively carried out by our developed gradient multilayer filtering materials. The technology of manufacturing (two- or multi-layer) FMs includes a step-by-step DRIP of powders of one composition (or powders mixture) on mandrel or matrix with the following sintering of the resulting powdered briquettes in the SHS mode with (or without) protective atmosphere (see **Figure *8a***).

The research was carried out on a mixture of titanium powder PTS-1 with particle size (-0.1...+0.063) mm with carbon of the technical mark PM-16E ($TiC_{0,5}$) and pure titanium powder PTK with particle sizes (-0.63...+0.4) mm. In the manufacturing of two-layer FM from a powders of different fractions to create a layer with small pore sizes we used a titanium powder PTS-1 with a particle sizes (-0.1...+0.063) mm and to create a basis layer (frame) - we used a titanium powder PTK with particle sizes (-0.63...+0.4) mm.

The compressed powder briquettes were sintered in a SHS-mode with a protective atmosphere and investigated their properties: pore sizes determined according to Ukraine state standard (GOST 26849-85), permeability coefficient according to Ukraine state standard (GOST 25283-82). The general view and structure of obtained two-layer FM based on $Ti+TiC_{0,5}$ is shown on **Figure 8 *b, c***. Obtained results were compared with the results given in [1], where the properties of two-layer powdered FM made by axial pressing in a steel mold are presented.

a) b) c)

Fig. 8. *a)* Scheme of step-by-step DRIP of powders on a mandrel; *b)* General view and *c)* Structure of two-layer FM based on titanium powders: internal frame layer - PTK powder (-0,63...+0,4) mm; external filter layer - a mixture of titanium powders: PTS(-0,1...+0,063) mm and carbon *C* in the stoichiometric proportion $TiC_{0,5}$ ($8Ti : 1C$)

Figure 9 shows the dependencies of the coefficient of permeability *K* from the average pores size D_{cp} of powdered FMs obtained by the DRIP method and FMs obtained by compression in a steel mold. The results show that using of the improved DRIP method allows us to increase the permeability at a given pore size on 35...50% compared with FMs obtained by pressing in a steel mold.

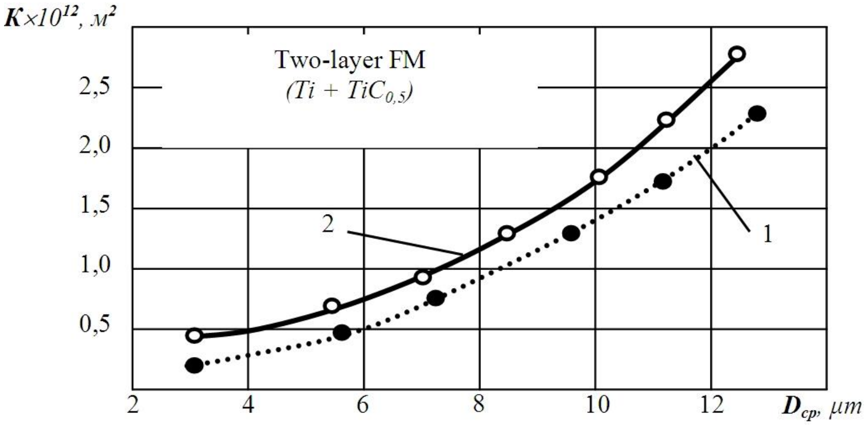

Fig. 9. Dependence of the coefficient of permeability *K* from the average pores size D_{cp}: 1 - two-layer powdered FM (axial pressing); 2 - two-layer powdered FM (DRIP+SHS)

On the basis of the obtained results, were manufactured experimental batches of gradient powdered FMs of simple and complex form (see **Figure 8**), which were tested for purification lubricants, liquid coolant (LC) and water (technical). Taking into account the increased chemical activity of the LC, the experimental FM batches were made on the basis of titanium carbide according to the technology developed by us. The results of the tests show that the using of two-layer FMs based on titanium carbide to purification such environments made it possible due to their improved properties (high chemical resistance, required mechanical strength, uniform distribution of pores along the entire filtration surface, increased permeability and pollutant capacity, the possibility of regeneration) increase duration of operation of obtained powdered FMs in 1,5-2,0 times. This confirms the feasibility of using developed technology to production of powdered filtering materials.

5 Conclusions

On the basis of theoretical and experimental researches was developed a technology for obtaining single- and multi-layer powdered FMs based on titanium carbide by dry radial-isostatic pressing method. As a result of the tests it was established that the proposed technology allows reducing energy consumption at the pressing stage in 2 times and at the stage of sintering – in 1,3-1,5 times due to the absence of external energy inputs for sintering (SHS-sintering). In addition, it has been established that the DRIP method in combination with the developed technology increases the uniformity of the pore distribution of single-layered FMs based on $TiC_{0,5}$ on 20-35% and increases the local permeability on 20-25% compared with similar FMs based on titanium powders Ti (PTS-1), which is related with the SHS combustion process ($Ti+C = TiC_{0,5}$), an increase in the average pores size, a more uniform distribution of density by volume and the absence of surface closure of pores.

The technology of obtaining a two-layer powdered FMs based on $Ti+TiC_{0,5}$ by the DRIP method increase the permeability at a given pore size on 35...50%, compared with powdered FMs obtained by axial pressing in a steel mold. The results of the tests show that the using of two-layer FMs based on titanium carbide makes it possible, due to their improved properties, to increase the duration of operation of the filtering material at a minimum in 1,5-2,0 times, which confirms the feasibility of using our technology for the production of gradient powdered FMs. Developed step-by-step technology DRIP of compactable materials also allows obtaining a high-performance FMs of new generation with unique operational properties, which in other ways practically impossible to obtain.

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