POROUS STRUCTURES AND THEIR EFFECT ON THERMOPHYSICAL PROPERTIES OF THERMAL PROTECTION ELEMENTS

Abstract: The improvement of the thermal insulating material thermophysical characteristics of the thermal protection elements by studying the porous structure is a promising direction of research. The article describes the effects of the porosity and coupling of the porous structure on the thermophysical characteristics of thermal insulating materials.

The article uses standard systematized techniques and instruments of scientific research applied in thermophysics. The research methodology of highly-porous material thermophysical properties is based on performance of empirical laboratory investigations of the samples obtained.

Keywords: thermophysical properties of the material, impurities, porous structure, swelling.

Introduction

It was found that for the pore structure effect on the material characteristics it is rational to use the following complex indices: porosity, number of pores, pore position in space, the pore form, pore formation energy. The article shows the effect of the porous structure on the thermophysical characteristics of the material. The complex parameters of the porous structure, which will allow to develop a new method of control of the porous structure, are proposed.

As a result of the experiment planning method, the regression equation of an effective coefficient of thermal conductivity for porous thermal protection structures was developed. It was established that for a more even distribution of the mixture in a volume it is necessary to minimize the size of the dispersed components, thereby increasing the area of their contacts.

The experimental method revealed that the moisture evaporation caused the formation of pores inside the clay. The shape of the pores was determined using electron microscope MMP-2P, both on the sample section and surface. The clearest clay has the greatest porosity (no iron oxide and calcium oxide). The pores have a spherical shape in it. The presence of impurities reduces the material porosity due to the increased clay viscosity.

Within the framework of energy independence development of Ukraine porous construction materials, being the thermal protection elements, are the most required insulating materials in the national economy. Within this group of materials highly-porous materials, obtained by steep swelling of the raw mixture, shall be considered separately. This group of materials shall be considered as special, because various materials may be obtained from one raw mixture by changing their final porous structure. The porous structure affects all thermophysical characteristics of the material. Due to this fact, study of porous structure is interesting within the frame of improvement of the material thermophysical characteristics.
Most authors estimate only the quantitative index, that is porosity, when studying macroporous materials. The sufficiency of this criterion for solid macroporous materials has not been determined so far.

**Literature review**

In [1] the study of thermal development of the forced convective heat transfer inside the channel, filled with porous medium, with its walls lapped on the constant heat flow (isoflas thermal boundary condition). The Darcy’s law and double energy equation (a local thermal non-equilibrium model) were studied. However, there is no final connection of the material porous structure appearance with its thermophysical characteristics considered in the article. The estimation technique of the porous structure is also not considered in the article.

In research work [2] hydrodynamic and mass exchange calculations of parametrized frame transportation in perfusion bioreactors were performed using the fluid structure interaction approach. It makes it possible to consider the porous structure as a compatible one. The model, studying the flow perfusion, was presented. However, such significant structural parameters as stress and deformation, that can affect pores in the material body, were not identified. It is almost certainly, that inadequacy of theory and experiment is caused by idealization of model structures [3]. Quite a number of other works [4-6] mention that the generalized theoretical substantiation of porous material thermal conductivity does not match with conducted experiments.

In [7] the results of performed theoretical and practical research of heat exchange processes of iron-containing waste of the steel surface etching were presented. Based on research results, new technological approaches to waste treatment to minimize environmental emission and reduce production costs were substantiated and practically approved. However, the analysis of the metal material porosity effect on the studied samples thermal conductivity was not presented.

The porous structure of ceramic products from silicon carbide (SiC) is considered in [8]. The main reactions of silicon carbide derivation and dependency of the derived ceramic product porosity on the synthesis of initial components were demonstrated. In the article the photos of the derived material structure and its porosity are presented, but absolutely different structure can be observed with the same porosity value. Other porous structure indices, besides porosity itself, are absent, thus, making it impossible to perform a profound analysis of thermophysical properties formation in ceramic products by formation of the predicted porous structures.

In article [9] deformation processes of titanium aluminides were studied. The compression pressure dependencies on the ingot geometric sizes and density for different types of titanium aluminides were determined. The study aimed at determination of various compression areas during pressing was also performed. The non-isostatic deformation coefficient was determined for titanium aluminides, when presses with casts. But in this research work change of the material thermal conductivity depending on the change of the porous material geometric characteristics was not considered.

Based on the literary sources analysis, the formation of thermophysical parameters of porous thermal insulating materials will depend on the porous structure itself, described by a number of complex indices and the material chemical composition. It is necessary to develop main complex indices that would fully reflect the porous structure and effects on the heat flow coming through the thermal insulating material.

In literary sources the fundamental studies were performed, aimed at the characteristic of absorption by the structural lightweight aggregate concrete (LWAC) capillary, considering various compositions with lightweight aggregates (LWA) with different porosity [10]. The effect of the following parameters was analysed: volume and initial water content in LWA, cement content and its substitution by ash, deposited ash or silicon dioxide and others; their effect on the material porous structure formation. However, research of the obtained material thermophysical properties was not sufficient.

It was determined that effective coefficient of thermal conductivity of fuel is greatly influenced by porosity [11], thus, porosity will form the main laws of heat-mass exchange process parameters.
In [12] the results of experimental research of thermal conductivity of dominant types of air cooler external pollutants were presented. The results were presented as thermal conductivity dependency on the pollutant density. It was demonstrated, that thermal conductivity greatly depends on the pollutant porosity, but porosity complex indices were not considered.

Theoretical substantiation of methodological fundamentals were determined to establish conditions of possible effects and post-effects of the hydraulic fracturing technology [13]. It was established, that the fundamental laws, determining formation and development of the hydraulic fracturing of productive formation technology post-effects include methodological instructions and criteria to predict breaking values and grinding effects.

Problem formulation

The existing experimental data according to the optimal formation conditions of the materials with macroporous structure, obtained during swelling, differ. These are, among others: foam glass, lightweight expanded clay aggregate, refractory materials. At present, there is no theory, generalizing the physical processes, occurring during porosity formation in solid materials during their swelling. For instance, it is recommended to heat foam glass initial mixture up to densification temperature (690°C) for 70 minutes and for 15 minutes [14].

The aim of this article is to determine existing methods of porous structure formation in thermal insulating and construction materials, used as thermal protection elements, define possibility of the structure control and also identify complex indices of the porous structure.

Results and Discussions

In [14] the glass swelling and crystallization processes with various chemical composition to determine the most effective temperature for glass swelling. By experimental data analysis it may be concluded, that porosity greatly increases in the glass with decreased crystallization temperature, but at this, the author of the research asserts that the initial early crystallization occurs locally. That is, to ensure higher swelling of foam glass, it is recommended to select the purest types of glass (with minimal number of impurities), the crystallization nuclei shall be formed by adding active foam impurities, which, after chemical reaction, form gas and solid substance with crystallization temperature exceeding swelling temperature. Glass with high content of Al₂O₃ (5.6-7.4%) swells in the most active manner at 830-850°C. Swelling of glass with high content of CaO (5.7-6.2%) and considerable content of K₂O (1.9-2.1%) is worth mentioning too. And, what is the most important, the connection between the foam glass thermal treatment temperature and swelling coefficient is obvious. Thus, thermal treatment mode affects the material structure and its thermophysical characteristics.

The author determines this dependency for a certain glass chemical composition using an experiment planning method. The following parameters were chosen as governing factors: carbon content in mixture, glass dispersion ability, thermal treatment temperature and its duration.

As it is seen from the performed experiment, the swelling coefficient decreases with increase of carbon content in the mixture, thus, forming foam. The effect of other parameters is not that obvious. The thermal treatment temperature and duration have the most considerable effect, when dispersion ability and carbon content have a weaker effect. But the combined influence of these factors according to pair interaction coefficients shall be also considered. The governing factors have a clear effect on the mass loss. The combined or separate increase of glass dispersion ability, thermal treatment duration and temperature cause increase in mass loss, meaning increase of gas emission from the mixture.

The author in [14] did not give proper attention to formation of the material structure itself, but pointed to the fact that porosity of the final material would be affected by a synthesis of initial raw components and gas forming agents (in a narrow range) and thermal treatment modes.

The material thermal treatment duration and temperature and initial moisture content of raw mixture were determined as main factors, affecting the porous structure. The pore porosity and diameter were
used as the main index of the porous structure evaluation, thus, making it impossible to perform a qualitative evaluation of the porous structure. The research result was determination of thermal characteristics dependency on the thermal treatment modes within a certain range. The necessity of combination of the porous structure and thermophysical properties remained an open issue.

Dependency of the final material thermal conductivity coefficient on the swelling coefficient proved to be non-linear. It allows to conclude that the quantitative index of porosity is not a criterion of the material qualitative evaluation. The increase of coefficient of thermal conductivity with increase of the porosity value is explained by the fact, that after a certain critical point pores start to grow in a non-systematic fashion, thus, increasing the convective component heat transfer and disturbing even distribution of pores by volume.

The attempt was also made to obtain empirical dependencies of the material thermophysical properties without the structure qualitative evaluation. Using the experiment planning method, dependencies of the silica material thermal capacity, thermal conductivity and density on the swelling modes were determined. The analysis of the dependency data showed, that a number of various factors affects the general density and swelling coefficient of the silica materials. At this, thermal treatment temperature and duration on swelling is comparatively equal. The thermal treatment duration has a more considerable effect on the coefficient of thermal conductivity of the silica material, but this effect is not definite. In case of long thermal treatment coefficient of thermal conductivity starts to grow. It, as it was mentioned before, is not typical of the foam glass swelling. The swelling time has a similar effect on the material thermal capacity. The main disadvantage of the specified dependencies is a narrow range of their application.

Increase of the pore size increases effective thermal conductivity by means of the convective component increase. At this, pressure inside pores decreases, thus, in its turn decreasing the convective component. The extremum of function of the convective component dependency on the material swelling modes shall exist. In well-known sources there are no data on research of the simultaneous effect of gaseous substance pressure and pore size on the effective coefficient of thermal conductivity. It makes it possible to formulate objectives for determination of the porous structure effect on the effective coefficient of thermal conductivity. It is possible to use theoretical and empirical methods for solution. To generalize obtained results concerning various technologies and materials, it is rational to establish theoretical bases of processes and structural elements, affecting the material swelling.

Strength characteristics are also important for the analysed materials. They depend on the material thermal treatment mode. The research shows that the main stage, affecting strength characteristics, is annealing and cooling of the swollen material. At this, the main factor, affecting cooling rate, is temperature conductivity. For instance, a safe cooling rate of foam glass at the process beginning may be equal to 1.2-1.8°C/min and 0.6-0.7°C/min at the end of the process. The structure defects and grain size are also important for strength. That is why a choice of the annealing temperature curve for various swollen materials is determined by the porous material structure that shall be considered, when cooling modes are chosen.

Thus, development of complex indices for porous structure and determination of its effect on thermophysical and strength characteristics of various porous materials is an urgent objective; its solution will make it possible to enhance the possibility to obtain materials with specified characteristics.

In research work [15] kinetic characteristics of carbon oxide and propane oxidation process on intermetallic catalyst with composition Ni-Co-Mn-Cu-Al were determined. Based on the modified model of Mars van Krevel, effective constants of reaction rates and energy activation were obtained. For carbon oxide oxidation reaction based on catalyst with composition Ni-Al-Co-Mn-Cu, activation energy is 37.2 kJ/mole, that is 1.4 times lower than activation energy of Ni-Al alloys. But in the research work no graphical experimental dependencies of the spherical silica-based swollen particle diameter change for different temperature values were given.
To perform experiments on formation of thermal protection thermal insulating elements, clays from various deposits, with silicon dioxide content from 48% to 65%, aluminium oxide from 3% to 10%, iron oxide not exceeding 11% and calcium oxide not exceeding 15% were selected.

The muffle-type electric furnace with temperature regulation by HK-0.1 thermocouples was used for thermal treatment. The samples got saturated up to the maximum humidity. After this, a part of each sample was dried using an indirect accelerated method (drying time was 10 minutes, furnace temperature was 130°C).

As it can be seen from the conducted experiment, moisture evaporation caused pore formation inside clays. The character and shape of pores were determined using electronic microscope MMR-2R, along the sample section and surface both. Clear clay (with no iron oxide and calcium oxide) has the highest porosity. It has spherically shaped pores. The presence of impurities decreases the material porosity due to increase of clay porosity. It shall be noted that impurities also affect the pore shape. The pores get elongated perpendicular to moisture diffusion lines, dividing the material in separate layers. A great number of impurities leads to crack formation. It has to do with uneven distribution of impurities by volume. Thus, during pore formation various stresses are generated inside the material. But impurities can increase the final material strength.

To determine the effect made by pore forming gases (CO₂, H₂O and CO, H₂, H₂S, SO₂), on swelling process, analyses samples were swollen at 750°C during 8 minutes. This temperature is sufficient for gas emission, but at this it is lower than the clay melting temperature. After thermal treatment the following changes were observed in all samples: pores are larger, compared to those in the previous experiments, but they are not spherical; sometimes a large pore inside the material arises, the material becomes stronger due to mullite formation, more obvious cracks appear, the clear clay material is brittle, its pores are more uneven and different in size.

To understand the structure effect of the analysed samples on their thermal capacity, the experiments were conducted to determine thermal conductivity of various porous materials. The compacted powdered gypsum were analysed (sample No. 1), samples of swollen clay (under various conditions) and have different structural characteristics (samples Nos. 2, 3, 4) and sample 3CaO·Al₂O₃·6H₂O (sample No. 5). The thermal conductivity measurement of all samples was performed using ІТ-λ-400. The measurement results are shown in figure 1.

![Figure 1. Dependency of samples thermal conductivity on temperature](image)

The thermal conductivity measurement error theoretically consists of geometric size (±0.8%), temperature (±1.7%), instrument reading (±2%) errors. Considering thermal losses, which cannot be
calculated due to complexity of temperature fields in the porous material, the total error is equal to ±5-7%. Practically, due to inhomogeneity of material and various experiment errors, this method error reaches 10-15%.

By the experiment results it may be concluded that with temperature increase from 50°C to 275°C, the thermal conductivity of porous materials increases. At this, thermal conductivity of pure Al₂O₃ with temperature increase (within this range) shall decrease [16]. It confirms the possibility of regulation of thermal conductivity-temperature dependency by increasing Al₂O₃ content. But based on the previous experiments, it may be asserted that increase of Al₂O₃ content in aluminium oxides will be justified only with the minimum of impurities.

From figure 1 it may be concluded, that the thermal conductivity change mode in all samples is the same, but in gas-concrete the dependency is more moderate, that is, it depends on the temperature at the minimum extent.

For all analysed samples it is typical, that dependencies of thermal conductivity on temperature may be described by linear or logarithmic dependencies (for logarithmic dependencies the determination coefficient does not differ by more than 5%). For samples 1, 2 and 5 logarithmic dependency is more accurate.

Temperature dependency of the aluminous thermal insulating material raw mixture thermal treatment on the thermal conductivity coefficient is rather ambiguous. The minimum thermal conductivity coefficient of thermal insulating material, based on aluminium oxide, was reached at thermal treatment temperature of 750°C. At this, during 650°C thermal treatment coefficient of thermal insulating material, based on aluminium oxide, is higher than at 750°C by 23%, and at 800°C – is almost twice higher. It is explained by evenness of pore distribution and their equal sizes at 750°C of thermal treatment and by a rational chemical structure.

Thus, in case of aluminium oxide raw mixture thermal treatment at 650°C – most pores in thermal insulating material are arranged in a uniform manner, but their size is less than pores of the thermal insulating material, swollen at 750°C. At 800°C much greater increase of some pores, but at this, the smallest pores disappear and despite the fact, that general material porosity is higher at 750°C of thermal treatment, the porosity is not uniform. Also, at 750°C and 800°C various chemical reactions occur, thus, affecting the results. It may be concluded, that the porous structure considerably affects thermal conductivity of porous thermal insulating materials based on aluminium oxide (29.9%).

It may be concluded, that porosity uniformity and pore size have a considerable effect on thermal conductivity of porous construction materials.

Most scientific studies of the material porous structures of thermal protection elements of industrial energy-generating plants consider the total porosity as the main structural characteristic of the thermal insulating material and other consider either the pore shape and their quantity or the pore type [17-21]. The performed analysis of the modern literature shows, that even simultaneous consideration of the total material porosity, the pore size and type is not sufficient for complete characteristic of the thermal insulating material porous structure. That is why, the main complex indices of the thermal insulating material porous structure and thermal protection element structure of energy-generating plants are proposed, that would fully reflect porous structure properties and make it possible to write a regression equation of dependency of thermal insulating material thermal properties on the proposed indices.

1) Porosity – Π, %. Porosity as a general index of density of thermal insulating material and thermal protection structure.

2) Number of pores – n, pcs/m³. The number of pores for homogeneous structure in combination with porosity gives a general idea about pore distribution in the material. The change of pore number in the process of thermal insulating material porous structure formation expresses the dynamic of pore formation process.
3) The pore distribution in space is described by Bravais translation system (Bravais lattice), where
the pore is a lattice nucleus with sizes less than Wigner-Seitz cell, or by statistical distribution of
pores in volume on the thermal insulating material.

4) The pore shape is a spatial coordinate function, describing the pore shape. It is possible to accept
the description of all pores as spheres with description of deformation, inherent to this sphere,
according to Poincare hypothesis or the pore dimensional sizes, or using a coefficient of the porous
structure geometric characteristic.

5) The indices of gas condition in pores are represented by the temperature gradient with convection
in pores depending on it and physical properties of heat transfer agent in the pore. It may also be
represented as the multiplication of Grashof number by Prandtl number.

6) To determine the energy content of formed porous thermal insulating materials and structures of
thermal protection elements used in industrial energy-generating plants, the energy of porous
structure formation.

\[
dQ_{pore} = T_{pore} dS + \varphi_{pore} dM_{pore}
\]

Considering given complex indices, using the experiment planning method, regression equations were
derived for thermal conductivity coefficient for the thermal protection porous structures.

\[
\lambda_{ef} = 0.04065 + 0.014 \ln(d_1) - 0.00527 \cdot \text{grad}(t) + 0.03423 \cdot \text{grad}(t)^2 + 0.00751 \lambda_m

-0.00947 \ln(d_1) \lambda_m + 0.01143 \cdot \ln(d_2) \cdot n + 0.01697 \cdot \text{grad}(t) \cdot n
\]

where:
\(\lambda_m\) – is a coefficient of the structure element thermal conductivity, having the logarithmic
dependency on the temperature (Eq. 1), \(\lambda_m \in [0.03; 0.9]\);
\(d_1\) – pore/void diameter of the structure along thermal flow, \(d_1 \in [4; 8]\) mm;
\(d_2\) – pore/void diameter of the structure perpendicular to thermal flow, \(d_2 \in [4; 8]\) mm;
\(\text{grad}(t)\) – temperature gradient along pore/void, \(\text{grad}(t) \in [10; 90]\), K;
\(n\) – number of pores/voids per volume unit, \(n \in [6.4 \cdot 10^{-5} \text{m}^3, \ n \in [1; 9] \text{.}

**Conclusions**

The analysis of literary sources and own experimental research on effect of porous material structure
in their thermophysical characteristics make it possible to draw the following conclusion: at present
there is no a single approach to evaluation of the porous structure effect on the material
thermophysical properties To study the pore structure effect on the material characteristics, it is
rational to use complex indices: porosity, number of pores, distribution of pores in space, pore shape,
pore formation energy.

As a research result, it was determined that:
- for more uniform mixture swelling by volume, it is necessary to minimize the size of disperse initial
  components, thus, increasing the area of their contacts;
- presence of impurities in aluminous materials, being swollen, decreases the final material porosity.
  The pores get elongated perpendicular to moisture diffusion lines, dividing the material in separate
  layers. A great number of impurities leads to crack formation;
- porosity uniformity has a considerable effect on thermal conductivity of porous construction
  materials;
- dependency of thermal conductivity coefficient on temperature for thermal insulating materials
  with microporous structure has a logarithmic character.
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