Development of technology for the production of thermally conductive carbon foams using microspheres and pitches

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Abstract. The technological process of obtaining thermally conductive carbon foams based on microspheres and pitches, including the stages of mixing the initial components, pressing the mixture of components, obtaining semi-finished "green" foam, low-temperature carbonization, carbonization, high-temperature heat treatment, pyro-compaction, mechanical processing has been developed. It is shown that the structure of the resulting foam is characterized by a lower content of voids, the layered structure of the walls of microspheres. The obtained values of thermophysical and physical-mechanical characteristics provide the possibility to use the foams for work in extreme conditions

1 Introduction

1.1 Relevance

The development of many industries necessitates the development of new and unique materials capable of working under extreme conditions while retaining their technical properties during operation. In recent decades a lot of attention is paid to the research aimed at development of carbon materials of the foam structure [1-9]. The main peculiarity of carbon materials as a class is a possibility of directed development of the porous structure during realization of the technological process by selection of fillers, additives and binders, heat treatment regimes. At the same time it is possible to regulate the total porosity, specific surface area and pore-size distribution in rather a wide range. Parameters of the porous structure have a great influence on physical-mechanical, thermal-physical and other properties of carbon foams [10-15].

One of the promising directions in the field of modern materials science is the development of chemically and corrosion-resistant high-temperature materials, including carbon-based ones. It is known that carbon materials exist in a wide variety of forms: carbon, graphite, diamond, fullerenes, glass carbon, graphene, highly oriented pyrolytic graphite, thermally expanded graphite, graphite polyhedral crystals, nanofibers, nanorods, single-layer and multilayer nanotubes, graphite whiskers, carbon black, carbon fibers, carbon foams, etc. Among the wide variety of listed materials, foam structure materials, including syntactic carbon foams, occupy a special place in terms of efficiency and prospects of application. A distinctive feature of syntactic carbon foams is the presence of a well-developed regular macroporous structure, which determines the maximum level of technical properties compared to other foamy materials at the same density. In addition, they have high specific strength characteristics, a heat conductivity coefficient adjustable in a wide range, high heat and heat resistance, electrical conductivity, resistance to aggressive media and other special properties.

Analysis of the situation in the field of obtaining and using carbon foams has shown that the problem of developing basic technological solutions for creating a new generation of heat-insulating and heat-conducting syntactic carbon foams with a wide range of values of the thermal conductivity coefficient and physical and mechanical characteristics, as well as approaches to modeling technological processes and designing products based on them, is extremely relevant.

Syntactic foams are the types of composite materials formed by binding hollow microspheres with a metal, polymer or ceramic matrix [6]. In this context, the term “syntactic” means “taken together”, and more precisely means the regularity of the structure, when an elementary cell can be isolated, the repetition of which can describe the structure of the foam macroform. The shells of hollow microspheres can be glass, polymer, carbon, ceramic, metal.

Basic requirements for microspheres are flowability, strength, defect-free, moisture and chemical resistance, hydrolytic strength, the possibility of changing the granulometric composition and volume filling coefficient within wide limits. Obtaining foams with optimal strength properties is possible only if the gas inclusions have a spherical shape. The diameter of microspheres, as a rule, is 1–500 microns, the wall thickness is 1–4 microns, the bulk density is 70–500 kg/m^3, the apparent density is 50–250 kg/m^3.

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Microspheres with a diameter of up to 40 mm are also used as hollow fillers of synthetic carbon foams.

The presence of hollow particles provides a low density of foams, a low coefficient of thermal expansion, and in some cases transparency for electromagnetic or acoustic waves. In the process of carbonization, oxidation, and solvent exposure, microspheres can transform to form foam with open cells. The structure of synthetic carbon foams provides for the presence of open pores, their connection with each other by a system of regular channels and a well-developed three-dimensional macroporous structure.

For operation of thermal-conductive foams in extreme conditions the following properties are required: bulk density – 0.1–1.0 g/cm^3; porosity – 60-97 %; thermal conductivity coefficient is from 10 to 180 W/m·K; thermal expansion coefficient – (2–8)· 10^{-6} K^{-1}; compressive strength – 0.3–20.0 MPa; fracture strength – 0.3–10.0 MPa; stability in inert environment – 2800°C, in air 600°C; carbon content is not less than 99%.

The aim of the work is to develop the technology, study the structure and operational properties of thermally conductive foams based on graphitizing, including mesophase-forming materials.

1.2 Input components

In order to obtain foams with high values of thermal conductivity coefficient we used raw materials that provide a high degree of graphitization during heat treatment. A necessary condition for this is the formation of a visco-plastic phase (mesophase as a liquid crystalline state of matter) during carbonization. This is ensured by the use of mesophase-forming coal and petroleum pitches with high values of the coefficient of thermal conductivity. In order to increase the physical and mechanical properties and the thermal conductivity coefficient of foams, it is effective to use additives of mesophase particles (microspheres), which helps to increase the degree of graphitization of the material. Carbon microspheres produced by carbonization of hollow phenol-formaldehyde resin (PFR) microspheres at 900°C were used as a filler. High-temperature coal tar pitch with a softening point of 120°C was used as a binder.

In carrying out this work, an integrated approach was used, according to which technologies for obtaining blanks of products with controlled properties based on syntactic carbon foams are considered as a set of interrelated processes for converting raw materials, which are consistently transformed at the stages of technological conversion into blanks of products, the properties of which are predetermined by the variety of relationships between the characteristics of the raw materials, as well as the operating parameters of the processes.

2 Materials and methods

Foams obtaining technology consists of the following stages: mixing of microspheres and pitch; formation of “green” foam by pressing a mixture of components; low-temperature carbonization of samples of “green” foam; high-temperature treatment; pyrocompaction of graphitized foam samples; mechanical processing.

2.1 Mixing of components

In a three-neck round-bottom flask of 500 ml we select and transfer portions of carbon microspheres (25.0±0.2 g), coal or oil pitch (25.0±0.2 g) in the form of plates, powder. A reflux condenser with chloralkalcium tube is attached to the flask and a stirring element of a mechanical stirrer with fluoroplastic working part is placed therein. While stirring at 60 rpm, 250 ml toluene is added to the contents and heated in an oil bath. The mixture was boiled under reflux while stirring at 100 rpm for 90 minutes, after which the contents of the flask was cooled to 30±5°C and portions of 150±50 ml were transferred into a 500 ml flask. The mixture is evaporated at a rotary evaporator (40°C, 250±50 mm Hg until complete removal of toluene). The mixture is then dried under vacuum while stirring on a rotary evaporator (120°C, 12±5 mm Hg, 60 min). The obtained granulate is removed from the flask and ground to a particle size of less than 250 microns to obtain a press powder.

The initial component is a coal or oil pitch with a mesophase yield of at least 20 wt. %. If necessary to work with pitches having a mesophase yield of less than 25 wt. %. Mesophase microspheres obtained by heat treatment of the initial pitch at a mesophase temperature (400–500 °C) followed by extraction of the soluble part in toluene can be added to increase the thermal conductivity of the foam. Mesophase microspheres are added to increase the mesophase yield from the pitch to 40–50 wt. %. Carbon micro- and nanoparticles in the form of finely ground carbon black, carbon nanotubes, natural graphite, graphene nanoparticles in the amount of 0.1–5.0 wt. % can be added to the pitch in order to increase the strength of the material.

The production of “green” foam. The powder is placed in a matrix with an inner diameter of 35 mm and shaped in a hydraulic press. Pressing regimes are loading speed of 0.25–0.35 tf/min, pressing pressure – 1.2 tf, holding at pressure for 3 minutes. The moulded billet is extracted, its overall dimensions, mass, apparent density are controlled.

Low temperature carbonization. Samples of “green” foam are wrapped in a double layer of paper, placed in a steel container, covered with a layer of graphitized swarf 5–10 cm high, the top is poured layer (0.5–1.5 cm) of high-temperature coal pitch, covered with a lid and placed in a muffle furnace. The samples in a container are heated at a rate of 2.5±0.5°C/min to the mesophase-forming temperature of the pitch (450 °C), held for 150 minutes, after which the furnace is turned off and cooled to 60±40°C for 12 hours. The samples are removed, the overall dimensions, shrinkage, apparent density, ultimate compressive strength and thermal conductivity coefficient are controlled.

Carbonization. Samples of "green" foam are wrapped in a double layer of paper, placed in a steel container, covered with a layer of graphitized swarf 5-10 cm high, on top of which we poured a layer of high-temperature coal pitch of height 2.5 mm, covered with a lid and placed in a muffle furnace. The samples in the container

are heated at a rate of 2.5±0.5 °C/min to 900 °C, incubated for 120 minutes, then the furnace is turned off and cooled to 60±40 °C for 12 hours. The samples are removed and the overall dimensions, shrinkage, apparent density, ultimate compressive strength and thermal conductivity coefficient are checked.

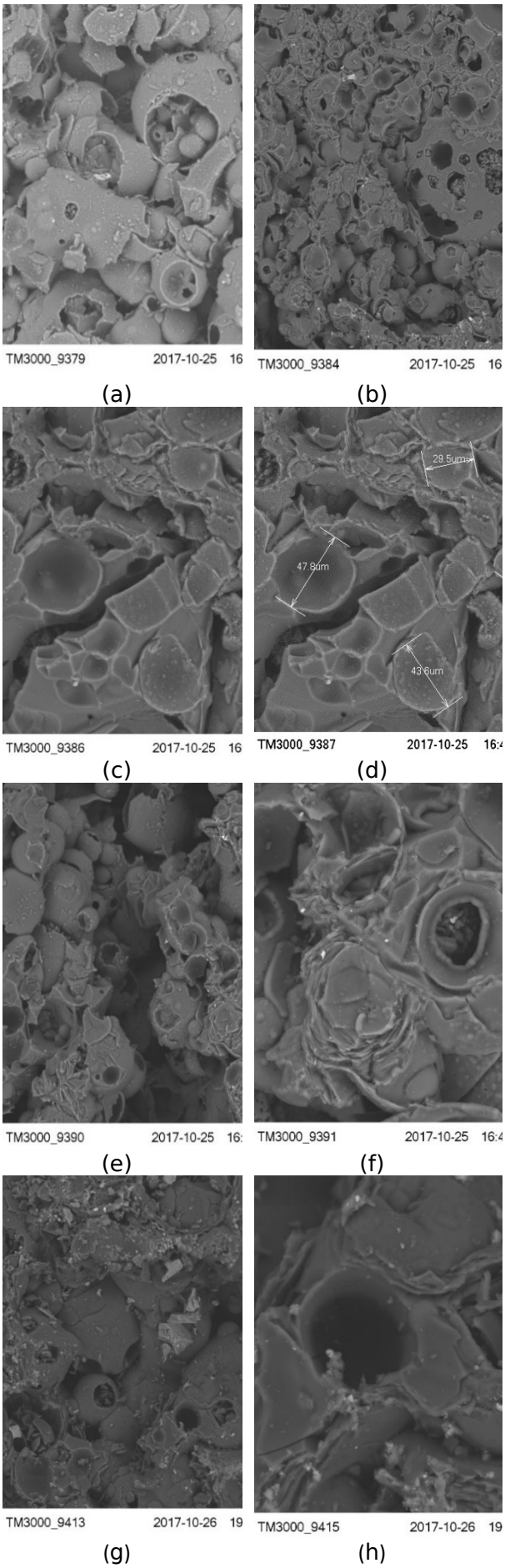
High temperature heat treatment. Obtained samples are placed in graphite crucibles with lids; the filler is poured as waste material from artificial graphite production. Crucibles are placed in an electric vacuum furnace, the furnace interior is evacuated to a residual pressure of less than 1 mm Hg. The furnace is heated for 8 hours to 2100 °C, allowed to stand for 2 hours and then cooled naturally. The samples are removed and the loss of mass, apparent density, compressive strength and heat transfer coefficient are monitored. The obtained samples are placed in graphite crucibles and the waste material from artificial graphite production is poured onto the crucibles. The crucibles are covered with a lid, placed in a graphite furnace and heated to 2700 °C and incubated for 60 minutes. Then the samples are extracted, weight loss, apparent density and true density, ultimate strength and compressive modulus of elasticity, thermal conductivity and thermal expansion coefficients, thermal and oxidation resistance are controlled.

Pyro-compaction. Samples of graphitized foam are loaded into the chamber of pyro-foam oven, the oven is sealed, purged with argon, then the samples are heated and kept at 800-1100 °C, methane pressure of 8-12 mm Hg for 20-120 hours. After that the samples are extracted, weight gain, apparent density, ultimate compressive strength and heat transfer coefficient are controlled.

Mechanical processing. Foam samples can be machined by cutting, drilling, milling, grinding at low tool feed rates with a Mohs hardness greater than 7.

3 Results and discussion

The results of scanning electron microscopy (SEM) examination of foams samples are shown in the figure. It can be seen that the basis of the obtained foams is microspheres with holes or partially destroyed probably due to the volatiles release during carbonization (Fig. 1, a, b). The size of obtained microspheres is less than 90 microns (average – 60 microns), bound by dense interlayers of binder which is a product of carbonization of pitch. The foam structure is characterized by a reduced content of voids due to the release of volatiles from the binder, which may be associated with a higher carbon content in the stove compared to the PFR. The binder layers are markedly textured, indicating the formation of graphite with a jet structure (Fig. 1, c–e). It is necessary to note also the formation of small isometric particles with the size less than 10 microns and chains of particles (fig. g-k) that specifies the course of secondary processes in a gas phase on the mechanism “liquid – steam – crystal” with the formation of soot-like particles from light fractions of pitch or not removed toluene residues.



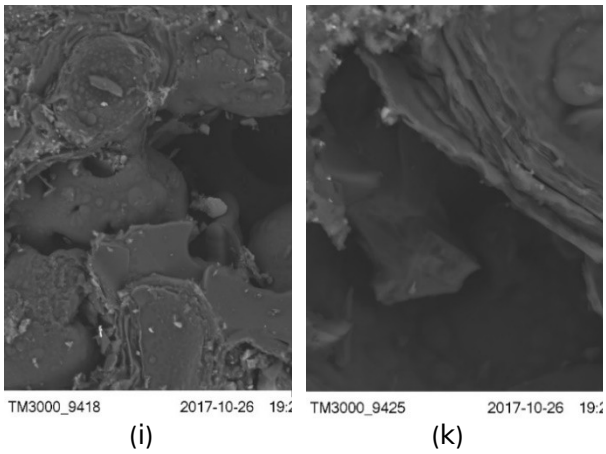


Fig. 1. SEM images of carbon foam samples.

A distinctive feature of the foam samples is the formation of a layered structure of the walls of the microspheres, indicating the course of coke formation, the subsequent graphitization of the binder on their surface, a change in the degree of graphitization of the walls material (Fig. 1, f, h, k).

The results of experimental studies of the basic technical properties of carbon foam samples obtained using the technology described above are shown in Figures 2–5.

Figure 2 shows the nature of the change in the apparent density of foams from the content of microspheres in the initial mixture. It can be seen that the dependence of the density is almost linear, which makes it possible to control the density of the material by changing the ratio of the initial components (filler – binder).

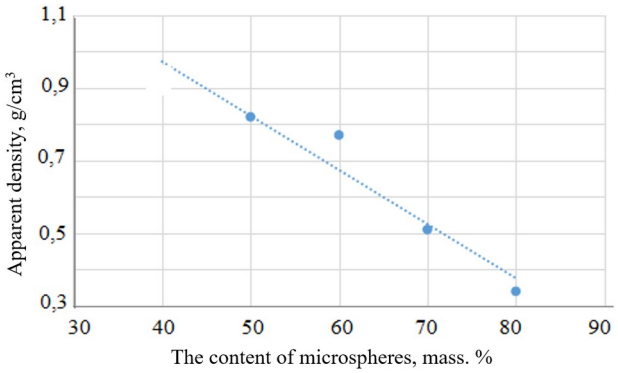


Fig. 2. Dependence of the apparent density samples on the content of microspheres.

Strength is the main requirement for structural materials, and the level of 20 MPa is sufficient for mechanical processing of the resulting foam samples. Figure 3 shows that the foam meets these requirements when the content of microspheres is 40 wt. % or less. In general, the strength naturally decreases with an increase in the content of microspheres, which corresponds to an increase in the porosity of the material.

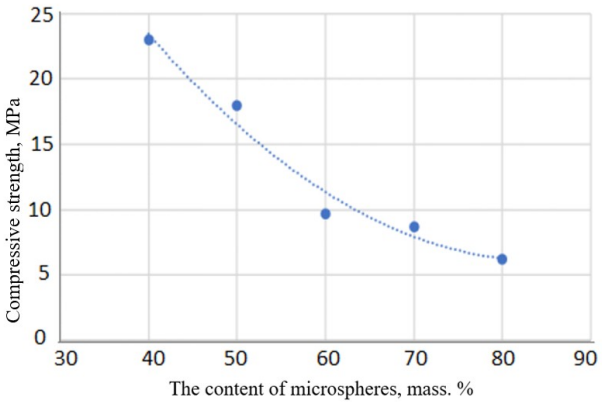


Fig. 3. Dependence of compressive strength samples on the content of microspheres.

Hardness is an important property that also determines the possibility of mechanical processing of foams. It can be seen that with an increase in the content of microspheres, the hardness of the foams decreases (Fig. 4) due to an increase in the porosity of the material.

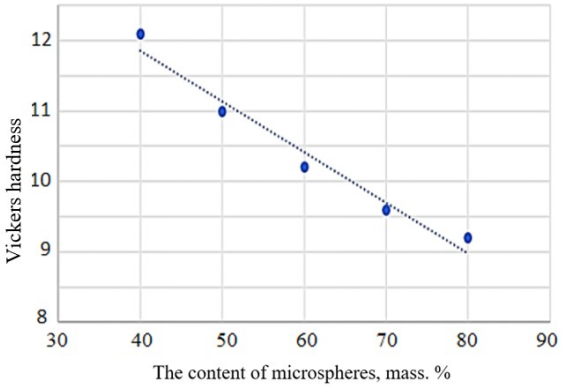


Fig. 4. Vickers hardness dependence foam on the content of microspheres.

Thermophysical properties determine the suitability of materials for use as high-temperature heat sink products. The tests carried out made it possible to establish that this class of materials satisfies the specified requirements in terms of temperature and oxidative resistance. The thermal conductivity coefficient clearly linearly depends on the content of microspheres (Fig. 5).

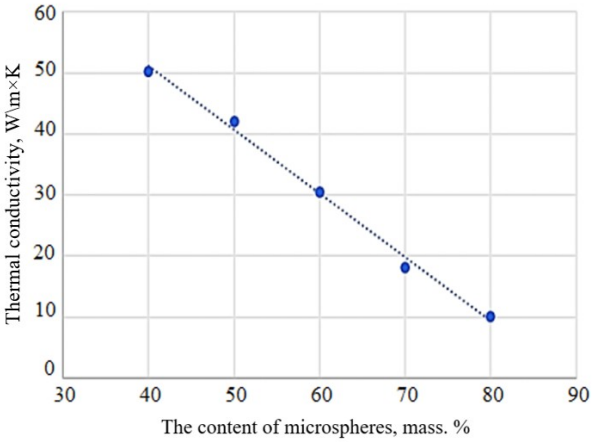


Fig. 5. The dependence of the coefficient of thermal conductivity foam on the content of microspheres.

4 Conclusion

Thus, a technological process of obtaining thermally conductive foams using carbon microspheres, coal or oil pitch was suggested and worked out. The process consists of the following stages: mixing the initial components in the form of carbon microspheres and coal or oil pitch in equal proportions; the formation of "green" foam by pressing the resulting mixture of components; low-temperature carbonization of samples of "green" foam; high-temperature heat treatment, pyrocracking of graphitized foam. The obtained values of the basic indices of the foams correspond to the predetermined characteristics, which makes it possible to use them for the manufacture of products operating under extreme conditions.

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