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Development of technologies for producing heat-conducting syntactic carbon foams with specified operational properties

E R Galimov¹, E E Sharafutdinova¹, N Ya Galimova¹, V M Samoylov² and E A Danilov²

¹Kazan national research technical university named after A.N. Tupolev, K. Marx street 10, Kazan, 420111, Tatarstan, Russian Federation

²JSC NIIGrafit, 2 Elektrodnyaya str., Moscow, 111524, Russia

kstu-material@mail.ru

Abstract. Technology for producing the articles based on the syntactic carbon foams is proposed. Components and regime parameters for producing the foams of open-porous cellular structure with specified thermophysical and strength characteristics are determined.

1. Introduction

Syntactic carbon foams (SCF) are one of the modern and promising classes of carbon composite materials their distinctive feature is the presence of a regular porous structure which provides high properties compared to materials of an irregular porous structure at the same density level [1-3]. Carbon materials are notable for the dependence of thermophysical and other physical-chemical properties on the structure parameters which makes it possible to obtain heat-insulating or heat-conducting materials with a wide range of thermal conductivity coefficient – from less than 0.1 W/m·K (for heat-insulating materials) up to 180 W/m·K (for heat-conducting materials) – when varying the raw material base and technological methods of their processing.

Carbon foams can be used in the design of heat sinks and heat insulation, the creation of porous electrodes, and for many other applications. Therefore, research aimed at developing the SCFs with given thermophysical and physical and mechanical properties is relevant.

2. Body text

The objective of this research is to develop technologies for the production of heat-conducting SCFs with given service properties.

Research techniques. Research of physical and mechanical (apparent density, ultimate compressive strength, hardness) and thermophysical (thermal conductivity coefficient) properties was carried out to determine the influence of composition and ratio of components, production technology of SCFs on their structure and operational characteristics. Density, ultimate compressive strength, and hardness were determined by standard techniques. Evaluation of the thermal conductivity coefficient of the samples was performed by the method of a stationary flow at a temperature of 20°C. The study of the SCF microstructure was conducted by the scanning electron microscopy (SEM) on a Hitachi TM3000. The samples were directly attached to a conductive carbon tape. Shooting conditions: accelerating voltage 15 kV, vacuum 10^{-6} mm Hg.

The initial components for producing the foams. There are different approaches to the production of SCFs with a controllable set of properties [4-10]. This paper presents a technological process for



producing foams with an average value of thermal conductivity coefficient – 10-50 W/m·K. Foams were obtained by the technology involving the use of filler and binder. Carbon microspheres obtained by carbonizing hollow microspheres from the phenol-formaldehyde resin at a temperature of 900°C were used as the filler; high-temperature coal tar pitch with a softening temperature of 120°C was used as the binder. It should be noted that the properties of foams can be varied in a very wide range because of the changes in porosity, proportions between the bonding carbon material and microspheres, their size, the gaseous medium composition, and etc.

Experimental part. The technological process of obtaining the foam includes the sequential carrying out of the following stages: the mixing of components, the formation of “green” foam, low-temperature carbonization, carbonization, high-temperature heat treatment, pyrocompaction, mechanical processing.

In the first stage, weighted carbon microspheres (25 g), coal tar or petroleum pitch (25 g) in the form of plates or powder were placed in the three-necked round-bottomed flask with a volume of 500 ml. A backflow condenser with calcium chloride tube was attached to the flask, and a mixing element of a mechanical stirrer with the fluoroplastic working part and a hermetic seal was placed into it. Under mixing at a speed of 60 rpm, 250 ml of toluene were added into the mixture, heated in an oil bath, and boiled using a backflow condenser (IKA C-MAG HS7) under mixing at 100 rpm for 90 minutes. After that, the content of the flask was cooled to a temperature of 30±5°C and transferred in portions of 150±50 ml to a 500 or 1000 ml round-bottomed or pear-shaped flask. The mixture was evaporated using a rotary evaporator IR-2M (ИР-2М) (vacuum pump LVS 105T with the integrated vacuum gauge and residual pressure regulator) at 40°C and residual pressure of 250±50 mm Hg until complete removal of toluene. Next, the resulting mixture was dried under vacuum with mixing using a rotary evaporator IR-2M at 120°C and residual pressure of 12 mm Hg for 60 minutes. The obtained granulate was removed from the flask and crushed in a mill until obtaining a powder with a particle size of less than 250 microns.

Coal tar or petroleum pitch with a mesophase yield of at least 35 wt. % can be used as the main initial component. If it is necessary to work with pitches that have a mesophase yield of less than 25 wt. % the mesophase microspheres of PMUG (ИМΥТ) brand or analogues obtained by heat treatment of the original pitch to a temperature of the mesophase formation (400-500°C) with subsequent extraction of the soluble part in toluene can be added to increase the thermal conductivity of the resulting product. The mesophase microspheres are added to increase the mesophase yield from the pitch up to 40-50 wt. %. Carbon micro- and nanoparticles (fine-grained soot, carbon nanotubes, natural graphite, graphene nanoparticles) can be added into the original pitch in an amount of 0.1-5.0 wt. % to increase product strength.

In the second stage, the formation of “green” foam was carried out. The powder was filled into a blind die with the inner diameter of 35.0±0.5 mm and molded using a PS-10 (ΠС-10) press with a loading rate of 0.25-0.35 tf/min at a pressing pressure of 1.2 tf for 3 minutes. The molded workpiece was extracted, and overall dimensions, mass, and apparent density were controlled.

In the third stage, the low-temperature carbonization was carried out. The obtained samples of the “green” foam were wrapped in a double layer of paper, placed in a steel container, covered by a 5-10 cm layer of broken graphite with a diameter of about 250 µm on top of which a 0.5-1.5 cm layer of high-temperature coal tar pitch with a diameter of 2.5 µm was poured it was covered with a steel lid and placed in a muffle furnace, equipped with a thermoregulator with the ability to control the speed and temperature of heating, as well as the exposure time. Samples in a steel container were heated at a rate of 2.5±0.5°C/min to pitch mesophase formation temperature (450°C) with an exposure at a final temperature for 150 min after which the furnace was turned off, cooled for 12 h to 60±40°C and samples were extracted.

In the fourth stage, the carbonization was carried out. The obtained samples of the “green” foam were wrapped in a double layer of paper, placed in a steel container, covered by a 5-10 cm layer of broken graphite with a diameter of about 250 µm on top of which a 0.5-1.5 cm layer of high-temperature coal tar pitch with a diameter of 2.5 µm was poured it was covered with a steel lid and

placed in a muffle furnace. Samples in a steel container were heated at a rate of $2.5 \pm 0.5^\circ\text{C}/\text{min}$ to a temperature of 900°C with an exposure at a final temperature for 120 min after which the furnace was turned off, cooled for 12 h to $60 \pm 40^\circ\text{C}$ and samples were extracted.

In the fifth stage, high-temperature heat treatment was carried out. The obtained samples were placed in graphite crucibles with lids backfilling (a scrap of artificial graphite production crushed to a particle size of less than 0.25 mm) was filled in. The crucibles were placed in an EVP-2500 (ЭВП-2500) vacuum furnace the working medium was pumped out to a residual pressure of less than 1 mm Hg (it is desired to fill the furnace with argon to displace air and then pump it out to a residual argon pressure of less than 1 mm Hg). The furnace was heated for 8 hours to 2100°C the samples were exposed for 2 hours then cooled naturally and extracted. The resulting samples were placed in graphite crucibles with lids the backfilling (a scrap of artificial graphite production) was filled in. The crucibles were placed in a graphitization furnace with the resistive principle of heating (such as Acheson or Tamman type) and heated to a temperature of at least 2700°C with exposure at a final temperature of at least 60 minutes. Alternatively, graphitization to a temperature of $2700\text{--}3000^\circ\text{C}$ can be carried out in a tubular or chamber furnace of a suitable design that provides an inert atmosphere (oxygen content not more than 10^2 vol. %).

In the next stage, the pyrocompaction was carried out. The obtained samples of graphitized foam were loaded into the pyrocompaction furnace chamber the furnace was sealed, blown through by argon, and after that, the samples were heated and kept at a temperature of $800\text{--}1100^\circ\text{C}$ and a pressure of 8-12 mm Hg for 20-120 hours.

In the last stage, if necessary, the obtained workpieces of foam were subjected to mechanical treatment by cutting, drilling, milling, grinding at low feed rates by a tool with a Mohs hardness of more than 7.

Comprehensive analysis of the apparent density, strength and thermophysical properties of SCFs obtained on the basis of carbon microspheres and coal tar or petroleum pitches were carried out. It is shown that the apparent density of the samples changes linearly depending on the content of microspheres in the initial mixture (figure 1) which allows adjusting the material density changing the ratio of filler and binder.

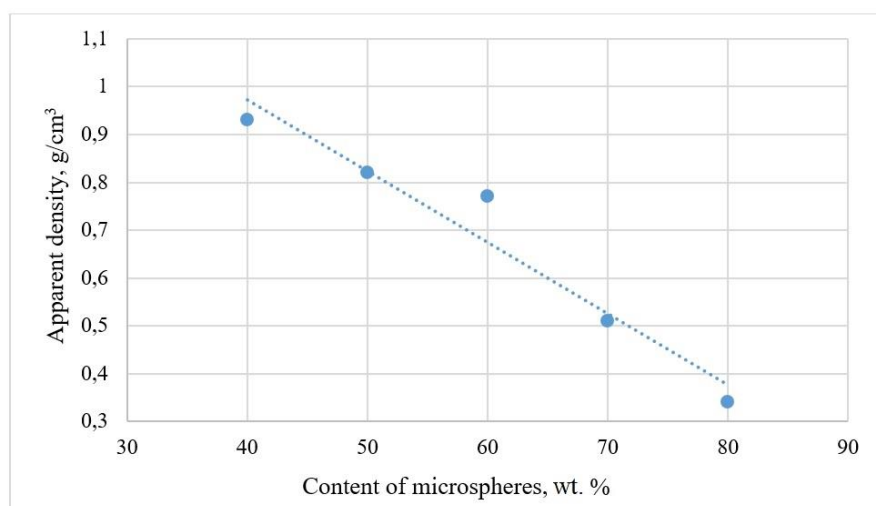


Figure 1. Change in apparent density of foam samples depending on the content of carbon microspheres

Strength is a fundamental requirement applicable to the structural materials. As a rule, the level of 20 MPa makes the materials acceptable for mechanical treatment using available methods (milling, cutting, and drilling). Figure 2 shows that SCFs produced according to the proposed technology satisfy this requirement when the microspheres content is 40 wt. % and less which allows their use for

manufacturing of products of complex geometric shapes for various functional purposes. In general, the strength expectedly decreases with increasing content of microspheres which corresponds to an increase of the material porosity.

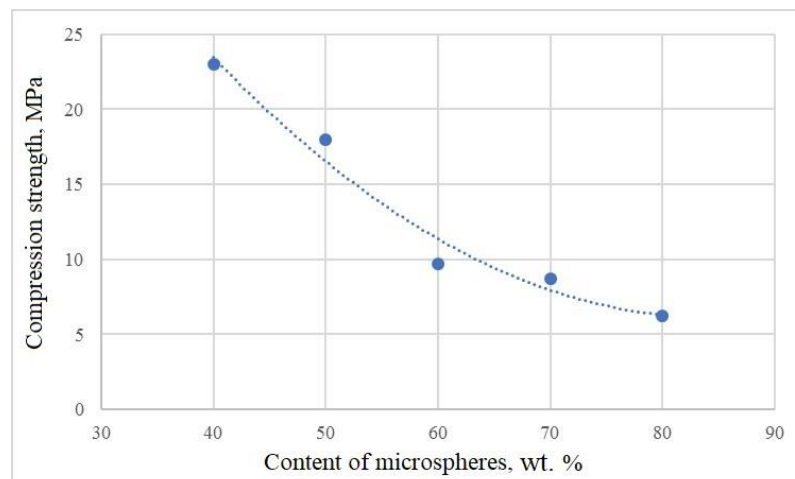


Figure 2. Change in compression strength of foam samples depending on the content of carbon microspheres

Hardness is also an important property that determines the possibility of mechanical treatment of materials. The data in figure 3 shows that the hardness of the studied foams samples allows their processing without using a special tool. With an increase of the microsphere content, the material hardness decreases which suggests that out of two trends – an increase of the average hardness because of the higher hardness of the coke of phenol-formaldehyde resin (microspheres material) compared to graphite from pitch, and decrease in it because of increase of the material porosity – the second one is predominant.

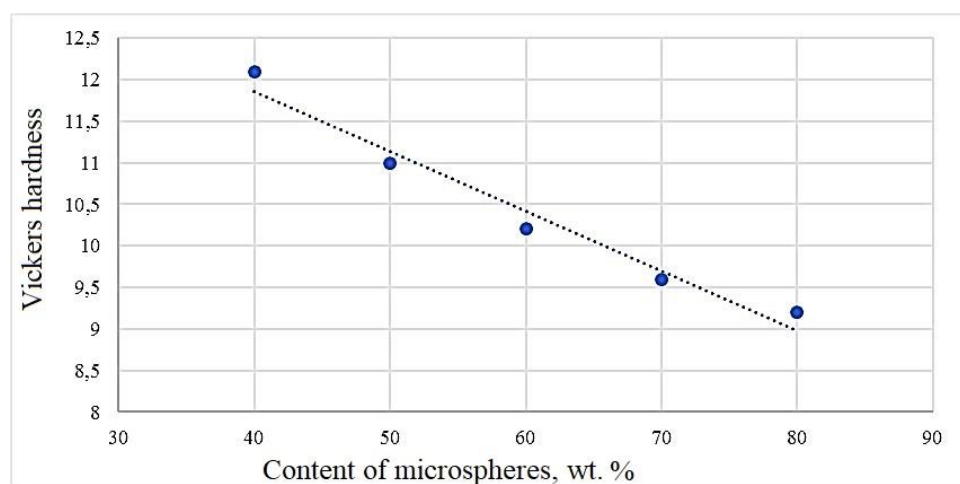


Figure 3. Change in Vickers hardness of foam samples depending on the content of carbon microspheres

Thermophysical properties determine the suitability of materials for use as products of high-temperature heat sink. The data in figure 4 shows that the thermal conductivity coefficient depends linearly on the content of microspheres and its values change approximately in the range from 10 to 50 W/m·K, that is, these foams fall in between thermal insulation materials with low thermal conductivity and isotropic heat-conducting graphite (90-110 W/m·K).

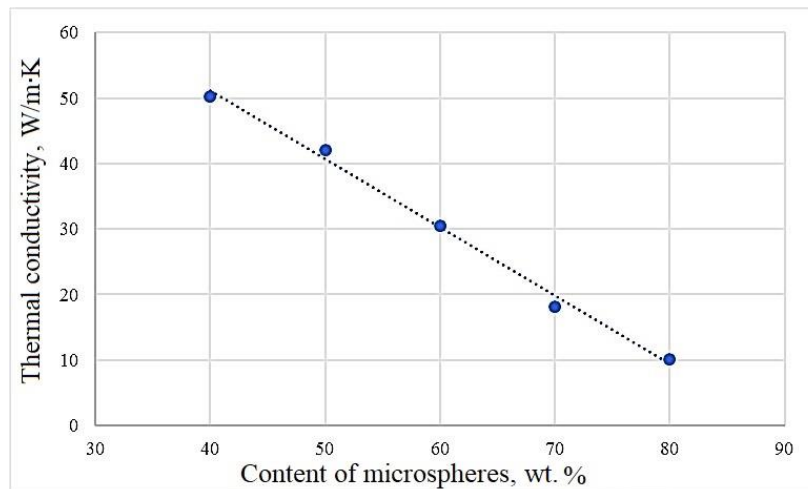
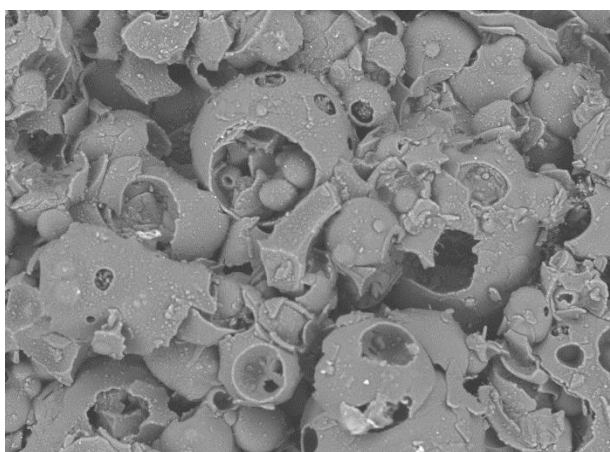


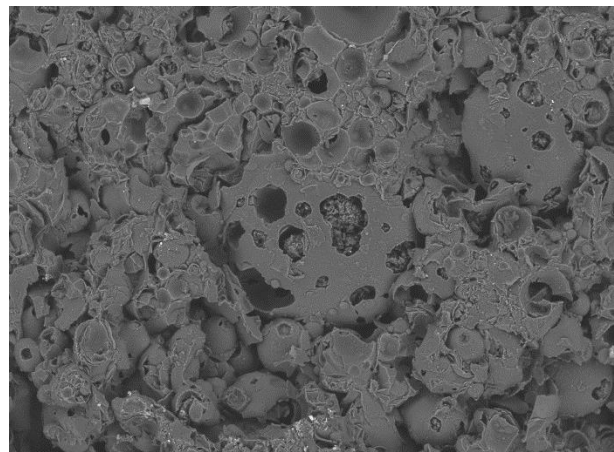
Figure 4. Change in thermal conductivity coefficient of foam samples depending on the content of carbon microspheres

The material microstructure was studied by scanning electron microscopy (figure 5). It can be seen that microspheres with holes or partially destroyed ones, probably because of the release of volatile substances during carbonization, form the basis of the obtained SCFs. The size of the obtained microspheres is less than 90 μm (the average is about 60 μm) which are connected by dense layers of binder (a product of the pitch carbonization). The binder interlayers are markedly textured which indicates the binder graphitization with the formation of graphite a striated structure (figure 5, *c-e*). Formation of small (less than 10 μm) isometric particles and chains of particles should also be noted (figure 5, *g-j*) which indicates the secondary processes occurrence in the gas phase (in the sort of “liquid-vapor-crystal”) with the formation of soot-like particles from light fractions of pitch or toluene residues that were not removed. The peculiarity of this class of materials is the formation of a layered structure of the microspheres walls which indicates both the process of coke formation and subsequent binder graphitization on their surface and the change of the graphitizability degree of the wall material (figure 5 *f, h, j*).



TM3000_9379

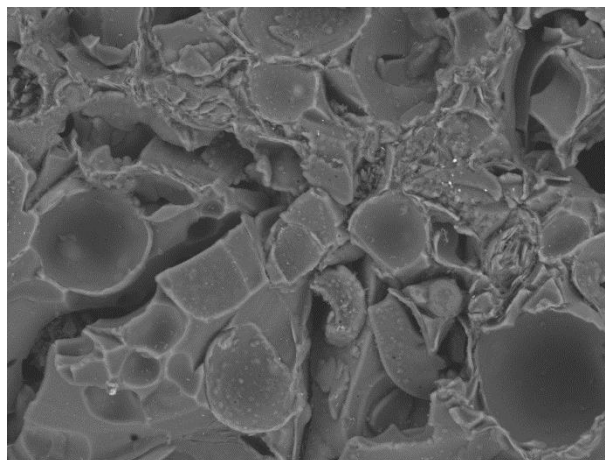
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a)

TM3000_9384

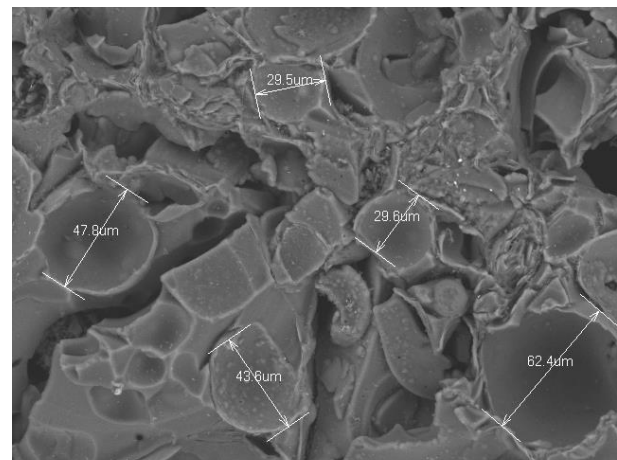
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b)



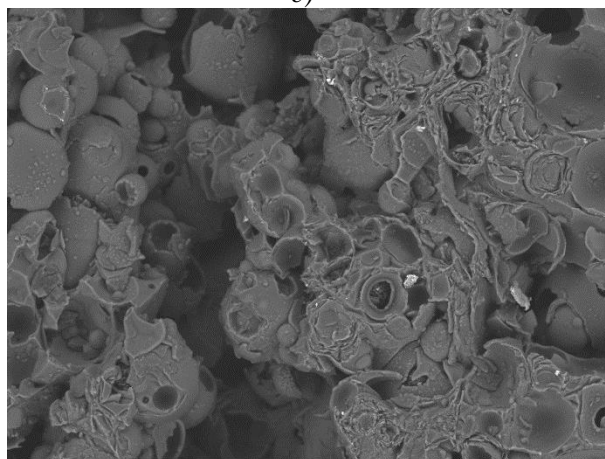
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c)



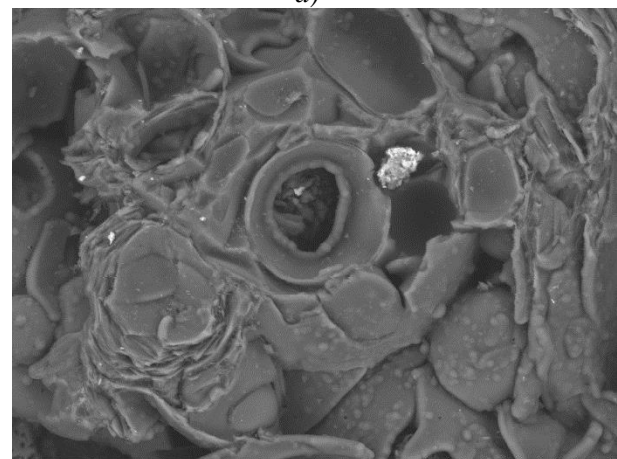
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d)



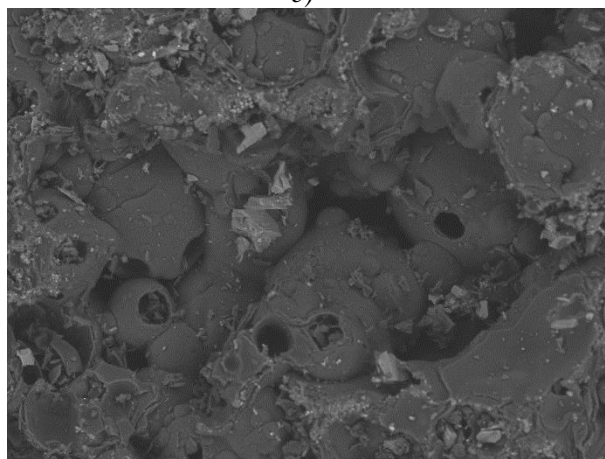
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e)



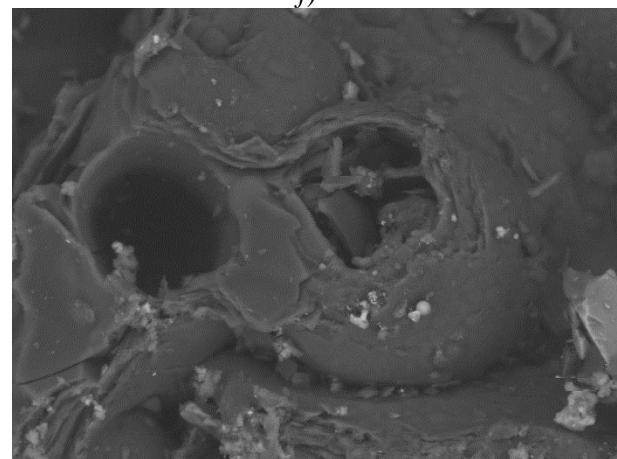
TM3000_9391 2017-10-25 16:46 H D3.9 x1.5k 50 um

f)



TM3000_9413 2017-10-26 19:18 H D4.1 x500 200 um

g)



TM3000_9415 2017-10-26 19:19 H D4.0 x2.0k 30 um

h)

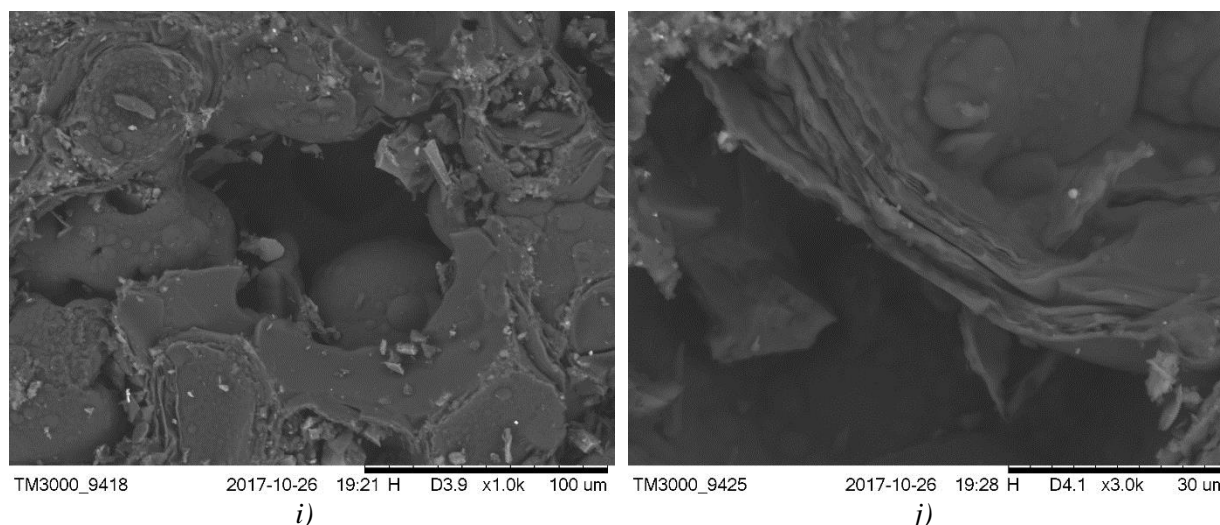


Figure 5. SEM photographs of foams obtained on the basis of carbon microspheres and coal tar pitches

3. Conclusions

Thus, the proposed technology allows obtaining SCFs with intermediate average values of the thermal conductivity coefficient (10-50 W/m·K) and satisfactory strength characteristics which makes it possible to use them for manufacturing of products including the ones with a complex surface geometry for which excessive heat sink is harmful or does not play a noticeable role (rocket technology and etc.).

4. Acknowledgment

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References

- [1] Tikhomirov V K 1975 *Foams. Theory and practice of their production and destruction* (Moscow: Khimiya Publ) pp 11-15
- [2] Galimov E R, Fedyaev V L, Galimova N Ya, Takhaviev M S and Siraev A R 2017 Mathematical modeling of processes occurring during deposition of sprayed particles of polymeric powder *Journal of Physics: Conf. Series* vol 789 **012007**
- [3] Salosina M O 2016 *The thermal conditions of the solar probe taking into account the impact of high-speed dust particles* (Moscow: Proceedings of MAI) p 86
- [4] Shutov F A Syntactic polymer foams 1986 *Advances in Polymer Science* pp 63–123
- [5] Inagaki M, Qiu J and Guo Q 2015 Review Carbon foam: Preparation and application *Carbon* Vol 87 pp128-52
- [6] Internet source: Firefly Energy Co. Available at: <http://fireflyenergy.com/>. (accessed 04.02.2018)
- [7] Anghelescu M S 2009 Integrated Engineering Thermal and Mechanical Analysis of Carbon Foam *Ph.D.* 122 p
- [8] Chen Y, Chen B, Shi X, Xu H, Shang W, Yuan Y and Xiao L 2008 Preparation and electrochemical properties of pitch-based carbon foam as current collectors for lead acid batteries *Electrochimica Acta* vol 53 pp 2245-49
- [9] Kashapov N F, Luchkin G S and Luchkin A G 2010 Vacuum technologies for the application of functional coatings “*Vestnik*” of Kazan State Technological University 2 number pp 340-45

- [10] Galimov E R, Shveyov A I, Shveyov I A, Lysanov D M and Galimova N Ya 2016 Development of combined technologies and multifunctional equipment for application of polymer powder coatings *International Journal of Applied Engineering Research* vol 11 number 3 pp 1583-89
- [11] Samoylov V M, Danilov E A, Galimov E R, Fedyaev V L, Galimova N Ya and Orlov M A 2017 Production of thermally conductive carbon foams and their application in automobile transport *IOP Conf. Series: Materials Science and Engineering* vol 240 **012062**
- [12] Galimov E R, Fedyaev V L, Galimova N Ya, Gimranov I R and Marat M M 2017 Formation of polymeric powder coatings *IOP Conf. Series: Materials Science and Engineering* vol 240 **012014**
- [13] Galimov E R, Fedyaev V L, Galimova N Ya, Gimranov I R and Siraev A R 2017 Dynamics of coalescence and spreading of liquid polymeric particles during coating formation *Journal of Physics: Conf. Series* vol 789 **012006**
- [14] Shafigullin L N, Shafigullina G R, Sarimov D R and Romanova N V 2017 Analysis of carbon plastics destruction causes based on epoxy binding *Turkish online journal of design art and communication* vol 7 pp 1872-78
- [15] Shafigullin L N, Gumerov I F, Ibragimov A R, Shafugullina G R, Nizamova A I and Romanova N V 2018 Aspects of using accelerated weather testing methods for polymeric materials *IOP Conference Series: Materials Science and Engineering* vol 412 issue 1 **012069**