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Technologies for producing heat-conducting carbon foams by method of pitches carbonization under pressure

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Abstract. Technology for producing syntactic carbon foams by the method of pitches carbonization under pressure is proposed. The components and optimal regime parameters for producing the foams with given thermophysical and strength characteristics are determined. The foams structure was studied using scanning electron microscopy.

1. Introduction

The technology for producing heat-conducting syntactic carbon foams obtained by the method of pitch carbonization under pressure is based on using the phenomenon of pore formation upon the release of volatile substances from coal tar or oil pitches their release is complicated by the application of external pressure.

2. Body text

The technological process consists of several stages. At the initial stage, the components are mixed. If it is necessary to work with pitches that have a mesophase yield of less than 25 wt. % the mesophase microspheres of PMUG brand or analogues obtained by heat treatment of the original pitch up 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 should be 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. When the loading is more than 1 kg, the components are mixed in a mixing machine with the Z-shaped blades at a temperature of 15-20°C higher than the softening temperature of the original pitch. When the loading is less than 1 kg, the mixing can be performed in a toluene solution.

The initial pitch and solvent (toluene) are loaded into a three-necked round-bottomed flask in an amount of 100 ml of solvent per 15 g of pitch the mixture is stirred by an anchor stirrer and boiled using a backflow condenser for 60 minutes. Then the mixture is cooled to a temperature of 40°C, and the solvent is removed by distillation under vacuum using a rotary evaporator followed by drying under vacuum using a rotary evaporator at a residual pressure of not more than 10 mm Hg and a temperature of 120°C for 60 minutes. After mixing, the mass is cooled to a temperature of 25°C and crushed to a particle size of less than 250 µm in a vibrating mill or hammer crusher.



In the second stage, the low-temperature carbonization under pressure is carried out. The moulding material of the crushed pitch with additives is placed in a cylindrical form made of carbon steel with a 0.5 mm thickness with one weld seam along the generatrix and one weld seam along the base. The form is filled not more than for 60% of the height. The form is placed in an autoclave with a limiting heating temperature of at least 600°C and a maximum attainable pressure of at least 16 MPa. Heating and pressure increase is carried out according to the mode shown in Figure 1. The pressure and temperature in the autoclave are controlled and regulated in close proximity to the container with samples.

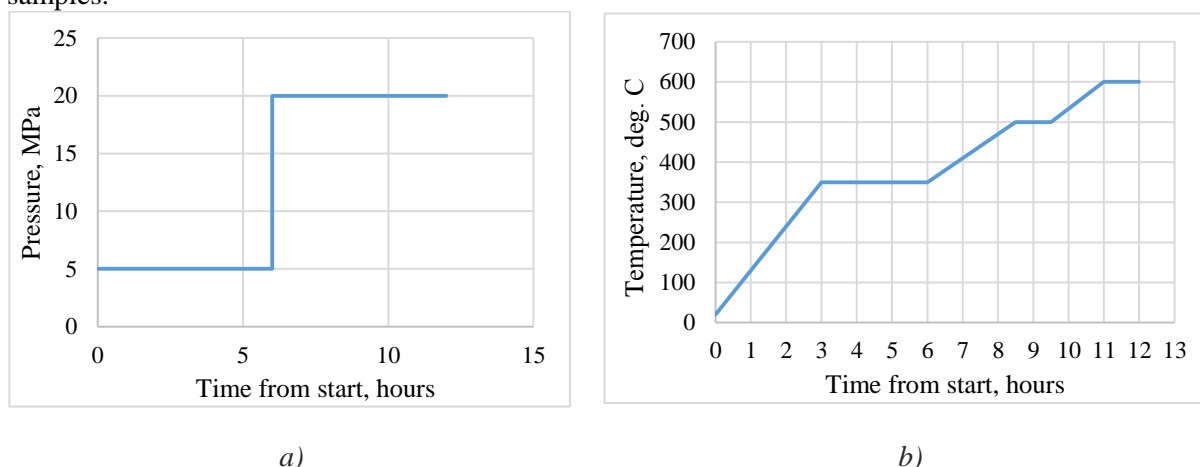


Figure 1. Diagram of pressure increase (a) and temperature (b) for low-temperature carbonization of workpieces of foam under pressure (pressure relieve – after 12 hours, cooling - natural)

After cooling of the autoclave working area to a temperature of 450°C, the pressure can be reduced to atmospheric, for this, capture of toxic impurities is provided in the autoclave system (cold trap and trap with benzene). After cooling of the autoclave working area to a temperature of 150°C it is unloaded, containers with samples are taken out and cut.

At the third stage, carbonization is 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 the container are heated at a rate of $2.5 \pm 0.5^\circ\text{C}/\text{min}$ to a temperature of 900°C with exposure at the final temperature for 120 min after which the furnace is turned off and cooled to a temperature of $60 \pm 40^\circ\text{C}$ for 12 hours. Samples are extracted, and overall dimensions, shrinkage, apparent density, ultimate compressive strength, and thermal conductivity coefficient are controlled. The obtained samples are placed in graphite crucibles with lids the filling (a scrap of artificial graphite production crushed to a particle size of less than 0.25 mm) is filled in. The crucibles are placed in an EVP-2500 (ЭВП-2500) vacuum furnace the working medium is pumped out to a residual pressure level 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 is heated for 8 hours to a temperature of 2100°C the samples are exposed for 2 hours then naturally cooled.

At the fourth stage, the graphitization process is carried out. The resulting samples are placed in graphite crucibles with lids the filling (a scrap of artificial graphite production crushed to a particle size of less than 0.25 mm) is filled in. The crucibles are placed in a graphitization furnace (such as Acheson or Tamman type) and heated to a temperature of 2700°C with exposure at the final temperature of at least 60 minutes.

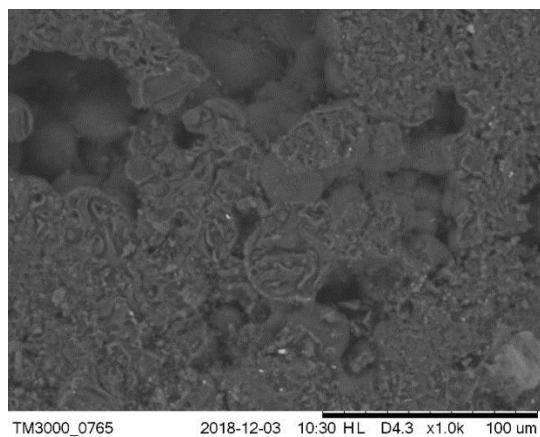
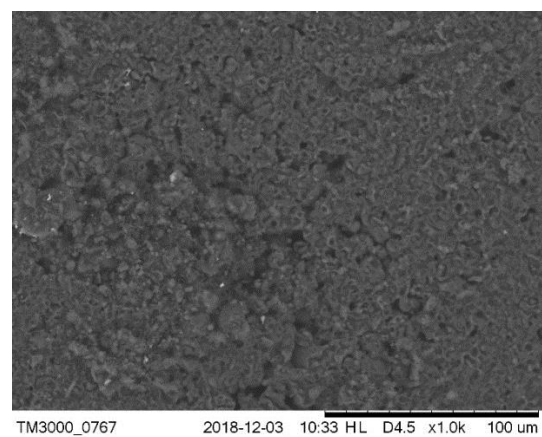
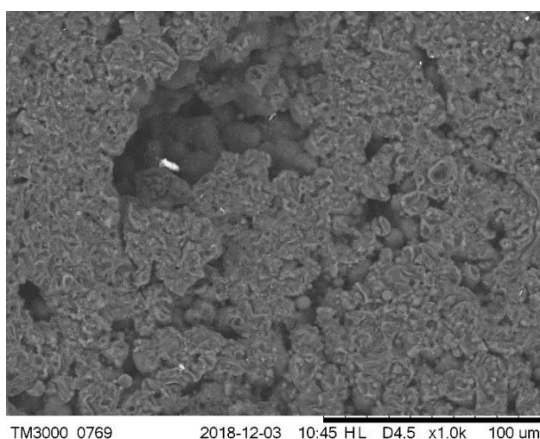
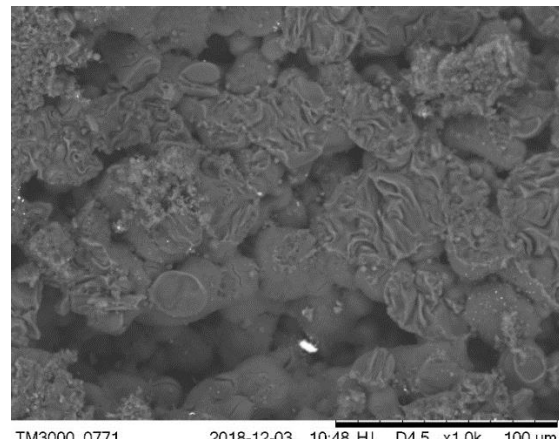
In the next stage, the pyrocompaction is carried out. The obtained samples of graphitized foam are loaded into the pyrocompaction furnace chamber the furnace is sealed, blown through by argon, and

after that, the samples are heated and kept at a temperature of at least 1100°C and the methane pressure of 8-12 mm Hg for 20-120 hours.

The final stage is the mechanical treatment of the obtained workpieces (cutting, drilling, milling, and grinding at low feed rates by a tool with a Mohs hardness of more than 6).

Carbon foams were obtained in an industrial autoclave by pitch impregnation of carbon-carbon composite materials at a pressure of 8.0 MPa and a temperature of 500°C, followed by carbonization up to a temperature of 2200°C. The resulting foam had a non-uniform macrostructure: the outer layer was a material with a density of about 1.2 g/cm³ and porosity observable with the naked eye, the inner layer had a density of about 0.7 g/cm³ and distinct porosity.

Figure 2 shows the SEM images of the outer (dense) layer. It can be seen that the porosity structure of the foam is non-uniform – there are small channel pores and large cracks in the material structure. In terms of the structure of the pore walls, the material is quite homogeneous and has a graphite-like structure of a spherulitic type with a spherulites size of about 20 µm. The sections show that spherulites are graphite-like carbon material at the stage of pre-graphitization.

*a)**b)**c)**d)*

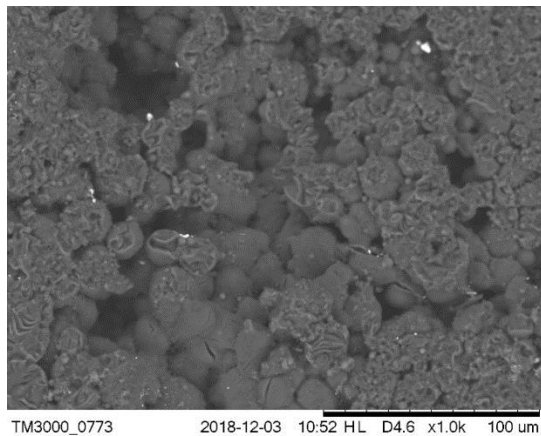
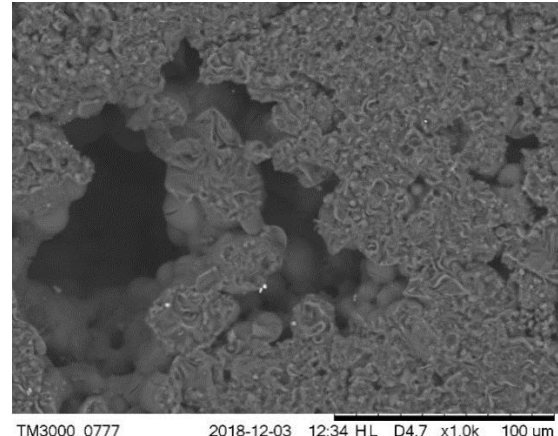
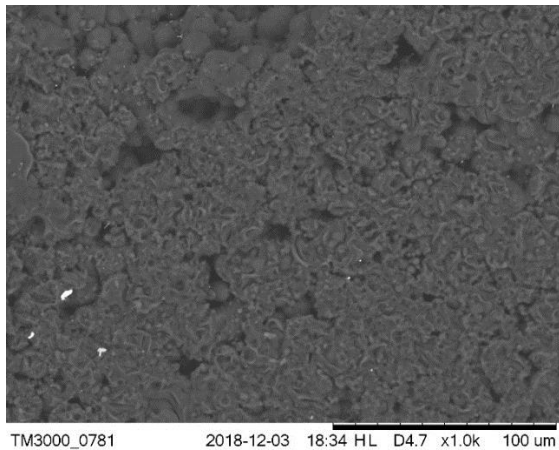
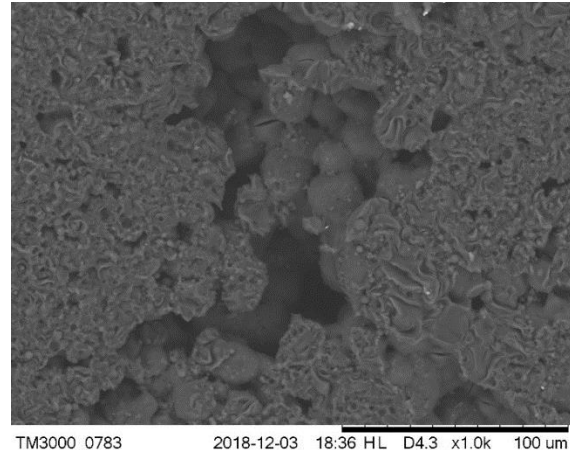
*e)**f)**g)**h)*

Figure 2. SEM images of carbon foams obtained by carbonization under pressure (outer surface of the sample)

Based on the analysis of 156 fields, a macropore size distribution was plotted (figure 3). The data on the figure shows that the pores are mostly small (up to 17.6 μm) this, apparently, is the reason for the main porosity of the material. The average pore size is 12.24 μm at a high standard deviation for the sample (12.68 μm) which further confirms the polymodal nature of the distribution.

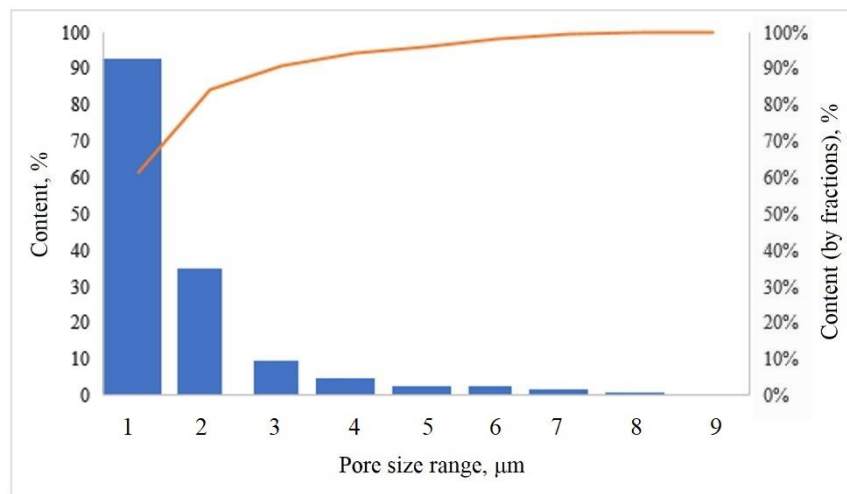
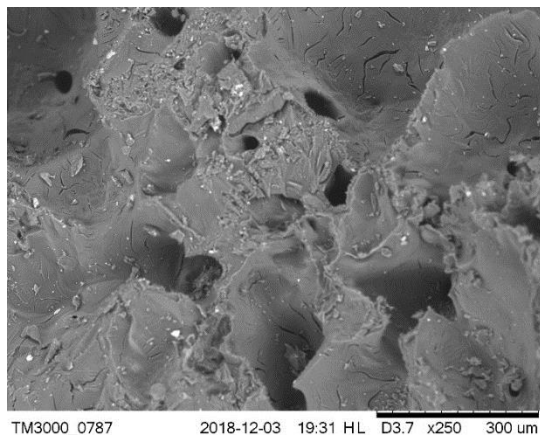
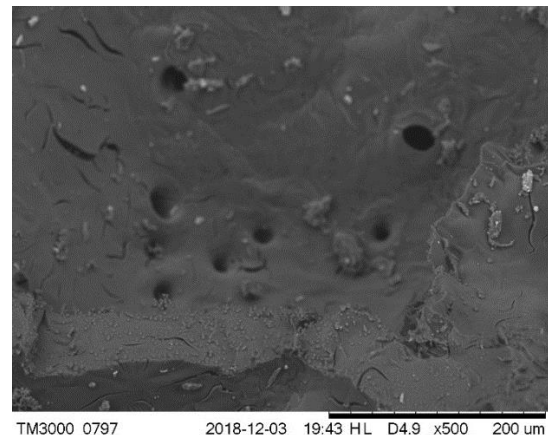


Figure 3. Macropores size distribution for carbon foams obtained by carbonization under pressure (outer surface of the sample): 1; 2; 3; 4; 5; 6, 7, 8, 9 – variation ranges of pore sizes respectively 1.02 – 9.32; 9.32 – 17.62; 17.62 – 25.92; 25.92 – 34.22; 50.82 – 59.12; 59.12 – 67.42; 34.42 - 42.52; 67.42 – 75.72; 42.52 - 50.82 μm

The internal porous part of the material is a foamy structure visible to the naked eye. Studies by the SEM method showed that the cuts and chips of the cell surface additionally contain canal-like macropores (figure 4) with a circular or elliptical section. In the interpore space, graphite has a striated structure and contains a large number of cracks with a width in the range of tens of nanometers. The secondary deposits of isometric particles are on the cell surface which indicates the carbon formation through the gas phase including due to volatile substances of the pitch.



a)



b)

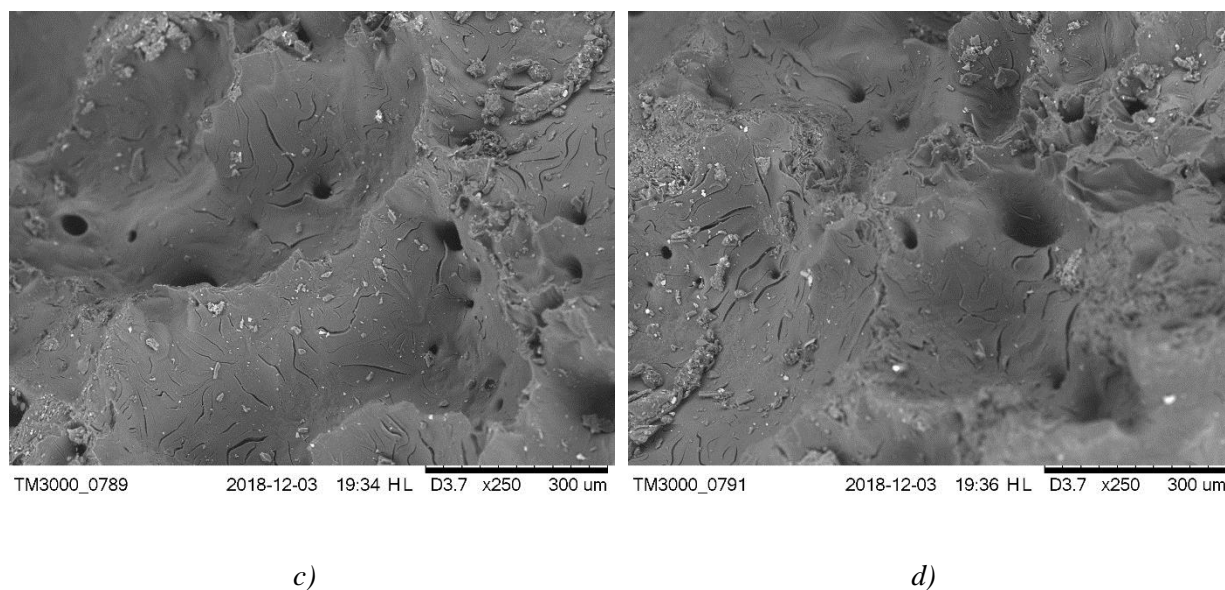


Figure 4. SEM images of carbon foams obtained by carbonization under pressure (inner part of the sample)

Based on the analysis of 128 fields, the macropores size distribution was plotted (figure 5). The data on the figure shows that the pores in this part of the sample are larger (the main part is in the range of 10-70 μm) this is the reason for the main porosity of the material. The pore diameter distribution is noticeable already at an average pore size of 41.79 μm at a standard deviation for a sample of 31.53 μm , which confirms the homogeneous nature of the material porosity.

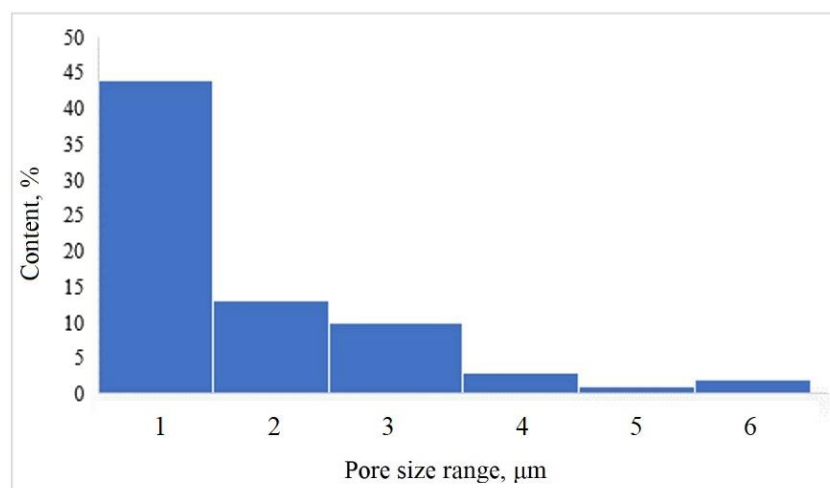


Figure 5. Macropores size distribution for carbon foams obtained by carbonization under pressure (inner part of the sample): 1; 2; 3; 4; 5; 6 – variation ranges of pore sizes respectively 10.80 – 35.84; 38.84 – 60.88; 60.88 – 85.92; 85.92 – 110.96; 110.96 – 136.00; > 136.00 μm

It should be noted that the wide pore size distribution does not allow classifying this class of carbon foams as syntactic.

Further, the experiments on carbonization under pressure of oil pyrolysis pitch with the softening temperature of 140°C at a pressure of 20 MPa and a temperature of 600°C were carried out, then the

samples were carbonized up to a temperature of 900°C processed in an electrovacuum furnace at 2100°C and graphitized in an Acheson type furnace up to a temperature of 2800°C.

Figure 6 shows the structure of the samples obtained by the SEM method. It can be seen that samples have pores of the approximately spherical cross-section with a narrow size distribution in the range of 250-300 μm , there are also inclusions of small spherulitic agglomerates of particles inside the pores which indicates the occurrence of secondary pyrolytic processes in the gas phase (soot formation and etc.). Moreover, the formed agglomerates have an isotropic structure and unexpressed texture despite the high final temperature of heat treatment.

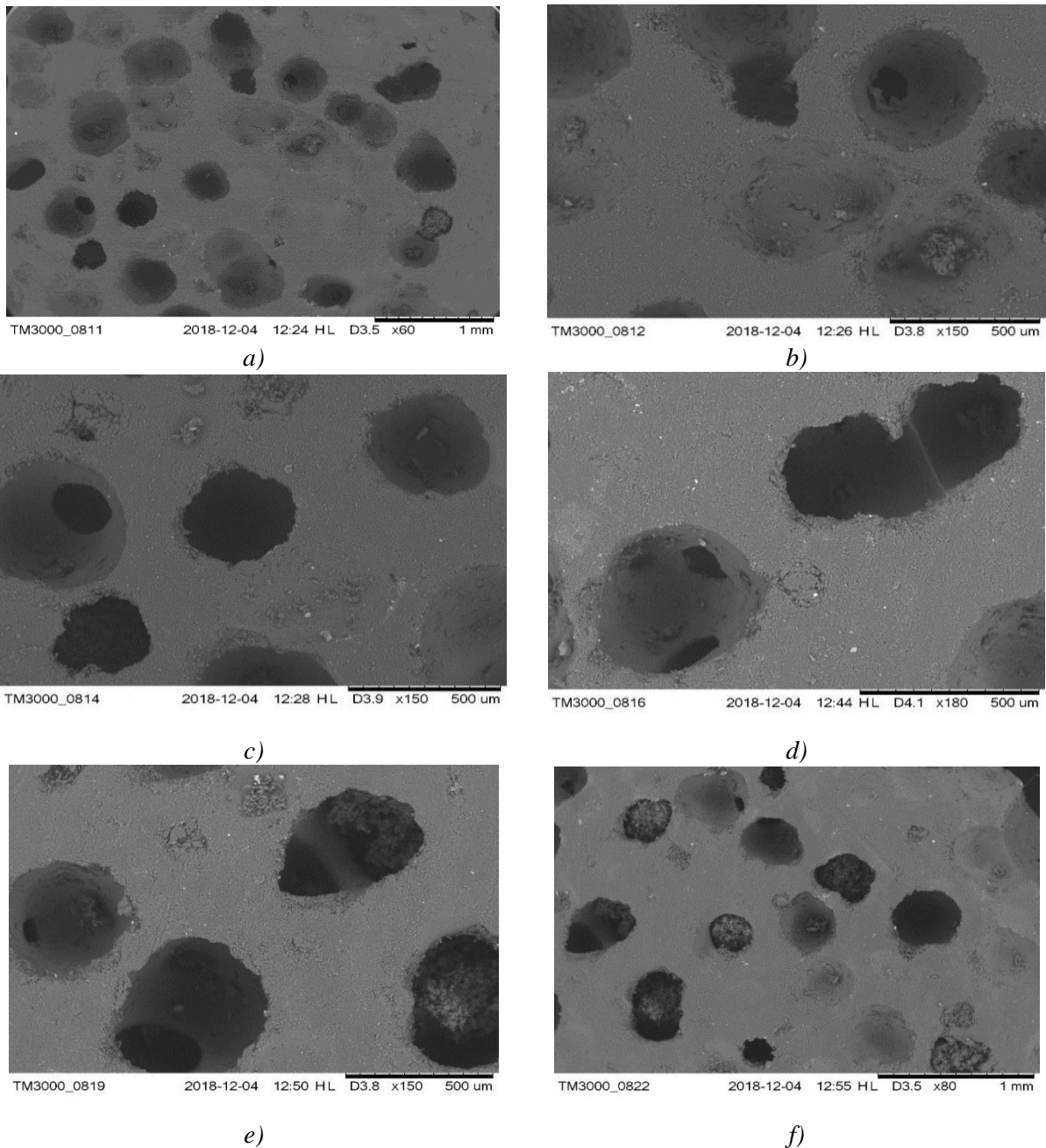
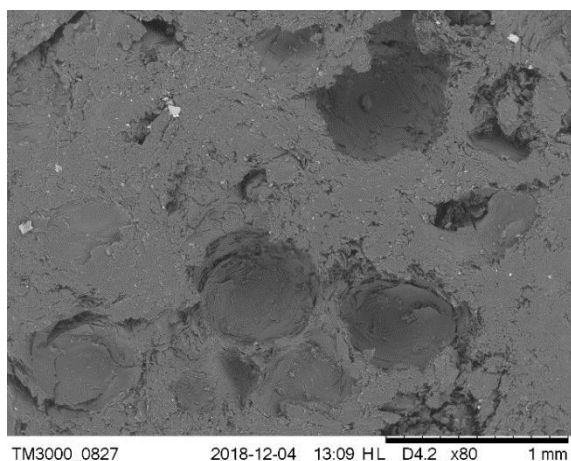
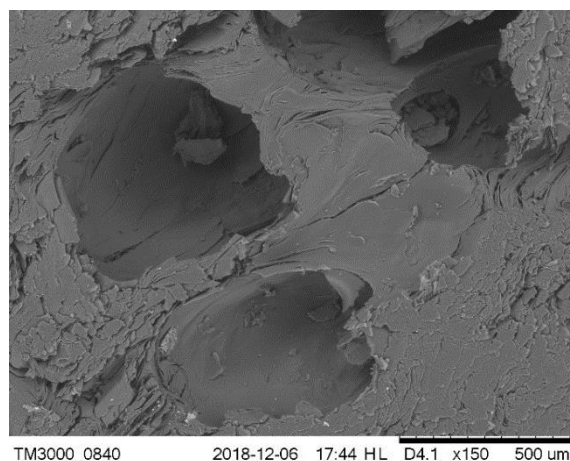
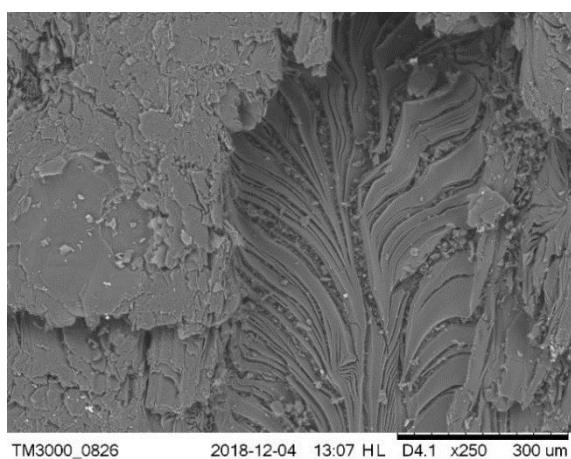
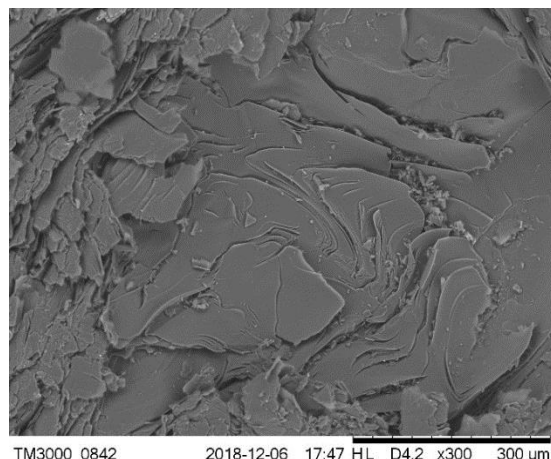


Figure 6. SEM images of carbon foams obtained by carbonization under pressure of oil pyrolysis pitch

The graphitized part of the sample has an isotropic structure, which indicates an insufficient content of the mesophase in the material. The characteristic graphite texture is expressed explicitly. The 10 wt. % of mesophase microspheres were added to the initial pitch and the material was processed in similar conditions to increase the content of the mesophase in the material.

Figure 7 shows the microstructure images of the obtained graphitized foam. It can be seen that pores have approximately the same character, but the structure of the interpore walls differs sharply from the previous material – walls have the high degree of graphitization with the striated structure of graphite (figure 7, *c* and *d*) there are also secondary deposits (figure 7 *a* and *b*), however, mainly walls have more pronounced graphite nature. In some places, cracks and pores of the elongated shape are observed (figure 7 *e* and *f*), which is possibly related to the thermal stresses arising at the low-temperature stage of the process that is conditioned by the filler presence. The presence of cracks can lead to a noticeable decrease in material properties.

The samples were also obtained on the basis of a special oil pitch with a mesophase content of more than 80 wt. % to decrease the resulting thermal stresses. The samples were obtained according to a similar scheme.

*a)**b)**c)**d)*

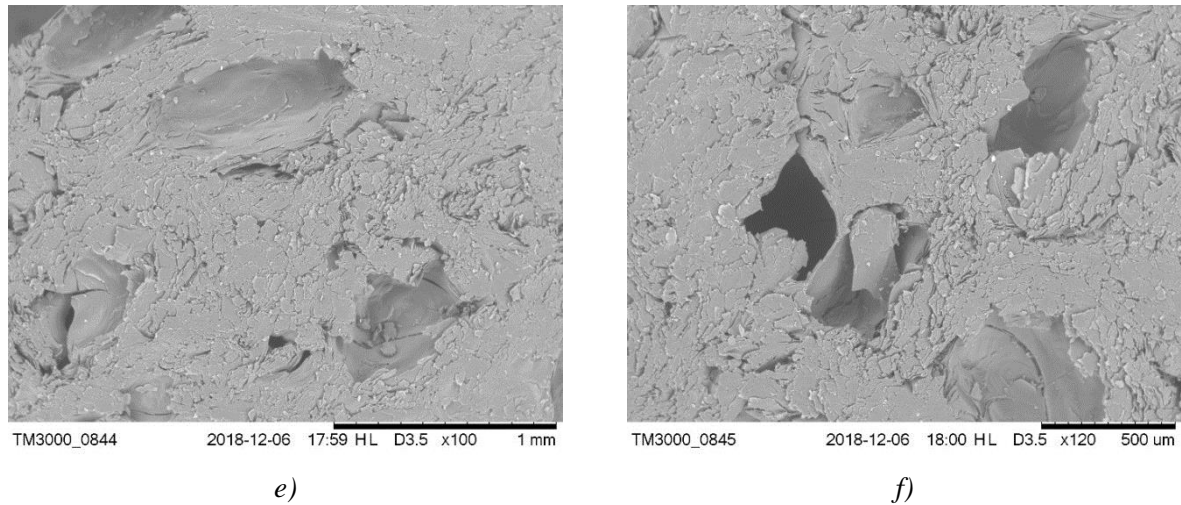
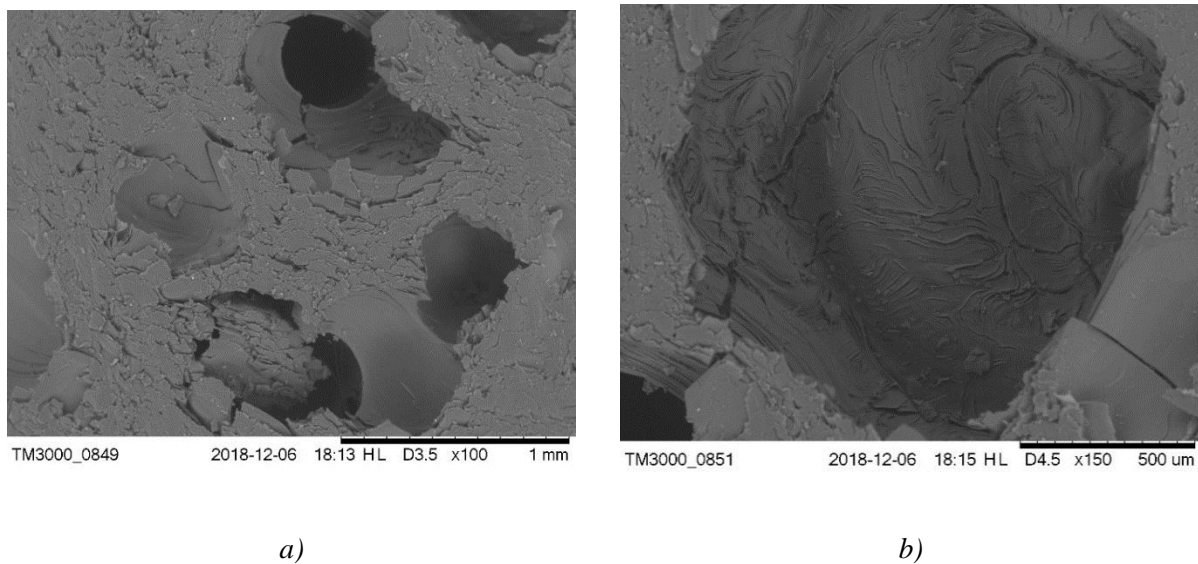


Figure 7. SEM images of carbon foams obtained by carbonization under pressure of oil pyrolysis pitch with the addition of 10 wt. % of mesophase microspheres

Figure 8 shows the images of the material microstructure. It can be seen that material has a structure with the high degree of anisotropy of the graphite component similar to the previous one. The presence of cracks in the structure of the inter pore walls which are visually comparable with those for the samples with mesophase microspheres can be seen.



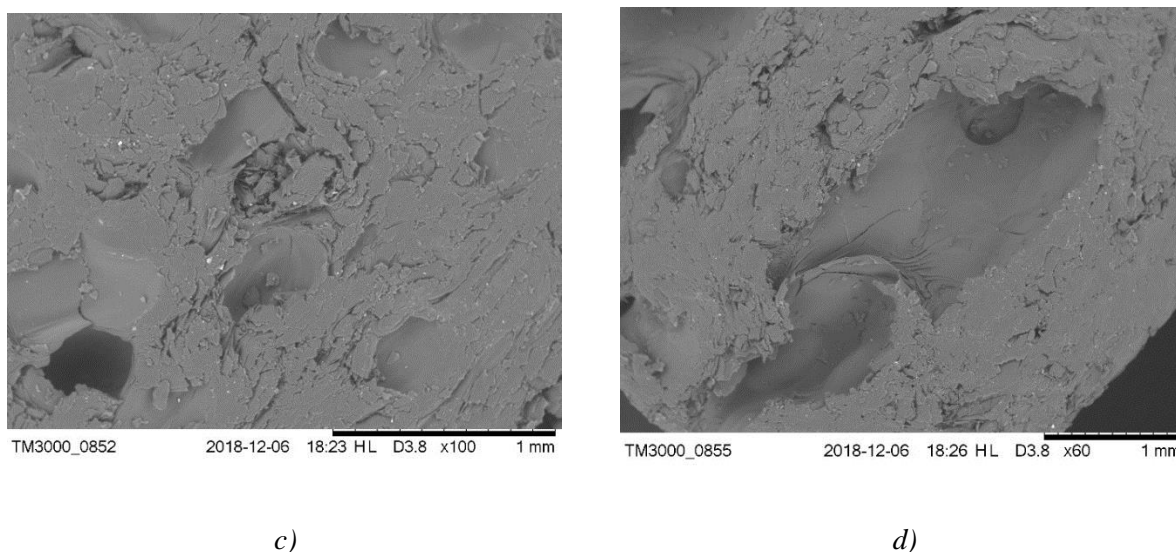


Figure 8. SEM images of carbon foams obtained by carbonization under pressure of special mesophase pitch

At the same time, studies of mechanical and thermophysical properties have shown that the properties of the given group of samples have a higher level which indicates the slightly higher degree of perfection of the graphite obtained using this technology.

3. Conclusions

Thus, the studies showed that the technology for producing foams by carbonization under pressure provides a fairly high level of thermophysical (heat-conducting) and physical and mechanical properties of products.

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