Influence of the composition and synthesis technology on the structure of syntactic carbon foams

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Abstract. The paper shows the influence of the composition and synthesis technology on the structure of syntactic carbon foams. It studies the foam technologies using carbon microballoons and phenol formaldehyde resin, and pitch carbonization under pressure. It reveals the influence of added mesophase microballoons in the starting pitch on the formation of a porous structure of syntactic carbon foams. It shows the macropore size distribution in carbon foams made by industrial carbonization under pressure.

1. Introduction
Carbon composite materials with a regular porous structure belong to the class of syntactic carbon foams where thermophysical properties depend significantly on synthesis technologies, starting components, and resulting structure [1-3]. Depending on the specified factors, it is possible to make syntactic carbon foams with thermal conductivity and thermal insulation properties, which can be changed in a wide range of thermal conductivity. Syntactic carbon foams are widely used as various functional materials in the aerospace, machine building, and many other current manufacturing industries [4-6].

2. Methodology
The microstructure of the syntactic carbon foams made using different process approaches was studied by scanning electron microscopy on Hitachi TM3000 instrument at an accelerating voltage of 15 kV, vacuum of $10^{-6}$ mm Hg, operating current of 150 nA, 60-3000x magnification. The studies were conducted for the syntactic carbon foams made using two process approaches [7].

3. Purpose and objectives of the study
The purpose of the paper is to study the influence of the composition and various synthesis technologies on the structural features of syntactic carbon foams (SCF).

4. Results
The first technology involves the synthesis of foams using carbon microballoons and phenol formaldehyde resin. The syntactic carbon foams of this type were made using the filler/binder technology. A filler was microballoons made by carbonizing hollow phenolic microballoons at a temperature of 900 ºC; a binder was phenol formaldehyde resin. The components were mixed in a
liquid phase, acetone was used as a solvent, which was removed by vacuum sublimation using the rotary evaporator. The resulting mixture was ground, pressed at the room temperature, carbonized at a temperature of 900 °C, and subjected to pyrocompaction at a temperature of 1100 °C with the special equipment [8-10].

SEM images (Figure 1) show that the resulting foams are based on microballoons having holes or destroyed partially, probably, due to the exit of volatile substances during the carbonization. The size of the resulting microballoons is lower than 90 μm (average size is approximately 60 μm). They are bound by layers of the binder (coke of phenol formaldehyde resin). The material has an isotropic structure, the texture is not distinct, the observed porosity depends heavily on the filler content. In addition, a significant number of voids is observed outside the surface of microballoons, which are likely to have been formed after the exit of volatile substances from the binder during the carbonization. The analysis of the resulting structures also shows thicker microballoon walls, which is indicative of orienting influence of the filler and carbonization of the binder, first of all, on its surface. It has been established that pyro-compaction does not have a major influence on the morphology of the resulting material.
Figure 1. Samples of the foam samples based on carbon microballoons and phenol formaldehyde resin. Magnification: (a) 1500x, (b) 500x, (c) 500x, (d) 1500x, (e) 1000x, (f) 500x, (g) 500x, (h) 1000x.

The second technology involves the synthesis of foams made by pitch carbonization under pressure. The foams were synthetized in an industrial autoclave by soaking carbon-carbon composite materials with pitch at a pressure of 8.0 MPa and a temperature of 500 °C, then carbonized at a temperature up to 2200 °C. The resulting foam had a prominent heterogeneous macrostructure: the outer layer was a material with a density of approximately 1.2 g/cm³ and porosity invisible with the naked eye, the inner layer had a density of about 0.7 g/cm³ and a prominent porosity.

Figure 2 shows SEM images of the outer (dense) layer. It can be seen that the structure of the material porosity is heterogeneous: there are small channel pores and large cracks in the structure of the material. In terms of the structure of pore walls, the material is sufficiently homogeneous and has a graphite-like spherulitic structure with a typical spherulite size of approximately 20 μm. The sections show that the spherulites are a graphite-like carbon material at the pregraphitization stage.
156 areas were analyzed to plot pore size distribution (Figure 3). The given data show that the pores are predominantly small (up to 17.6 μm), which contribute to the most of the porosity of syntactic carbon foams. The average size of pores is 12.24 μm, with a high standard sampling deviation (12.68 μm), which provides an additional confirmation of the polymodal nature of their distribution.

The inside porous part of the material is a foamy structure visible with the naked eye. SEM studies show that there are also channel circular or elliptical macropores (Figure 4) on the saw cuts and spalls of the cell surface. In the interpore space, the graphite has a laminar structure and includes a large number of cracks with a width in the range of tens of nanometers. Besides, there are secondary deposits of isometric particles on the surface of the cells, which is an indirect indication of carbon formation via the gaseous phase in particular due to volatile pitch substances.
Figure 4. Samples of the foams made by industrial carbonization under pressure (the inner surface of the sample). Magnification: (a) 250, (b) 500x.

128 areas were analyzed to plot the pore size distribution (Figure 5). The data in the figure show that this area has larger pores, and the size of the most of the pores is $10-70 \, \mu m$. It is important to note that a relatively broad pore size distribution makes it impossible to attribute this foam class to syntactic foams.

Figure 5. Nature and ranges of the pore size distribution for foams made by industrial carbonization under pressure (the inner surface of the sample).

The structure was studied in the samples of carbon foams made by carbonization under pressure of pyrolyzed petroleum pitch with a softening temperature of $140 \, ^\circ C$ at a pressure of $20 \, MPa$ and a final temperature of $600 \, ^\circ C$. Then the samples were carbonized by heating up to a temperature of $900 \, ^\circ C$, subjected to heat treatment in an electric vacuum furnace at a temperature of $2100 \, ^\circ C$, and graphitized in an Acheson furnace at a temperature of $2800 \, ^\circ C$. Figure 6 shows the structures of the studied samples. It can be seen that the samples feature more or less spherical pores with a narrow size distribution in the range of $250-300 \, \mu m$. The inclusions of small spherulitic agglomerates of the particles inside the pores stand out, which is indicative of secondary pyrolytic processes in the gaseous...
phase (soot formation, etc.). And the resulting agglomerates have an isotropic structure and non-prominent texture, despite the high final temperature of heat treatment. It can be seen that the graphitized part of the sample has an isotropic structure, which is indicative of too low mesophase content in the material. The texture intrinsic to graphite is prominent in the sample.

![Figure 6](image)

Figure 6. Samples of the foams made by carbonization under pressure of pyrolyzed petroleum pitch. Magnification: (a) 150x, (b) 80x.

10 wt. % of mesophase microballoons were added to the starting pitch, and the material was processed in similar conditions to increase the mesophase content. Figure 7 shows the microstructure of the resulting graphitized foam. It can be seen that the pores have approximately the same nature, but the structure of the interpore walls is starkly different from that of the previous material: the walls have a very high degree of graphitization, with the laminar structure of graphite (Figure 7, (b)). There are also secondary deposits (Figure 7 (a), however, the samples generally have a more prominent graphite nature. Cracks and elongated pores (figure 7 (c)) are observed in some areas, which can be caused by the thermal stresses at the low temperature process stage due to the filler presence. Cracks can lead to a noticeable decrease in the material properties.

The samples were also made from a special petroleum pitch with a mesophase content of more than 80 wt. % to decrease the arising thermal stresses. The material was made using the similar technology.
Figure 7. Samples of the foams made by carbonization under pressure of pyrolyzed petroleum pitch, with 10 wt. % of mesophase microballoons. Magnification: (a) 150x, (b) 250x, (c) 120x.

Figure 8 shows the microstructure of the resulting samples. It can be seen that the material has a structure with a high degree of anisotropy of the graphite component. Cracks can be observed in the structure of the interpore walls.

Figure 8. Samples of the foams made by carbonization under pressure of special mesophase pitch. Magnification: (a) 100x, (b) 150x.

4. Conclusions
Therefore, the studies determined that the structure of syntactic carbon foams was heavily influenced by the starting components and synthesis technologies. It is found that:
- the foams made by the first technology are a classical heterogeneous filler-binder system where both filler and binder are isotropic materials similar to glassy carbon, and the cells are clearly based on the hollow filler microballoons;
- the foams made by the second technology are characterized by near-spherical shapes of cells and a narrow diameter spread, which corresponds to the conditions of formation (the size of gas bubbles should be defined mostly by external pressure during foam formation); special mesophase pitch and added mesophase microballoons have a major influence on the degree of perfection of graphite structure, which should have a positive effect on the properties.
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