Comparative study of structural properties of syntactic carbon foams made using different process approaches

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Abstract. The structural properties of syntactic carbon foams made using different process approaches were studied by scanning electron microscopy. The paper shows that foam technology has a major influence on the formation of the foam structure.

1. Introduction
Carbon foams, including syntactic ones, belong to one of the advanced and promising classes of composite materials, which feature a regular porous structure that provides higher properties as compared to materials with an irregular porous structure, with a similar density. Syntactic carbon foams are distinguished by dependence of their thermophysical and other physical chemical properties on the structure parameters. Due to the variation of raw materials and process methods, it makes it possible to manufacture thermal insulation and thermally conductive materials with a wide range of thermal conductivity [1-5].

2. Methodology
The microstructure of syntactic carbon foams made using various process approaches was studied by scanning electron microscopy (SEM) on Hitachi TM3000 instrument. The samples were directly secured on a conductive carbon adhesive tape. The imaging conditions were an accelerating voltage of 15 kV, vacuum of 10⁻⁶ mm Hg, operating current of 150 nA, 60-3000x magnification.

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
Syntactic carbon foams made by template carbonization. The foams of this type (with their structure based on carbon material similar to glassy carbon (coke of phenol formaldehyde resin)) were synthetized by soaking the template (open-cell melamine with a cell size of 100-150 μm) in 20 % wt. solution of phenol formaldehyde resin in ethanol and acetone at a residual pressure of 40-50 mm Hg, followed by drying, curing of resin at a final temperature of 150 °C, carbonization at a final temperature of 900 °C, and pyrocompaction at a temperature of 1100 °C.
SEM images (Figure 1) show that the material as a whole inherits the structure from the polymer template, i.e., it has a cell structure with a cell size of 100-150 μm.

Figure 1. SEM images of the syntactic carbon foams made by template carbonization. Magnification: (a) 100x, (b) 250x, (c) 500x, (d) 500x, (e) 2500x, (f) 2000x.
It is observed in some areas that the cells are filled with coke of phenol formaldehyde resin (Figure 1, a-c), interpore walls and interstices become thicker (Figure 1, e, f). The carbon material has an isotropic structure, the texture is not prominent, the porosity observed with the microscope is more than 80%.

Syntactic carbon foams based on carbon microballoons and coal tar pitch. A filler was carbon microballoons made by carbonizing hollow phenolic microballoons at a temperature of 900 ºC; a binder was high-temperature coal tar pitch (softening temperature of 120 ºC). The components were mixed in toluene, and then it 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 ºC and then in an electric vacuum furnace at a temperature of 2100 ºC, and subjected to pyrocompaction at a temperature of 1100 ºC.

SEM images (Figure 2) 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 dense layers of the binder (product of pitch carbonization). The foams have a lower number of voids that are formed due to the exit of volatile substances from the binder. The binder layers have a prominent texture, which is indicative of noticeable binder graphitization with the formation of laminar graphite (Figure 2, c-e). It is also important to note the formation of small (less than 10 μm) isometric particles and chains of particles (Figure 2, g-j), which is indicative of secondary processes in a gaseous phase (liquid-vapor-solid), with the formation of soot-like particles from light pitch fractions or residual toluene. The distinctive feature of this material class is the formation of a lamellar structure of microballoon walls, which indicates the coke formation and subsequent binder graphitization on their surface, as well as change in the degree of graphitizability of the wall material (Figure 2, f, h, j).
Figure 2. SEM images of the syntactic carbon foams based on carbon microballoons and coal tar pitch. Magnification: (a) 500x, (b) 250x, (c) 1000x, (d) 1000x, (e) 500x, (f) 1500x, (g) 500x, (h) 2000x, (i) 1000x, (j) 3000x.

Syntactic carbon foams made using a volatile blowing agent. In a strict sense, the foams of this type are syntactic due to the method of their synthesis, and not due to the structure of the resulting pore system. The foams were synthetized by vibro-milling coal tar pitch, sodium chloride, and natural graphite; by pressing the mixture at a temperature of 40-60 °C and pressure of 12 MPa; carbonization at a temperature of 900 °C; heat treatment in an electric vacuum furnace where the blowing agent is melted and evaporated at 2000-2100 °C; graphitization at a temperature of 2800 °C in an inert atmosphere.

Figure 3 shows SEM images of the resulting samples. It can be seen that the material is a typical highly porous graphite with a high degree of crystalline perfection in terms of its microstructure. The crystallites with a size of up to several micrometers are visible by an electron microscope (Figure 3, a-c, and, most notably, e), the macroscale texture is not prominent, which can be associated with the rapid exit of the blowing agent. The macropores with a size of approximately 10 μm look like channels, which is also likely to be associated with the conditions of the blowing agent evaporation. The size of pores is an order of magnitude smaller than the size of sodium chloride particles (100-250 μm), which is indicative of secondary micromechanical processes during the graphitization (crack relaxation, creep).
Figure 3. SEM images of the syntactic carbon foams made using a volatile blowing agent. Magnification: (a) 600x, (b) 600x, (c) 400x, (d) 2000x, (e) 1200x, (f) 1000x, (g) 1500x, (h) 1200x, (i) 400x, (j) 800x.

The observed number of pores (15-20% of the section) does not correspond to the material density (0.3-0.5 g/cm³) and theoretical porosity [6-10], which indicates that the bulk of pores are nanometric. It makes these materials interesting and promising as adsorbents in various manufacturing industries.

4. Conclusions
The syntactic foams made using different technologies (template carbonization; based on carbon microballoons and coal tar pitch; using a volatile blowing agent) are characterized by a distinctive structure that depends on the selected starting components and process conditions. The SEM studies of structural features of foams revealed:
- the foams made by template carbonization are similar to open-cell polymer foams known in the industry, and consist entirely of isotropic carbon;
- the foams made using carbon microballoons as a filler and coal tar pitch as a binder are a classical heterogeneous filler-binder system where both filler and binder are isotropic materials, with the cells clearly based on hollow filler microballoons;
- the foams made using a volatile blowing agent are characterized by high porosity and degree of graphitization, as well as by an extensive system of slit-shaped micro- and mesopores; the graphite pore walls have a clear texture to ensure high thermophysical properties; the macropores are circular or elliptical channels due to the nature of the blowing agent exit.

Acknowledgments
The work was carried out with the financial support of the Ministry of Education and Science of the Russian Federation within the framework of the Federal Target Program “Research and development in priority areas of development of the scientific and technological complex of Russia for 2014–2020” agreement No. 14.583.21.0057 of July 28, 2016 (Project ID RFMEFI58316X0057).

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