

# Study of the influence of synthesis technologies on the properties of syntactic carbon foams

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**Abstract.** The paper studied the influence of starting components and operating conditions of synthesis processes on the performance properties of syntactic carbon foams. The studies determined the behavior and ranges of hardness, ultimate compressive strength, apparent density, and thermal conductivity of foams made by template carbonization and using carbon microballoons, depending on heat treatment temperature. They determined the influence of a volatile blowing agent (sodium chloride) with wide and narrow fraction on a change in the studied properties of syntactic carbon foams.

## 1 Introduction

Carbon materials are represented by a very wide range of natural and artificial substances with a combination of useful mechanical properties, which are widely used in many current manufacturing industries. Of particular interest are man-made materials where the properties depend on two key factors: a combination and ratio of starting raw materials that are used for production, and manufacturing methods.

Production of carbon materials includes the following major operations: preliminary preparation of starting components by grinding and subsequent heat treatment with no air at elevated temperatures. Heat treatment process is accompanied by preshrinking, removal of volatile compounds, increase in specific gravity, increase in electrical conductivity and mechanical strength of materials. Solid carbon materials, both natural (graphite, anthracite) and artificial (coke, soot), are mixed with binders (pitch, synthetic resins) in certain combinations and ratios, and pressed with special equipment at most suitable operating conditions. Resulting intermediate products in the form of “green” workpieces are subjected to heat treatment at elevated temperatures with no air.

In recent decades, many advanced industrial countries have conducted the comprehensive experimental and theoretical research to develop a wide range of carbon materials with various structures. Of particular interest among them are syntactic carbon foams. The distinctive feature of such foams is a regular porous structure that provides higher thermophysical properties as compared to materials with an irregular porous structure, with

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a similar density [1-7]. Syntactic carbon foams are distinguished by a significant dependence of their properties on the structure parameters. Due to the variation of raw materials, production methods, and processing conditions, it makes it possible to produce thermal insulation and thermally conductive materials with a wide range of thermal conductivity: from less than 0.1 W/m·K (for thermal insulation ones) to 180 W/m·K (for thermal conductive ones). Carbon foams are used to make heat sinks and thermal insulation, porous electrodes, and many other products for various applications. Thus, the studies focused on development of syntactic carbon foams with tailor-made thermophysical and physical mechanical properties are relevant and important. The purpose of this study is to study the influence of the composition and synthesis technologies on the properties of syntactic carbon foams.

## 2 Research techniques

The physical mechanical (apparent density, ultimate compressive strength, hardness) and thermophysical (thermal conductivity) properties were studied to determine the influence of the composition and ratio of components, foam technology on the structure and performance properties of foams. Density, ultimate compressive strength, and hardness were determined using the existing standard techniques. Thermal conductivity was assessed with constant heat flux method at a temperature of 20 °C.

Starting components for synthesis of foams. There are different approaches to synthesis of syntactic carbon foams with a controllable set of properties [8], which can be varied in a very wide range by changing porosity, ratios between binding carbon material and microballoons, their sizes, composition of gas filling, etc. For the studies, carbon foam samples with various structures were synthesized by three methods: using microballoons and pitch; template carbonization, using a volatile blowing agent.

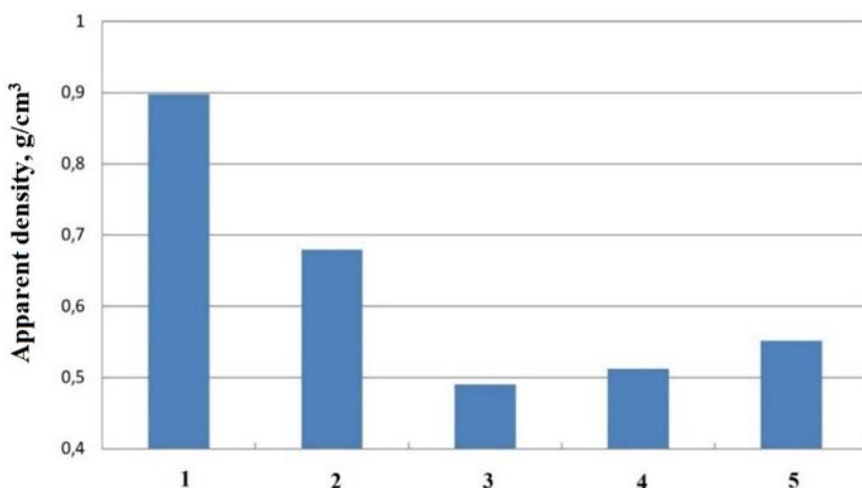
Foams based on carbon microballoons and coal tar pitch. Syntactic carbon foams of this type were synthesized using the filler/binder technology. A filler was carbon microballoons made by carbonizing hollow phenolic microballoons at a temperature of 900 °C; a binder was high-temperature coal tar pitch with a softening temperature of 120 °C. The components were mixed in a liquid phase (toluene), then the solvent 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 then in an electric vacuum furnace at a temperature of 2100 °C, and subjected to pyrocompaction at a temperature of 1100 °C.

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 synthesized 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 temperature of 150 °C, carbonization at a temperature of 900 °C, and pyrocompaction at a temperature of 1100 °C.

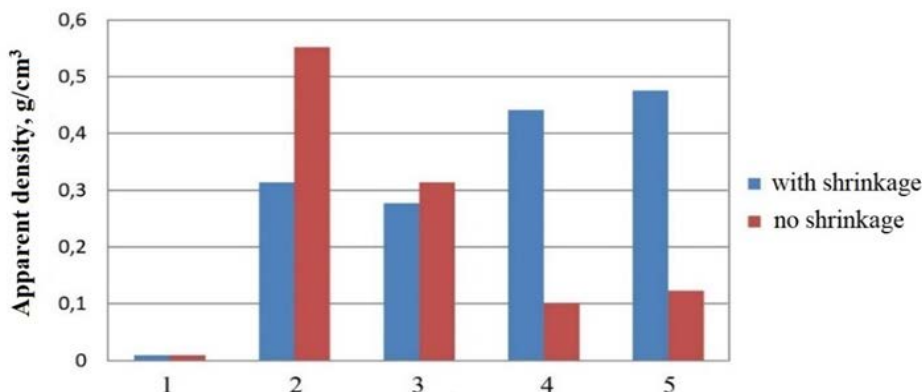
Foams made using a volatile blowing agent. Foams of this type were synthesized by vibromilling a mixture of high-temperature coal tar pitch with a softening temperature of 120 °C as a binder, sodium chloride, and (for certain samples) natural graphite followed by pressing in a blanking die at a temperature of 40-60 °C and pressure of 12 MPa. Then it was subjected to carbonization at a temperature of 900 °C, heat treatment in a electric vacuum furnace at 2000-2100 °C (the process was accompanied by melting and evaporation of the blowing agent), and graphitization at a temperature of 2800 °C in an inert atmosphere in a special furnace [9].

### 3 Body text

The comprehensive experimental research was conducted to adjust the properties of syntactic carbon foams made with different methods. Figures 1 and 2 show the relationships between the density of workpieces based on carbon microballoons and based on melamine, and heat treatment temperature at different stages of the process cycle. For syntactic carbon foams made from microballoons, it can be seen that all the stages with a loss of volatile substances (curing, carbonization) are accompanied by a decrease in density, i.e., mass loss prevails over shrinkage processes. Such a phenomenon is typical for highly-porous materials with a rigid backbone formed by carbon microballoons [10]. Although pitch binders act differently when heated (they melt and form liquid crystal phase), the samples based on carbon microballoons and pitch feature the similar density behavior. Generally, similar patterns are also typical for melamine-based samples made by template carbonization.

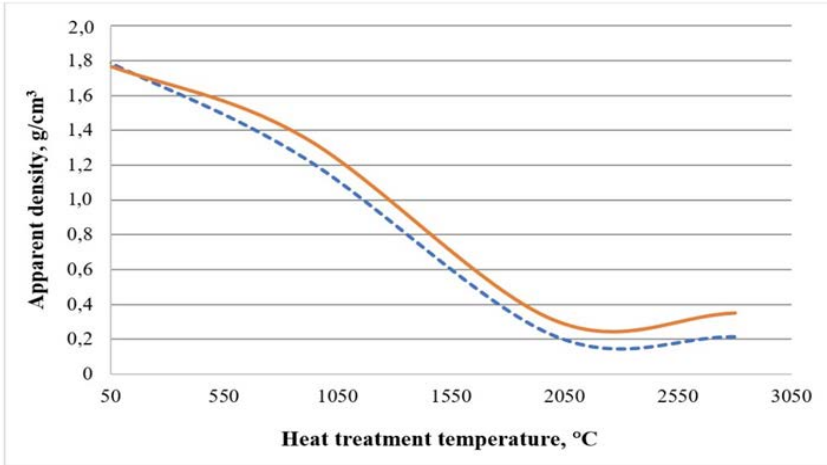


**Fig. 1.** Change in density of the workpieces at different stages of synthesis process cycle for foams based on carbon microballoons: (1) pressing; (2) heat treatment at 150 °C; (3) carbonization at 900 °C; (4) pyrocompaction at 1050 °C for 20 hours; (5) pyrocompaction at 1050 °C for 44 hours.



**Fig. 2.** Change in density of the melamine workpieces at different stages of synthesis process cycle: (1) starting melamine; (2) soaking; (3) curing at 150 °C; (4) carbonization at 900 °C; (5) pyrocompaction at 1050 °C.

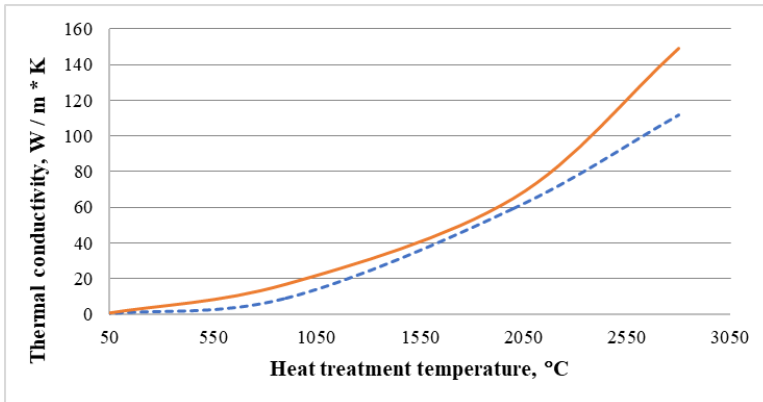
Figure 3 shows the relationship between the density of pitch workpieces made using a volatile blowing agent and heat treatment temperature, with wide and narrow fraction of salt.



**Fig. 3.** Density of the pitch workpieces made using a volatile blowing agent vs heat treatment temperature: dashed line for wide fraction of salt; solid line for narrow fraction of salt (100-250 μm).

It is evident from the above data that after carbonization at 900 °C the density decreases slightly due to a loss of pitch mass, however, a rigid salt backbone that does not tend to deform at such temperatures remains unchanged, and no shrinkage occurs. When temperature rises above 1600 °C it results in salt removal and rapid mass loss, which is accompanied by a noticeable decrease in density (by 3-5 times). During graphitization, the density increases slightly due to the shrinkage of the porous material, which corresponds to the theoretical data about the behavior of these graphite types [11]. It is important to note that foams made using narrow and wide fraction of filler have similar apparent density.

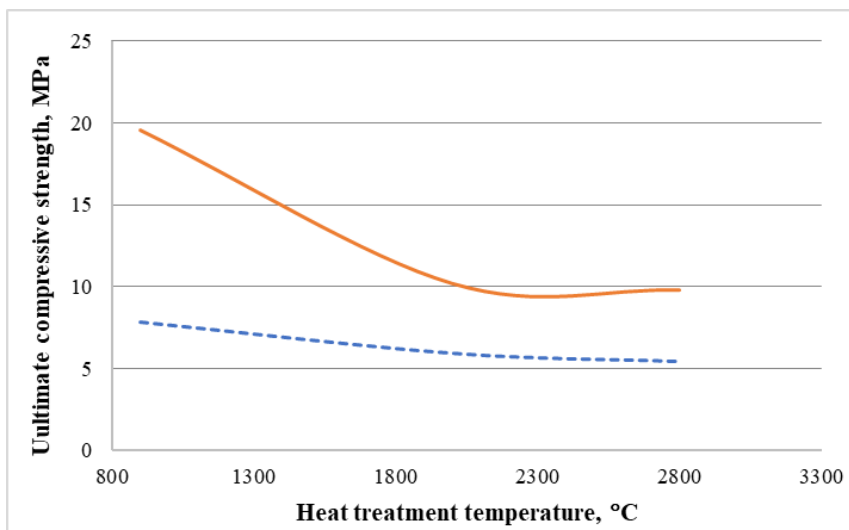
Figure 4 shows the relationship between thermal conductivity of foams made using a volatile blowing agent and heat treatment temperature. It can be seen that thermal conductivity increases steadily as heat treatment temperature rises. The observed effect is not typical for artificial graphite which feature a plateau in the range of 800-2200 °C and a subsequent rapid increase in thermal conductivity. This effect can be associated with the facilitation of graphitization process in the thin layers on the surface of filler or pores, as well as with the good conditions of heat transfer at elevated temperatures.



**Fig. 4.** Thermal conductivity of the pitch workpieces vs heat treatment temperature: dashed line for wide fraction of salt; solid line for narrow fraction of salt (100-250 μm).

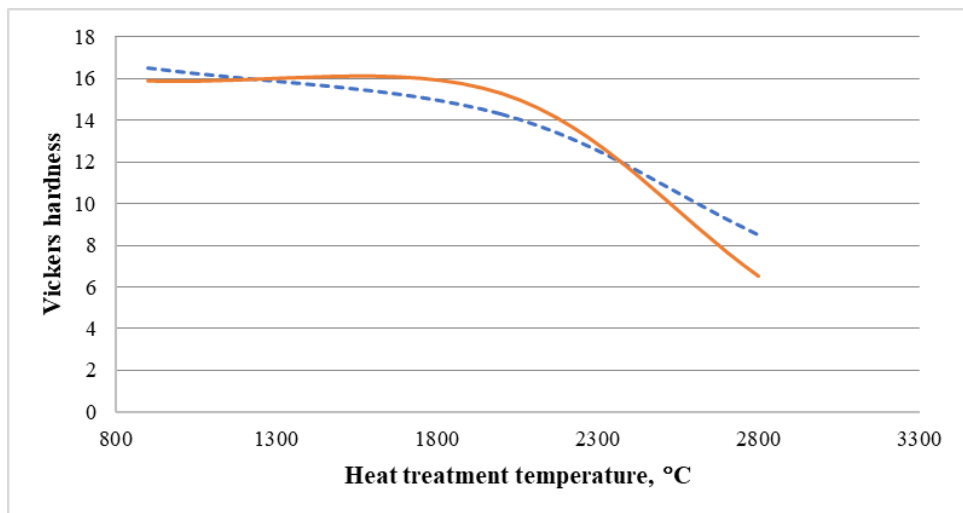
It is important to note that the samples made from narrow fraction of salt have higher properties, which is associated with a more uniform shrinkage and graphitization rearrangements. The relationship between ultimate compressive strength and heat treatment temperature for foams made using a volatile blowing agent (Figure 5) shows that this characteristic is significantly lower than the properties of structural graphite (80-120 MPa).

This effect can be explained by the negative influence of pores and decrease in the effective working cross-section during testing. It is important to note that the performance of the sample based on narrow fraction of salt is generally typical for graphite despite its low properties, i.e., a decrease in the strength is observed during heat treatment, with a small increase in this value between the stages of pre-graphitization and graphitization due to flow of graphite, which leads to “healing” of cracks. In the samples based on wide fraction, a system of cracks formed during baking due to thermal stresses is likely not to go through noticeable transformations during further processing. It results in a consistently low level of strength, with its slight decrease at a higher heat treatment temperature, which is associated with graphitization.



**Fig. 5.** Ultimate compressive strength of the pitch workpieces vs heat treatment temperature: dashed line for wide fraction of salt; solid line for narrow fraction of salt (100-250  $\mu\text{m}$ ).

The behavior of Vickers hardness depending on heat treatment temperature for workpieces made using a volatile blowing agent (Figure 6) corresponds to the existing theoretical concepts [12]. Generally, coke has a higher hardness than graphite. Therefore, high-temperature graphitization is preferable for foams made using a volatile blowing agent as it provides the required thermal conductivity and density, a slightly higher strength, and lower hardness of workpieces, which facilitates their subsequent machining.



**Fig. 6.** Vickers hardness of the pitch workpieces vs heat treatment temperature: dashed line for wide fraction of salt; solid line for narrow fraction of salt (100-250 μm).

## 4 Conclusions

Therefore, the studies determined the influence of starting components and operating conditions of synthesis processes on the performance properties of syntactic carbon foams. The studies laid down the behavior and ranges of the basic properties of carbon foam samples (hardness, ultimate compressive strength, apparent density, and thermal conductivity) made by three different methods. They show the influence of wide and narrow fractions of filler (sodium chloride) on a change in the studied properties of foams.

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