SOME ISSUES OF ISOSTATIC CARBONIZATION OF COAL TAR PITCH IN THE PRODUCTION OF CARBON-CARBON COMPOSITE MATERIALS

Alexander A. Antanovich[1], Sergey F. Kolesnikov[2]

[1]Vereshchagin Institute for High Pressure Physics, Russian Academy of Sciences,
14 Kaluga highway, 108840, Moscow, Troitsk, Russia

[2]Joint-Stock Company "Scientific-research Institute of structural materials based on graphite",
2 Electrode street, 111524, Moscow, Russia

Abstract

The dynamics of changes in the density, mechanical and structural properties of carbon-carbon composite materials (CCCM) has been experimentally investigated depending on the number of carbonization processes of coal tar pitch carried out using isostatic technology. A high-pressure and high-temperature apparatus of large volume for research and industrial applications is described.

Keywords: *carbon-carbon composite materials, isostatic carbonization, carbon fiber, coal tar pitch, carbon matrix, ultimate strength, graphitization, thermal conductivity*

1. INTRODUCTION

Carbon – carbon composite materials (CCCM) consist of a carbon filler and a carbon matrix. As a carbon filler, high-modulus carbon fibers are mainly used. The matrix is made of organic polymers by high-temperature treatment in the volume of the future workpiece.

Organic products (matrix precursors) contain a lot of carbon: coal and oil pitches (up to 50 -65 %) or phenol-formaldehyde resins (up to 50 – 70 %). Use as methane, propane, benzene with carbon content up to 60 – 85 %.

The advantages of using coal pitches as a precursor to the production of CCCM carbon matrices have been known for a long time (Panagiotis ,Matzinos , Pil 1995). Coke from coal pitches has higher density, thermal conductivity and oxidation resistance.

Even earlier, the advantages of increased pressure during carbonation of the carbon matrix in the volume of a 3-dimensional carbon-carbon frame were shown (Weber et al. 1977). The pressure in the process affects the structure of the resulting carbon matrix. There are more dense carbon structures. Such isostatic technologies have found practical application in modern practice. Despite some differences, isostatic technologies involve three main stages in the production of CCCM. We will show it on our example of receiving details from large-size three-dimensional reinforced preparations of CCCM. A photo of one of these parts is shown in Figure 1.

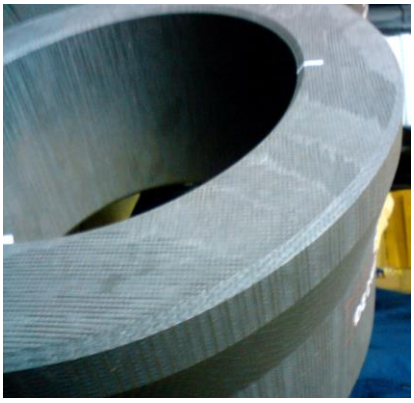


Fig. 1. Photograph of a detail of three-dimensional reinforced CCCM

The first stage: preparatory. A three-dimensional reinforced frame with an initial density of ~ 0.6 g/cm^3, made on the basis of high-modulus carbon fibers, impregnate with medium-temperature coal tar pitch and carbonize the pitch at atmospheric pressure and temperature 750ºC. This process is repeated (usually up to three times) until the density of the preforms is 1.0 g/cm^3. At this density level, the carbon-carbon material acquires compressive strength of ~ 10 MPa, which allows to withstand subsequent cycles of impregnation with high-temperature coal pitch and carbonation at high pressure without deformation and destruction.

The second stage: impregnation and carbonation under pressure (PIC). Prepared at the first stage, the workpiece CCCM impregnate with high-temperature coal pitch and carbonize the pitch at a pressure of up to 100 MPa and a temperature of up to 750ºC. This operation is carried out repeatedly (up to 4-6 times) to achieve the desired density of the material. The density of the material at this stage increases during the impregnation process.

Third step: high-temperature treatment (HTT). After each impregnation and carbonization process under pressure, the CCCM workpiece is subjected to high-temperature vacuum treatment at a temperature of up to 2170ºC. After this stage, the density of the material decreases as a result of chemical transformations.

The joint change in density as a result of the PIC and the HTT will be called a cycle of densification of the material.

In our work (Antanovich, Kolesnikov 2017, 2018) the study of the basic regularities of the technological production process of carbonization at high pressure was carried out. The kinetics of increasing the density of CCCM for a number of products has been studied. At the same time, the mechanism of influence of the medium pressure on the carbonation processes of coal pitches passing from liquid, low-viscosity to high-viscosity and solid state remains insufficiently clarified.

The technology described above is used to create CCCM parts (figure 1) with a density of at least 1.93 g/cm^3. For other applications it is possible to use UCM with lower density. In this regard, it is of some interest to trace the dynamics of changes in the properties of the material at each of the above stages of production of CCCM. The results of such studies, given below, can be used to select the appropriate number of technological stages of production of the material.

2. MATERIALS AND METHODS

The technology of isostatic carbonization is as follows. The CCCM workpiece obtained after the preparatory stage is placed in a thin-walled metal container, the diameter and height of which is greater than the diameter and height of the workpiece. All the free space of the container in a special installation is filled with liquid pitch. After that, the container is sealed and subjected to thermobaric treatment. First, the container is heated to a temperature at which the pitch has a minimum viscosity. Then, at this temperature, the pressure in the container begins to increase, resulting in impregnation - filling the open pores of the workpiece with liquid pitch. After the impregnation is completed, the temperature is raised at the same pressure, resulting in the carbonation of the pitch to form a coke structure.

To create a high pressure on the walls of the container and the liquid pitch in it, a high-pressure apparatus was used, in which a bulk medium, for example, dry quartz sand, is used as a medium that transmits pressure. The scheme of such a device is shown in figure 2.

We have a set of such devices with internal diameters of 150, 560, 800 and 1000 mm. In the figure, the power cylinder is dialed from four rings 1. To increase or decrease the height of the workpiece CCCM number of such rings can be increased or reduced. The force on the pistons 2, necessary to obtain high pressure in the apparatus, is created by means of a hydraulic press. Water cooling channels are made in each of the rings. Electric power is supplied to the heater 9 through the hollow current leads 5, also filled with sand. The heater is made of stainless steel sheet with a thickness of 0.1 mm and allows you

to create a temperature of up to 800ºC. To create higher temperatures, more heat-resistant materials should be used.

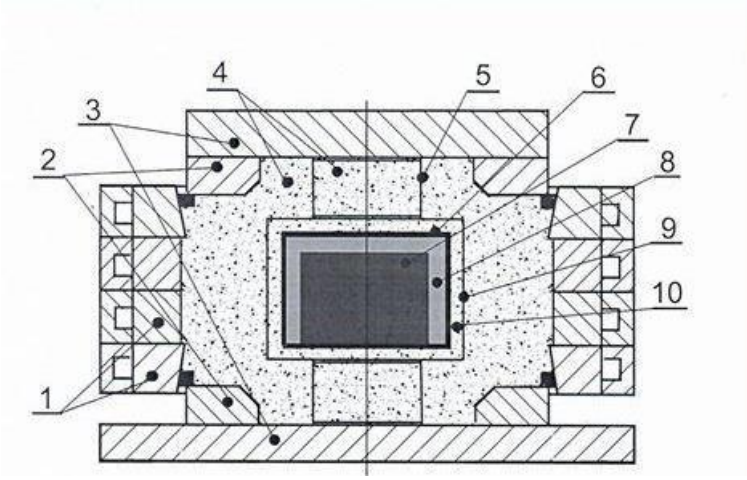


Fig. 2. Diagram of high-pressure apparatus

1 - power rings, 2 - pistons, 3- base plate, 4 - dry sand, 5 - current lead, 6 - hermetic container, 7 - CCCM blank, 8 - coal tar pitch, 9 – heater, 10 - thermal insulation (a layer of dry sand)

3. RESULTS

3.1. Density

Figure 3 shows the results of apparent density measurements for large-sized CCCM workpieces (up to 400 mm in diameter) after each densification cycle.

Here are the average density values based on the results for 170 CCCM billets.

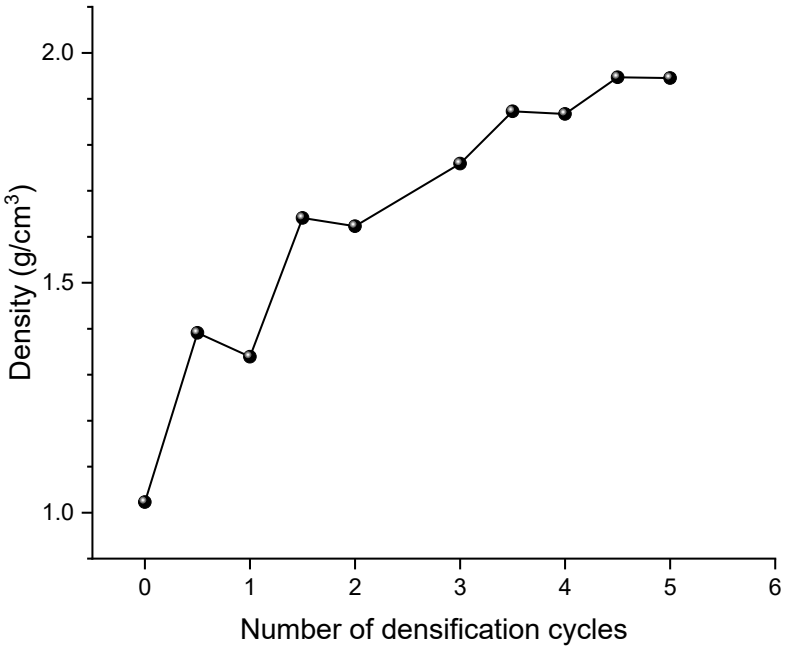


Fig. 3. The change in the density of the material after each cycle of the densification

As mentioned above, in each sealing cycle, the density first increases (PIC) and then falls slightly (HTT). The third densification cycle in addition to PIC and HTT provides for more machining, when the workpiece dimensions (diameter and height) are ground on a lathe at 10-15 mm to remove the less dense porous layer of the material.

3.2. Strength

In the process of compaction UCM formed levels of strength and other physical and mechanical characteristics of the material. The levels of these characteristics were determined on samples cut from the UCM blanks and intended for research. The dependences of the tensile and compressive strength are shown in figures 4 and 5.

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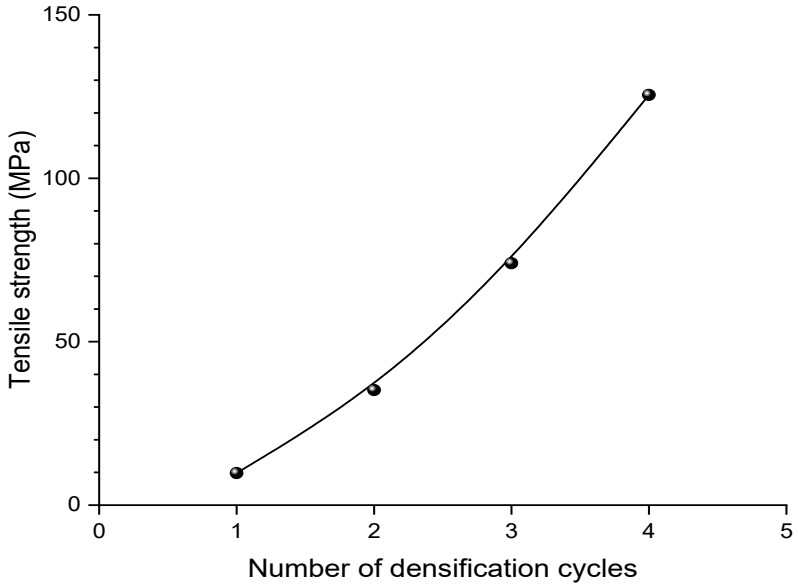


Fig. 4. The dependence of the tensile strength on the number of densification cycles

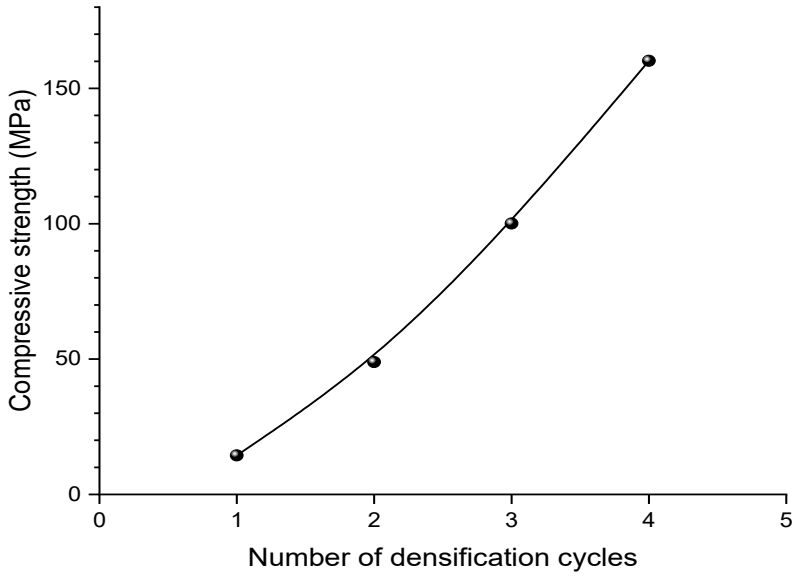


Fig. 5. The dependence of the compressive strength on the number of densification cycles

3.3. Thermal conductivity

As we mentioned above, parallel to the compaction of the CCCM, other physical properties of the material are formed. Changes in the coefficient of thermal conductivity in the process of compacting the material are shown in figure 6.

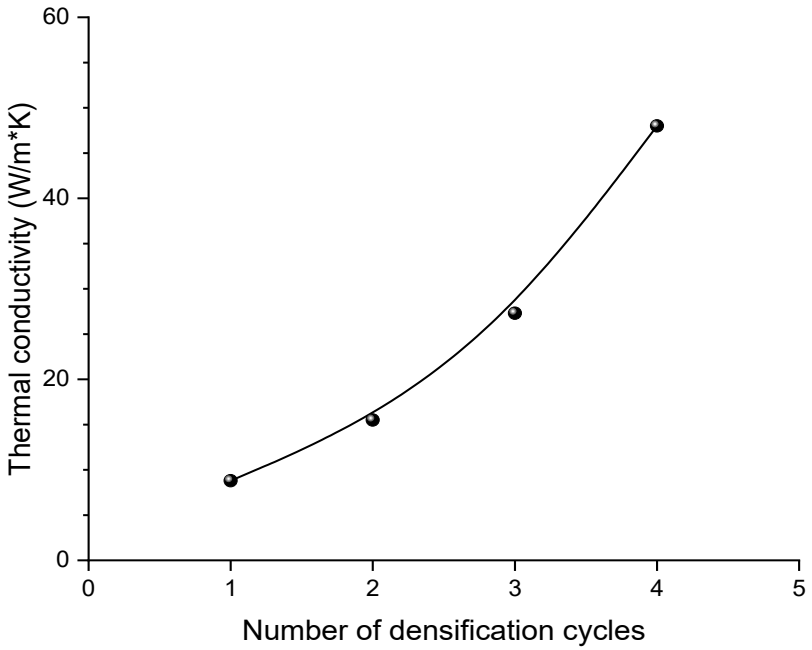


Fig. 6. The dependence of the coefficient of thermal conductivity on the number of densification cycles

3.4. The degree of graphitization

We also study the processes for improving the crystalline structure of the CCCM in the process of densification of the material in the four consecutive cycles. Since carbon fiber and the carbon matrix are the main elements in CCCM, structural changes are expected to occur in both of these components. The values of the degree of graphitization *g* were determined on the basis of x-ray structural analysis of the structural characteristics of the material samples by the formula

$$g = \frac{d_{002} - 0{,}335}{0{,}344 - 0{,}335} \qquad (1)$$

Here, d_{002} is the d-value in the structure of the investigated component of CCCM in nanometers, 0.335 is the d-value in the structure of natural graphite, 0.344 is the d-value in the turbostratic structure of graphite.

It was found that the structure of carbon fibers does not change significantly: the thickness of L_C crystallites increases slightly from 4 to 6.3 nm, the width of *La* crystallites remains almost constant at the level of 4 nm, and the interplanar distance d_{002} decreases from 0.349 to 0.345 nm. The structure of the carbon matrix during compaction of the material changes more significantly: the *Lc* value increased from 29 nm to 36 nm, the *La* value – from 17 nm to 28 nm, d_{002} decreased from 0.341 nm to 0.337 nm. In the end, the degree of the graphitization of the matrix CCCM has grown from 35 to 70%. The dependence of the degree of graphitization of the matrix against the number of cycles of compaction is presented in figure 7.

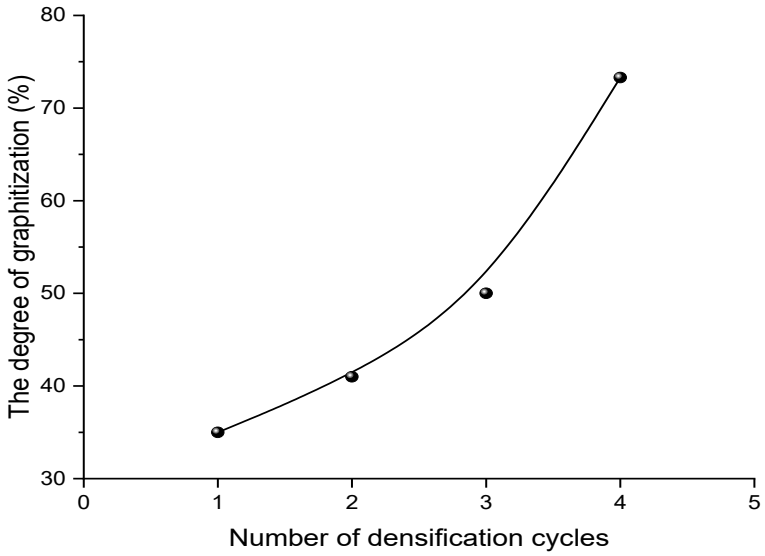


Fig. 7. The dependence of the degree of graphitization of the matrix on the number of densification cycles

4. CONCLUSIONS

The results presented in the article show the dynamics of changes in the physical and mechanical properties of CCCM from the number of compaction cycles and can be used to select the appropriate number of these cycles to obtain a material with specified properties.

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