An invention relates to composite materials, in particular, carbon-based composite materials and methods of obtaining thereof, and may be used in aerospace and aviation industries and in processing metals, natural stones or other hard and superhard materials. A method of obtaining a carbon-based composite material is claimed, comprising the exposure of a mixture of a carbon-containing material and a filler to high pressure and temperature, characterized by the addition to the mixture of a sulfur-containing compound, preferably carbon disulfide, with the said exposure being conducted in the temperature range of 600-2000°C and a pressure of 0.1-20 GPa. The material obtained by the above method is characterized with high strength and low density, high hardness (not less than 10 GPa) and high heat resistance in the air.
Method of obtaining a carbon-based composite material, and the composite material obtained thereby

FIELD OF THE INVENTION

The present invention relates to composite materials, in particular, to carbon-based composite materials, and methods of obtaining thereof, and may be used in aerospace and aviation industries, for processing metal, natural stone and other hard and superhard materials.

STATE OF THE ART

Composite materials (composites) are multi-constituent materials consisting of a polymer, metal, carbon, ceramic or other base (matrix, or binder), reinforced with fillers such as fibers, filamentary crystals, finely dispersed particles etc. By selecting the composition, matching the properties of the matrix and reinforcement, determining the proportion thereof and orientation of the reinforcement material, it is possible to obtain materials with a required combination of operational and processing properties.

According to the structure of the filler, composite materials are subdivided into fiber-based (reinforced with fibers and filamentary crystals), layered (reinforced with film, plates or layered fillers), and particle reinforced, or dispersion-strengthened (with a filler in the form of finely dispersed particles). The matrix in composite materials ensures consolidation of the material, transmission and distribution of tension in the filler, and determines heat, moisture, fire and chemical resistance.

According to the nature of the matrix material, composites are subdivided into polymer, metal, carbon, ceramic and other types.

Composite materials reinforced with high-strength and high-modulus continuous filaments (fibers) have become the most widely used in engineering applications. Of a special interest are the following types:

- composite materials with carbon as a base, reinforced with carbon fibers (carbon-carbon materials);

- composite materials on the basis of ceramics, reinforced with carbon, silicon carbide and other heat-resistant fibers.

Great attention is now given to the creation of new composite materials on the basis of both known and relatively recently discovered modifications of carbon with other elements. An opportunity is now emerging to design materials with pre-determined properties assembled of atomic clusters with needed physical and chemical properties.
At present, there has been described an allotropic form of carbon called fullerene, which is used, for example, as a source material to produce diamonds ("The fullerenes", edited by H.W. Kroto, J.E. Fischer, D.E. Cox, Pergamon Press, Oxford, New York, Seoul, Tokyo, 1993).

A fullerene is a molecule, in which atoms of carbon (60-240 and more in number) are interconnected in such a way as to form a hollow body of an almost spherical shape. Thus, for example, the C_{60} fullerene molecule reminds of a football being formed with 20 hexagons and 12 pentagons. Interatomic distances in the C_{60} fullerene molecule remain almost as short and strong as in a layer of graphite (i.e. graphene); the diameter of a molecule being about 0.7 nm.

A superhard carbon material and method of obtaining thereof are known, wherein an allotropic form of carbon namely C_{60} fullerene is used as a source carbon material (RF patent No 2127225, 1996).

C_{60} fullerene is subjected to a pressure of 7.5-37 GPa and a temperature selected from the range of 20-1,830°C in toroid type, Bridgeman anvil type and other high pressure apparatuses. Under the exposure of the initial fullerene to pressure and temperature, polymerization of fullerene molecules or fragments of molecules occurs. Compact samples of the material possess high mechanical and electrophysical properties.

However, in spite of the high mechanical properties of the superhard materials described above, their thermal conductivity is extremely low.

This, in particular, restricts the use of such materials in cutting tools, because the absence of the withdrawal of heat which is intensively emitted in the area of contact between the processed item and the tool greatly restricts the productivity of the tool and results in its failure due to overheating.

Besides, high pressure apparatuses known at this time (7.5-37 GPa) have small sizes; therefore they limit the size of a product that can be produced from the material obtained in such apparatuses. Thus, it would be easy to make the tip of a cutting tool 1 cm in length, but it would be quite impossible to produce an aircraft body part one meter long.

That is why items capable of being produced from a material obtained by the known method are mostly cutting tool tips.

A superhard composite material and method of obtaining thereof are known (RF patent 2491987, 2011). The method comprises an exposure to high pressure and temperature of a source carbon constituent it being a diamond and binder constituent, with the said carbon constituent additionally containing fullerene and/or nanodiamond; and the binder constituent
being one or more substances selected from the group consisting of: silicon bronze alloy, Monel alloy and hardmetal.

The material is obtained in two stages, wherein at the first stage the mixture of source constituents is exposed to a dynamic pressure of 10-50 GPa under temperatures in the range of 900-2,000°C, and at the second stage the material thus obtained is put into a high pressure apparatus and exposed to a static pressure of from 5 to 15 GPa in the temperature range of 700-1,700°C for at least 20 sec.

The known method allows obtaining a carbon material with high microhardness, elasticity and enhanced wear resistance, which enables it to be used in mining, stone processing and metal processing industries.

However, high pressure apparatuses known at this time (7.5-37 GPa) have small sizes; therefore they limit the size of a product that can be produced from the material obtained in such apparatuses, which prevents the use of the material described above in aerospace and aviation industries.

Aluminum alloy B95 and a composite material based on carbon fibers and epoxy resin are known that can serve as examples of a strong and light material at the same time. The said materials have the highest values of strength - $\sigma^*/\rho$ of about 200 (the strength indicator is a ratio of tensile or flexural (cross-bending) strength (in MPa) to density (in g/cm$^3$) $\sigma^*/\rho$.)

However, both the materials possess low hardness of less than 1-2 GPa, to say nothing of heat resistance (operating temperature less than 200 °C).


Another known material, boron carbide $B_4C$, is light (density 2.52 g/cm$^3$), very hard (hardness about 35 GPa) and heat-resistant (operating temperature up to 2,000 °C), but for all that extremely brittle, so much so that the above-said parameter ($\sigma^*/\rho$) is virtually impossible to determine (G.V. Samsonov, T. Ya. Kosolapova, T.T. Domasevich "Properties, production methods and application areas of hard-melting carbides and alloys based thereon", Kyev, 1974).

A work is known ("Hard disordered phases produced at high-pressure-high-temperature treatment of $C_{60}$" by V.D. Blank, V.N. Denisov, A.N. Ivlev, B.N. Mavrin, N.R.Serebryanaya, G.A. Dubitsky, S.A.Sulynov, M.Yu. Popov, N. Lvoa, S.G. Buga and G.Kremkova. Carbon, V.36, P 1263-1267 (1998)), wherein a method is described of obtaining a very hard (with hardness between 10 GPa and that of cubic BN (50 GPa)) carbon material from molecular $C_{60}$.
fullerene, and the material itself, which is called in the work a "layered laterally bound disordered carbon material". A very hard (with hardness between 10 GPa and 50 GPa) layered laterally bound disordered carbon material, hereinafter called "VT fullerite", is obtained in high pressure apparatuses (at 7 - 8 GPa and 600-1,600 °C).

The density of VT fullerite is about 2.1 g/cm³, and its hardness H, as noted above, is over 10 GPa. Using the known relationships between strength and hardness, we can expect a σ*/ρ ratio of over 1,000 for VT fullerite.

Besides high hardness, VT fullerite possesses the effect of a virtually complete elastic imprint recovery on indenture, which testifies to its unique mechanical properties when used as a structural material.

A high pressure apparatuses known at present (7.5-37 GPa) have small sizes; therefore they limit the size of a product that can be produced from the material obtained in such apparatuses.

Therefore, the known material cannot be used as a structural material in aerospace and aviation industries.

Moreover, in the process of VT fullerite formation from C₆₀ fullerene there occurs a significant volume jump: the density of the source fullerene is 1.7 g/cm³, while the density of VT fullerite is 2.1 g/cm³, which results in considerable stress in the sample and, consequently, the cracking thereof. Low thermal conductivity of the source fullerene (0.4 W/mK) and VT fullerite (about 10 W/mK) leads to big temperature gradients during synthesis, which also results in the cracking of the sample.

In invention patent application "Composite materials containing a nanostructured carbon binder phase and high pressure process" by B. Kear and O. Voronov No. US 2005/01 861 04 dated March 23, 2004, the authors offer a composite material consisting of a "matrix phase" and "binder phase". As a binder phase, materials are proposed obtained from fullerene by thermobaric treatment of a mixture of fullerene and a "matrix phase". As a matrix phase, a variety of carbides, borides and oxides are proposed, as well as diamond and carbon fibers. The work asserts that high-strength materials may be obtained from fullerene at pressures below 7 GPa.

However, that assertion is not true. According to research conducted by the authors, materials possessing high strength (and also high hardness of over 10 GPa) are obtained from C₆₀ fullerene only in high pressure apparatuses at 7 - 8 GPa and 600-1,600 °C, which, as noted
above, does not allow obtaining material for items more than several centimeters in size, and excludes the use of such material as a structural material in aerospace and aviation industries.

The closest technical solution to the claimed invention is the method mentioned above relating to obtaining a superhard composite material (RF patent 2491987, 201 l). The method includes the exposure of the source carbon constituent to high pressure and temperature, the said constituent being diamond, and a binder constituent, with the carbon constituent additionally containing fullerene and/or nanodiamond, and the binder constituent being one or more substances selected from the group consisting of: silicon bronze alloy, Monel alloy and hardmetal.

However, even if the known material possesses microhardness, elasticity and enhanced wear resistance, it is very brittle, while item sizes of over 1 cm cannot be obtained due to small sizes of the existing high-pressure cells.

Therefore, the state-of-the-art technical solutions existing at present do not allow obtaining strong, light, hard and at the same time heat-resistant carbon-based composite structural materials.

**BRIEF SUMMARY OF THE INVENTION**

The technical purpose of this invention is to provide the possibility to produce a carbon-based composite material with low density, high bending strength, high hardness and heat resistance, and manufacture products from the said material with a characteristic size of 1-100 cm (the term "characteristic size" being used in this case to describe typical dimensions of items that can be manufactured from the proposed composite material).

**DETAILED DISCLOSURE OF THE INVENTION**

The goal of this invention is to create a method of obtaining a high-strength, high-hardness, heat-resistant and light carbon-based composite material suitable for the production of items with a characteristic size of 1-100 cm that may be used in aerospace and aviation industries as well as in the processing of metals, natural stones and other hard and superhard materials.

For that purpose, a method of obtaining a carbon-based composite material is claimed comprising the exposure of a mixture of a carbon-containing material and a filler to pressure and temperature, wherein a sulfur-containing compound is added to the said mixture and the treatment is conducted in the temperature range of 600-2,000 °C and the pressure range of 0.1-20 GPa.

Preferably, the sulfur-containing compound is added in an amount of from 0.1 to 3 mass % of sulfur relative to the weight of the carbon-containing material.
As a sulfur-containing compound, carbon sulfur or a compound out of the group of mercaptans is used, or a product of interaction of a compound out of the group of mercaptans with elemental sulfur.

As a carbon-containing compound, molecular $C_{60}$ fullerene or fullerene-containing soot is used.

Preferably, boron carbide is used as a filler in an amount of from 30 to 70 mass % of the weight of the carbon-containing material.

Preferably, carbon fibers, diamond, nitrides, carbides, borides or oxides are used as a filler in an amount of from 1 to 99 mass % of the weight of the carbon-containing material.

Preferably, the treatment is conducted in the temperature range of 800-1,200 °C and a pressure of from 0.5 to 10 GPa.

Also, a composite material is claimed obtained by the method according to any of claims 1-8.

Preferably, the composite material is intended for the production of items therefrom with a characteristic size of 1-100 cm.

It is known that high mechanical properties of carbon-based composite materials are determined by the formation of chemical bonds between the matrix and the binder phases.

However, as already noted, at present it is only possible to obtain a composite material with good mechanical properties in high pressure apparatuses (at 5-15 GPa), where strong association (determined by the formation of chemical bonds) is ensured during synthesis between the matrix and the binder. At lower pressures, both matrix phase hardness and the strength of association between the matrix and the binder are extremely low, and such composite material will not possess any meaningful hardness under the conditions of tensile stress (tensile or flexural strength).

According to the authors’ research, it is possible to figure out substances that would serve as initiators of chemical bond formation both among $C_{60}$ molecules and between $C_{60}$ and other constituents of the composite material even under lower pressures and temperatures. Besides the initialization of the $C_{60}$ - 3D polymerization reaction (i.e. a three-dimensional reaction wherein covalent bonds connecting $C_{60}$ molecules are formed in all directions), such substance should be uniformly distributed over the volume of the source material. If such initiator is uniformly distributed over the entire fullerene in the composite, one can expect the more uniform process of composite formation (accompanied by the formation of chemical bonds) and, ultimately, the more uniform distribution of physical and mechanical properties in the composite obtained.
According to the authors' research, it may be a sulfur-containing compound, e.g. carbon sulfur or a compound out of the group of mercaptans, in particular, isoamyl mercaptan, or a product of interaction of a compound out of the group of mercaptans with elemental sulfur.

It turned out that in that group, carbon disulfide \( \text{CS}_2 \) ("carbon sulfur") satisfies the above-mentioned requirements in the greatest degree. Carbon disulfide \( \text{CS}_2 \) potentially possesses the both mentioned properties. Indeed, under the conditions of composite material sintering, it disintegrates giving forth elemental sulfur (Tonkov EY, High Pressure Phase Transformations Handbook Vol. 1. Amsterdam: OPA; 1992). Thanks to a high affinity with carbon, sulfur atoms (after \( \text{CS}_2 \) disintegration) will form covalent C-S bonds with fullerene and transform the fullerene molecule into a radical, which in turn will induce bonding with the surrounding molecules or other constituents of the material. Besides, \( \text{CS}_2 \) is a good solvent of molecular \( \text{C}_{60} \) fullerene, and, consequently, easily penetrates the molecular crystal of the source \( \text{C}_{60} \). Thus, sulfur atoms can be uniformly distributed over the space occupied by fullerene. Since such initialization centers are uniformly distributed over the space occupied by fullerene, an isotropic product is ultimately produced.

The filler plays an important role in composite material synthesis. When the matrix is being formed from \( \text{C}_{60} \) fullerene, there is a considerable volume jump, the density of the initial fullerene being 1.7 g/cm\(^3\) and the density of the matrix 2.1 g/cm\(^3\), which results in considerable stresses in the sample and, consequently, the cracking thereof. Besides, the low thermal conductivity of the source fullerene (0.4 W/raK) and the matrix obtained therefrom (about 10 W/mK) results in great temperature gradients during synthesis, which also results in the cracking of the sample. The filler, due to its resilience and higher thermal conductivity, offsets the above effects, making it possible to obtain composite materials without cracks.

The authors used of the following known methodologies in their research:

To characterize the structure of the obtained samples, the known X-ray diffraction analysis technique was used.

To control the elementary composition of the obtained samples, they were analyzed by the known energy-dispersive and wave spectroscopy with the help of a scanning electron microscope.

To characterize mechanical properties, measurements of hardness and flexural strength were made according to known methods.

Hardness was measured by the Knoop or Vickers pyramid in accordance with GOST 9450-76.
Cross-bending strength $\sigma^*$ was measured by a three-point bending test in accordance with GOST 20019-74.

Elastic moduli were determined by the known ultrasonic method.

The values of elastic moduli allow to evaluate the bonding between the constituents of the composite material. High elastic moduli testify to the presence of a chemical bond between the filler and the carbon-based material produced by synthesis.

The sample density $p$ was measured by the known method of hydrostatic weighing.

The ultimate parameter widely used in engineering to evaluate the potential ability of a material to be used in aerospace and aviation industries is the ratio of strength to density $\sigma^*/\rho$.

The sample heat resistance was determined by the known method of thermogravimetric analysis.

DESCRIPTION OF DRAWINGS.

Fig. 1 shows the results of cross-bending strength measurements of a sample of composite material synthesized from a 50/50% (by weight) mixture of $C_6O$ and $B_4C$ in the presence of $CS_2$ at a pressure of 2 GPa and temperature of 1,000 °C. The cross-bending strength $\sigma^*_{\text{bend}}$ was equal to 570 MPa.

Fig. 2 shows the results of compression strength measurements of a sample of composite material synthesized from a 50/50% (by weight) mixture of $C_6O$ and $B_4C$ in the presence of $CS_2$ at a pressure of 2 GPa and temperature of 1,000 °C. The compression strength $\sigma^*_{\text{compression}}$ was equal to 2,250 MPa.

Fig. 3 shows the results of thermogravimetric analysis of the samples conducted at a temperature of up to 1,400 °C in the air. The lower curve corresponds to the sample of composite material synthesized from a 50/50% (by weight) mixture of $C_6O$ and $B_4C$ in the presence of $CS_2$ at a pressure of 2 GPa and temperature of 1,000 °C. The upper curve corresponds to the source boron carbide powder.

The following examples illustrate the claimed invention without restricting it as to its substance.

EXAMPLES

Example 1. Obtaining a composite material in accordance with the present invention at a pressure of 0.1 GPa.
B₄C boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with molecular C₆₀ fullerene powder (with an average grain size of 1 μm) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill.

Carbon disulfide CS₂ was added to the resulting mixture of C₆₀ and B₄C in the amount of 0.05 ml of CS₂ per 1 g of the mixture. Then the mixture of C₆₀, B₄C and CS₂ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples.

For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 0.1 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the sample was examined with the help of X-ray diffraction, Raman spectroscopy, transmission electron microscope and thermogravimetric analysis, and studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the materials obtained in this example was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength conducted according to the three-point bending test technique (GOST 20019-74) gave a value of cross-bending strength σ*₁₈₅ₐ equal to 400 MPa.

Density was measured by the hydrostatic weighing method. The sample density ρ was 2.20 g/cm³.

The σ*/ρ ratio was equal to 180, meaning that the obtained material surpasses many materials used in aerospace and aviation industries.

Thermogravimetric analysis of the sample, conducted at a temperature under 1,400 °C in the air, showed an increase in the mass of about 3%, beginning from the temperature of 800 °C, which was related to boron carbide oxidation. In general, the sample was heat-resistant.

Thus, the composite material of the obtained sample was at the same time strong, light, hard and heat-resistant.

Example 2. Obtaining a composite material in accordance with the present invention at a pressure of 0.5 GPa.
B₄C boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with molecular C₆₀ fullerene powder (with an average grain size of 1 µm) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill.

Carbon disulfide CS₂ was added to the resulting mixture of C₆₀ and B₄C in the amount of 0.05 ml of CS₂ per 1 g of the mixture. Then the mixture of C₆₀, B₄C and CS₂ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples.

For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell with a working diameter of 100 mm, stressed to a fixed pressure of 0.5 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. The obtained sample had a diameter of 100 mm. It is possible to produce from samples of that size, e.g., a heat shield or a turbine blade.

After unstressing the sample was examined with the help of X-ray diffraction, Raman spectroscopy, transmission electron microscope and thermogravimetric analysis, and studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the materials obtained in this example was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength conducted according to a three-point bending test technique (GOST 20019-74) gave a value of cross-bending strength σₚ,cr equal to 500 MPa.

Density was measured by the hydrostatic weighing method. The sample density p was 2.23 g/cm³.

The σₚ/ρ ratio was equal to 220, meaning that the obtained material surpasses many materials used in aerospace and aviation industries.

Elastic moduli were determined by the ultrasonic method. Average values of the sample elastic moduli were: Young’s modulus E=150 GPa, pressure modulus K=110 GPa, shear modulus G=60 GPa. High elastic moduli testify to the presence of a chemical bond between boron carbide and the carbon-based material produced by synthesis.
Thermogravimetric analysis of the sample, conducted at a temperature under 1,400 °C in the air, showed an increase in the mass of about 3%, beginning from the temperature of 800 °C, which was related to boron carbide oxidation. In general, the sample was heat-resistant.

Thus, the composite material of the obtained sample was at the same time strong, light, hard and heat-resistant.

Example 3. Obtaining a composite material in accordance with the present invention at a pressure of 2 GPa.

B₄C boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with molecular C₆₀ fullerene powder (with an average grain size of 1 μm) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill. Carbon disulfide CS₂ was added to the resulting mixture of C₆₀ and B₄C in the amount of 0.05 ml of CS₂ per 1 g of the mixture. Then the mixture of C₆₀, B₄C and CS₂ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 2 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the sample was examined with the help of X-ray diffraction, Raman spectroscopy, and transmission electron microscope and thermogravimetric analysis, and studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength conducted according to a three-point bending test technique (GOST 20019-74) gave a value of cross-bending strength σ* being equal to 570 MPa (Fig. 1) and compression strength being equal to 2,250 MPa (Fig. 2).

Density was measured by the hydrostatic weighing method. The sample density p was 2.3 g/cm³.

The σ*/ρ ratio was equal to 250.

Elastic moduli were determined by the ultrasonic method. Average values of the sample elastic moduli were: Young’s modulus E=190 GPa, pressure modulus K=120 GPa, shear
modulus $G=75$ GPa. High elastic moduli testify to the presence of a chemical bond between boron carbide and the carbon-based material produced by synthesis.

Thermogravimetric analysis of the sample, conducted at a temperature under 1.400 °C in the air, showed an increase in the mass of about 3%, beginning from the temperature of 600 °C, which was related to boron carbide oxidation (Fig. 3, lower curve). In general, the sample was heat-resistant. For comparison, Fig. 3 shows thermogravimetric analysis data for the source boron carbide, with said thermogravimetric analysis conducted under the identical conditions. In the latter case, a mass increase of about 100% related to oxidation was observed, in spite of the fact that boron carbide is a heat-resistant material (Fig. 3, upper curve). Consequently, the composite material demonstrates a considerable increase in heat resistance relative to the source $\text{B}_4\text{C}$.

Thus, the composite material of the obtained sample was at the same time strong, light, hard and heat-resistant.

Example 4. Obtaining a composite material in the temperature range of 600 - 2.000 °C in accordance with the present invention.

Several samples were produced. For that purpose, $\text{B}_4\text{C}$ boron carbide powder (with an average grain size of 100 nm) was mixed with molecular $\text{C}_{60}$ fullerene powder (with an average grain size of 1 $\mu$m) in proportion of 30/70% and 70/30% by weight in a vibration mill. The total weight of the mixture in each case was 2 g. Carbon disulfide $\text{CS}_2$ was added to the resulting mixture of $\text{C}_{60}$ and $\text{B}_4\text{C}$ in the amount of 0.05 ml of $\text{CS}_2$ per 1 g of the mixture. Then the mixture of $\text{C}_{60}$, $\text{B}_4\text{C}$ and $\text{CS}_2$ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 1 GPa and heated to a fixed temperature with a fixed exposure time at the said temperature. Samples were obtained at the temperatures of 600, 700, 800, 900, 1000, 1100, 1200, 1300, 1400, 1500, 1600 and 2000 °C with the exposure times of 0.1, 1, 10, 30, 60, 120 and 180 sec. After unstressing the samples were examined with the help of X-ray diffraction, Raman spectroscopy, transmission electron microscope and thermogravimetric analysis, and studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the samples obtained in this example was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis
showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength were conducted according to a three-point bending test technique (GOST 20019-74). Density was measured by the hydrostatic weighing method. The $\sigma^*/\rho$ ratio of the samples obtained - not lower than 200. The samples were stable at least up to 1,400 °C.

Thus, the composite material of the obtained samples was at the same time strong, light, hard and heat-resistant.

Example 5. Obtaining a composite material in accordance with the present invention, wherein fullerene-containing soot is used as a carbon-containing material.

$B_4C$ boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with fullerene-containing soot powder (with an average grain size of 1 μm) with a $C_{60}$ content of 60% in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill. Carbon disulfide $CS_2$ was added to the resulting mixture of fullerene-containing soot and $B_4C$ in the amount of 0.05 ml of $CS_2$ per 1 g of the mixture. Then the mixture of fullerene-containing soot, $B_4C$ and $CS_2$ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 1 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the sample was studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength were conducted according to a three-point bending test technique (GOST 20019-74). Density was measured by the hydrostatic weighing method. The $\sigma^*/\rho$ ratio of the obtained samples was 100. The samples were stable at least up to 1,400 °C.

Thus, the composite material of the obtained samples was at the same time strong, light, hard and heat-resistant.
Example 6. Obtaining a composite material in accordance with the present invention.

Several samples were made. For that purpose, each of diamond, silicon carbide SiC, aluminum nitride AlN and aluminum oxide Al2O3 powders in the amount of 1 g were mixed with molecular C60 fullerene powder in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill. Carbon disulfide CS2 was added to the resulting mixture of C60 and each of the said powders (SiC, AlN and Al2O3) in the amount of 0.05 ml of CS2 per 1 g of the mixture. Then the mixture obtained by the addition of CS2 was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, each of the mixtures was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 1 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the samples were studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength were conducted according to a three-point bending test technique (GOST 20019-74). Density was measured by the hydrostatic weighing method. The σ/ρ ratio of the samples obtained was not lower than 100. The samples were stable at least up to 1,000 °C.

Thus, the composite material of the obtained samples was at the same time strong, light, hard and heat-resistant.

Example 7. Obtaining a composite material in accordance with the present invention, wherein carbon fibers are used as a carbon-containing material.

Carbon disulfide CS2 was added to molecular C60 fullerene powder in the amount of 0.05 ml of CS2 per 1 g of C60. Then the mixture was ground in an agate mortar until a homogeneous consistency was obtained. Carbon fibers were then added to the obtained mixture in the proportion of 50% by weight to C60 fullerene and carefully mixed with a spatula. Then the mixture in the amount of 2 g was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 2 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the sample was studied for mechanical properties.
Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.

Measurements of cross-bending strength were conducted according to a three-point bending test technique (GOST 20019-74). Density was measured by the hydrostatic weighing method. The $\sigma^*/\rho$ ratio of the samples obtained was not lower than 100. The samples were stable at least up to 1,000 °C.

Thus, the composite material of the obtained samples was at the same time strong, light, hard and heat-resistant.

Example 8. Obtaining a composite material in accordance with the present invention, wherein cubic boron nitride (borazon) is used as a filler

$c$-BN cubic boron nitride powder (with an average grain size of about 1 $\mu$m) in the amount of 1 g was mixed with molecular $C_{60}$ fullerene powder (with an average grain size of 1 $\mu$m) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill. Carbon disulfide $CS_2$ was added to the resulting mixture of $C_{60}$ and c-BN in the amount of 0.05 ml of $CS_2$ per 1 g of the mixture. Then the mixture of $C_{60}$, c-BN and $CS_2$ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 2 GPa and heated to a temperature of 1000 °C with the exposure time of 100 sec. After unstressing the sample was examined with the help of X-ray diffraction. Raman spectroscopy, and transmission electron microscope, and studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Elemental analysis was conducted by the methods of energy-dispersive and wave spectroscopy with the help of a scanning electron microscope. The conducted elemental analysis showed the presence of sulfur in the obtained material of less than 0.01 %, i.e. sulfur was eliminated from the obtained material during synthesis.
Measurements of cross-bending strength conducted according to a three-point bending test technique (GOST 20019-74) gave a value of cross-bending strength $\sigma^b_{\text{bend}}$ equal to 300 MPa.

Density was measured by the hydrostatic weighing method. The sample density $\rho$ was 2.8 g/cm$^3$.

The samples were stable at least up to 1,000 °C in the protective atmosphere.

Thus, the composite material of the obtained samples was at the same time strong, light, hard and heat-resistant.

Example 9. Obtaining a composite material at temperatures beyond the range of 600 - 2,000 °C.

Several samples were produced. For that purpose, $B_4C$ boron carbide powder (with an average grain size of 100 nm) was mixed with molecular $C_{60}$ fullerene powder (with an average grain size of 1 µm) in proportion of 50/50% by weight in a vibration mill. The total mixture weight in each case was 2 g. Carbon disulfide $CS_2$ was added to the resulting mixture of $C_{60}$ and $B_4C$ in the amount of 0.05 ml of $CS_2$ per 1 g of the mixture. Then the mixture of $C_{60}$, $B_4C$ and $CS_2$ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples. For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 2 GPa and heated to a fixed temperature with a fixed time of exposure to the said temperature. Samples were obtained at the temperatures of 400 and 2,400 °C with the exposure time of 100 sec. After unstressing the sample was studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the obtained samples was lower than 10 GPa, which does not allow the material to be classified as a high-hardness one.

Thus, the composite material of the obtained samples was not a high-hardness material.

Example 10. Obtaining a composite material beyond the pressure range of 0.1-20 GPa.

$B_4C$ boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with molecular $C_{60}$ fullerene powder (with an average grain size of 1 µm) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill.

Carbon disulfide $CS_2$ was added to the resulting mixture of $C_{60}$ and $B_4C$ in the amount of 0.05 ml of $CS_2$ per 1 g of the mixture. Then the mixture of $C_{60}$, $B_4C$ and $CS_2$ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples.
For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 0.05 GPa (production of samples at pressures above 20 GPa was technically difficult) and heated to a temperature of 1000 °C with the exposure time of 100 sec. After unstressing the sample was studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the obtained samples was lower than 10 GPa, thus the material was not a high-hardness one.

Thus, the composite material of the obtained samples was not a high-hardness material.

Example 11. Obtaining a composite material in accordance with the present invention using mercaptan instead of carbon disulfide.

B₄C boron carbide powder (with an average grain size of 100 nm) in the amount of 1 g was mixed with molecular C₆₀ fullerene powder (with an average grain size of 1 μm) in the amount of 1 g (in proportion of 50/50% by weight) in a vibration mill.

Isoamyl mercaptan C₃H₁₁SH was added to the resulting mixture of C₆₀ and B₄C in the amount of 0.05 ml of C₃H₁₁SH per 1 g of the mixture. Then the mixture of C₆₀, B₄C and C₃S₂ was ground in an agate mortar until a homogeneous consistency was obtained and used for the production of samples.

For that purpose, the mixture was loaded into a piston-cylinder type high pressure cell, stressed to a fixed pressure of 2 GPa and heated to a temperature of 1,000 °C with the exposure time of 100 sec. After unstressing the sample was studied for mechanical properties.

Hardness was measured by the Knoop or Vickers pyramid (GOST 9450-76). The hardness of the material obtained was in the range of 10-70 GPa, which makes it a high-hardness material.

Measurements of cross-bending strength conducted according to a three-point bending test technique (GOST 20019-74) gave a value of cross-bending strength \( \sigma_{bend}^* = 530 \) MPa.

Density was measured by the hydrostatic weighing method. The sample density \( \rho \) was 2.3 g/cm³.

The \( \sigma^*/\rho \) ratio was equal to 230.

Thermogravimetric analysis of the sample, conducted at a temperature below 1,400 °C in the air, showed that the sample was heat-resistant.

Thus, the composite material of the obtained sample was at the same time strong, light, hard and heat-resistant.
Thus, the material obtained according to the claimed technical solution is characterized by high strength and low density, with a ratio of cross-bending strength (in MPa) to density (in g/cm$^3$) $\sigma^* / \rho$ of at least 200, high hardness of at least 10 GPa and high heat resistance in the air of at least 1,400 °C.
What is claimed is:

1. A method of obtaining a carbon-based composite material, comprising the exposure of a mixture of a carbon-containing material and a filler to high pressure and high temperature, wherein a sulfur-containing compound is added to the said mixture and the treatment is conducted in the temperature range of 600-2000 centigrade and a pressure of 0.1-20 GPa.

2. The method according to claim 1, wherein the said sulfur-containing compound is added in the amount of from 0.1 to 3 mass % of sulfur relative to the weight of the carbon-containing material.

3. The method according to claim 1, wherein the said sulfur-containing compound is carbon disulfide.

4. The method according to claim 1, wherein the said sulfur-containing compound is a compound from the group of mercaptans, or a product of interaction of a compound out of the group of mercaptans with elemental sulfur.

5. The method according to claim 1, wherein the carbon-containing material is molecular C60 fullerene.

6. The method according to claim 1, wherein the carbon-containing material is fullerene-containing soot.

7. The method according to claim 1, wherein the filler is boron carbide in the amount of from 30 to 70 mass % relative to the weight of the carbon-containing material.

8. The method according to claim 1, wherein the filler is carbon fibers, or diamond, or nitrides, or carbides, or borides, or oxides in the amount of from 1 to 99 mass % relative to the weight of the carbon-containing material.

9. The method according to claim 1, wherein the exposure is preferably conducted in the temperature range of 800-1,200 centigrade and the pressure range of 0.5-10 GPa.

10. A composite material obtained by the method according to any of claims 1-9.

11. The composite material according to claim 9, intended for the production of items therefrom with characteristic sizes of 1 to 100 cm.
Fig. 1.

Fig. 2.
Fig. 3
INTERNATIONAL SEARCH REPORT

A. CLASSIFICATION OF SUBJECT MATTER

INV. C04B35/52 B01J3/06 C01B31/02 C04B35/528 C04B35/581
ADD.

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

C04B B01J C01B

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practicable, search terms used)

EPO-Internal, COMPENDEX, INSPEC, WPI Data

C. DOCUMENTS CONSIDERED TO BE RELEVANT

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* Special categories of cited documents:

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"E" earlier application or patent but published on or after the international filing date

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

Further documents are listed in the continuation of Box C.

See patent family annex.

Date of the actual completion of the international search
31 March 2015

Date of mailing of the international search report
09/04/2015

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Buffet, Noemie

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