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Hydrophobic coating based on tetraethoxysilane on graphite foil

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In this work, a hydrophobic coating was obtained on the surface of graphite foil pressed from thermally exfoliated graphite. The original graphite foil contains residual oxygen groups on the surface, which are formed at the boundaries of crystallites during the production of expandable graphite and are preserved even after thermal shock. The uncoated material was characterized by a water contact angle of 65°, which indicates the hydrophilicity of the material. The coating was deposited from a solution of tetraethoxysilane in isopropyl alcohol with the addition of water and an aqueous solution of ammonia. Different tetraethoxysilane/water ratios were used for the hydrolysis-condensation process and the production of the coating. With a fixed amount of aqueous ammonia and with a decrease in the amount of added water, an increase in the static water contact angle of the material with water to 96° was observed. Using X-ray phase analysis, it was shown that the coating is an amorphous silicon oxide; using IR spectroscopy, the presence of residual ethoxy groups in the coating composition was confirmed, which lead to an increase in the hydrophobicity of the material.

Keywords: carbon materials, organosilicon compounds, hydrophobicity, contact angle.

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Introduction

Thermally exfoliated graphite (TEG) — a carbon material that corresponds to graphite by its structure, but has extremely high porosity and ability to compact without a binder into compacts with various density. The compacted materials based on TEG with density of 0.5 g/cm^3 and above are called a graphite foil (GF). GF is a promising sealing material, and combines such characteristics as elasticity, compressibility and stability at high temperature and in presence of acids or vapors of organic solvents, which makes it possible to use this material as a sealant to seal various media, including water vapors and aqueous solutions [1,2]. Reliable sealing plays an important role in maintaining public and environmental safety, and also brings economic benefits to the enterprises, reducing the risk of accidents and frequency of repair works. The third unsealing in the Russian segment of the International Space Station in a year, multiple oil leaks caused by pipeline unsealing all over the country — some of many examples of how important it is to design and use chemically resistant sealing materials, which will be immune to drastic temperature fluctuations and pressure differences.

GF production may be divided into several stages: intercalation, hydrolysis, thermal expansion and compaction [3–6]. At the first stage, the intercalated graphite compound (IGC) is formed, by interaction of the flaky graphite with nitric or sulphuric acid in the presence of the oxidant. The oxidant, for example, potassium dichromate or potassium permanganate, oxidizes the graphite matrix, converting it into a macrocation, and certain substance (intercalate) is introduced into the interlayer space of the graphite crystalline lattice, increasing at the same time the interlayer distance and the identity period, which is confirmed by the X-ray diffraction (XRD) analysis [6–8]. Then IGC hydrolysis is carried out, in process of which macrocations of graphite matrix are reduced, oxidized graphite (OG) is formed, which contains many oxygen functional groups in its composition, such as −CHO, −OH, −COOH etc. [4,6,9]. At the next stage the produced OG is thermally treated to form TEG. In process of thermal expansion the remains of intercalate and oxygen-containing groups are destroyed and release various gases [10]. At the last stage TEG is compacted into GF.

The source graphite manifests hydrophobic properties, however, depending on the conditions of production, GF may also manifest hydrophilic properties. Some studies show that the TEG produced in the air atmosphere has a contact angle within 53−68°, and the contact angle of TEG produced in the inert atmosphere of argon, achieves even 45° [11]. This is explained by partial destruction of the oxygen groups under thermal treatment of OG and presence of residual hydrophilic oxygen-containing groups in TEG and GF. Previously the presence of the oxygen groups in OG [9] and residual oxygen groups in TEG [12,13] was confirmed. Therefore, the TEG-based materials are hydrophilic materials with water contact angle of less than 90°, which promotes water penetration into GF pores [12]. Hydrophilic behavior deteriorates sealing in respect to water media (aqueous solutions, water vapors) due to liquid penetration into material pores.

To reduce material wetting with water, various hydrophobic coatings may be applied onto GF. Some of most common compounds for modifications of the surface with the purpose to improve the material hydrophobic behavior are various organosilicon compounds with hydrophobic functional groups. Organofunctional silanes combine functionality of organic groups and reactive inorganic silicates in a single molecule, act as molecular binders between inorganic substrates and organic polymers and bind these two diverse materials through the boundaries [14–17]. One of the methods to produce hydrophobic materials is sol–gel process, its main advantages are — simplicity and low cost. There are examples of such coatings being applied onto metals and glasses. The coating may be applied from organic solution of silanes with organic substitutes by their hydrolysis and condensation in presence of water [14,18].

Speed and mechanism of hydrolysis are highly dependent on catalyst. During acid catalysis at the first stage of hydrolysis the protonation of one of alkoxy-groups takes place, and the Si−O bond in the substituted group becomes more polarized, which will further facilitate its break. At the next stage the water molecule nucleophilically attacks silicon at the opposite side from the substituted group. An intermediate compound is produced, where the silicon coordination number is 5, and the molecule looks like a trigonal bipyramid. Groups $-OH_2$ and $-OHR$ occupy perpendicular positions relative to the plane, where the silicon atom and remaining alkoxy groups are located. Then an alcohol molecule breaks off, and the end product again acquires a tetrahedral configuration, and the molecule turns in a mirror-like manner relative to non-substituted groups [19].

The speed and mechanism of condensation reaction also depend on the medium. In process of acid-catalyzed condensation at the first stage, protonation also takes place, but now for the hydroxy-group, and the oxygen in the substituted group gains a positive charge. At the second stage condensation occurs between the protonated and non-protonated hydroxy-groups, a siloxane bridge is formed, and a hydroxonium ion breaks off as a catalyst [19].

In process of hydrolysis catalyzed with the base, the hydroxide-ion is nucleophilically joined to the silicon atom, as a result of which, as in the case of acid catalysis, an intermediate compound is formed with the trigonal bipyramid configuration. One of alkoxy groups acquires a negative charge on the oxygen atom and together with the hydroxy-group is located on the line perpendicular to the plane, where the silicon atom and the remaining alkoxy-groups are located. Then a negatively charged alkoxy-group breaks off, and a molecule turned in mirror-like manner is formed with one hydrolyzed group [19].

During alkaline catalysis, at the first stage of condensation the hydroxide ion attacks the substituted hydroxy-group, which causes its deprotonation to form a water molecule. Then at the second stage the negatively charged atom of oxygen and hydroxy-group of the other molecule are condensed to form a bond −Si−O−Si− and to break off the hydroxide-ion [19].

Therefore, the speed of both hydrolysis and condensation highly depend on pH. Formation of organosilicon particles may be divided into three stages: monomer polymerization with particle formation, particle growth and binding of the particles into chains, which finally change into gel [20]. In the acid medium the hydrolysis speed is higher, and more fine particles are formed [15]. Even though at $\mathrm{pH} < 2$ the speed of condensation also starts rising at the expense of strong protonation of silane and reaction behavior:

$$\equiv \mathrm{S{-}OH_2^+} + \mathrm{HO{-}Si} \equiv \to \equiv \mathrm{Si{-}O{-}Si} \equiv + \mathrm{H^+}.$$

At neutral and low-alkaline pH hydrolysis is very slow, and condensation, on the contrary, is fast [15]. In this medium the solubility and dissolution speed of silane increase, and silane particles are ionized to a considerable degree, therefore, particles grow without aggregation and gel formation [20]. In case of alkaline catalysis, condensation mostly occurs, and particle size increases, at the expense of condensation by reaction:

$$\equiv \mathrm{Si{-}O^-} + \mathrm{HO{-}Si} \equiv \to \mathrm{Si{-}O{-}Si} \equiv + \mathrm{OH^-}.$$

Condensation reaction products also depend on the solution medium. In the weak-base medium only the condensation process mostly occurs, and in the acid one first the hydrolysis stage, and then condensation take place. In acid catalysis there is a significant trend towards formation of silanols at the hydrolysis stage. For the primary catalysis most often the ammonia solution is used, which provides low-alkaline pH. At the same time no silanols are formed as intermediate compounds, and particle deposition accelerates.

A bond is formed to the material surface at the expense of interaction of functional groups of a condensed particles with hydroxy-groups on the surface of the modified material [15].

Based on the importance of improvement of the sealing properties in sealants, the objective of this paper was to improve the hydrophobicity of GF by production of a coating based on tetraethoxysilane on the GF surface and to study the composition, structure and surface properties.

1. Experimental part

To produce the intercalated compound of graphite of stage 1 with sulphuric acid, the natural flaky graphite (purity of 99.9 %) interacted with 96 %-th solution of sulphuric acid and potassium dichromate at mass ratio $m(\text{graphite}):m(K_2Cr_2O_7):\mathrm{m}(H_2SO_4) = 1 : 0,17 : 7,4$. The stage number of the intercalated compound of graphite — is a number of graphite layers between the nearest layers of intercalate, i.e. in this case sulphuric acid is introduced into each interlayer space of the graphite crystalline structure. Besides, in process of intercalation the graphite matrix is charged positively, forming a macrocation, and the negatively charged acid residues are incorporated into interlayer space of the crystalline lattice

$$6\cdot 24\mathrm{C} + 22\mathrm{H_2SO_4} + \mathrm{K_2Cr_2O_7} = 6\mathrm{C_{24}^{+}HSO_4^{-}}\cdot 2\mathrm{H_2SO_4}$$
$$+\,\mathrm{Cr_2(SO_4)_3} + \mathrm{K_2SO_4} + 7\mathrm{H_2O}.$$

The mixture was mixed in a teflon glass for 2 h. After that a large part of the produced mix was slowly poured out into a glass with cold water and mixed for 1 min. When IGC is treated with excess water, irreversible deintercalation occurs. And OG is formed — adduct containing residual molecules of water and acid in the intercrystalline space and multiple oxygen groups on its surface. During hydrolysis the intercalate molecules diffuse from the graphite matrix. Water reduces the graphite lattice with the positive charge to release oxygen:

$$2\mathrm{H_2O} - 4\mathrm{e^-} \rightarrow \mathrm{O_2} + 4\mathrm{H^+},$$

$$\mathrm{C_p} + +\mathrm{qe^-} \rightarrow \mathrm{C_{p\text{-}q}^{+}} + \mathrm{C_q^{0}}.$$

Water excess was filtered from the produced oxidized graphite on a glass porous filter. OG was washed on a filter with hot water ($T = 50-60\,^\circ$C) at mass ratio of $m(\mathrm{H_2O}) : m(\mathrm{H_2SO_4}) \sim 7:1$. The resulting OG was dried in a drying oven at 60 °C for 6 h.

The OG thermal expansion process was carried out at 800 °C in a pipe furnace in the air atmosphere. The produced TEG was compacted into graphite foil with thickness of 0.5 mm and density of 1 g/cm^3.

To produce the coating based on TEOS $\mathrm{Si(OC_2H_5)_4}$ (TEOS), a beaker was filled with 30 ml isopropyl alcohol, with addition of 5 ml TEOS, then water was added to the produced solution using a pipette, and 25 %-th ammonia solution at molar ratio of $\mathrm{TEOS/H_2O/NH_3{\cdot}H_2O} = 1:0,6:0,04$; 1 : 1 : 0,04; 0,6 : 1 : 0,04. The mix was mixed in a magnetic mixer at 30 °C for 20 min. Then GF plates were placed into a beaker with the mix. GF was soaked in the solution for around 24 h. GF was removed from the mix, dried on air for 8 h and placed into a desiccator for storage.

The specimen structure was studied by XRD method on diffractometer Rigaku Ultima IV (radiation CuK_α, $\lambda = 1.5418$ Å).

The morphology of the produced specimens and their elemental composition were studied by method of scanning electron microscopy (SEM) and energy-dispersive X-ray spectroscopy (EDX) on electron microscope TESCAN VEGA3 LMU.

Infrared spectroscopy (IR) was done on IR Fourier spectrometer Bruker Tensor27 in the range of 4000−500 cm^{-1} in the light. The studied specimen was mixed with KBr at mass ratio 1 : 100, and rubbed in an agate mortar and compacted into a pellet with weight of 50 mg and diameter of 5 mm.

The static water contact angle was measured by sessile drop method. To measure a contact angle, a goniometer was used that was designed on the basis of a horizontal microscope and a digital camera. A drop of distilled water was placed with a pipette on the GF surface, then the angle was determined between the tangents at the phase interface of water–air and water–GF. For statistics, the measurement was carried out five times for each specimen of GF, then the average value of the contact angle was calculated, and the relative error of such calculation did not exceed 5 %.

2. Results and discussion

The 1 stage IGC structure means alternating layers of graphene and intercalate. The XRD method was used to calculate the identity period of the produced IGC, which made 7.98 Å. The identity period corresponds to the height of the repeated fragment in the crystalline lattice of graphite filled with intercalate. In case of stage 1 of IGC, this fragment corresponds to the thickness of the graphene layer and the intercalate layer that alternate between each other. At the next stage the hydrolysis of the produced IGC was carried out to form oxidized graphite. XRD data showed that the interplanar spacing of OG (3.39 Å) is slightly increased compared to the natural graphite (fig. 1, *a*). During hydrolysis the large part of intercalate is removed, and oxygen functional groups are formed (−COOH, −C=O, −C−OH) on the OG surface, the presence of which is confirmed by the method of IR spectroscopy (fig. 1, *b*). The intercalation and oxidation processes often lead to considerable deformation and flaking of the OG particle, which is observed on the SEM image (fig. 1, *c*).

After thermal treatment of the produced oxidized graphite at 800 °C TEG was formed. In process of thermal expansion the remains of intercalate and oxygen-containing groups are destroyed and release various gases ($\mathrm{SO_3}$, $\mathrm{SO_2}$, $\mathrm{H_2O}$, $\mathrm{O_2}$, $\mathrm{CO_2}$, CO). This results in the break of the bond between certain layers of graphite and multiple increase of the graphite particle in the volume. Besides, the interplanar spacing of TEG (3.36 Å) is kept close to the interplanar spacing of graphite (fig. 1, *d*). The method of IR spectroscopy demonstrated presence of residual oxygen groups in TEG after the thermal treatment of OG: C−O−H, C=O, C−O−C, =C−O, peaksof which are in the range of 1800−1000 cm^{-1} on IR spectrum (fig. 1, *e*). TEG particles represent a foam-like macroporous mass with multiple flaked graphite packs (fig. 1, *f*).

Due to large area of the surface and the volume increased many times, the TEG weight is compacted easily into GF without a binder. At the same time the chemical composition of the material will not change, and GF in their structure and composition would not differ from TEG in any way. Due to residual oxygen groups, the foil has rather marked hydrophilic behavior, the water contact angle of GF is 65°.

Hydrophobic coating on the GF surface was applied from the TEOS solutions $\mathrm{Si(OC_2H_5)_4}$ (TEOS) in isopropyl

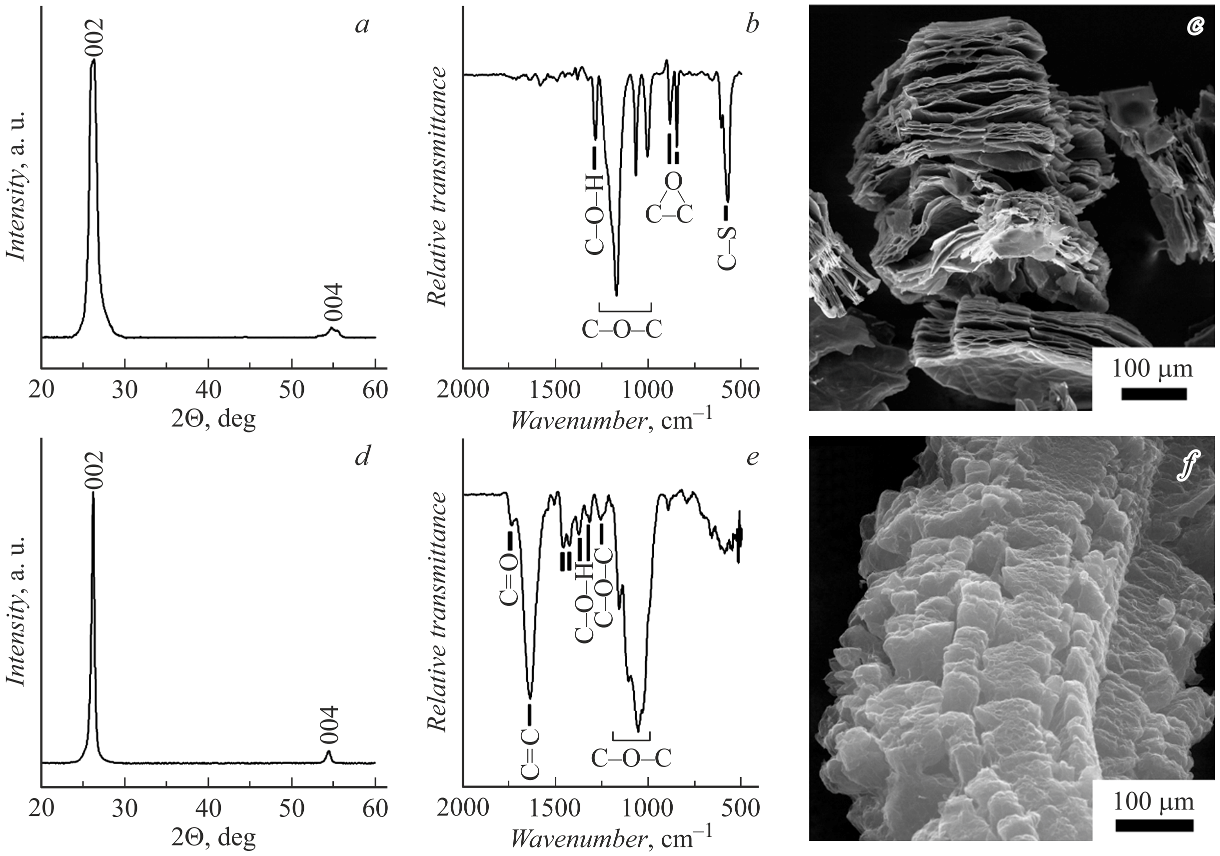

Figure 1. X-ray images, IR spectra and SEM images (*a–c*) of oxidized graphite and (*d–f*) TEG.

alcohol with different amount of water added for hydrolysis: $TEOS/H_2O = 0{,}6:1$; $1:1$; $1:0{,}6$. The coating formation was confirmed by the SEM methods with elemental analysis. The SEM images without a coating demonstrate the graphite sheets pressed to each other (fig. 2, *a*). Elemental analysis showed that the material without the coating contains mostly carbon, and also some oxygen (fig. 2, *a*). On SEM images of GF with the TEOS-based coating you can see many nanoscale particles that are less than tenths of a micrometer, forming an even layer on the GF surface (fig. 2, *b–d*). The elemental analysis confirms the presence of silicon within the coating composition (fig. 2, *b–d*).

GF X-ray images with the TEOS-based coating only contain peaks 002 and 004 related to the graphite phase (fig. 3). The calculated interplanar spacing in GF is 3.36 Å.

To specify the structure of the coating itself, a powder was produced separately, which represents particles of condensed silane, by evaporation of impregnation solution, from which the coating was applied. The X-ray image of this powder shows a broad peak at $2\Theta \sim 23^\circ$ with low intensity, related to phase of SiO_2 (fig. 4, *a*), so one may conclude on the absence of the periodical crystalline structure of the coating and the presence of the silicon-containing phase on the GF surface in amorphous state. The peak related to the amorphous SiO_2 is not observed on GF X-ray images due to its extremely low intensity compared to the peaks of the graphite phase (fig. 3).

The TEOS-based coating structure was studied in more detail by the IR spectroscopy method (fig. 4, *b*). Band at $\sim 1100-800\,\mathrm{cm}^{-1}$ is related to oscillations of Si–O- and Si–O–Si-bonds formed from TEOS condensation. Si–O–Si-bonds are the frame of the condensed silane particle. In process of hydrolysis and condensation, the particle surface forms –OH-groups, which is indicated by the band in the area of $1650\,\mathrm{cm}^{-1}$, related to the oscillations of Si–O–H-bond. Partial hydrolysis causes the preservation of some ethoxy-groups on the surface of silicon oxide, where Si–O–C-bonds $(1300-1130\,\mathrm{cm}^{-1})$ and C–H-bonds $(1500-1370\,\mathrm{cm}^{-1})$ are present in C_2H_5-fragment. The broad band at $900-1500\,\mathrm{cm}^{-1}$ was decomposed into components. The peak at $934\,\mathrm{cm}^{-1}$ is related to oscillations of Si–O in the silanol fragment. Low intensity peaks in the range of $1000-1100\,\mathrm{cm}^{-1}$ at $1010\,\mathrm{cm}^{-1}$, $1031\,\mathrm{cm}^{-1}$ and high intensity peak at $1070\,\mathrm{cm}^{-1}$ are related to oscillations of Si–O–Si-bond in cyclic fragments $(R_2SiO)_n$ of the condensed part of silane, and the peak position is related to number *n*. The peak at $1182\,\mathrm{cm}^{-1}$ is related to oscillations of Si–O–Si-bond in $Si-OC_2H_5$-fragments within the condensed particle of silane. Therefore, some $Si-OC_2H_5$-groups are preserved in the process of hydrolysis

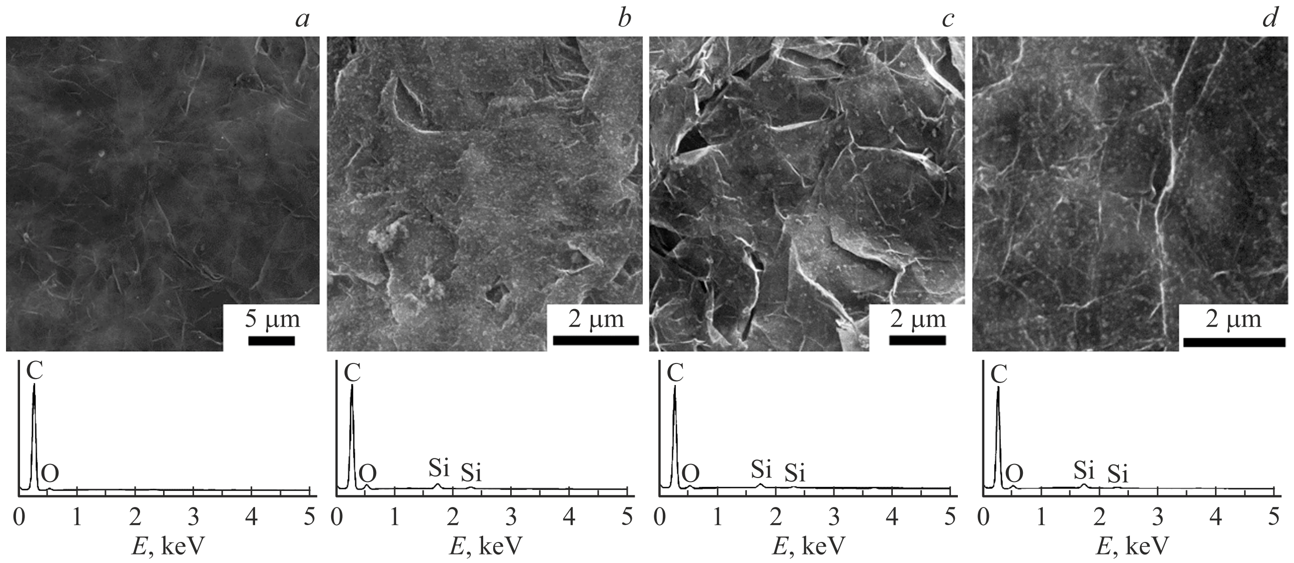

Figure 2. SEM images and EDX-spectra (*a*) of GF without coating, GF with coating based on TEOS/H_2O at the ratio of (*b*) 0,6 : 1; (*c*) 1 : 1; (*d*) 1 : 0,6.

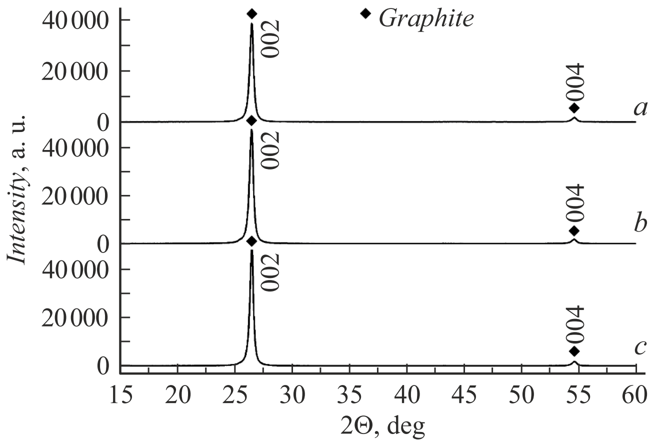

Figure 3. X-ray images with GF with coating based on TEOS/H_2O at the ratio of (*a*) 0,6 : 1; (*b*) 1 : 1; (*c*) 1 : 0,6.

and condensation and results in the growth of the coating hydrophobicity.

As it was shown, TEG and GF compacted from TEG contains residual oxygen groups (fig. 1, *e*), which reduces its hydrophobicity ($\theta_{H_2O} = 65^\circ$) (fig. 5, *b*). In process of hydrolysis and condensation of TEOS the amorphous silicon oxide is formed, which is deposited on the GF surface and forms a coating (fig. 5, *a*). If the share of water decreases in the impregnation solution of isopropyl alcohol, θ_{H_2O} increases from 79 to 96° (fig. 5, *c–e*).

In process of hydrolysis in the presence of excess of water vs the quantity of silane (TEOS : H_2O=0,6 : 1) the ethoxy groups is substituted practically fully with hydroxy groups. Hydrophilic OH-groups prevail on the surface of the formed particle of the condensed silane (fig. 5, *c*). Besides, the insignificant quantity of hydrophobic ethoxy groups remains on the surface, and their presence causes some increase of the water contact angle of coated GF compared to the source GF. As the quantity of water reduces in the

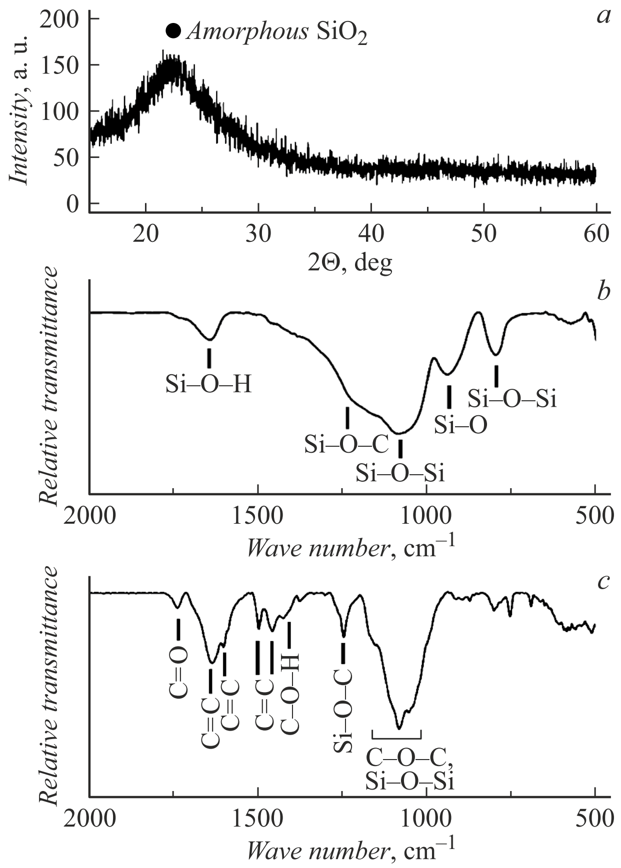

Figure 4. *a* — X-ray image, *b* — IR spectrum of TEOS-based coating particles/H_2O at the ratio of 1 : 0,6; *c* — IR spectrum of GF with the coating.

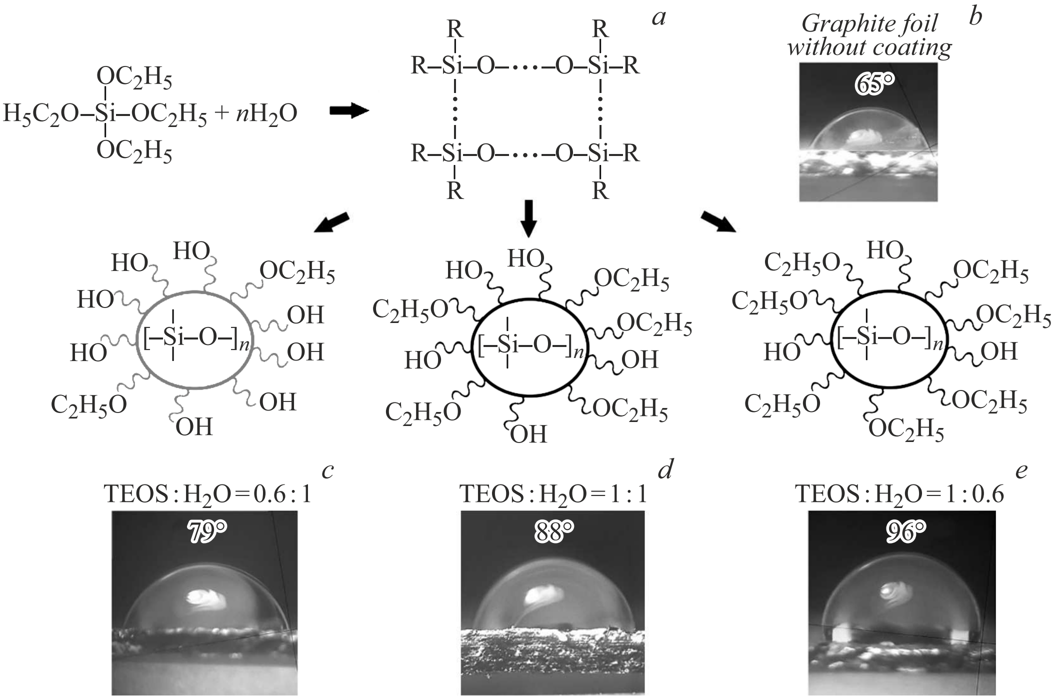

Figure 5. *a* — schematic image of coating produced on the basis of condensed TEOS and images of contact angle (*b*) GF without coating and with coating on GF surface, produced using TEOS/H_2O at the ratio of *c* — 0,6 : 1; *d* — 1 : 1; *e* — 1 : 0,6.

impregnation solution, only partial substitution of ethoxy groups with hydroxy groups occurs in silane, and the share of the remaining hydrophobic ethoxy groups is growing in the formed particles of the condensed silane (fig. 5, *d, e*). These particles are condensed on the GF surface and form a coating on the entire surface. Therefore, you can substantially increase the GF hydrophobicity by application of the coating from the TEOS solution and variation of TEOS/water ratio.

Conclusion

GF was produced with hydrophobic coating based on TEOS by hydrolysis and condensation of silane in the presence of water and aqueous solution of ammonia (as catalyst of hydrolysis–condensation processes). It was shown with the help of IR spectroscopy that TEG, from which GF was compacted, contained residual oxygen functional groups, which were not decomposed at thermal expansion of the source oxidized graphite at 800°C. These groups within TEG and GF on its basis cause reduction in GF hydrophobicity: GF had water contact angle less than 90°. Application of the coating by hydrolysis and condensation of TEOS in the presence of water causes increase in the contact angle. As quantity of water decreases for silane hydrolysis as the coating is applied, the material hydrophobicity increases, and water contact angle of coated GF increases to 96°. In process of TEOS hydrolysis–condensation, the amorphous particles of condensed silane are formed, the surface of which contains hydrophobic ethoxy groups. These particles coat the GF surface, increasing its hydrophobicity.

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Conflict of interest

The authors declare that they have no conflict of interest.

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