Analysis of the structure of foam graphite by optoacoustic spectroscopy and scanning electron microscopy

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A specimen of foam graphite foil is shown to have an anisotropic structure and consists of layers (stacks) of crystallite sheets weakly bound to one another.

The increasing interest in the use of metastable carbon nanostructures of low dimensionality (nanoclusters) in the fields of catalysis,[1] superconductivity,[2] astronomy,[3] combustion processes[4] and environmental protection[5] has necessitated the development of effective production methodologies. One promising direction is the target-directed solid-phase modification of graphite materials with reduction of their dimensionality at micro- and nano-levels by physicochemical methods[6] as the first step towards the preparation of nanoclusters.

The unusual thermal and mechanical properties of these materials, *e.g.* those obtained by heating oxidised graphite,[6] have been noted in a number of our studies. Considerable interest was attracted by the low heat of vaporisation of this thermoexpanded (foam) graphite,[7,8] indicating vaporisation of large graphite fragments which can be used for the synthesis of carbon nanoclusters.[9] The qualitative difference between the mechanisms of vaporisation of foam graphite and conventional polycrystalline graphite is obviously due to the structural properties of these materials.[7,8]

The ideal crystalline graphite with density $\rho_{cg} = 2.25$ g cm^{-3} is an infinite crystallite consisting of two-dimensional graphite layers 3.35 A apart, which leads to anisotropic properties.[10] Polycrystalline graphite (PCG) with density $\rho_{pcg} = 1.7$ g cm^{-3} differs in that it has a close packed array of chaotically oriented separate crystallites of 50–500 A and has spatially isotropic properties.[10] Foam graphite foil is produced by milling thermoexpanded graphite with a bulk density of 2–5 g dm^{-3} consisting of capsules approximately 100 μm in diameter and up to several mm long, constituted by separate crystallites of 100–500 A with a controlled vacancy density.[6] The density of the resulting material, ρ_{fg}, is 0.70 ± 0.05 g cm^{-3}, and the average disorientation angle of the crystallite basis plane with respect to the surface of the material θ does not exceed 35°. The manner in which the crystallites fill the bulk, and the arrangement of air vacancies, which occupy about 66% of the material volume, substantially influence the character of the heat transfer during laser vaporisation; however, they still remain unknown.

To study the structure of the foam graphite foil we used a laser source of ultrasonic waves which is widely used in defectoscopy, in investigations of physical properties of materials and to verify the geometrical dimensions of objects.[11] A Nd:YAG laser ($\lambda = 532$ nm) with a pulse duration (FWHM) of 10 ns and a pulse repetition frequency of 0.9 Hz was chosen as the radiation source. The absorption of the radiation in a thin near-surface layer (less than 10^{-7} m thick) of a target with a thickness of 600 μm created a surface thermoacoustic source of longitudinal acoustic waves, recorded at the back side of the target by a piezoelectric ceramic sensor running at no-load and by a C-122 oscilloscope. Waves propagation within the material led to a delay in their recording by the sensor with respect to the beginning of the laser pulse, this delay being proportional to the thickness of the target (Figure 1).

In ideal crystalline graphite, longitudinal acoustic waves propagate at different rates in different directions, namely, $V_{par} = 2 \times 10^4$ along the basis plane and $V_{perp} = 3.5 \times 10^3$ m s^{-1} in the direction perpendicular to the basis plane.[12] Apart from the crystalline phase, foam graphite foil contains air vacancies, the average total length of which in a direction normal to the surface is L_{cr} and L_{air}, respectively. The sound propagates in the vacancies at the velocity of sound in air, $V_{air} = 330$ m s^{-1}. Then, in the general case, the time required for the wave to pass through the target T_{pass} [within the accuracy of the constant equal to 1.2 ± 0.1 μs, which is the time needed for the wave to pass through a 3 mm thick brass disk protecting the sensor from the direct action of radiation] is expressed in the following way

$$T_{pass} = L_{par}/V_{par} + L_{perp}/V_{perp} + L_{air}/V_{air} + 1.2$$

where L_{par} and L_{perp} are the overall distances covered by the wave within the target along the basis plane of the crystallites and normally to it, respectively. For the two extreme cases, namely, the chaotic orientation of crystallites with isotropic filling of the whole bulk and an ordered arrangement of crystallites as weakly joined layers (stacks) separated by air gaps (sandwich structure) with clear-cut anisotropy, L_{par}, L_{par} and L_{air} are related to L_{cr} and to the material density by the following expressions:

$$L_{par} = 0.66L_{cr},\ L_{par} = 0.33L_{cr},\ L_{air} = \sqrt[3]{(\rho_{cg}/\rho_{fg} - 1)}L_{cr}$$

in the former case and $L_{par} = L_{cr}\sin\theta$, $L_{perp} = L_{cr}\cos\theta$, and $L_{air} = 2.21L_{cr}$ in the latter case. The curves for the theoretical dependence for each of the extreme cases are shown in Figure 1.

Curve *3* [anisotropic structure, $V_s = (4.6 \pm 0.3) \times 10^2$ m s^{-1}] is in better agreement with the experimental plot [curve *1*, $V_s = (4.3 \pm 0.3) \times 10^2$ m s^{-1}] than curve *2* [isotropic structure,

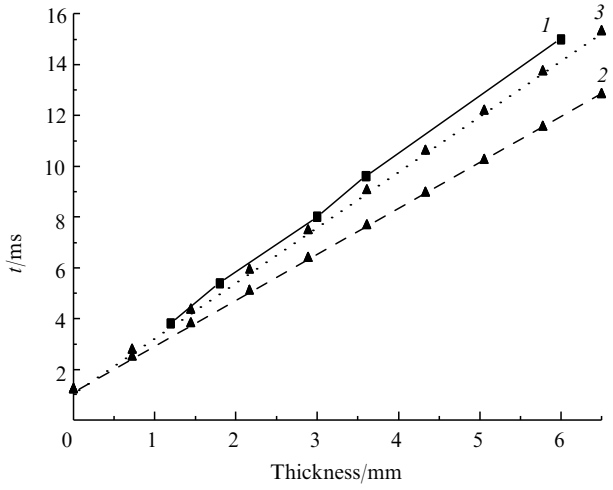

Figure 1 Dependence of the time required for the thermooptical pressure wave to pass through the target on its thickness.

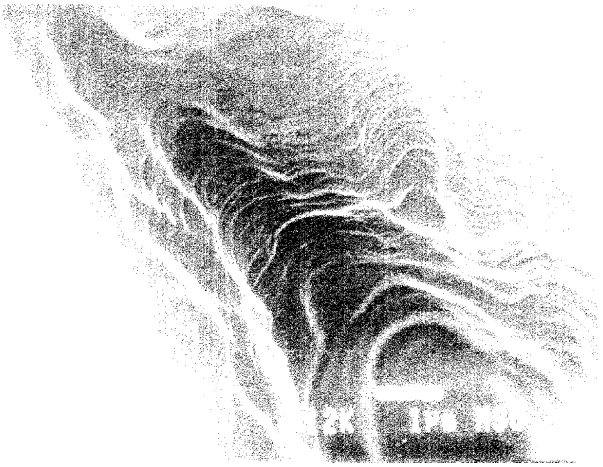

Figure 2 Micrograph of the crater wall (magnification 12 000).

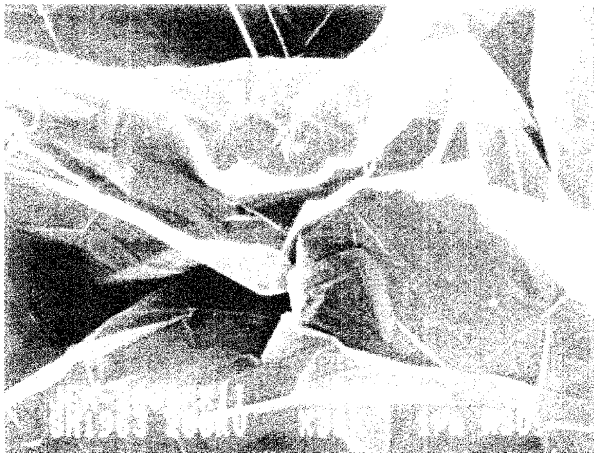

Figure 3 Micrograph of a crystallite sheet (magnification 30 000).

$V_s = (5.6 \pm 0.4) \times 10^2$ m s^{-1}]. It is obvious that even the simplified views on the character of sound propagation in graphite make it possible in this case to conclude that the foam graphite foil has a layered structure with air gaps and that the interaction between the layers (stacks) of crystallites is weak.

The average spacing between the layers (stacks) of crystallites in the structure of the foam graphite foil was measured at the wall of a crater formed due to the radiation from a Nd:YAG laser (λ = 532 nm) with a normal intensity distribution, a pulse duration (FWHM) of 25 ns and a pulse repetition frequency of 12.5 Hz. The radiation was focused by a lens (F = 28 cm) and directed through a shutter window onto a target at right angles to its surface. The target was exposed to 1, 3, 5 and 10 laser pulses in the laser flux range 0.08–2.4 J cm^{-2}. The structure of the crater wall formed under the influence of the radiation with a laser flux of 2.4 ± 0.1 J cm^{-2} (Figure 2) was studied using a JEM 2000FX-II scanning electron microscope with an LaB_6 cathode (the maximum magnification of the microscope was 800 000 and the accelerating voltage of the electron beam was 200 kV). The specimens were studied in the regime of recording of secondary electrons.

The spacing between the layers (stacks) of crystallites was found from the average number of steps (layers) on a fragment of the crater wall. The length of this fragment was defined as 1.0 ± 0.1 μm along the radius R divided by the sine of the angle between the crater axis and the crater wall in the region where the measurement was carried out. The angle was determined from the expression $\mathrm{tg}\,\alpha = \mathrm{d}X/\mathrm{d}\varepsilon \times \mathrm{d}\varepsilon/\mathrm{d}R$, where X and ε are the average depth of the crater per pulse and the laser flux taken from the previous paper.[7] In the case of normal distribution of the laser flux with $\sigma = 80 \pm 5$ μm and $\varepsilon_0 = 2.4 \pm 0.1$ J cm^{-2}, the angle α near the bottom of the crater is 10°. Here the average repetition period of the layers is 0.66 ± 0.07 μm, and 0.46 ± 0.05 μm of it is the total air gap within the layers. The remaining 0.20 ± 0.02 μm are filled by individual crystallites (0.01 μm thick and up to 0.05 μm in diameter) according to the 'crumpled sheet' principle (Figure 3), the average angle of the disorientation of the basis plane of crystallites with respect to the material surface not exceeding 35°.

Thus, a foil of foam graphite has an anisotropic structure and consists of 0.66 ± 0.07 μm thick two-dimensional graphite layers, 0.20 ± 0.02 μm of which are filled with deformed weakly interacting sheets with a thickness of 0.01 μm consisting of separate crystallites oriented in the sheet plane.

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