# Two-step mechanism of the laser vaporisation of foam graphite

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**Laser ablation of a foam graphite foil is governed by the splitting off of 'cold' weakly bound layers (stacks) of crystallites following the recoil pulses of the thermal vaporisation of the material.**

Laser vaporisation of graphite is one of the most frequently used methods for the preparation of carbon clusters.[1] Small clusters containing up to a hundred carbon atoms are obtained directly by condensation in a supersonic nozzle of small molecules vaporized from the graphite surface.[2,3]

The target-directed synthesis of nanotubes and nanofibres larger than several thousands of atoms in size can be achieved by the coalescence of large 'structural blocks', *i.e.* fragments,[4] but the preparative-scale synthesis of these large precursors is difficult.

Previously we have reported on the anomalously low heat of vaporisation of foam graphite (FG), the magnitude of which (30–40 kJ $mol^{-1}$) suggests the possibility of laser vaporisation of large carbon clusters. The unusual character of the vaporisation of foam graphite compared with usual polycrystalline graphite (PCG)[7] may be due to specific features of the structure of FG, namely, the arrangement of crystallites in layers and the high density of vacancies in the crystallites which exert an influence on the mechanical stress and heat transfer within the material during laser vaporisation. The laser vaporisation of PCG is mostly quasi-stationary.[7] The phase state of the near-surface layer of graphite with a thickness of several interatomic distances is determined by the instantaneous temperature field and by the stress field of the recoil pulse according to the Clausius–Clapeyron law; the near-surface layer as a dynamic system moves during the laser pulse along the sublimation–vaporisation curves. An equation relating the saturated vapour pressure $p$ and the temperature $T$ in the near-surface layer to the intensity of the laser radiation $I_L$ and to the characteristics of the medium during the quasi-stationary vaporisation has been derived from the boundary condition of the Stefan problem with allowance for the expression for the recoil pressure:[7]

$$(1-R)I_L V_{vap}/H_{gas}(p,T) = P(T) = P_0 \exp[-\lambda/kT]$$

$P_0$ is the parameter characterising the variation of the pressure with increase in temperature; $\lambda$ is the heat of vaporisation, $R$ is the light reflection coefficient, $H_{gas}$ is the total heat of heating–vaporisation; and $V_{vap}$ is the velocity of the vapour emission.

The values of the integral of the thermooptical and ablation components of the acoustic signal, which characterise the temperature and stress fields on the surface, averaged over the time of the laser pulse action and over the volume of the target heated by radiation,[8] increase linearly for PCG with increase in the radiation intensity along the curve of vaporisation in the phase diagram of carbon above the triple point ($0.5\times10^8$ W $cm^{-2}$) (Figures 1 and 2). The heat of heating–vaporisation

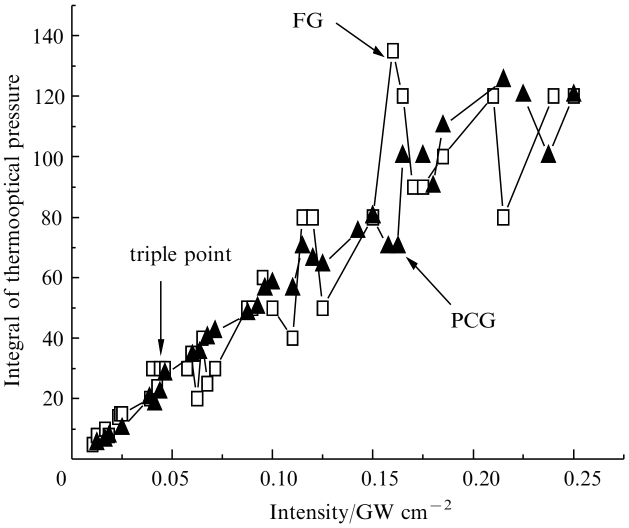


**Figure 1** Dependence of the integral of thermooptical pressure on the intensity of laser radiation for foam (FG) and polycrystalline graphite (PCG).

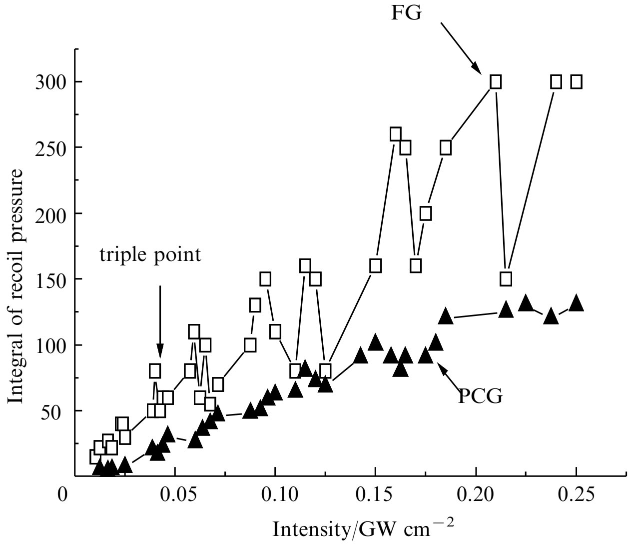


**Figure 2** Dependence of the integral of recoil pressure on the intensity of laser radiation for foam (FG) and polycrystalline graphite (PCG).

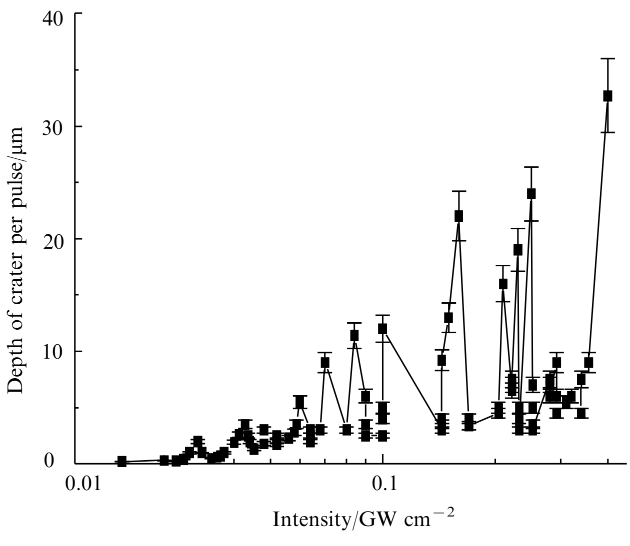


**Figure 3** Dependence of the average increase in the depth of a crater per radiation pulse on the radiation intensity for foam graphite (FG).

calculated from the dependence of the average depth of a crater on the intensity equalled 540±100 kJ $mol^{-1}$ (the reflection coefficient was taken to be 10%) and coincides with that calculated for the range between the triple and critical points in the phase diagram of carbon (530 kJ $mol^{-1}$).[7]

The slightly non-monotonic character of the variation of the thermooptical pressure and of the recoil pressure (TOP and RP) with increase in the intensity has been accounted for by the thermal instability of the quasi-stationary movement of the vaporisation front on the rough graphite surface, predicted by Anisimov *et al.*[9] During intense vaporisation, the thin near-surface layer is cooled and the transfer of energy to it from the region where radiation is absorbed occurs by thermal conductivity. The depth of the absorption of light is much greater than the thickness of the near-surface layer so the temperature increases deep into the medium, attaining a maximum at a certain distance from the surface. The stationary vaporisation becomes unstable, since, when a spot of the front is displaced in opposition to the temperature field gradient, the heat flow to it increases. The movement of the spot is accelerated, because the temperature in the spot-surface rises, which, like the initial disturbance of the front, increases proportionally to $\sim \exp(iky + \gamma t)$, where $k$ is the wavenumber of the corresponding Fourier component of the spectrum of the roughness of the surface, $y$ is the coordinate on a unidimensional surface, $\gamma$ is an increment of the disturbance growth, and $t$ is time in the laser-pulse timescale. The amplitude of the displacement of the spot does not exceed the distance at which the maximum of the temperature field is attained, and the layer with this thickness is destroyed by the shortwave perturbations more rapidly than the stationary vaporisation regime is established, the substance of this layer being removed. The maximum non-stationary growth of certain components of the Fourier spectrum of the roughness of the surface relief occurs in a narrow range of laser intensity $k_{max} \sim (C_1 - C_2 \ln I_L)^{0.5}$ ($C_1$ and $C_2$ are characteristics of the substance), and supershort high-power pressure pulses are generated due to the recoil momentum of the vaporised substance.

The influence of the roughness of the FG surface on its vaporisation was studied using the opticoacoustic setup described previously.[5,6] A graphite target was vaporised by a Nd:YAG laser ($\lambda$ = 532 nm, $\tau$ = 10 ns, $f$ = 0.9 Hz); the integral of the amplitude of the longitudinal acoustic compression waves over the compression half-period for TOP and RP was measured in the intensity range $I_L$ 0.1–$2.5\times10^8$ W $cm^{-2}$ using a piezoelectric ceramic sensor and a wide-band storage oscilloscope after averaging 50 pulses. The average increase in the crater depth over one laser pulse was measured in the intensity range $I_L$ 0.2–$4\times10^8$ W $cm^{-2}$ using a Nd:YAG laser ($\lambda$ = 532 nm, $\tau$ = 25 ns, $f$ = 12.5 Hz) with a normal intensity distribution. The radiation was focused onto a target at right angles to its surface and the number of radiation pulses needed to burn completely through the target of known thickness or the decrease in the time needed for a TOP wave to pass through the target (coming off the crater bottom closer to the acoustic sensor on the back of the target) was recorded (Figure 3).

The resulting non-monotonic dependence of the crater depth in FG on the intensity implies that two processes are involved in ablation: the minima in Figure 3 correspond to quasi-stationary vaporisation (linear dependence, heat of heating–vaporisation about 500 kJ $mol^{-1}$), while the maxima reflect the shock splitting off of 'cold' weakly bound stacks of crystallites in the bulk of the material with a heat of heating–vaporisation of 30–40 kJ $mol^{-1}$ (Figure 3).

It follows from Figure 1 that in the intensity range studied, the distribution of the temperature field over the surface of FG almost coincides with that in the case of PCG, which confirms the surface character of light absorption (at a depth of about 0.15 μm) by the FG target. On the other hand, the curves for the recoil pressure and for the crater depth in Figures 2 and 3 indicate the occurrence of intense ablation of FG, having the resonance character of the radiation intensity and with a low heat of vaporisation (the increase in the crater depth per pulse is up to 30 μm), while the correlation of the positions of peaks in Figures 1, 2 and 3 reflects a relationship between the disturbance of the temperature field at certain intensity values and the increase in the vaporisation velocity.

The above facts suggest that in the case of FG, against the background of stationary vaporisation non-stationary thermal vaporisation occurs at certain values of the radiation intensity, probably due to the thermal instability of the vaporisation front at various components of the roughness spectrum of the defective surface of FG. The supershort recoil pulses of the vaporised substance being generated cause both the destruction of the heated layer on the surface and the shock splitting off of 'cold' weakly bound stacks of crystallites within the bulk of the material.

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