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# Characteristic features of the laser ablation of foam graphite

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**Anomalously high ablation efficiencies and their markedly non-monotonic dependence on the energy density have been noted in the laser ablation of foam graphite.**

Graphite is the traditional source of carbon for the deposition of carbon films and for the preparation and study of carbon clusters.[1] It has recently attracted special interest in connection with the development of physicochemical methods for the specific modification of its structure at the micro- and nano-level.[2] At the same time, its structural characteristics may determine its thermophysical and optical properties and may influence significantly the nature of its ablation on exposure to the laser radiation.

The ablation of graphite is to a large extent determined by the nature of the diffusion of heat within it following exposure to laser radiation. Typical thermal diffusivities of graphite are of the order of 0.01–0.1 $cm^2\ s^{-1}$, so that the characteristic heat diffusion distance during the application of a nanosecond laser pulse amounts to a fraction of a micrometer for all graphite modifications. Therefore the differences in the character of the ablation of foam and the usual crystalline graphite are associated exclusively with the difference between their structures, namely between a layered type of structure and a high density of defects on the atomic scale.

Foam graphite is obtained by compressing graphite capsules (approximately 100 μm in diameter and up to 1000 μm long)[2] assembled from scales approximately 0.01 μm thick and with the orientation of an individual scale at right angles to the axis of the capsule. Each scale consists in its turn of layers of 100–1000 Å graphite crystallites with a multiplicity of edge dislocations and a measureable density of vacancies in the crystallite. As a result, the density of the material is $\rho = 0.7\ g\ cm^{-3}$ and the velocity of sound in it is $c = 450\ m\ s^{-1}$, which is comparable to the velocity of sound in air and is significantly lower than the velocity of sound in crystalline graphite, while the thermal conductivity in the crystallite is $\lambda_{||} = 1000\ W\ m^{-1}\ K^{-1}$ and that between the layers is $\lambda_{\perp} = 3–5\ W\ m^{-1}\ K^{-1}$ and is close to that of crystalline graphite.[3]

We have investigated pulsed laser ablation by an opticoacoustic method which makes it possible to measure with a high degree of accuracy the average depth of a crater on the target surface created during the application of the laser pulse.[4] In the experiments, we used an opticoacoustic set up similar to that described by Esenaliev *et al.*[4] The second harmonic emission from a Nd:YAG laser with pulse energy $E = 5$ mJ ($\lambda = 532$ nm), a normal spatial intensity distribution ($\omega = 0.6$ mm at the outlet mirror), a divergence of radiation $\alpha = 0.5$ mrad, a pulse duration (FWHM) $\tau = 22$ ns, and a pulse tracking frequency $f = 12.5$ Hz was focused by a lens ($F = 10$ cm) onto a graphite target with a thickness $l = 0.6$ mm after attenuation to the required intensity by neutral calibrated filters. A portion of the radiation (5%) was directed by means of a glass beam splitter into a photodiode – pyroelectric system in order to synchronise the system for recording and measurement of the energy of the laser radiation in each pulse (the stability of the output laser energy in the second harmonic was 6%). The opticoacoustic measurements were performed with the aid of a piezoelectric ceramic sensor in the cold run regime. The electric signal, proportional to the amplitude of the displacement of the surface of the sensor, was recorded by means of a wide-band storage oscillograph.

In the course of the measurements, the longitudinal acoustic compression waves were recorded and the time shift of the leading front of the thermooptical signal was measured as a

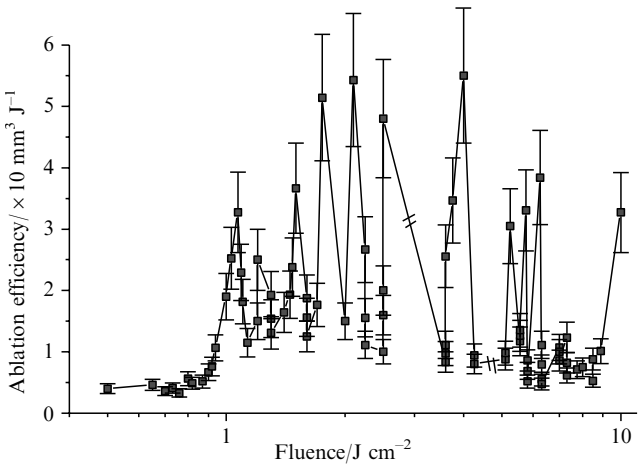


**Figure 1** Dependence of ablation efficiency on laser fluence for foam graphite.

function of the number of laser pulses (after averaging over 100 pulses of the laser radiation). Knowing the velocity of sound, this made it possible to calculate the average increase in the depth of a crater per pulse for the given energy density of the radiation on the surface of the target. The resulting average depths of a crater were found to agree satisfactorily with determinations of the average crater depth made from the number of pulses necessary to burn completely through a graphite target of known thickness.

The variation of the ablation efficiency, *i.e.* the ratio of the amount of vaporised substance to the absorbed energy of the laser radiation, was calculated from the observed variation of the average increase in the depth of a crater per radiation pulse for foam graphite by dividing it by the energy density (Figure 1). We obtained a markedly non-monotonic relation (not observed previously for other modifications of graphite),[5] the maxima of which corresponds to the heat of vaporisation of foam graphite $Q' = 30$–$40$ kJ mol$^{-1}$. This is comparable to the literature values of the heats of formation of large carbon clusters[6] and to the interlayer bond energy in crystallites ($E_{bond} = 30$–$40$ kJ mol$^{-1}$).[7] Thus the ablation products may be both large clusters[8] and even fragments of individual crystallites ejected from the surface by the recoil shock wave,[9] accumulating up to 10% of the energy of the laser pulse.[10] We note that in the case of polycrystalline graphite, characterised by a high thermal conductivity and low density of structural defects, the crater depth per pulse, which we measured by a similar procedure in the range of energy densities indicated, do not exceed 0.2 μm, wich is consistent with a heat of vaporisation above 1 MJ mol$^{-1}$, while the composition of the vaporised substance is limited to small carbon clusters.[5]

In interpreting the results obtained for foam graphite, we first took into account the fact that in the band spectrum of crystalline graphite there is no forbidden band between the valence and conductive bands of the high-level valence π electrons.[11] This is responsible for the metallic character of the thermal and electrical conductivities of graphite, pointing to a thermal mechanism of the vaporisation. In this case, the non-monotonic structure of the dependence of the ablation efficiency on the energy density may be accounted for by the thermodynamics of the non-equilibrium quazi-stationary processes involving the injection of energy into the near-surface heated layer and its dissipation in the form of the vaporisation of clusters, because the condition for the existence in this layer of a local thermodynamic equilibrium is ensured by a stationary vaporisation regime.[12]

Thus for each peak on the plot (Figure 1) of the ablation efficiency against the energy density there is a corresponding range of intrinsic energy densities or, in other words, temperatures of the graphite surface, in which a phase transition may occur during vaporisation from one size distribution of clusters to another, which in the case of metals has been noted for ions of different charge types.[5] The temperature of the near-surface layer corresponding to the bulk density of the thermal energy (equal to vaporisation energy of the clusters with a given size distribution) is attained at the peak maximum. Accordingly, at the leading front of the peak the bulk density of the thermal energy in the graphite layer increases, intensifying the vaporisation of a particular distribution of clusters, whereas at the trailing front of the peak this increase suppresses their vaporisation, favouring the vaporisation of clusters with a different distribution.

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