Formation of large carbon clusters during laser ablation of foam graphite

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Vaporisation from rough surface areas during the laser ablation of foam graphite under vacuum generates a shock wave of recoil pressure of the vaporised substance which destroys the layer heated by radiation by desorbing large fragments from the material surface.

In recent years, metastable carbon nano-structures (nano-clusters) have found wide use in the fields of medicine,[1] biology,[2] photophysics[3] and electronics,[4] and because of this the search for effective production methods is continuing. The highly defective foam graphite[5] (FG), together with carbon black[6] and carbon mesophase,[7] is one of the most promising sources of large carbon clusters, because the ablation energy during laser ablation is low compared with that of usual polycrystalline graphite (PCG).[8,9] Since the structure of a separate crystallite in PCG is close to an ideal crystal structure, the products of the laser vaporisation are small primary ions.[10] Therefore, in the case of FG with a rough surface, one can expect vaporisation of large carbon clusters.

Intense vaporisation of graphite starts in the region above the triple point in the phase diagram of carbon; this corresponds to the laser radiation intensity range in which the electron absorption in the vapours by the reverse decelerating absorption mechanism becomes significant.[11] The vaporisation products are fragmented and ionised by fast electrons thus forming a plasma layer on the surface; the rate of these processes rapidly increases with increase in the radiation intensity on the nanosecond laser-pulse timescale. The mass spectrum of the primary ions formed presents fairly completely not only the thermal ions emitted from the surface but also the fragments of vaporised neutral species which were ionised by electron impact in the plasma.

The dependence of the spectrum of the primary ions of FG on the intensity of laser radiation was studied on an MX-7304 quadrupole mass spectrometer, the ion optics of which were modified for recording the time-of-flight mass spectra (Figure 1). The radiation of the second harmonics of an Nd : YAG laser with pulse energy $E = 5$ mJ ($\lambda = 532$ nm), a normal intensity distribution, an angular divergence of 0.3 mrad, a pulse duration (FWHM) of 25 ns and a pulse repetition frequency of 12.5 Hz was attenuated by neutral filters and then focused by a lens ($F = 28$ cm) through a quartz window in a vacuum chamber (pressure $< 10^{-7}$ Torr) onto a grounded rotating graphite target (ring shaped) perpendicular to its surface. Part of the radiation (5%) was directed to a photodiode–pyroelectric system by virtue of a beam splitter in order to synchronise the systems of recording and control of the laser radiation energy in each pulse (the stability of the output laser energy in the second harmonics was 6%). When the laser radiation hit the target, the primary ions of the vaporised substance arising in the plasma were extracted and accelerated by a pulse electric field with a voltage of 100 V and with a pulse duration of 0.1–10 μs, applied to a grid installed 4 cm from the target. After passing through the grid, the ions travelled a distance of 45 cm in a field-free space and entered the input of the secondary electron multiplier. After discrimination of noise and preamplification, the pulse bursts corresponding to separate ions were read by a counter located at a computer board. The count cycle was 1.25 μs, which corresponds to the resolution of the mass spectrometer, $R = 18$ for $M \sim 300$ amu, for the laser radiation intensity I_L being lower than 0.03 GW cm^{-2} (at higher radiation intensities the peaks of separate ions are blurred due to increase in the forward temperature of the plasma, and the instrument operates in the probe mode). The digital signal was averaged over 1000 radiation pulses and then it was graphically processed (Figures 2 and 3).

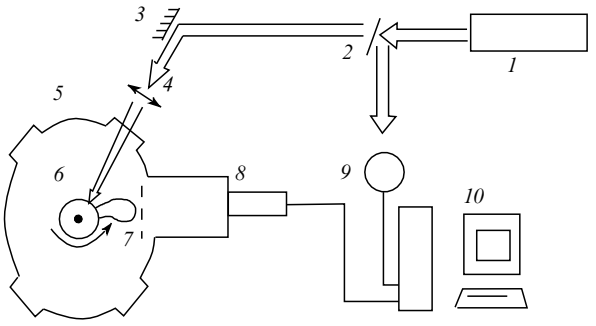

Figure 1 Experimental set up: laser (*1*), beam splitter (*2*), non-transparent mirror (*3*), focusing lens (*4*), vacuum chamber (*5*), rotating graphite target (*6*), extracting/accelerating grid (*7*), secondary electron multiplier with a discriminator and an preamplifier (*8*), photodiode–pyroelectric (*9*), computer with a pulse-counter board (*10*).

In a study of the laser ablation of foam graphite under atmospheric pressure,[8] it was shown that the surface roughness and intense vaporisation above the triple point of the phase diagram (0.016 GW cm^{-2}) are key factors for the manifestation of the effect of the shock ablation of FG. Despite the fact that the distribution of the temperature field on the surface of FG (at a depth of about 0.15 μm) in the intensity range 0.01 to 0.25 GW cm^{-2} virtually coincides with that for PCG, the curves for the recoil pressure of the vaporised substance and for the average crater depth per pulse indicate that there occurs unusually intense ablation of FG, having a resonance character regarding the emission intensity

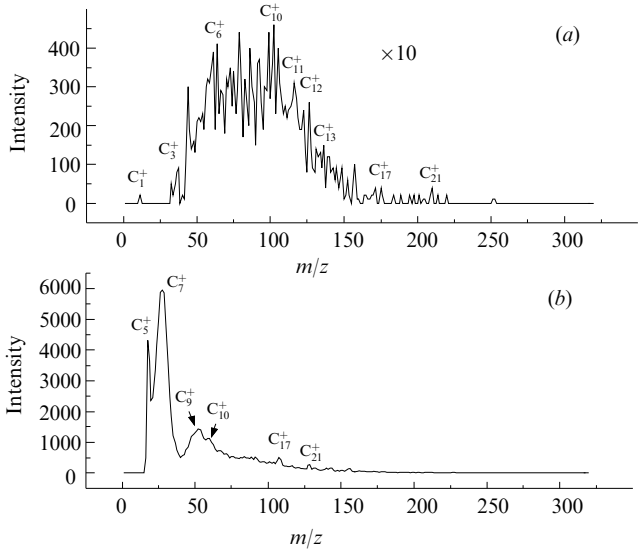

Figure 2 Time-of-flight mass spectrum of foam graphite (ion intensity, arbitrary units/time of flight, μs) at laser radiation intensity, GW cm^{-2}: 0.013 (*a*), 0.026 (*b*).

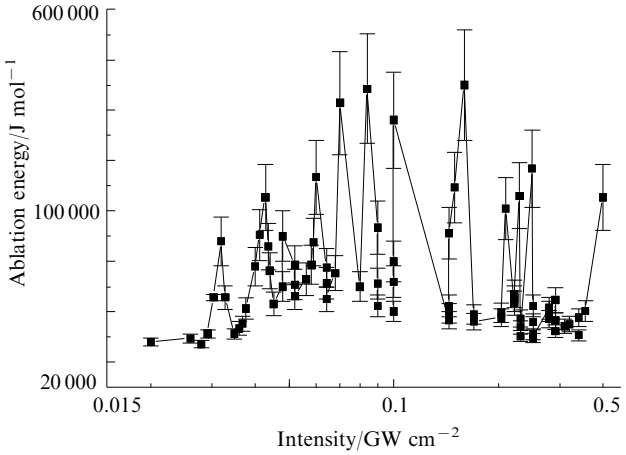

Figure 4 Dependence of the ablation energy of foam graphite on the intensity of laser radiation under atmospheric pressure.

and with a low ablation energy (the increase in the crater depth per pulse is up to 30 μm).[8] The correlation of the peak positions in the plots for the thermooptical pressure, recoil pressure, and the average crater depth per pulse reflects a relationship between the disturbance of the temperature field at certain values of the intensity and the increase in the vaporisation velocity, caused by the thermal instability of the vaporisation front at various components of the spectrum of the surface roughness (surface clusters) of FG.[8,12] The generated pulse of recoil of the vaporised substance leads to the destruction of the heated near-surface layer and to the shock-induced spalling of 'cold' weakly joined sheets of crystallites in the bulk of the material.[8]

When an FG sample is evacuated, the sound-conducting medium (air) is removed from the gaps between the crystallite sheets. Therefore, during vaporisation, the vapour fills the gaps only in the heated near-surface layer, and the shock wave of the recoil pulse, confined to this volume, disperses it.

When the radiation intensity is 0.013–0.026 GW cm^{-2}, the absorbing layer on the FG surface reaches the neighbourhood of the triple point, where the vaporisation of the material is weak and the mass spectrum of the primary FG ions does not differ from that for the PCG ions (C_1^+–C_{11}^+)[10] (Figure 2). However, starting from 0.08 GW cm^{-2}, the mass spectra recorded for FG, in addition to the low-mass component C_1^+–C_5^+ typical of PCG, contains a high-mass component C_{30}^+–C_{110}^+ (Figure 3), which is broadened towards the low mass region due to fragmentation by electron impact in the near-surface plasma and due to the development (caused by the instability of the radiation energy) of unstable vaporisation on some of the components of the roughness spectrum. Since the thermodynamics of vaporisation of PCG and FG are similar (identical distributions of the temperature field on the surface

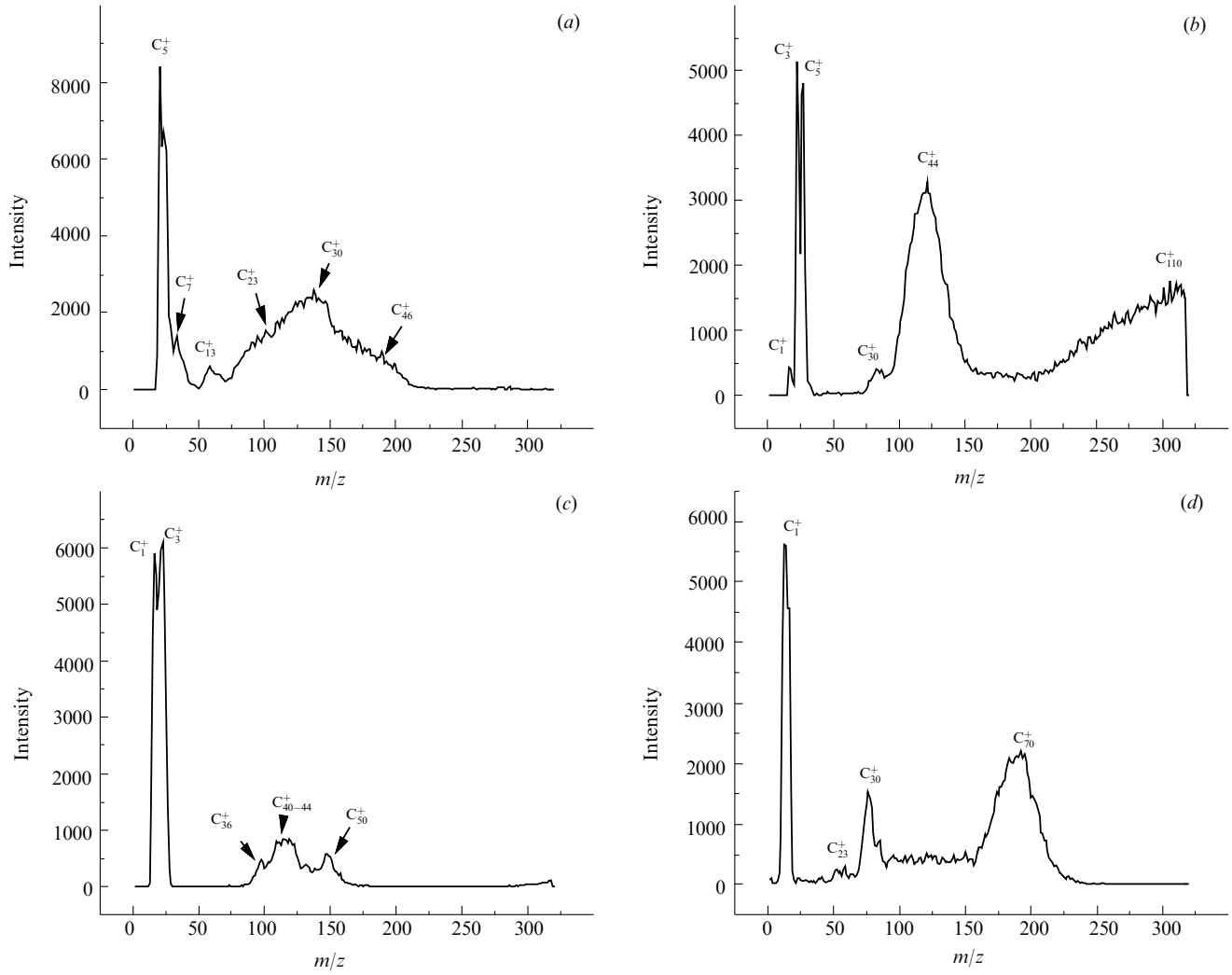

Figure 3 Time-of-flight mass spectrum of foam graphite (ion intensity, arbitrary units/time of flight, μs) at laser radiation intensity, GW cm^{-2}: 0.08 (*a*), 0.13 (*b*), 0.44 (*c*), 1.3 (*d*).

and identical amounts of substance vaporised per pulse),[8] the modal character of the spectrum in the case of FG (vapour-drop mixture)[12] for intensities of more than 0.08 GW cm^{-2} indicates that the formation of large cluster ions during the laser ablation under vacuum occurs by a 'desorptional' rather than by a condensational mechanism.

The correlation between the ablation energy of FG (energy per unit of volume vaporised)[8] (Figure 4) and the greatest size of cluster ions detected in the mass spectra at various intensities reflects the influence (noticeable even from 0.2 GW cm^{-2}) of the plasma arising near the target surface on the course of the vaporisation of graphite during a laser pulse (absorption in the plasma, increase in the specific amount of the radiation energy consumed per unit of substance removed, due to the strong over-heating and ionisation of the vapour, and shielding of the target with the plasma).

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References

1 T. N. Savateeva, M. K. Shevtchuk and P. P. Iakoutseni, *Abstracts of the 2nd International Workshop 'Fullerenes and Atomic Clusters'*, St. Petersburg, 1995, p. 174.

2 G. V. Andrievsky, L. M. Samokhina, A. V. Zhmuro and A. D. Roslyakov, *Abstracts of the 2nd International Workshop 'Fullerenes and Atomic Clusters'*, St. Petersburg, 1995, p. 172.

3 O. I. Shevaleevsky, L. L. Larina and L. A. Chernozatonsky, *Abstracts of the 2nd International Workshop 'Fullerenes and Atomic Clusters'*, St. Petersburg, 1995, p. 175.

4 A. F. Hebard, *Physics Today*, 1992, 26.

5 S. I. Kudryashov, N. B. Zorov, A. A. Karabutov and Yu. Ya. Kuzyakov, *Mendeleev Commun.*, 1997, 20.

6 H. Y. So and C. L. Wilkins, *J. Phys. Chem.*, 1989, **93**, 1184.

7 I. J. Dance, K. J. Fisher, G. D. Willet and M. A. Wilson, *J. Phys. Chem.*, 1991, **95**, 8425.

8 S. I. Kudryashov, N. B. Zorov, A. A. Karabutov, S. V. Kuznetsov and Yu. Ya. Kuzyakov, *Izv. Akad. Nauk, Ser. Fiz.*, 1996, **3**, 2 (in Russian).

9 S. I. Kudryashov, S. V. Sokolov, N. B. Zorov, A. A. Karabutov and Yu. Ya. Kuzyakov, *Mendeleev Commun.*, 1997, 25.

10 J. J. Gaumet, A. Wakisaka, Y. Shimizu and Y. Tamori, *J. Chem. Soc., Faraday Trans.*, 1993, **89**, 1667.

11 N. B. Delone, *Vzaimodeistvie lazernogo izlucheniya s veshchestvom* (*Interaction of laser radiation with matter*), Nauka, Moscow, 1989, pp. 190–204 (in Russian).

12 S. I. Anisimov, M. I. Tribel'skii and Ya. G. Epel'baum, *Zh. Eksp. Teor. Fiz.*, 1980, **78**, 1597 [*J. Exp. Theor. Phys.*), 1980, **51**, 802].

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