Appearance of the supercritical state of carbon in the laser evaporation of low-density graphite foil

Sergei I. Kudryashov,* Sergei G. Ionov, Alexander A. Karabutov and Nikita B. Zorov

Department of Chemistry, M. V. Lomonosov Moscow State University, 119899 Moscow, Russian Federation.
Fax: +7 095 932 8846; e-mail: serg@laser.chem.msu.su

A high concentration of nonequilibrium defects in crystallites and a low bulk density of the graphite foil obtained from thermally expanded graphite favour the explosive decomposition of the laser-heated surface layer of the substance in the supercritical state.

Low-density carbon materials such as graphite foil are of considerable interest because of the possibility of generating various high-temperature states of carbon by the action of intense laser radiation. Due to the high (up to 80%) porosity of the low-density graphite foil, quasi-equilibrium evaporation into the pores occurs in the near-surface region of laser radiation absorption with a thickness greater than 100 nm. The average size of the pores, according to small-angle X-ray back scattering data, is 10–20 nm (less than the free path length of vapour species). Depending on the ratio between the material density ρ and the density of carbon in the critical state $\rho_{cr} = 0.64$ g cm^{-3},[1] the critical state of the substance ($\rho = \rho_{cr}$), the labile state of the liquid phase with pre-critical parameters ($\rho < \rho_{cr}$), or the supercritical state of the substance ($\rho > \rho_{cr}$) in the immediate vicinity of the critical point can be formed. The structure of graphite foil is metastable[2] due to the presence of nonequilibrium chemically induced defects; therefore, the heats of laser-induced phase transitions in graphite foil can differ from similar parameters for polycrystalline graphite (PCG) chosen for the study as the reference sample.

In this work, for studying the mechanism of the laser-induced decomposition of graphite foil, we used the method of photoacoustic spectroscopy, which is widely used for the investigation of phase transitions occurring in the bulk and on the surface of condensed matter under the action of laser radiation.[3] Previously, in the study of laser evaporation of dense PCG (bulk density $\rho = 1.7$ g cm^{-3}) by the photoacoustic procedure, we have observed the threshold-like (by laser power density, $I_0 \approx 0.3$ GW cm^{-2}) formation of the surface layer of the liquid phase of carbon at the thermodynamically unstable (labile) state, which is decomposed due to hydrodynamic removal of the products of spinodal decomposition of this state: nuclei of the liquid and gas phases.[4] The disappearance of the thermoacoustic pulse of rarefaction of negative polarity in the acoustic signal detected by the photoacoustic procedure was used as a criterion of formation and hydrodynamic decomposition of the labile state of the liquid phase of carbon. In fact, the compression wave of the thermoacoustic nature (with a positive polarity) on the free surface of the labile liquid phase of carbon is not reflected with the appearance of the following rarefaction wave (with a negative polarity), but is transformed into a directed flow wave of the gas–liquid mixture of the products of spinodal decomposition. Thus, the recoil pressure of the substance evaporated on the target surface is equal to the thermoacoustic pressure in the labile phase (Figures 1 and 2) and is approximately half the pressure of saturated carbon vapour at the given temperature, provided its value is not greater than the critical temperature of carbon.[4]

In this work, we chose a graphite foil sample, which differs from a PCG sample in bulk density (0.7 g cm^{-3}) and high concentration of nonequilibrium structural defects, as the object of photoacoustic studies. In experiments, we used a photoacoustic setup similar to that described in ref. 4. An Nd:YAG laser ($\lambda = 532$ nm, $\tau = 10$ ns, $f = 0.9$ Hz) heated and evaporated the graphite target with a thickness of 600 μm. The absorption of radiation in the thin (less than 10^{-7} m) surface layer of the target, followed by thermalization of the absorbed energy to the energy of the phonon subsystem and evaporation of the substance, created surface thermoacoustic and evaporation sources of longitudinal acoustic waves, which were detected on the back side of the target by a ‘thick’ piezoelectric ceramic PZT-19 detector (thickness $d = 1.5\pm0.1$ mm, time constant *ca*. 500 ms) and an S8-12 oscilloscope with an input resistance of 1 MΩ. The thickness of the acoustic detector provided a time ‘window’ with a duration of 400–500 ns for the direct detection of the acoustic signal without reflection in the piezocrystal. The acoustic detector worked in the idling regime, *i.e.*, the signal detected was proportional to the displacement amplitude (the integral value for the vibrational velocity). However, a path length L_{path} of about 4 mm for the acoustic wave in the graphite target and a protective brass disk in the acoustic detector were

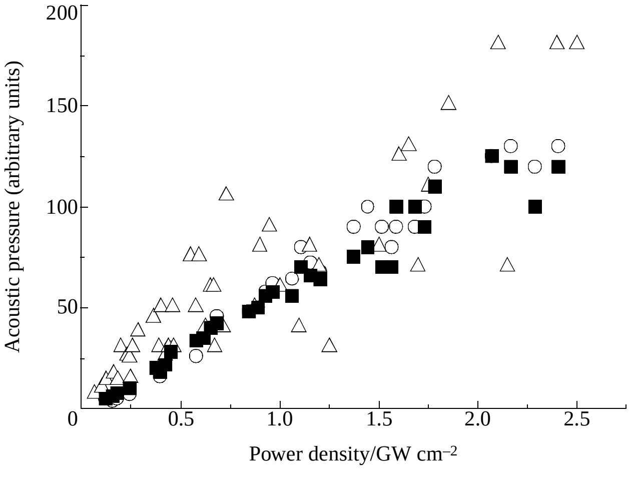

Figure 1 Dependence of the thermoacoustic pressure (■), recoil pressure for PCG (○) and thermoacoustic pressure for graphite foil (△) on I_0 (RSD ≤ 10% for each acoustic pressure value).

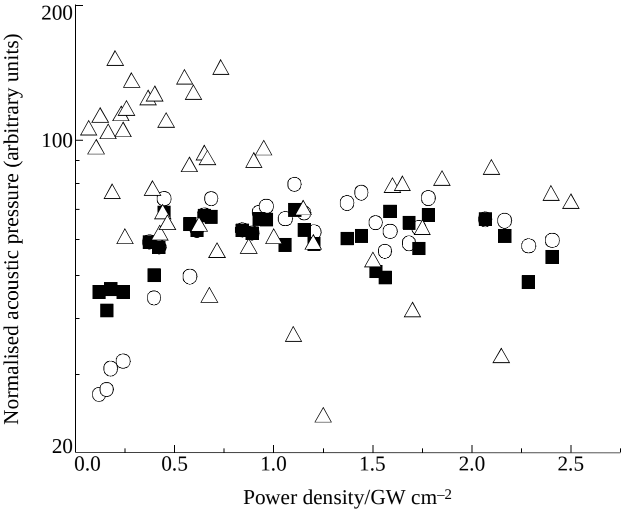

Figure 2 Dependence of normalised values (divided into I_0) of the thermoacoustic pressure (■), recoil pressure for PCG (○) and thermoacoustic pressure for graphite foil (△) on I_0 (RSD ≤ 16% for each normalised value).

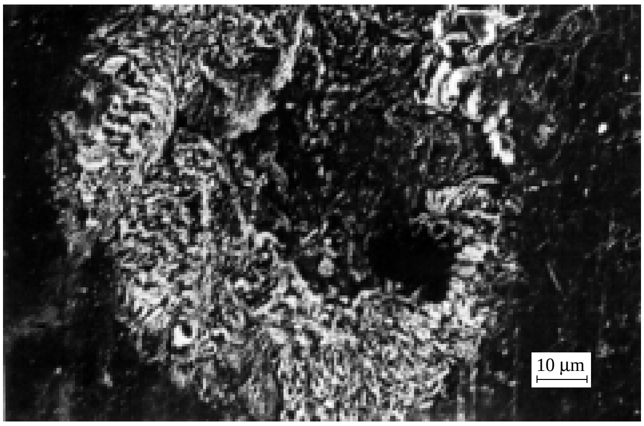

Figure 3 SEM image of the surface of the graphite foil sample laser irradiated with a power density greater than 0.006 GW cm^{-2}.

chosen in such a way that the detector was localized in the far diffraction zone [$L_{path} >> L_{diffr} = (d^2_{source} f)/V_{sound} \leq 200$ µm for sizes of the acoustic source $d_{source} \approx 150$ µm, sound velocity $V_{sound} \approx 450$ m s^{-1}, and a frequency of the main spectral component of the acoustic signal $f \approx 5$ MHz]. Due to this arrangement of the acoustic detector, when the acoustic signal was propagated in the target, diffraction exerted a differentiating effect on the signal shape. As a result of the successive action of differentiating effects (due to diffraction) and integration (idling regime), the detected signal presents the real spatial and temporal distribution of thermoelastic stresses in the region of acoustic generation predicted by the photoacoustic theory.[5]

The signal observed upon laser irradiation of the graphite foil target takes the form of a single compression pulse (with a positive polarity) over the whole studied range of laser power density ($I_0 = 0.06$–2.5 GW cm^{-2}), *i.e.*, it is formed under conditions of hydrodynamic removal of the substance. The direct experimental evidence for the explosive and bulk character of formation of the acoustic compression pulse during laser decomposition of the graphite foil sample was obtained by scanning electron microscopy (SEM), studying the shape of the crater in the graphite foil target irradiated with a power density of 0.003–1 GW cm^{-2}. The structure of partially torn off packets of crystallites is observed on the target surface only beginning from the threshold value $I_0 = 0.006$ GW cm^{-2} corresponding to the deposition of radiation energy of *ca.* 200 kJ mol^{-1} to the absorption layer on the target surface (Figure 3). For incident power density $I_0 > 0.015$ GW cm^{-2}, a smooth crater surface is observed, which indicates complete removal of the laser-heated layer of the substance.

It is likely that the hydrodynamic mechanism of acoustic generation during laser evaporation of graphite foil ($\rho > \rho_{cr}$) can be related to the expansion of the laser-heated layer of carbon in the supercritical state (thickness to 100 nm for the given sample of graphite foil with a bulk density of 0.7 g cm^{-3}). In fact, the amplitude of the acoustic compression pulse generated in the graphite foil target (Figures 1 and 2), taking into account greater dissipation of the longitudinal acoustic wave in the foil as compared to the PCG target (thickness of the targets 600±25 µm, correction coefficient for graphite foil 1.3±0.2), is two to three times greater than the amplitude of the acoustic compression pulse appeared during the spinodal decomposition of the labile liquid phase of carbon in the PCG target at $I_0 = 0.3$–2.5 GW cm^{-2}. This implies that the internal quasi-static vapour pressure in closed cavities of graphite foil exceeds by 2–3 times the value of the recoil pressure during the nonequilibrium hydrodynamic decomposition of the surface layer of the labile liquid phase in the PCG target and, hence, exceeds by 1–1.5 times the value of the equilibrium pressure of saturated carbon vapour at the same evaporation temperature, and corresponds to the formation of the supercritical state of carbon. Taking into account the calibration of the acoustic detector during laser evaporation of PCG,[6] the maximum pressure in the graphite foil target volume occupied by the substance in the supercritical state is 3400±500 bar at $I_0 = 2.5$ GW cm^{-2}, which considerably exceeds the value of the critical carbon pressure (2210 bar[1]).

As follows from the SEM and photoacoustic spectroscopy data, the supercritical state of carbon appears in the graphite foil target at $I_0 < 0.06$ GW cm^{-2} (for PCG at $I_0 > 0.3$ GW cm^{-2}), which indicates a significant decrease in the total heat of formation of the supercritical state of carbon from 270[7] to 200 kJ mol^{-1} due to the contribution of the energy of nonequilibrium chemically induced defects of the crystallites (more than 70 kJ mol^{-1}).

The authors are grateful to the Russian Foundation for Basic Research for support (grant no. 98-03-32679).

References

1 H. R. Leider, O. H. Krikorian and D. A. Young, *Carbon*, 1973, **11**, 555.

2 S. I. Kudryashov, S. G. Ionov, A. A. Karabutov and N. B. Zorov, *Mendeleev Commun.*, 1998, in press.

3 I. A. Veselovskii, B. M. Zhiryakov, A. N. Korotchenko and A. A. Samokhin, *Kvantovaya Elektronika*, 1985, **12**, 381 (*Sov. J. Quantum Electronics*, 1985, **15**, 246).

4 S. I. Kudryashov, A. A. Karabutov and N. B. Zorov, *Mendeleev Commun.*, 1998, 6.

5 V. E. Gusev and A. A. Karabutov, *Lazernaya Optoakustika* (*Laser Photoacoustic*), Nauka, Moscow, 1991 (in Russian).

6 S. I. Kudryashov, A. A. Karabutov, M. A. Kudryashova, V. I. Beketov and N. B. Zorov, *Mendeleev Commun.*, 1998, 29.

7 *Termodinamicheskie svoistva individual'nykh veshchestv* (*Thermodynamic Properties of Individual Substances*), ed. V. P. Glushko, Nauka, Moscow, 1979, vol. 2, p. 10 (in Russian).

Received: Moscow, 25th May 1998
Cambridge, 6th August 1998; Com. 8/04727H