Mendeleev Commun., 1998, 8(1), 29–30

Laser-induced phase transitions of carbon

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The rate of laser-induced phase transitions (melting and evaporation) of carbon in the subcritical region of the phase diagram is determined by optical characteristics of the air–melt–graphite layered system.

During laser-induced phase transitions (LIPT) of carbon, the optical feedback channel apparently exerts a greater influence on the LIPT dynamics than the heat-conduction mechanism, for which thermal resistance of the melt is the key factor in the feedback mechanism.[1] In this case, the reflectance, transmittance and absorbance of a film of the carbon melt vary as functions of the film thickness due to interference, and thus control the dynamics of melting and evaporation. However, up to now only a few studies dealing with laser-induced melting and evaporation of carbon have been carried out. The separate results of these studies do not permit an elucidation of the roles of both feedback channels in the LITP dynamics. It is known that when the surface of graphite is heated by laser radiation to the graphite–liquid–vapour triple point T_{tr}, *ca.* 5000 K, a heat wave and phase transition fronts of melting and evaporation begin to propagate deep into the material. The movement of the melting front into the target in the case of the moderately absorbing graphite melt [α(532 nm) = $8 \pm 2 \times 10^5$ cm^{-1})] with low heat conductivity is maintained as a result of heating and melting of graphite at the interface by the radiation that has passed through the melt. The depth of penetration of the melting front (the thickness of the melt film Y) during a 25 ns laser pulse reaches a value of the order $2\alpha^{-1}$(532 nm) = 2.4×10^{-5} cm, which is in better agreement with the experimental result[2] Y(532 nm) = $= 1.8 \times 10^{-5}$ cm than the depth of penetration of the heat wave: $\sqrt{2\chi(4000\ \mathrm{K})\tau}$ 10^{-5} cm (at a temperature conductivity of graphite[3] χ(4000 K) = 2.5×10^{-3} cm^2 s^{-1}).

The thickness Y of the molten film existing due to dissimilar velocities of propagation of the melting and evaporation fronts

$$\frac{\mathrm{d}Y}{\mathrm{d}t} = V_{\mathrm{melt}}(t) - V_{\mathrm{evap}}(t) \qquad (1)$$

which differ in the heats of transition [H(liq.; P_{tr}, T_{tr}) = = 200 kJ mol^{-1} and $_{\mathrm{evap}}H(P_{tr}, T_{tr})$ = 265 kJ mol^{-1}],[3,4] determines the reflectance (R), transmittance (T) and absorbance (A) of the air–melt–graphite l ayered medium [Figure 1, for n(532 nm) = = 0.84 ± 0.01, k(532 nm) = 0.45 ± 0.15][1] owing to the interference of radiation in the molten film.[5] These values determine the following velocities of propagation of phase transition fronts

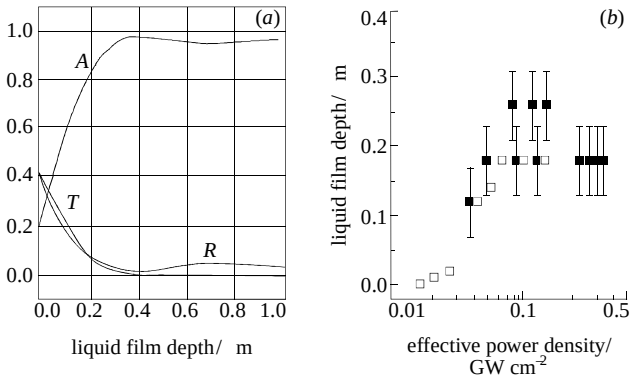

Figure 1 (*a*) Dependences of the reflectance (R), transmittance (T) and absorbance (A) of the air–liquid carbon–graphite medium on Y. (*b*) Dependences of the thickness of the liquid carbon film $Y(I_0, \tau/2)$ and $Y(I_0, \tau)$: dark and light squares.

induced by radiation with instantaneous intensity $I(t)$, equations (2) and (3),

$$V_{\mathrm{melt}}(t) = \frac{T(Y)I(t)V_{\mathrm{m}}}{H(\mathrm{liq.}, P_{tr}, T_{tr})} \qquad (2)$$

$$V_{\mathrm{evap}}(t) \cong \frac{[1 - R(Y) - T(Y)]I(t)V_{\mathrm{m}}}{H_{\mathrm{eff}}(P, T)} \qquad (3)$$

[V_{m} is the molar volume of graphite, $H_{\mathrm{eff}}(P, T)$ is equal to the sum of $_{\mathrm{evap}}H(P, T)$ and H(liq.; P_{tr}, $T_{tr} \rightarrow P$, T)] and thus complete the feedback mechanism.

In a study carried out by laser reflectometry,[1] we discovered interference of the laser radiation in the air–m elt–pol ycrystalline graphite (PCG) layered medium formed at a power density of 0.017–0. 7 GW cm^{-2}. The interference extrema are manifested by the angular dependence of the intensity of the reflected radiation at an optical thickness of the film Y specified by relationships for the minima and maxima of reflectance:

$$(2m + 1 - \frac{2(\varphi_{23} - \varphi_{12})}{\pi})0.25\lambda = Y(I_0)n(\sqrt{n^2 - \sin^2\theta_1})^{-1} \qquad (4)$$

$$(m - \frac{(\varphi_{23} - \varphi_{12})}{\pi})\,0.5\lambda = Y(I_0)n(\sqrt{n^2 - \sin^2\theta_1})^{-1} \qquad (5)$$

where $\varphi_{12} = -1.2 \pm 0.1$ rad and $\varphi_{23} = 0.2 \pm 0.1$ rad are phase shifts of the light wave at the vapour–mel t (12) and melt–graphite (23) interfaces.[1] The presence of characteristic interference maxima in the range of effective (with allowance for the incidence angle) power density of 0.06–0. 3 GW cm^{-2} made it possible to elucidate the dependence of the film thickness in the middle of the radiation pulse $Y(I_0, \tau/2)$ (Figure 1); this dependence reproduces the profile of the $Y(I_0, \tau)$ curve found by TEM measurements of the re-crystallised layer thickness of highly oriented pyrolytic graphite melted by laser radiation with similar characteristics.[2] In both cases, the thresholds for the beginning of melting (0.015 and 0.020 GW cm^{-2}) and for flattening of the curves (0.054 and 0.062 GW cm^{-2}) are virtually identical; in addition, a clear-cut plateau is observed, *i.e.* there is a steady-state regime when a film with Y_{st} = 0.18 m is maintained during a laser pulse. According to equation (1), this plateau can be attributed to the beginning of intensive

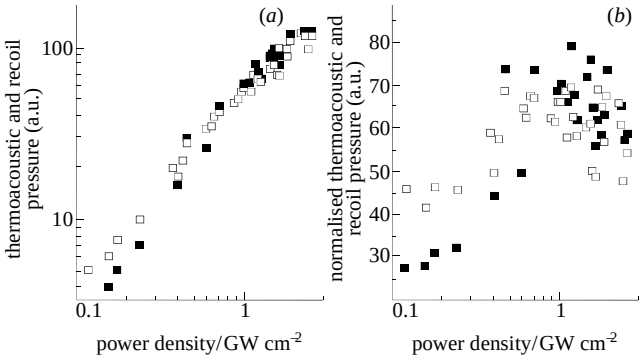

Figure 2 (*a*) Dependences of $P_{ta}(I_0)$ and $P_{rec}(I_0)$ (light and dark squares) for PCG. (*b*) Dependences of the normalised P_{ta}/I_0 and P_{rec}/I_0 values (light and dark squares).

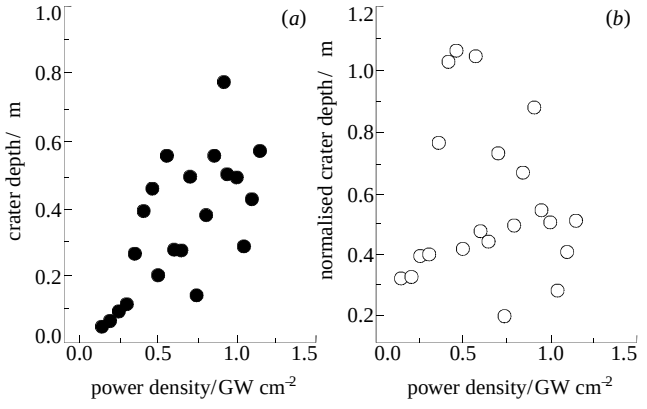

Figure 3 Dependences of the average crater depth for polycrystalline graphite: (*a*) $X(I_0)$ and (*b*) normalised X/I_0.

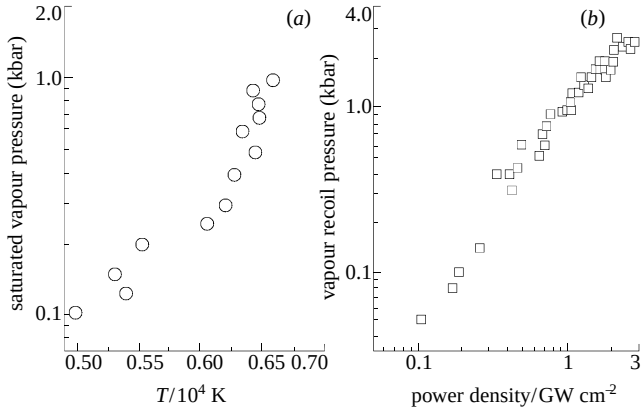

Figure 4 (*a*) Temperature dependence $P_{sat}(T)$ according to published data[4] and (*b*) dependence of the normalised (in bar) recoil pressure $P_{rec}(I_0)$.

evaporation at a power density I_0 higher than the threshold value equal to 0.05 GW cm^{-2}.

In fact, when the film of the melt occurs under steady-state conditions in the power density range 0.06–0.3 GW cm^{-2}, $R(Y)$ and $T(Y)$ reach their minimum values (0.06 and 0.2), whereas the absorbance, conversely, reaches its maximum (0.74) (Figure 1). Consequently, starting from 0.06 GW cm^{-2}, a fast linear increase is observed in the plot for the integrated thermoacoustic pressure $P_{ta}(I_0)$ (Figure 2) characterising the energy absorbed per unit liquid phase[6]

$$\int_0^\tau P_{ta}(t)\mathrm{d}t = \rho_0 c_0 \int_0^\tau V_f(t)\mathrm{d}t = \frac{[1 - R(Y) - T(Y)]\beta}{C_p} I_0 \qquad (6)$$

(V_f is the vibrational velocity, β, C_p and α are temperature expansion and isobaric heat capacity coefficients and the absorbance coefficient of liquid carbon, respectively, ρ_0 is the density of graphite and c_0 is the speed of sound in the direction perpendicular to the basis plane). Since the β value depends only slightly on the temperature in the 5000–6100 K range of the subcritical region in the curve of evaporation of carbon,[7] according to equation (6), the constancy of the specific value

$$\frac{P_{ta}}{I_0} = \frac{[1 - R(Y) - T(Y)]\beta}{C_p}$$

in the corresponding range of I_0 confirms the invariance of the absorbance capacity of the carbon melt film.

The intensive evaporation of carbon in the range of I_0, higher than the threshold equal to 0.05 GW cm^{-2} and correlating with the establishment of the steady-state thickness of the film, is stimulated by the high absorbance ability of the latter. The average deepening of the crater $X(I_0)$ and average recoil pressure of the evaporation products $P_{rec}(I_0)$ per pulse directly describe the integrated velocity of the evaporation front per pulse (Figures 2,3). The linearity of these dependences in the range 0.06–0.3 GW cm^{-2} implies that the $A(Y)$ value is constant, since $H_{eff}(P, T)$ scarcely changes in the subcritical range of the evaporation curve.[4,8]

The expression for determining $P_{rec}(t)$ in terms of $V_{evap}(t)$:

$$P_{rec}(t) = \rho_{vap} V_{vap}[T(t)]^2 = \rho_0 V_{evap}(t) V_{vap}[T(t)] = 0.5 P_{sat}[T(t)] \qquad (7)$$

(where V_{vap} and ρ_{vap} are the velocity and the vapour density) not only describe qualitatively the steady-state character of the P_{rec}/I_0 and $P_{rec}(I_0)$ dependences in the range 0.1–0.3 GW cm^{-2} (Figure 2), but also make it possible to calculate $P_{sat}(T)$ for a steady-state regime for destruction and to normalise $P_{rec}(I_0)$. In fact, when carbon is vaporised under the action of nanosecond laser pulses on the surface, only thermal equilibrium is established, because the flux of radiation energy falling on the surface from the environment is counterbalanced by the reverse flux of energy carried away by the vaporised substance. Conversely, neither mass-exchange nor mechanical equilibrium is established on the surface, because the substance is transferred in virtually one direction. As a result, the instantaneous gas-dynamic recoil pressure P_{rec} on the target surface becomes half the saturated vapour pressure under steady-state evaporation conditions at the same instantaneous temperature of the surface.

The average V_{evap} per radiation pulse τ = 25 ns needed for calculations was found from the X value. The velocity of vapour in the free path distance from the target surface corresponds to the velocity $\sqrt{kTM^{-1}}$ of the products of decomposition of an activated complex on the surface at temperature T and mass of the removed fragment M; for the species C_3, which predominates in the vapour in the temperature range 5000–6100 K,[3] it is equal to (1.1–1.2)×10^3 m s^{-1}. The values $P_{sat}(T)$ = 120–230 atm for the region of steady-state destruction of PCG, 0.15–0.3 GW cm^{-2}, calculated from the formula

$$P_{sat}(T) = 2\rho_0 \frac{X}{\tau}\sqrt{\frac{kT}{M}} \qquad (8)$$

lie within the subcritical branch (Figure 4) according to the published data.[4] This confirms the adequacy of the model proposed in our study for the appearance of recoil pressure and also attributes the steady-state regime of LIPT to the subcritical region of variation of the thermodynamic variables characterising the state of carbon. Since the average P_{rec} over the radiation pulse in the case of steady-state destruction of PCG does not depend on its duration τ, the calculated and experimental values of P_{rec} should coincide; this makes it possible to normalise the $P_{rec}(I_0)$ dependence in bar outside the subcritical region (Figure 4).

The authors are grateful to the Russian Foundation for Basic Research (grant no. 96-03-33324) for financial support.

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Received: Moscow, 25th July 1997
Cambridge, 25th October 1997; Com. 7/05902G